Synthesis, Reactivity and Computational Studies of 1,4-Dialkyl-1,2,4-Triazol-5-ylidene Phosphorus(I) Cations

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Synthesis, Reactivity and Computational Studies of 1,4-Dialkyl-1,2,4-Triazol-5-ylidene Phosphorus(I) Cations

By

Fawzia Omar Elnajjar

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

Windsor, Ontario, Canada

2019

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Synthesis, Reactivity and Computational Studies of 1,4-Dialkyl-1,2,4-Triazol-5-yldene Phosphorus(I) Cations

by

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Declaration of Co-Authorship / Previous Publication

I. Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows: Most of the work contained in Chapter 2 of the dissertation was published in the journal article with the title: 1,2,4-Triazol-5-ylidenes versus Imidazol-2-ylidenes for the Stabilization of Phosphorus(I) Cations “F. O. Elnajjar, J. F. Binder, S.C.Kosnik, C. L. B. Macdonald, Z. Anorg. Allg. Chem. 2016, 642,1251–1258” I synthesized and characterized all the compounds in the manuscript except X-ray crystallography and elemental analysis. Justin F. Binder performed the X-ray crystallography, elemental analysis experiments and the writing. Stephanie C. Kosnik performed elemental analysis. My supervisor, Dr. Charles L.B. Macdonald performed the computational studies and provided the editing of the manuscript.

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Abstract

The Macdonald research group has been active in the synthesis of low-oxidation main group elements, particularly, compounds containing phosphorus in the (+I) oxidation state (P\textsuperscript{I}). One of the routes the group uses to stabilize phosphorus(I) center is through the use of N-heterocyclic carbenes (NHCs). Generally, NHC-P\textsuperscript{I} compounds are synthesized via ligand replacement reactions with the precursor [(dppe)P\textsuperscript{I}]\textsuperscript{+} which was previously developed by the research group.

Chapter 1 provides a review of the current status of low oxidation state P(I) chemistry as it presents an overview of the stabilization of P(I) centre through a synthesis of a remarkable compound (triphosphenium cation) using different reported routes. In addition, NHCs show a great ability to stabilize phosphorus in low oxidation state via producing various phosphacynine compounds employing imidazoles by different preparation methods. Accordingly, the properties of the analogue triazole compounds are also presented in order to illustrate their electronic and structural properties.

In chapter 2 various derivatives of 1,2,4-triazol-5-ylidene phosphorus(I) compounds were synthesized. This was performed by following these steps: (1) synthesizing 1,4-dialkyl-1,2,4-triazolium salts; (2) deprotonation of these salts using a suitable base and producing carbenes; (3) addition of [(dppe)P\textsuperscript{I}]\textsuperscript{+} salt to the resultant carbene in-situ to give the target phosphorus(I) compound. Metathesis reactions were employed to 1,4-dialkyl-1,2,4-triazolium iodide salts and the precursor [(dppe)P\textsuperscript{I}]\textsuperscript{+}Br by addition of NaBPh\textsubscript{4} in order to improve their solubilities and obtain pure materials of the desired products. The electronic properties of 1,2,4-triazol-5-ylidene phosphorus(I) compounds were assessed and compared with those of the previously reported 1,3-imidazol-2-ylidene phosphorus(I) adducts using \textsuperscript{31}P NMR spectroscopy and X-Ray crystallography.
data in conjunction with theoretical studies. The results revealed that the triazolylidenes are superior \( \pi \)-acids than their imidazolyl analogues and that the resulting P\( \text{I} \) complexes are less basic.

Chapter 3 provides a study of the reactivity of TAZ\( \text{II}_2 \)P\( \text{I} \) compounds in order to investigate to what extent the two pairs of electrons on the phosphorus centre are available to coordinate to Lewis acids as the phosphorus centre displayed higher \( \pi \)-acceptor properties than the previously reported imidazoles. This was accomplished via reactions with a variety of oxidation reagents such as elemental sulfur, triflic acid and methyl triflate, and coordination to transition metals such as gold, iron and cobalt. The observed results indicated that the TAZ\( \text{II}_2 \)P\( \text{I} \) complexes with both main group elements and transition metals are unstable in solution and leading to decomposition in some cases. Theoretical studies show that the snapping energy of metal-ligand bond for the TAZs complexes is much weaker than that of IMIDs complexes which agrees well with the experimental results.

In chapter 4, we treated 1,4-dialkyl-1,2,4-triazolium ions with phosphinidenes and elemental selenium to explore the electronic nature of the carbenes associated with \( \pi \)-accepting and \( \sigma \)-donor properties of the carbenes using NMR spectroscopy. Accordingly, various selenone derivatives of TAZs were synthesized and fully characterized. Experimental results along with theoretical studies revealed that TAZ carbenes have higher \( \pi \)-acceptor properties and lower donor properties than their analogues IMID carbenes. Among the TAZ carbenes, the diisopropyl substituted TAZ carbene is the strongest donor and weakest \( \pi \)-acceptors, however; dimethyl substituted TAZ carbene is the highest \( \pi \)-acceptor and the worst donor.
For

Alhussein

Mustafa and Basmalah
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List of Abbreviations, Symbols, Nomenclature

NHCs  N-heterocyclic carbenes
CAAC  cyclic (alkyl)(amino)carbene
R     Alkyl group
TAZs  1,4-dialkyl-1,2,4-triazol-2-ylidenes
IMIDs imidazol-2-ylidenes
MeTAZ 1,4-dimethyl-1,2,4-triazol-4-ylidene
[D₃]MeCN  Deuterated acetonitrile
Dppe  1,2-bis(diphenylphosphino)ethane, Ph₂P(CH₂)₂PPh₂
BPh₄  Tetraphenyl borate
NMR  Nuclear magnetic resonance
MHz  MegaHertz
Et₂O·BF₃  Boron trifluoride etherate
DFT  density functional theory
NBO  Natural bond orbital
DCM  Dichloromethane
MeCN  Acetonitrile
MP  Melting point
HR-ESI-MS  High resolution electrospray ionization mass spectrometry
THF  Tetrahydrofuran
scXRD  Single Crystal X-ray Diffraction
Et₂O  Diethyl ether
Me   Methyl
Et   Ethyl
iPr  Isopropyl
Bz   Benzyl
ppm  Parts per million
<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>n-Bu</td>
<td>n-butyl ((\text{CH}_2)_3\text{CH}_3)</td>
</tr>
<tr>
<td>E_H</td>
<td>Energy of homo orbitals</td>
</tr>
<tr>
<td>E_L</td>
<td>Energy of Lumo orbitals</td>
</tr>
<tr>
<td>LP</td>
<td>Population of lone pairs</td>
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<tr>
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</tr>
<tr>
<td>Ch</td>
<td>Chalcogens</td>
</tr>
<tr>
<td>OTf</td>
<td>Triflate, trifluoromethanesulfonate</td>
</tr>
<tr>
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<td>Dimethylsulfide</td>
</tr>
<tr>
<td>Ptr</td>
<td>m-phenol-1,2,4-triazole</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
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<td>Amino-1,2,4-triazole</td>
</tr>
<tr>
<td>2pytr</td>
<td>4-(pyrid-2-yl)-1,2,4-triazole</td>
</tr>
<tr>
<td>'Bu</td>
<td>Tert-butyl group</td>
</tr>
<tr>
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<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
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Chapter 1: Introduction

1.1 General Introduction

The chemical elements of group 15 (or group 5A) of the periodic table include nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). This group is known as the pnictogens "Pn" or nitrogen family.\(^1\) The name pnictogen originally refers to the Greek word "pniktos" which means "choke or strangle".\(^2\) One of the most important element among these pnictogens is phosphorus. Phosphorus-containing compounds have exhibited great attention in academic and industrial fields. Elemental phosphorus is a nonmetal and is found in three allotropes which are white, red and black phosphorus. The most common allotropes at room temperature are white phosphorus and red phosphorus. White phosphorus has the form \(\text{P}_4\) and is found to be stable only under water (or inert atmospheres) while the red allotrope forms polymeric molecule and is stable in air.\(^3,4\)

Because of its importance, the chemistry and chemical properties of phosphorus has been widely discussed.\(^5\) Phosphorus has the electron configuration: \(1s^22s^22p^63s^23p^3\), this electronic distribution is illustrated in Figure 1.1. Phosphorus contributes in molecular bonding with other periodic table elements and forms many types of compounds. Some common compounds containing

![Figure 1.1: Atomic energy levels of phosphorus atom\(^6\)](image-url)
phosphorus are PH$_3$, PCl$_5$, PF$_5$ and POCl$_3$. Phosphorus atom has the ability to form multiple bonds via back-donation since it has a low energy d orbital that could bind with other orbitals have the same symmetry as the empty d orbital from phosphorus. The wealth chemistry of phosphorus has led us to investigate further aspects of phosphorus compounds. The main goal of this dissertation is to synthesize, characterize and study electronic properties of N-heterocyclic carbene complexes of phosphorus in a low oxidation state, in particular; substituted 1,2,4-triazole-stabilized phosphorus (I) cations.

1.2 Oxidation States

The term oxidation state of an atom is among the basic concepts that may be used to explain the structural features, bonding and reactivity of a molecule. The oxidation state concept is defined as the charge on an atom that results from removing number of electrons from an atom within a molecule. The oxidation state is a fundamental feature that would be utilized to study the chemistry of an atom in question. According to the established counting rule, oxidation states are determined based on the relative electronegativity of the atom in the molecule. By applying such rules, H is +1 oxidation state, O is -2 oxidation state, and phosphorus is assigned oxidation state from -3 to +5, for example; phosphorus in PF$_3$ is +3 and in PF$_5$ is +5.

The use of the oxidation state or oxidation number is very important, for example, in balancing oxidation and reduction reactions, however; applying these rules can be misleading because the method does not consider the actual electronic distribution and the chemical behavior of a molecule. For example, for the following Lewis bases, PH$_3$, PMe$_3$ and P(NMe$_2$)$_3$, the oxidation state of phosphorus atom is -3, +3 or -3 and +3 respectively in spite of their similarity in chemical behavior and electronic structures.
The concept of the valence state is another way to assign the oxidation state of an atom within a molecule. The valence state is defined as the number of electrons which an atom utilizes for bonding (or chemistry) in a molecule. In CH$_4$ molecule, for example; carbon atom uses its 4 electrons in bonding which therefore means it has a valence state of 4. Hydrogen atom uses its one electron to form a bond with the carbon which means it has a valence state of 1. As a result, in order to determine the valence state, identifying the electronic distribution of the atoms within a molecule is necessary which in turn is very helpful for understanding the reactivity, and electronic and structural behavior of the molecule. However, in some cases the valence state shows some ambiguities and do not agree with the oxidation number (Figure 1.2)

![Figure 1.2: Differences between oxidation numbers and valence state on phosphorus atoms within one molecule.](image)

An alternative method that can be used to define the oxidation state of an atom in a molecule is by counting the number of non-bonding electrons that are presenting on the atom in question. This method is used in the Macdonald group and it decreases the ambiguity of using the two previous counting rules of the oxidation states. This model (Figure 1.3) is more fruitful since it highlights the similarities in electronic structures, chemical behavior and geometrical characteristics of compounds involving elements in a particular oxidation state. For example, according to the counting rule, the phosphine PMe$_2$H has a phosphorus atom with an oxidation state +1:
whereas, in the compound AsMe₂H which has similar structural and chemical properties to the phosphine, the oxidation state of As is +3. However, by applying the non-bonding electrons rule outlined in Figure 1.3, the oxidation state of both centers, P and As is considered as III oxidation state and both compounds have different chemical and structural properties than Pnictogen(I) compounds.

![Figure 1.3: Oxidation states of pnictogens according to the non-bonding electrons rule](image)

When compounds containing a pnictogen with +5 oxidation state (Pn(V)), it means there are no non-bonding valence electrons present. When the pnictogen atom has an oxidation state of +3 (Pn(III)), this means there is a single lone pair presenting on the pnictogen center. For more illustration see Figure 1.4 and Figure 1.5.

![Figure 1.4: Some bonding environments detected for compounds containing Pn(V)](image)
The chemistry of low oxidation main group elements has a widespread development for many years and in particular the area of phosphorus in low oxidation state. An example of well-known stable compounds of phosphorus (I) is the triphosphonium salts of the general formula \([R_3P—P—PR_3]^{+}\). The central dicoordinate phosphorus atom has an oxidation state of (+1) which describes the atom as an electron rich centre. Consequently, such species comprise a low oxidation state phosphorus (+1) centre possess different structural and electronic properties and unique reactivities when compared to phosphorus in oxidation states of +3 and +5.

In 1982, Schmidpeter reported the synthesis and characterization of the first cyclic triphosphonium cation. The P(I) cation \([(dppeP)]^{+}\) was produced via the reduction of \(\text{PCl}_3\) with \(\text{SnCl}_2\) in the presence of \(\text{dppe}\); bis(diphenylphosphino)ethane. This method was used to prepare a various cyclic and acyclic triphosphonium salts with the use of different reducing agents (Scheme 1.1).

Later, in 2001, Dillon et al. illustrated that the reaction of \(\text{PX}_3\) (X = Cl, Br, I) with dppe produced a five membered ring of P(I) cations in the absence of a reducing agent. In this case the phosphine ligand acts as a reducing agent that reduces P(III) to P(I) as it is oxidized to the corresponding halophosphonium halide P(V). \(^{31}\text{P}\) NMR spectroscopy indicated the presence of a

**Figure 1.5: Some bonding environments reported for compounds containing Pn(III)\(^9\)**
triplet and doublet patterns that are comparable with Schmidpeter cyclic triphosphonium cation. Other examples of cyclic triphosphonium cations which include six- and seven-membered rings have been synthesized via the use of dppp (1,2-bis(diphenylphosphino)propane) and dpb (1,2-bis(diphenylphosphino)butane) precursors respectively. However this general method of preparing triphosphonium salts has a disadvantage associated with the formal formation of \( \text{X}_2 \) which reacts with diphosphane producing a halo-phosphonium salt as a by-product. These by-products are difficult to isolate and prevents isolation of pure and crystalline triphosphonium adducts. During later years, additional chemistry was accomplished on triphosphonium adducts in order to investigate their reactivity such as alkylation and protonation in which methyl triflate and triflic acid were used to oxidize P(I) centre to P(III).

In 2003, Macdonald et al. reported the synthesis and isolation of triphosphonium adducts from the reaction between \( \text{Pl}_3 \) and diphosphane (Scheme 1.2) in a similar manner to the previously mentioned. The by-product( \( \text{I}_2 \) ) was readily washed off with THF or ether allowing for the isolation of pure crystalline [dppeP]I as a white solid for the first time (Figure 1.6). The group also attempted to use
Scheme 1.2: Synthesis of triphophenium cation using PI₃.¹⁶

Figure 1.6: X-ray structure of triphosphenium salt obtained by Macdonald et al.¹⁶

PCl₃ and PBr₃ in a similar manner as with PI₃, but it did not result in a pure triphosphenium salt ion. It was suggested that, the produced halogens Cl₂ and Br₂ in this case are very reactive comparing to I₂ and readily oxidize the diphosphane ligand forming many side products as observed in the ³¹P NMR spectra. It is worth noting that triphosphenium iodide is air stable and its stability is attributed to the back bonding of the electrons on the electron rich phosphorus (I) centre in triphosphenium cation to the anti-bonding orbitals of the dppe ligand.

A few years later, the Macdonald group reported the development of a novel synthesis pathway that produced pure solid of triphosphenium bromide salt in a high yield (up to 96%). Their new method involved the addition of one equivalent of PBr₃ and three equivalents of cyclo-hexene to a slight excess dppe in DCM solvent under inert atmosphere (Scheme 1.3). The reaction
produced Br\(_2\) which was excluded through the interacting with cyclohexene forming 1,2-dibromo-
cyclohexane which in turn easily removed under vacuum. This effective method has been exten-
sively used in Macdonald lab to easily prepare pure triphosphenum bromide salt that is a worthy 
source of phosphorus(I) that could be transferred to obtain various derivatives of stabilized P\(^I\) com-
pounds.\(^{65}\)

\[
PBr_3 + 1.1 \text{Ph}_2\text{P} - \text{PPh}_2 + 3 \text{cyclohexene} \rightarrow \text{DCM} \quad \begin{array}{c}
\text{Ph}_2\text{P}^+ \text{PPh}_2^- \\
\text{Br}_2
\end{array}
\]

**Scheme 1.3: More efficient method to synthesize triphophenium cation using PBr\(_3\).\(^{65}\)**

### 1.4 Carbenes

Carbenes have displayed a very important role as transient intermediates in organic and 
organometallic chemistry since the early work of Doering (1950s)\(^{66}\) and Fischer (1964)\(^{67}\). Car-
benes are compounds that have a divalent carbon atom with 6 valence electrons around the carbon 
atom center. The carbon atom in the carbene molecule could be in linear geometry with sp hybrid-
ization or bent geometry with sp\(^2\) hybridization. The carbon atom in the linear geometry has two 
non-bonding degenerate orbitals (\(p_x, p_y\)), however; the bent molecule, orbitals \(p_x\) and \(p_y\) have dif-
ferent energy levels. Whereas the orbital \(p_y\) remains unaffected (called \(p_\text{a}\)), the orbital \(p_x\) is stabi-
lized and since it has more of s orbital character, it is called \(\sigma\) orbital. Since most carbenes are bent, 
their frontier orbitals are called \(\sigma\) and \(p_\text{a}\) (Figure 1.7).\(^{17}\)
Figure 1.7: Different carbene geometries and their frontier orbitals

Figure 1.8: Different electronic structures of carbenes

Figure 1.8 illustrates four different electronic structures in which the two non-bonding electrons can be in either $\sigma$ or $p_\pi$ orbitals or in both. The two non-bonding electrons can occupy $\sigma$ and $p_\pi$ orbitals ($\sigma^1p_\pi^1$) with parallel spins and leads to a triple state. In contrast, these two electrons can be in opposite spin producing singlet state in different cases. One case, the two electrons can occupy $\sigma$ orbital and have an electronic configuration of $\sigma^2$. Another case, the two electrons can occupy $p_\pi$ orbital forming an electronic configuration $p_\pi^2$. The last case is that, the two electrons might locate in both $\sigma$ and $\pi$ orbitals and form $\sigma^1p_\pi^1$. The multiplicity of the ground state of carbenes is very important character that influences their reactivity. The multiplicity of the ground state depends on the energy gap between $\sigma$ and $p_\pi$ orbitals. In a similar manner to the crystal field
theory in which a strong ligand field results in a low spin and a weak ligand field results in a high spin, the singlet ground state of carbenes prefers a large $\sigma-p_\pi$ energy gap ($\geq 2$ eV), however; smaller energy gap ($\leq 1.5$ eV) causes a triplet ground state.\textsuperscript{17}

The ground-state multiplicity of carbenes can be influenced by the type of substituents introduced to the carbene molecule in terms of their electronic effects which include inductive and mesomeric effects, and steric effects.

1.4.1 Electronic Effects

1.4.1.1 Inductive Effects

This involves the influence of the substituents' electronegativity on the carbene multiplicity. It is well recognized that $\sigma$-electron withdrawing substituents favor the singlet state over the triplet state which is due to the fact that $\sigma$-electron withdrawing substituents stabilize the $\sigma$ orbitals by increasing the s character and keeping $p_\pi$ orbital unchanged and thus increases the $\sigma-p_\pi$ distance leading to the singlet state. On the other hand, $\sigma$-electron donating substituents decrease the $\sigma-p_\pi$ difference and therefore the triplet is favored.\textsuperscript{17}
Figure 1.9: Illustration of the substituents' electronegativity effect on the ground state spin multiplicity of carbenes.

1.4.1.2 Mesomeric Effects

In comparison to the inductive effects of the substituents on the ground state spin multiplicity of some carbenes, the mesomeric effects play a more important rule on the stabilizing of either of the two ground state spin multiplicities. The substituents that interact with carbene centre can be categorized into two types of groups, X and Z, where X = π-electron donating groups, and Z = π-electron withdrawing groups. Accordingly, the singlet state carbenes can be classified into highly bent carbenes (X-X), linear carbenes (Z-Z) and quasi linear carbenes (X-Z). The mesomeric effects of these carbenes involve the interaction between carbene orbitals (σ, pₓ or pₓ, pᵧ) and p or π orbitals of the two types of substituents. As shown in Figure 1.10, in the case of the bent carbenes (X,X), the singlet state is p referred due to the interaction between the vacant orbital pₓ on the carbene and the p orbital lone pairs on the substituent which leads to an increase in the energy.
level of the $p_\pi$ orbital whereas the $\sigma$ orbital of the carbene remains unchanged. This change in energy increases the energy gap $\sigma - p_\pi$ and therefore the singlet state is favored. The presence of $\pi$-electron donating group (X) generates a polarized four-electron three-centre $\pi$-system. The linear singlet carbenes (Z,Z) form from an interaction between the substituent vacant orbitals with the $p_y$ orbital. In this interaction, the $p_x$ orbital remains unchanged and therefore the ($p_x$, $p_y$) degeneracy is broken leading to a singlet state even if these carbenes are linear. The presence of these substituents results in a polarized three-centre two-electron bond. The last type, quasi-linear (X,Z) carbenes arises from the combination of both substituents X and Z. The X substituent lone pairs interact with the $p_y$ orbital, whereas the Z substituent vacant orbital interacts with the $p_x$ orbital. This interaction results in the singlet state being favored because the vacant $p_y$ orbital is destabilized, while the filled $p_x$ orbital is stabilized. This quasi-linear structure forms a polarized allene-type system.\[^{17}\]

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**Figure 1.10: Illustration of the polarized three-centre $\pi$-system\[^{17}\]**

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\[^{17}\] Refer to the original source for detailed images and explanations.
1.4.2 Steric Effects

The steric effects may influence the ground-state spin multiplicity in the absence of electronic effects. In carbenes of linear geometry, when the carbene frontier orbitals are degenerate, the triplet ground state will be favored. This can be obtained by increasing the steric effect which therefore increases the carbene bond angle resulting in a favored triplet ground state. For example, di(tert-butyl)- and diadamantylcarbenes have triplet ground states, however; dimethylcarbene shows a singlet ground state. Moreover, compounds such as cyclopentylidene and cyclopropenylidene have singlet ground states due to angular constraint and both angular constraint and aromaticity respectively.\(^{17}\)

1.5 N-Heterocyclic Carbenes

N-heterocyclic carbenes (NHCs) are one of the most studied carbenes types. The term NHC is commonly used to describe heterocyclic species that involve at least two nitrogen atoms linked to the carbon carbene centre with a general formula of \([\text{R}_2\text{N}]_2\text{C}^\cdot\]. These species have been widely recognized and broadly applied in fields of organocatalysis and organometallic, transition metals and main group chemistry. An early work was established by Wanzlick and Schönherr to prepare a metal-carbene complex without isolation of the free carbene, however; later in 1991 Arduengo et al. isolated the first carbene by addition of NaH and catalyst DMSO in THF to imidazolium chloride (Scheme 1.4).\(^{18,19}\)
Arduengo et al. attempted to identify the reason behind the stability of this carbene whether it is due to steric or electronic effects through the synthesis and isolation of stable carbenes with less hindrance effects of the N-substituents. They concluded that the stability of the carbenes was not due to just steric effects, but it could be electronic or a combination of both electronic and steric effects. Later in 1995, Arduengo and coworkers postulated that the stability of the carbenes could be due to the aromaticity of the imidazole ring, however; they were able to synthesize and isolate a carbene with a saturated imidazole ring confirming the aromaticity was not a main factor for the stability of the carbenes (Scheme 1.5).

Later work by Boehme and Frenking that involved theoretical studies used natural bond order (NBO) calculations and indicated the presence of $p_{\pi}-p_{\pi}$ delocalization between nitrogen atom and the carbene carbon on the ring framework. At the same time, Heinemann et al. published a detailed study proved that the stability of the carbenes is not related to the $p_{\pi}-p_{\pi}$ conjugation. They performed some isodesmic calculations on acyclic carbenes and aminocarbenes which suggested
that even when conjugation is not present, the carbene is still stabilized by the electron withdrawing properties of the neighboring nitrogen atoms, however; the conjugation is still an important factor that supports the stability of the carbenes.\textsuperscript{23}

1.6  \textbf{N-Heterocyclic Carbenes Complexes of p-Block Elements}

Even though N-heterocyclic carbenes with transition metals have been reported extensively, their adducts with main group elements have been also growing widely. Like NHC-metal complexes, interactions between \textit{p}-block elements and NHCs occur through \(\sigma\)-donation from the carbene orbitals to the \(\sigma\)-accepting orbitals of the low valent main group elements. These adducts own high stability which provide unique properties that promote the opportunity to investigate their bonding nature, reactivity and possible applications.\textsuperscript{24,25,26}

1.6.1 \textbf{Electronic Effects and Bonding in NHC-p-Block Complexes}

N-Heterocyclic carbenes contain nitrogen atoms adjacent to the carbene carbon that has a significant effect on the electronic properties of the carbene. The effect of the nitrogen atoms as \(\sigma\)-electron-withdrawing and \(\pi\)-electron-donating results in an increase in the energy gap between the frontier orbitals, which because of a decrease in the HOMO (\(sp^2\)-hybridized lone pair orbital, \(\sigma\)-orbital) energy and an increase in the LUMO (unoccupied \(p_\pi\) orbital) energy. This effect on the frontier orbitals controls different properties of the carbene such as the high stability, nucleophilicity and \(\sigma\)-donor and \(\pi\)-acceptor abilities.
N-Heterocyclic carbenes complexed to main group elements possess an interesting three types of bonding as shown in Figure 1.12. Structure (I), single dative covalent $C_{\text{NHC}}$–$E$ bond, represents the ylide resonance form where there is no $\pi$-back contribution from $E$. Structure (II), double bond between NHC and $E$, represents the ylene resonance form. Structure (III), dative bond between NHC and $E$, represents donor-acceptor complex form.

The relative contribution of structures (I) and (II) relies on the $\pi$-back electron donation of $E$ and the $\pi$-accepting properties of the carbene. In the case of light elements such as C, N and O the classic double bond $C$=$E$ is the dominant (ylene structure), whereas; for the heavy elements,
the decrease towards the hybridization causes dative covalent bond to be the favorable (ylide structure). The structure (III) is a single dative bond and it is different form structure (I) and it occurs between a doubly filled valence orbital of the carbene and a vacant valence orbital of E.\textsuperscript{42}

Sharing double bonds can be formed between E and a triplet state of the carbene, while dative double bonds can be found in the case of E with singlet carbenes. Singlet carbenes might form sharing double bonds as well if the carbene has high π-acidic properties (e.g. CAAC; Cyclic Alkyl Amino Carbene) and E is lighter element with high electronegativity such as O and N.\textsuperscript{27,42}

1.6.2 NHC-Stabilized Phosphorus(I) Cations

The chemistry of N-heterocyclic carbenes with phosphorus has been known since 1964 (although it was not considered in that context until much later), when Dimroth and Hoffmann discovered two-coordinate phosphorus compounds, known as phosphacyanines\textsuperscript{68} (b)(Scheme 1.6). This discovery is an important development in phosphorus and main group element chemistry. The compounds were synthesized by reacting 2-chlorobenzothiazolium salts (a) with tris(hydroxymethyl)phosphine or reacting the same salt (a) with tris(trimethylsilyl)phosphine. The phosphacyanine salt possesses unique features that involve the near co-planarity of the two benzothiazole rings as the twisting angle is 3° and a short S—S distance which suggests a significant interaction between the two atoms.

In 1983, Schmidpeter and co-workers\textsuperscript{69} described a new route to the synthesis of phosphacyanine salts by the reaction of bis(imidazolidin-2-ylidenes) (c) with triphosphinenium salt. It was suggested that the reaction involved an insertion of a phosphorus (I) fragment into the C═C double bond and loss of two phosphine molecules.
More recently, Macdonald and co-workers have developed a novel strategy to produce similar systems by employing NHCs in their synthesis (Scheme 1.7). First, they reacted 3 equivalents of the corresponding carbene with phosphorus trichloride and produced phosphacyanine adduct, however; the method has some deficiency due to the difficulty with purification as the product and by-product has similar solubility. Accordingly, a new approach was used to overcome the problem of removing the by-product by utilizing triphosphonium salt \([(dppe)P][X]\) \([dppe = 1,2\text{-bis}(diphenylphosphino)ethane]\) with the carbene to produce the product and the by-product dppe which is easy to remove in this case by washing with non-polar solvents.
They found that this method seems to work with carbenes with small alkyl substituents ($R_1 = \text{Et, } \text{^3Pr}$) on nitrogen atoms, but bulkier substituents ($R_1 = \text{tBu, adamantyl}$) did not form the target product. They presented the experimental data of the cations and showed a significant $^{31}\text{P}$ NMR chemical shifts appear in high field region (-124.2 to -129.2 ppm). In addition, the structural features which involve elongation in the bonds $\text{P—C}$ 1.823(2) and 1.824(2) Å and small twisting in $\text{C—P—C}$ angle of 97.35(9)$^\circ$ as well as the established computational investigations proved that these cations contain a phosphorus(I) centre.
Additional phosphorus cations involving cyclic bis(NHC)-stabilized P(I) cations and P-thiazol-2-ylidene salts (SNHC-P(III)), Figure 1.13 (c) were also prepared by the Macdonald group using the same triphosphonium salt as a phosphorus source. The cyclic cations bear a P(I) centre based on the $^{31}$P NMR chemical shifts at high field (82 ppm) and also the theoretical calculations proved the presence of two electron pairs on the phosphorus atom similar to that for acyclic analogues. However, in case of P-thiazol-2-ylidene salts, $^{31}$P NMR signals were shifted more downfield (77 ppm) and the theoretical studies proved the presence of one lone pair of electrons on the phosphorus atom, which supports the assignment as P(III). The reactivity of phosphorus centre in
the acyclic and cyclic NHC and their analogues SNHC were tested through the reaction with various transition metals and towards some oxidizing agents such as sulfur, triflic acid and methyl triflate (Figure 1.14).²⁹,⁴²

![Chemical structures](image)

**Figure 1.14: Compounds of P(I) cations with oxidizing agents and transition metals, M=Cr, Co, W.**⁴²

Early in the 1980s, phosphaalkenes which include benzimidazolin-2-ylidene phosphine and mono and diamino adducts were reported.⁷¹ These phosphaalkenes possess an ylidylic resonance structure due to the π-donation of the nitrogen atoms leaving a negative charge on the phosphorus atom (dative bond). Such ylidylic structures exhibit high-field resonance shift of the phosphorus and increase the bond distance between the carbene carbon and phosphorus. These structures have advantages in the phosphinidene transfer reactions that require the cleavage of a C—P dative bond.
1.7 NHC Complexes of Group 16 Heavy Elements:

Numerous NHCs containing chalcogen elements (S, Se, Te) have been synthesized and characterized, in addition to the studies performed to understand the nature of carbene—chalcogen interactions. Most NHC-Chalcogen compounds that are well known are the adducts represented by the mono-coordination to a chalcogen atom. These adducts are called chalcogenones or chalcogeno-ureas. Compounds such as acyclic chalcogenones (R₂C=Ch, R = Alk, Ar) comprise a C═Ch double bond found to be less stable with heavier chalcogens (S, Se, Te) which is a result of the low tendency towards hybridization that in turn lowers the overlap between the 2p orbitals of the carbene carbon and np orbital of the chalcogen. However, in the case of CNHCs—Ch bond showed higher stability due to the conjugation with the nitrogen atoms on the ring framework and therefore a contribution of the ylidic resonance form is the dominant.⁷²

Numerous free NHCs or those generated in situ have been reacted with sulfur, selenium and tellurium to produce the corresponding NHC-Ch adducts. ³⁰,³¹,³²,³³,³⁴,³⁵,³⁶,³⁷,³⁸ Thione adducts were well recognized compounds as they exhibit straightforward synthetic methods and therefore act as accessible starting materials in various synthetic processes. ³⁹,⁴⁰,⁴¹ The reported CNHC-Ch bond distance increases as going down the group of the periodic table. The CNHC-Ch bond distances are (1.66−1.69 Å), (1.82−1.86 Å) and (2.050−2.087 Å) where Ch = S, Se and Te respectively.⁴² The ⁷⁷Se NMR chemical shifts of NHC–Se adducts are used to assess the π-accepting properties of various derivatives of NHCs. ³⁵,³⁶,⁴³ A number of NHC-thiones showed interesting biological behaviors in the medicinal field in addition to their attracting applications in the transition metal and main group chemistry which has led to more attention to develop the chemistry of the heavier analogues. ³¹,⁴⁴,⁴⁵
Scheme 1.8: Preparation of NHC-Chalcogen compounds, Ch = S, Se and Te

Protonation and methylation of NHC-Chalcogens using triflic acid and methyl triflate were reported and stable compounds were isolated. The $C_{NHC}$-Ch bond distance is longer than the parent chalcogens and $^{77}$Se NMR and $^{125}$Te NMR spectra, showed more down-field chemical shifts than that of the parent adducts that was interpreted as being indicative of a decrease in the electron density on the elemental chalcogens.\textsuperscript{46} NHC-supported chalcogen dications $[\text{NHC}_2\text{Ch}]^{2+}$ were reported, and these compounds mimic NHC-stabilized phosphorus(I) cations $[(\text{NHC})_2\text{P}]^+$. The first adduct of this category of compounds was the sulfur compound (a) in Figure 1.15. The compound was synthesized via methylation of nitrogen atoms of the bis-heterocycle sulfide adduct using methyl triflate. The compound $[(\text{IMe}_4)_2\text{S}][\text{SbCl}_6]$; Figure 1.15(b) was obtained accidently by refluxing a mixture of the thione (IMe$_4$)S and dimethylformamide.\textsuperscript{47} Di-coordinated Se and Te adducts were obtained by a transfer of the corresponding chalcogen from diazabutadiene ligand to two equivalents of the NHC ligand resulting in the dication adduct. $C_{NHC}$–Se bond distances are 1.915(3) and 1.920(3) Å which are shorter than the $C_{NHC}$–Te bond distances of 2.136(4) and 2.138(3) Å. The C–Te–C bond angle (91.5(1)°) is smaller than the C–Se–C angle (96.3(1)°) in the lighter homologue (Figure 1.15 (d)). However; the presence of 4 equivalents of the carbene yielded tetra-coordinated NHC-Te adduct (Figure 1.15 (c)). The dicordinate Se and Te adducts are coordinated through the chalcogen centre to the oxygen of the triflate anions. The bond distances $\text{Ch} \cdots \text{O}$ are (2.755 and 2.969Å) and (2.740 and 2.921Å) respectively.\textsuperscript{48,49}
Another interesting NHC-Ch adduct is the one with T-shaped geometry (Figure 1.16). The dicationic tris(selenone) complex is a unique example of these species and it is obtained by the oxidation of the corresponding selenone (IMe\textsubscript{2})Se with Cu(OTf)\textsubscript{2}.\textsuperscript{50} The C\textsubscript{NHC}–Se bond length is 1.885(4) Å similar to that of the starting selenone (IMe\textsubscript{2})Se (1.884(10) Å). The Se–Se–Se bond angle is 174.11(2)°, and the average Se–Se bond length is 2.6501(8) Å.
The chemistry of five-membered N-heterocycle compounds is considerable and has found a variety of biological and industrial applications. Tetrazol (CH$_2$N$_4$), triazoles (C$_2$H$_3$N$_3$), and their substituted derivatives are the most important species within the five-membered N-heterocyclic compounds that display a significant and continuous development in different areas. Triazoles were first discovered by the scientist Bladin in 1885 and assigned the name triazole to the nitrogen carbon ring system and its derivatives. Triazole is a five-membered heterocyclic ring, which possesses three nitrogen atoms 1,2, or 1,2,3 positions. Triazole exhibits two isomer forms for each type (1,2,3-triazole and 1,2,4-triazole) (Figure 1.17).

Among these organic compounds, 1,2,4-triazoles have attracted researchers' attention due to their significant role in many aspects of the chemical industry in which they assisted to prevent the formation of fog in photographic emulsions as well as their use as herbicides and convulsants.
1,2,4-triazole derivatives are among the important five-membered heterocyclic species that have lower toxicity than imidazole derivatives.\textsuperscript{51}

1.8.1 Structural properties of 1,2,4-triazole

1,2,4-triazole shows a significant stability which could be mainly rationalized to the aromaticity of this ring. The molecule forms a $6\pi$ system through the two double bonds and one pair of electrons from a nitrogen atom. Also, the stability of the molecule could be a result of the tautomeric structures this molecule exhibits. The two tautomeric forms are $1H$-1,2,4-triazole and $4H$-1,2,4-triazole, and it was indicated that the isomer $1H$-1,2,4-triazole is more stable than the isomer $4H$-1,2,4-triazole. Tautomerization has been seen in substituted 1,2,4-triazoles as well (Figure 1.18). The compound 3-mercapto-1,2,4-triazole exhibits two tautomeric structures in which the hydrogen atom binds to a nitrogen atom forming thione or the hydrogen atom binds to sulfur atom forming thiol. The thione is the most favorable form. Chloro-1,2,4-triazole displays three tautomeric forms; 3-chloro-$1H$-1,2,4-triazole (most stable), 3-chloro-$4H$-1,2,4-triazole (least stable) and 5-chloro-$1H$-1,2,4-triazole. Also, 3-amino-1,2,4-triazole shows three tautomeric forms; 3-amino-$1H$-1,2,4-triazole (most stable), 3-amino-$2H$-1,2,4-triazole and 3-amino-$4H$-1,2,4-triazole (least stable).\textsuperscript{52}

The geometric and chemical properties similarity between triazoles and imidazoles, and the fact that 1,2,4-triazoles is a combination of pyrazoles and imidazoles (Scheme 1.9) have widely promoted the field of using these remarkable species in various areas\textsuperscript{56} and particularly in coordination chemistry\textsuperscript{57} as appealing ligands and thus offers exciting possibilities.
Figure 1.18: Tautomerization forms in substituted 1,2,4-triazoles.52

Scheme 1.9: Structural similarity between both imidazole and pyrazole, and triazole

1.8.2 Coordination Modes of Substituted 1,2,4-Triazole

Because of the presence of the donor atoms on both sides of the ring, and the heterocyclic \( \pi \)-conjugated system, these species are able to bridge transition metals and form different geometries depending on the donor atom of the ligand and the metal properties. This varied bonding mode is often found on nitrogen atoms N1 and N4 and even on the three nitrogen atoms, N1,N2, and N4 (Figure 1.19).53,54,55 While numerous multidentate of the unsubstituted 1,2,4- triazole complexes that form polymeric structures have been known, it is uncommon to find unsubstituted 1,2,4-triazoles acting as monodentate ligand which could be attributed to the poor solubility of the complexes or the production
of microcrystalline materials. Accordingly, substituted 1,2,4-triazoles were the target to derive more structures in the area of coordination chemistry which leads to higher opportunity to study their potential coordination modes and the possible applications.

There are usually four coordination modes of the substituted 1,2,4-triazole and are as the following:

a) N1, N2, N4-bridging mode; the three nitrogen atoms of the substituted 1,2,4-triazole coordinate to metal ions forming a planar system. In this case, presence of bulky substituents on positions C3 and C5 prevents 1,2,4-triazole from bridging the metal ions due to the hindrance effect. Series of complexes have been reported to show the monodentate ability such as complexes of 1,2,4-triazole with Zn(II) ion, Figure 1.20(a).

b) N1, N2-bridging mode; many substituted 1,2,4-triazoles have shown coordination of transition metals on nitrogen atoms on positions N1 and N2 especially when the position N4 or the positions C3 and C5 are occupied with other species. An example of such bridging exists in the compound
[Cd₃(ptr)₆(H₂O)₆](ClO₄)₆·2H₂O·2DMF·2C₂H₅OH (ptr = (m-phenol)-1,2,4-triazole), Figure 1.20(b).⁵⁷

c) N1, N2-bridging mode; this type of bridging mode is slightly found because by the reaction with transition metals the two isomers 1H-triazole and 4H-triazole present in solution, however; the isomer 4H-triazole is more stable, which gives the chance to the existence of N1, N2-bridging mode more than N2, N4-bridging mode. Such bridging is occurring in the complex [Cd(3atr)₂(H₂O)₂](SiF₆)₆, (3atr = 3-amino-1,2,4-triazole) as shown, Figure 1.20(c).⁵⁷

d) N1 or N2-bridging mode; this type of bridging is uncommon, and it exists when the other positions except N1 and N2 are occupied by other bulky groups and thus force the substituted 1,2,4-triazole to coordinate as monodentate ligand. Such a case is seen in the complex [Cd(2pytr)₂(NCS)₂]ₙ, (2pytr = 4-(pyrid-2-yl)-1,2,4-triazole), Figure 1.20(d).⁵⁸ In 1981, chromium and tungsten pentacarbonyl complexes with the mono substituted 4-methyl and 4-phenyl-1,2,4-triazole were reported where the triazole existed as a monodentate ligand.⁵⁸
1.8.3 Triazol-5-ylidenes

1,2,4-Triazole derivatives have also been involved in the synthesis of stable carbenes, 1,2,4-triazol-5-ylidenes which was first reported by Enders et al. in 1996.59 These carbenes possess incredible features such as high stability at a high temperature up to 125°C in oxygen and moisture free atmosphere and great σ-donor properties due to the electron density on the carbene carbon. The 1,2,4-triazol-5-ylidene, Figure 1.21(a) was prepared38 by deprotonation of the corresponding triazolium salt with NaOMe in MeOH to form 5-methoxytriazoline, Figure 1.21(b), and then MeOH was removed under reduced pressure at 80°C. 13C NMR (δ(C5) = 214.6ppm) and C5–N bond lengths (1.351(3) Å and 1.373(4)Å) and the small N–C5–N bond angle (100.6(2)1) are comparable with the unsaturated imidazol-2-ylidenes. The reactivity of the carbene was investigated towards insertion, addition and transition metals, main group elements and cycloaddition reactions proving its great nucleophilicity resembling the imidazolylidene carbenes.59,60 Other triazolyli-idenes were obtained from C5 deprotonation of triazolium salts, Figure 1.21(d, e) and used as nucleophiles in organocatalysis.61,62 Bertrand et al. prepared the 1,2,4-triazolium salt Figure 1.21(c)
and the efforts to isolate the free carbene upon deprotonation of the triazolium salt were not successful.\textsuperscript{63} Peris et al. prepared a diiridium complex by reaction of (c) with two equivalents of [IrCl(COD)]\textsubscript{2} in the presence of KOtBu. In addition, a heterobimetallic IrI/RhI complex was obtained by reaction of (c) with [IrCl(COD)]\textsubscript{2} and [RhCl(COD)], (COD = 1,5-cyclooctadiene).\textsuperscript{64}

In 2003, Korotkikh \textit{et al.} reported the synthesis of new 1,2,4-triazol-5-ylidenes from the corresponding triazolium salts (Figure 1.22).\textsuperscript{37} They prepared triazolium bromide salts by heating the 3,4-diaryl-1,2,4-triazols with 1-bromo adamantane in acetic acid, and then an ion exchange was applied to the bromide salts by using an aqueous solution of NaClO\textsubscript{4}. Two new convenient methods were used to prepare their triazolyldienes. First method, a suspension of the triazolium perchlorate was treated with potassium tert-butoxide in benzene. Second method, a solution of the triazolium perchlorate in acetonitrile was reacted with a 55% dispersion of sodium hydride in mineral oil. The yields they collected were similar to Enders' carbene. The reactivity of these species was investigated through different routes. They reacted the corresponding triazolyldiene compound with CH\textsubscript{3}CN via C-H insertion to form 1-(1-adamantyl)-3,4-diphenyl-5-cyanomethyl-5H-1,2,4-triazoline, which is the first results that involve the heteroaromatic carbene with CH\textsubscript{3}CN. As we mentioned in the previous part that Enders \textit{et al.} attempted the insertion reaction to C-H bond for their substituted phenyl triazolyldiene, however it was unsuccessful. In addition, they reacted the elemental sulfur and elemental selenium with the corresponding triazolyldiene and form thione and selenone adducts.\textsuperscript{37}
Figure 1.21: a) 5-methoxytriazoline; b) Enders's carbene 1,2,4-triazolylidene; c), d) and e) 1,2,4-triazolium salts.

Figure 1.22: Korotkikh's carbene 1,2,4-triazolylidene and its insertion reaction, $R_1 = C_6H_5$, $p$-$C_6H_4Br$; $R_2 = C_6H_5$, $\alpha$-$C_{10}H_7$, $p$-$C_6H_4Br$; $X = ClO_4^-$
1.9  Dissertation Overview

The synthesis and characterization of compounds containing low oxidation state atoms of p-block elements and the study of their reactivity have been the area of the interest of Macdonald group for several years. This dissertation contains the synthesis and characterization of new N-heterocyclic carbene stabilized P(I) compounds. Chapter 2 details the synthesis and characterization of a series of 1,4-dialkyl-1,2,4-triazolium iodide and tetraphenylborate salts featuring methyl, ethyl, isopropyl and benzyl substituents and their use as precursors, in conjunction with triphosphonium reagents, to generate 1,4-dialkyl-1,2,4-triazol-5-ylidene-stabilized phosphorus(I) ions. The structural and spectroscopic features of the products are compared to those of analogous ions featuring 1,3-imidazol-2-ylidene ligands. Chapter 3 explores the coordination chemistry of the generated 1,4-dialkyl-1,2,4-triazol-5-ylidene-stabilized phosphorus(I) ions involving reactions with both main group and transition metal electron acceptors. These compounds have different bonding modes in which they could coordinate via phosphorus atom or the unsubstituted nitrogen atoms on the framework of the triazole ring. To help explain the reactivity of 1,4-dialkyl-1,2,4-triazol-5-ylidene-stabilized phosphorus(I) ions and their bonding modes, computational chemistry is used for these compounds and imidazole-stabilized P(I) ions for acidity and stability comparison purposes. Chapter 4 includes the synthesis and characterization of 1,4-dialkyl-1,2,4-triazol-5-selenone compounds in order to examine the acidity of the corresponding carbenes. In addition to exploring the reaction of the carbenes with other p-block elements such as sulfur produced the respective thione and then examining their reactivity towards some of transition metals. Finally, Chapter 5 summarizes the previous chapters and includes some suggestions and aspects for future work.
1.10 References:


(3) Aylett, B. J. *Polyhedron* 1985, 4 (10), 1799.


Chapter 2: 1,2,4-Triazol-5-ylidene-Stabilized Phosphorus(I) Cations

2.1 Introduction

The discovery of the first “bottle-able” singlet carbenes in the late 80s and early 90s sparked a revolution in the field of ligand design.\textsuperscript{1,2} Although these divalent carbon donors were initially employed as phosphine mimics, they now comprise their own diverse family of compounds ranging from acyclic species to cyclic species with varying ring sizes and heteroatom compositions.\textsuperscript{3,4,5,6} N-heterocyclic carbenes (NHCs) in particular are probably most well-appreciated for their application as ligands in transition metal chemistry, \textsuperscript{7,8,9,10} but a significant number of main group-element NHC complexes have emerged in recent literature and these are now a topic of considerable interest within the inorganic chemistry community and more generally.\textsuperscript{11,12,13}

In regard to the stabilization of low-oxidation state phosphorus, carbene chemistry has proven particularly fruitful. The seminal work by Cowley and Arduengo on phosphinidene adducts (Figure 2.1a) illustrated that carbenes could indeed stabilize such reactive species in the form of adducts;\textsuperscript{14,15} a large variety of such complexes are now known even including adducts of the parent phosphinidene (PH).\textsuperscript{16,17,18,19} Similarly, Bertrand’s work on the activation of white phosphorus by various types of carbenes has yielded carbene-capped phosphorus(0) clusters ranging from one to twelve phosphorus atoms (Figure 2.1b);\textsuperscript{20,21,22,23} Robinson and Bertrand reported NHC- and cyclic (alkyl)(amino)carbene- (CAAC-) stabilized diphosphorus(0) species (Figure 2.1c), which can be oxidized to form remarkable radicals;\textsuperscript{22,24,25} and our group and others have discovered new routes to monoatomic carbene complexes of phosphorus(I) (Figure 2.1d).\textsuperscript{26,27,28,29,30}
Figure 2.1: (a) An NHC-phosphinidene adduct. (b) An NHC-capped P₄ cluster. (c) NHC-stabilized “diphosphorus”. (d) A phosphamethine cyanine cation (X = S, NR). (e) The nomenclature scheme for imidazol-2-ylidenes (IMIDs) used in this work; only one substituent label is used for compounds bearing identical alkyl substituents on both N atoms. (f) The nomenclature scheme for 1,4-dialkyl-1,2,4-triazol-2-ylidenes (TAZs) used in this work.

Many of these main group carbene compounds have garnered significant interest recently but it must be emphasized that some examples of these species had already been known for decades. The first examples of carbene-stabilized diphosphorus were given by Romanenko in 1985,³¹ although the carbenic nature of bis(alkylamino)carbene fragment was not fully appreciated at the time.³² Likewise, phosphamethine cyanine cations provided the first examples of monoatomic carbene-stabilized phosphorus(I),³³,³⁴,³⁵ but the carbenic nature of thiazolyl³⁶ and benzimidazolyl³⁷ fragments was similarly not recognized at the time of their discovery.

Using our research group’s modern and optimized synthetic approach to carbene-stabilized phosphorus(I) salts²⁶,²⁷,²⁸,³⁸ and the now-well-established library of carbenes, which are readily accessible by today’s standards, we present herein the synthesis of the first examples of 1,2,4-
triazolylidene- (TAZ-) stabilized phosphorus(I) ions. It must be emphasized that the crystalline so-called “Enders’ carbene” based on the TAZ framework was reported in 1995 and that this class of carbene has been mostly studied as organocatalysts in asymmetric synthesis. The use of such carbenes as ligands towards transition metals has been greatly overshadowed by the use of NHCs based on the 1,3-imidazol-2-ylidene (IMID) core, and there are few examples of TAZ-ligated main group moieties (consisting of a handful of borane adducts, selenones, and thiones). Figure 2.1, e and f depict the nomenclature scheme, which is used in the current work to distinguish between the different alkyl substituents on the given TAZ or IMID, respectively. When both substituents on the TAZ are the same (i.e. when $R_1=R_2$) only one group is represented (i.e. 1,4-dimethyl-1,2,4-triazol-4-ylidene is abbreviated to MeTAZ).

2.2 Experimental

Reagents and General Procedures. All manipulations were carried out using standard inert atmosphere techniques. 1-Methyl-1,2,4-triazole was purchased from Alpha Aesar and used without further purification and all other chemicals and reagents were obtained from Sigma Aldrich. [D$_3$]MeCN was dried with calcium hydride or phosphorus pentoxide, [D$_2$] dichloromethane and [D]chloroform were dried with phosphorus pentoxide. All other solvents were dried on a series of Grubbs’ type columns and were degassed prior to use. Cyclic triphosphonium salts ([dppe]P[Br]) and [(dppe)P][BPh$_4$], $i$PrIMID$^+$, 1-ethyl-1,2,4- triazole, and 1-isopropyl-1,2,4-triazole were all synthesized according to literature methods.

Instrumentation. NMR spectra were recorded at room temperature with Bruker Advance III 500 MHz, Bruker Advance Ultrashield 300 MHz, or Bruker Advance DPX 300 MHz spectrometers. Chemical shifts are reported in ppm relative to internal standards for $^1$H and $^{13}$C (the given
deuterated solvent) and external standards for $^{31}\text{P}$ (85% H$_3$PO$_4$) and $^{11}\text{B}$ (Et$_2$OBF$_3$). Coupling constants $|J|$ are given in Hz. Melting points were determined in sealed (under nitrogen) or open capillary tubes using an Electrothermal Mel-Temp® melting point apparatus. Elemental Analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a Perkin Elmer 2400 combustion CHN analyzer. High-resolution electrospray ionization mass spectrometry was performed at the McMaster Regional Centre for Mass Spectrometry.

**Theoretical Methods.** Calculations were performed with the Gaussian 09 suite of programs$^{50}$ using Compute Canada’s Shared Hierarchical Academic Research Computing Network (SHARCnet). Model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method$^{51,52,53}$ in conjunction with the TZVP basis sets for all atoms.$^{54,55}$ Geometry optimizations were started using models in which the relevant phosphorus, nitrogen, and carbon atoms were placed at the positions found experimentally using X-ray crystallography and the hydrogen atoms were placed in geometrically appropriate positions using Gaussview.$^{56}$ Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical information. Natural bond orbital (NBO) analyses$^{57}$ to determine orbital contributions, Wiberg Bond Indices and orbital energies were obtained using the routine included in the Gaussian distributions.$^{58}$ Summaries of the calculated results, including Cartesian coordinates are presented in the sections below.

**X-ray Crystallography.** Crystals for investigation were covered in Nujol®, mounted on to a goniometer head, and then rapidly cooled under a stream of cold N$_2$ of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were collected using the
APEXIII software suite\textsuperscript{59} with a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with Mo-K\(\alpha\) (\(\lambda = 0.71073\) Å) or Cu-K\(\alpha\) (\(\lambda = 1.54178\) Å) radiation. For each sample, data were collected at low temperature. APEXIII software was used for data reductions and SA-DABS\textsuperscript{60} was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX\textsuperscript{61} software suite as implemented in the WinGX\textsuperscript{62} or OLEX2\textsuperscript{63} program suites. Validation of the structures was conducted using PLATON.\textsuperscript{64}

**Preparation of 1,4-Dimethyl-1,2,4-triazolium Iodide, 2.1**

The spectroscopic properties of this salt are consistent with those previously reported.\textsuperscript{65} Crystals suitable for scXRD were obtained by slow evaporation of a DCM solution.

**Preparation of 1,4-Diethyl-1,2,4-triazolium Iodide, 2.2**

Ethyl iodide (15.808 g, 101.4 mmol) and potassium carbonate (6.002 g, 43.43 mmol) were added sequentially to a flask containing triazole (2.000 g, 28.96 mmol) and MeCN. The mixture was heated to 60 °C for 5 d. After cooling to room temperature, the suspension was filtered and all volatiles were removed from the filtrate under reduced pressure. Yield: 95% (6.983 g, 27.60 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a DCM solution. Mp: 85 °C. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}CN, 25 °C): \(\delta = 1.52\) [\(t, 3J_{H,H} = 1.5, NCH\textsubscript{2}CH\textsubscript{3}\)], 4.32 (q, \(3J_{H,H} = 7.5, 2\) H, NCH\textsubscript{2}CH\textsubscript{3}), 4.40 (q, \(3J_{H,H} = 7.5, 2\) H, NNCH\textsubscript{2}CH\textsubscript{3}), 8.77 (s, 1 H, NCH), 9.94 (s, 1 H, NCH). \textsuperscript{13}C NMR (300 MHz, CD\textsubscript{3}CN, 25 °C): \(\delta = 14.0\) (s, NCH\textsubscript{2}CH\textsubscript{3}), 15.1 (s, NNCH\textsubscript{2}CH\textsubscript{3}), 44.6 (s, NCH\textsubscript{2}CH\textsubscript{3}), 48.8 (s, NNCH\textsubscript{2}CH\textsubscript{3}), 142.8 (s, C3), 144.8 (s, C5). \textbf{HRESI-MS:} calcd. for C\textsubscript{6}H\textsubscript{12}N\textsubscript{3}
Preparation of 1,4-Diisopropyl-1,2,4-triazolium Iodide, 2.3

Isopropyl iodide (17.23 g, 101.4 mmol) and potassium carbonate (6.002 g, 42.42 mmol) were added sequentially to a flask containing triazole (2.000 g, 28.96 mmol) and MeCN. The mixture was heated to 60 °C for 5 d. After cooling to room temperature, the suspension was filtered and all volatiles were removed from the filtrate under reduced pressure. Yield: 68% (5.591 g, 19.88 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a DCM solution. Mp: 163 °C. \( ^1H \) NMR (300 MHz, CD\(_3\)CN, 25 °C): \( \delta = 1.58 \) [d, \( ^3J_{H,H} = 6.9, 6 \) H, NCH(C\(_3\)H\(_2\))], 1.60 [d, \( ^3J_{H,H} = 6.9, 6 \) H, NNCH(C\(_3\)H\(_2\))] (the two former doublets overlap and appear as a 1:2:1 triplet), 4.80 [sept, \( ^3J_{H,H} = 6.9, 1 \) H, NCH(CH\(_3\))], 4.83 [sept, \( ^3J_{H,H} = 6.9, 1 \) H, NNCH(CH\(_3\))], 8.88 (s, 1 H, NCH), 10.05 (s, 1 H, NCH). \( ^13C \) NMR (300 MHz, CD\(_3\)CN, 25 °C): \( \delta = 21.6 \) [s, NCH(CH\(_3\))], 22.7 [s, NNCH(CH\(_3\))], 53.5 [s, NCH(CH\(_3\))], 57.0 [s, NNCH(CH\(_3\))], 140.7 (s, C3), 143.7 (s, C5). HR-ESI-MS: calcd. For C\(_8\)H\(_{16}\)N\(_3\) [M – I]+ \( m/z = 154.1339 \), found: 154.1339. C\(_8\)H\(_{16}\)N\(_3\)I (281.137): C 33.08 (calcd. 34.18); H 5.48 (5.74); N 14.36 (14.95)%.

Preparation of 4-Isopropyl-1-methyl-1,2,4-triazolium Iodide, 2.4

A flask containing 1-methyltriazole (1.000 g, 12.03 mmol), isopropyl iodide (2.047 g, 12.04 mmol), and MeCN (20 mL) was heated to 60 °C overnight. After cooling to room temperature, all volatiles were removed under reduced pressure and the remaining material was triturated with Et\(_2\)O (20 mL) to give a white solid. Yield: 18% (0.535 g, 2.11 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a DCM solution. Mp: 178 °C. \( ^1H \) NMR (300 MHz, CDCl\(_3\), [M – I]+ \( m/z = 126.1026 \), found: 126.1027. C\(_6\)H\(_{12}\)N\(_3\)I (253.084): C 29.54 (calcd. 28.47); H 4.90 (4.78); N 15.37 (16.60)%.
25 °C): \(\delta = 1.73 \text{ [d, } J_{HH} = 7.2, 6 \text{ H, CH(CH}_3)_2\text{], 4.28 (s, 3 \text{ H, CH}_3\text{), 5.04 [sept, } J_{HH} = 7.2, 1 \text{ H, CH(CH}_3)_2\text{], 8.59 (s, 1 \text{ H, NCH}, 11.44 (s, 1 \text{ H, NCH})}]. \) 13C NMR (300 MHz, CDCl3, 25 °C): \(\delta = 23.2 \text{ [s, CH(}C\text{H}_3)_2\text{], 40.1 (s, CH}_3\text{), 53.5 [s, CH(CH}_3)_2\text{], 141.5 (s, C}_3\text{), 142.8 (s, C}_5\text{).} \) HR-ESI-MS: calcd. For C6H12N3 [M – I]⁺ \(m/z = 126.1026\), found: 126.1029. C6H12N3I (253.084): C 28.32 (calcd. 28.47); H 4.57 (4.78); N 16.29 (16.60)%.

**Preparation of 1-Ethyl-4-isopropyl-1,2,4-triazolium Iodide, 2.5**

A flask containing 1-ethyltriazole (1.332 g, 13.71 mmol), isopropyl iodide (2.331 g, 13.71 mmol) and MeCN (20 mL) heated to 60°C overnight. After cooling to room temperature, all volatiles were removed under reduced pressure and the remaining material was triturated with THF (20 mL) to give a white solid. Yield: 5% (0.195 g, 0.730 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a DCM solution. Mp: 168 °C. 1H NMR (300 MHz, CDCl3, 25 °C): \(\delta = 1.67 \text{ (t, } J_{HH} = 7.5, 3 \text{ H, CH}_2CH}_3\text{), 1.74 [d, } J_{HH} = 6.6, 6 \text{ H, CH(CH}_3)_2\text{], 4.62 (q, } J_{HH} = 7.5, 2 \text{ H, CH}_2CH}_3\text{), 5.06 [p, } J_{HH} = 6.6, 1 \text{ H, CH(CH}_3)_2\text{], 8.45 (s, 1 \text{ H, NCH}, 11.75 (s, 1 \text{ H, NCH})}. \) 13C NMR (300 MHz, CDCl3, 25 °C): \(\delta = 14.0 \text{ (s, CH}_2CH}_3\text{), 22.7 [s, CH(CH}_3)_2\text{], 48.9 (s, CH}_2CH}_3\text{), 53.6 [s, CH(CH}_3)_2\text{], 141.6 (s, C}_3\text{), 143.8 (s, C}_5\text{).} \) HR-ESI-MS: calcd. for C7H14N3 [M – I]⁺ \(m/z = 140.1182\), found: 140.1182. C7H14N3I (267.11): C 31.04 (calcd. 31.48); H 5.17 (5.28); N 15.28 (15.73)%.

**Preparation of 1,4-dibenzyl-1,2,4-triazolium bromide, 2.6**

MeCN solvent was added to a flask contains sodium hydroxide (0.200 g, 5.000 mmol) and left under stirring for 10 min. Triazole (0.346 g, 5.000 mmol) was added and the mixture was left to stir for 1 hour at room temperature. (2.060 g, 12.00 mmol) of benzyl bromide was added and
the mixture was heated to 65°C for 24 h. After cooling to room temperature, the suspension was filtered and all volatiles were removed from the filtrate under reduced pressure. The white material collected was rinsed with ethyl acetate solution to remove impurities. Yield: 62% (1.022 g, 3.100 mmol). $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 5.68 (s, 2 H, NCH$_2$Ph), 5.74 (s, 2 H, NNCH$_2$Ph), 7.41 (m, 4 H, H-Ar), 7.55 (m, 6 H, H-Ar), 8.42 (s, 1 H, NCH), 11.96 (s, 1 H, NNCH). $^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 52.20 (s, NCH$_2$Ph), 56.4 (s, NNCH$_2$Ph), 129.3-132.1 (m, Ar-C), 142.7 (s, C3), 143.8 (s, C5).

**Preparation of 1,4,5-tribenzyl-1,2,4-triazolium bromide, 2.7**

Benzyl bromide (17.33 g, 101.0 mmol) and potassium carbonate (6.002 g, 43.00 mmol) were added sequentially to a flask containing triazole (2.000 g, 28.95 mmol) and MeCN. The mixture was heated to 60 °C for 24 h. After cooling to room temperature, the suspension was filtered and all volatiles were removed from the filtrate under reduced pressure. Yield: 61% (7.393 g, 28.95 mmol). Crystals suitable for scXRD were obtained from MeOH/acetone solvent combination. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 4.99 (s, 2 H, C(3)CH$_2$Ph), 5.58 (s, 2 H, NCH$_2$Ph), 5.64 (s, 2 H, NNCH$_2$Ph), 6.71 (d, $^3$J$_{H,H}$ = 7.4, 2 H, H-Ar), 7.31-7.10 (m, 13 H, H-Ar), 9.3 (s, 1 H, NCH). $^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 30.7 (s, C(3)CH$_2$Ph), 51.6 (s, NCH$_2$Ph), 55.8 (s, NNCH$_2$Ph), 128.29-132.39 (m, Ar-C), 144.3 (s, C3), 152.5 (s, C5).

**Preparation of N,N-Dialkyl-1,2,4-triazolium Tetraphenylborates**

The compounds were synthesized by anion exchange with sodium tetraphenyl borate in deionized water. Once precipitated from water, the BPh$_4$ salts were filtered and washed with diethyl ether and dried under reduced pressure for several hours.
Preparation of \(\text{[(iPrTAZ)}_2\text{P}][\text{BPh}_4]\), 2.8

A solution of K\(_{tBuO}\) (0.040 g, 0.36 mmol) in THF (10 mL) was added to a stirring solution of \(\text{[iPrTAZ]}[\text{BPh}_4]\) (0.170 g, 0.359 mmol) in THF (15 mL), resulting in the formation of a colorless precipitate. After 30 min of stirring, a solution of [dppeP][BPh\(_4\)] (0.134 g, 0.179 mmol) in THF (10 mL) was added, resulting in a yellow mixture. After 2 h of stirring, the white precipitate was filtered off, and the filtrate was concentrated to approximately 5 mL. Et\(_2\)O (50 mL) was added to precipitate the product, which was collected by filtration, washed with Et\(_2\)O (3 \times 5 mL) and dried under reduced pressure. This material may be further purified by dissolving in DCM and filtering off trace amounts of [K][BPh\(_4\)]. Yield: 56% (0.065 g, 0.101 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a \([\text{D}_3]\)MeCN solution. Mp: 168 °C (dec). \(^1\)H NMR (300 MHz, CD\(_3\)CN, 25 °C): \(\delta = 1.36 \) [d, \(^3\)J\(_{H,H} = 6.6\), 12 H, NCH(CH\(_3\))\(_2\)], 1.43 [d, \(^3\)J\(_{H,H} = 6.9\), 12 H, NNCH(CH\(_3\))\(_2\)], 4.49 [dsept, \(^3\)J\(_{H,H} = 6.6\), \(^4\)J\(_{H,P} = 2.7\), 2 H, NCH(CH\(_3\))\(_2\)], 4.62 [dsept, \(^3\)J\(_{H,H} = 5.0\), \(^4\)J\(_{H,P} = 1.5\), 2 H, NNCH(CH\(_3\))\(_2\)], 6.84 (m, 4 H, BPh\(_4\)), 7.00 (m, 8 H, BPh\(_4\)), 7.28 (m, 8 H, BPh\(_4\)), 8.56 (s, 2 H, NCH). \(^1\)B NMR (500 MHz, CD\(_2\)Cl\(_2\), 25 °C): \(\delta = -5.4\) (s, BPh\(_4\)). \(^{13}\)C NMR (500 MHz, CD\(_3\)CN, 25 °C): \(\delta = 21.4\) [s, NCH(CH\(_3\))\(_2\)], 22.2 [s, NNCH(CH\(_3\))\(_2\)], 52.4 [d, \(^3\)J\(_{C,P} = 6.9\), NCH(CH\(_3\))\(_2\)], 55.0 [d, \(^3\)J\(_{C,P} = 5.2\), NNCH(CH\(_3\))\(_2\)], 122.7 (s, BPh\(_4\)), 126.5 (m, BPh\(_4\)), 136.6 (m, BPh\(_4\)), 142.7 (s, NCHN), 161.7 (d, \(^1\)J\(_{C,P} = 102\), PCN), 164.7 (q, \(^1\)J\(_{C,B} = 49.2\), BPh\(_4\)). \(^{31}\)P\(_{\{\text{H}\}}\) NMR (300 MHz, CD\(_3\)CN, 25 °C): \(\delta = -125.9\) (s). HR-ESI-MS: calcd. For C\(_{16}\)H\(_{30}\)N\(_6\)P \([\text{M} - \text{BPh}_4]\)^+ \(m/z = 337.2264\), found: 337.2267. C\(_{40}\)H\(_{50}\)N\(_6\)PB (656.648): C 74.02 (calcd. 73.16); H 8.07 (7.67); N 12.31 (12.8)%.
Preparation of \([i^{Pr}{\text{IMID}}H]^2\text{P}[\text{BPh}_4]\), 2.9

A solution of \([\text{dppeP}][\text{BPh}_4]\) (0.368 g, 0.492 mmol) in THF (10 mL) was added to a stirring solution of 1,3-diisopropylimidazol-2-ylidene (0.075 g, 0.493 mmol) in THF (15 mL). After stirring for 30 min, \(\text{Et}_2\text{O}\) (40 mL) was added and the yellow precipitate was tritutrated twice with \(\text{Et}_2\text{O}\) (10 mL). After drying under reduced pressure, MeCN was used to wash the solid and remove excess \([\text{dppeP}][\text{BPh}_4]\), giving the product as a yellow powder. Yield: 80% (0.128 g, 0.196 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a DCM solution. Mp: 205 °C (dec). \(^1\text{H NMR}\) (300 MHz, \(\text{CD}_3\text{CN}, 25^\circ\text{C}\)): \(\delta = 1.27 \ [d, \ 3J_{\text{H,H}} = 6.9, \ 24 \text{ H}, \ \text{NCH(CH}_3)_2] \), \(4.82 \ [d\text{sept}, \ 3J_{\text{H,H}} = 6.9, \ 4J_{\text{H,P}} = 3.6, \ 4 \text{ H}, \ \text{NCH(CH}_3)_2], \ 6.88 \ (m, \ 4 \text{ H}, \ \text{BPh}_4), \ 7.03 \ (m, \ 8 \text{ H}, \ \text{BPh}_4), \ 7.06 \ (s, \ 4 \text{ H}, \ \text{H}_{\text{imid}}), \ 7.31 \ (m, \ 8 \text{ H}, \ \text{BPh}_4) \). \(^{11}\text{B NMR}\) (500 MHz, \(\text{CD}_2\text{Cl}_2, 25^\circ\text{C}\)): \(\delta = -6.1 \). \(^{13}\text{C NMR}\) (500 MHz, \(\text{CD}_2\text{Cl}_2, 25^\circ\text{C}\)): \(\delta = 22.7 \ [s, \ \text{NCH(CH}_3)_2], \ 52.1 \ [d, \ 3J_{\text{C,P}} = 7.5, \ \text{NCH(CH}_3)_2], \ 119.1 \ (d, \ \text{NCHCHN}), \ 122.2 \ (s, \ \text{BPh}_4), \ 126.0 \ (m, \ \text{BPh}_4), \ 136.3 \ (s, \ \text{BPh}_4), \ 157.4 \ (d, \ 1J_{\text{C,P}} = 99.2, \ \text{PCN}), \ 164.4 \ (q, \ 1J_{\text{C,H}} = 49.3, \ \text{BPh}_4) \). \(^{31}\text{P NMR}\) (300 MHz, \(\text{CD}_3\text{CN}, 25^\circ\text{C}\)): \(\delta = -133.7 \ (\text{pent}, \ 4J_{\text{P,H}} = 3.5) \). \(\text{HR-ESI-MS: calcld. for C}_{18}\text{H}_{32}\text{N}_4\text{P}[\text{M – BPh}_4]^+ m/z = 335.2359, found: 335.2365. C}_{42}\text{H}_{52}\text{N}_4\text{PB} (654.672): C 77.05 (calcd. 77.05); H 8.26 (8.01); N 8.57 (8.56)\%.

2.3 Results and Discussion

A typical route for the preparation of free triazole-5-ylidenes involves the deprotonation of a suitable triazolium precursor. We were surprised to see that very few 1,4-dialkyl-1,2,4-triazolium iodide salts with small substituents had been reported, and that none had been structurally characterized. To fill this apparent gap, we prepared and fully characterized those precursors including single-crystal X-ray diffraction in most cases. The synthesis of the 1,4-dialkyl-1,2,4-triazolium
iodide salts was conveniently accomplished using established methods, wherein the given 1-alkyl-1,2,4-triazole was heated with the chosen iodoalkane to 60 °C in acetonitrile (MeCN). After workup, the resultant salts are collected as white solids, and material suitable for single-crystal X-ray diffraction (scXRD) was grown by evaporation of dichloromethane (DCM) solutions (see the Experimental Section for details). The NMR chemical shift data for these salts are similar to those of other reported examples and metrical parameters and crystallographic data of the cations (depicted in Figure 2.2) are summarized in Tables 2.1, 2.2 and 2.3.

With these TAZ precursors in hand, we attempted to employ an in-situ approach for the generation of the desired TAZ-stabilized phosphorus(I) salts. We have observed previously that the triphosphenium precursor [dppeP][Br] is not indefinitely stable in the presence of strong bases (like potassium hydride and potassium hexamethyldisilazide), so a stepwise, one-pot reaction was attempted first. We started with the methylated derivative 1,4-dimethyl-1,2,4-triazolium iodide [MeTAZ][I], treating this salt with potassium tert-butoxide in tetrahydrofuran (THF) as the first step. Very little change was observed since both reagents and products (MeTAZ, and potassium iodide) are colorless. The reaction mixtures were stirred for several hours at room temperature and then one half equivalent of [dppeP][Br] was added to the mixture (Scheme 1). This addition resulted in an immediate color change to pale yellow in each case. We have observed previously that such ligand exchange reactions with both bromide and iodide counter anions typically generate iodide salts of the desired PІ cations. [In this work, valence states are indicated using a superscripted Roman numeral (e.g. PІ means “univalent”), whereas formal oxidation states are indicated with parentheses, e.g. phosphorus(I).] In anticipation of the formation of such a product, the precipitate was extracted into DCM and then precipitated through the addition of diethyl ether (Et₂O) to produce a pale-yellow material.
Scheme 2.1 Synthesis of TAZ-stabilized P^I salts. When X = I, Br, there are significant amounts of triazolium salt remaining. When X = BPh₄, pure material can be isolated.

Table 2.1: Selected bond lengths /Å and angles /° of the triazolium cations depicted in Figure 2.2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>[MeTAZ]^+</th>
<th>[EtTAZ]^+</th>
<th>[PrTAZ]^+</th>
<th>[MePrTAZ]^+</th>
<th>[EtPrTAZ]^+</th>
<th>[BzTAz]^+</th>
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<td>C5—N4</td>
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<td>1.334(4)</td>
<td>1.328(4)</td>
<td>1.334(4)</td>
<td>1.328(4)</td>
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<td>1.315(9)</td>
<td>1.316(5)</td>
<td>1.309(4)</td>
<td>1.313(4)</td>
<td>1.325(4)</td>
<td>1.324(3)</td>
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<tr>
<td>N4—C3</td>
<td>1.370(10)</td>
<td>1.358(5)</td>
<td>1.359(4)</td>
<td>1.358(4)</td>
<td>1.364(5)</td>
<td>1.360(2)</td>
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<tr>
<td>N1—N2</td>
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<td>1.366(4)</td>
<td>1.362(4)</td>
<td>1.367(4)</td>
<td>1.361(5)</td>
<td>1.372(2)</td>
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<tr>
<td>N2—C3</td>
<td>1.305(11)</td>
<td>1.303(5)</td>
<td>1.298(5)</td>
<td>1.300(4)</td>
<td>1.308(5)</td>
<td>1.303(3)</td>
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<tr>
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<td>105.9(3)</td>
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Table 2.2: Summary of crystallographic data for the triazolium cations depicted in Figure 2.2

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<td>b/Å</td>
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<td></td>
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# Table 2.3: Summary of crystallographic data for the triazolium cations depicted in Figure 2.2

<table>
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<th>Identification code</th>
<th>[Me_iPrTAZ-H][I] 2.4</th>
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<th>[BzlTAZ-Bzl-H][Br] 2.7</th>
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Figure 2.2: Thermal ellipsoid plot (50% probability surface) of 1,4-dialkyl-1,2,4-triazolium iodide salts and 1,4,5-tribenzyl-1,2,4-triazolium bromide. Hydrogen atoms and iodide anions are omitted for clarity. Selected bond lengths /Å and angles /° are summarized in Table 2.1
$^{31}$P NMR spectroscopy revealed that the desired cation had indeed been formed and that the dppe by-product had been completely removed using the afore mentioned protocol. The chemical shift for the cation appearing at −116 ppm is consistent with a highly shielded phosphorus environment, as one would anticipate for such inversely polarized phospha-alkenes; the chemical shift data are comparable to those of related cations. Unfortunately, $^1$H NMR spectroscopy revealed that a significant amount of [MeTAZ]$^+$, 2.1 was also present in the sample. Because of the similar solubilities of these two species, the complete purification of the desired TAZ-stabilized iodide salts was not possible in our hands.

Nevertheless, we attempted crystallizations of the crude solid in the hopes that it would furnish single crystals of the TAZ-stabilized phosphorus(I) iodide salt we had targeted. We were indeed able to obtain suitable material for one of these: the salt [(Me$_2$TAZ)$_2$P][I] recrystallizes from DCM in the space group C2/c and the molecular structure of the cation and relevant metrical parameters are given in Figure 2.3 and Table 2.4. The phosphorus atom sits on a 2-axis and the crystallographically identical P–C bonds of 1.795(4) Å and the C–P–C angle of 95.1(2)° are similar to those of closely related IMID-stabilized $^1$P cations bearing N-methyl substituents. Likewise, the twisting of the heterocycles from the C–P–C planes of 41.4° is consistent with the 36–48° found in the most analogous IMID-stabilized $^1$P cations. It is also worthy of note that the NN fragment within each triazolyl ring is oriented approximately anti to the inferred σ-type lone pair on the phosphorus atom.
Given that the impure material from these reactions was not ideal for further study in terms of reactivity or characterization, we sought a better approach for the preparation and isolation of pure material. Recognizing that the starting materials ([\text{MeTAZ}]^+[^I] and [dppeP][Br]) are quite insoluble under the given reaction conditions, we posited that increasing the solubility of these ions could improve the reaction outcomes. Thus, the halide anions in each of the starting reagents were exchanged to produce the corresponding tetraphenylborate (BPh\textsubscript{4}) salts, which are much more soluble in THF.

With these new salts in hand, the same synthetic protocol was reinvestigated. We observed that when a THF solution of K\text{tBuO} is added to a solution of [\text{PrTAZ}][BPh\textsubscript{4}] in THF, precipitation of potassium tetraphenylborate ([K][BPh\textsubscript{4}]) as a white solid occurs. After stirring for a few minutes, addition of the [dppeP][BPh\textsubscript{4}] THF solution results in the formation of a yellow mixture. Filtration of this mixture (to remove [K][BPh\textsubscript{4}]) and precipitation with Et\textsubscript{2}O provides a pale yellow material of similar appearance to that obtained from the reaction of the halide salts, but \textsuperscript{1}H NMR spectroscopy of the precipitate exhibits almost no unreacted triazolium salt. This observation suggests that solubility plays an important role in the deprotonation step and perhaps the P\textsuperscript{+} transfer...
step as well. Extraction into DCM followed by filtration (to remove residual [K][BPh₄]) and recrystallization provided the analytically pure material which we sought, Figure 2.4. Proton NMR spectra of the material collected from the reaction involving the isopropyl-substituted triazolium with halide salts (blue) and with BPh₄ (green) are shown in Figure 2.5 to exemplify the improvement conferred by the use of the BPh₄ salts. Specifically, the signals for the C3 and C5 protons (which integrate to 1:1) overlap the one C3 proton environment of [(iPrTAZ)₂P]⁺, 2.8. The presence of the triazolium contaminant can also be inferred from the presence of multiple isopropyl methine proton signals between δ = 4 and 5 ppm.

**Figure 2.4:** Thermal ellipsoid plot (50% probability surface) of [(iPrTAZ)₂P][BPh₄], 2.8. Hydrogen atoms are omitted for clarity
Figure 2.5: Proton NMR spectra of the material isolated from the reaction outlined in Scheme 1 (for R = iPr) after the described workup. The top (blue) spectrum represents when X = I, Br and the bottom (green) spectrum represents when X = BPh₄ (i.e. the product is pure [(iPrTAZ)₂P][BPh₄], 2.8).

Based on the success obtained to produce pure [(iPrTAZ)₂P][BPh₄], 2.8, we attempted to follow the same procedure using the other triazolium tetraphenyl borate with other alkyl groups, however; unreacted triphosphenium precursor [dppeP][BPh₄] and the triazolium salts still appeared in the ³¹P NMR and ¹H NMR spectra. An effort to obtain crystals from these attempts led us to grow crystals of the compound [(EtTAZ)₂P][BPh₄], 2.10 recrystallized from MeCN in the space group P-1 and the molecular structure of the cation and relevant metrical parameters are given in Figure 2.6 and Table 2.4. Another protocol was used as well to overcome the presence of unreacted [dppeP][BPh₄] and triazolium salts by the addition of an excess of the base to ensure that all triazolium salt has converted to the carbene and then followed by adding less equivalents of [dppeP][BPh₄] to avoid any unreacted molecules of it. According to the observations through the synthesis of TAZ-P(I) derivatives, 1,4-diisopropyl-1,2,4-triazole-stabilized phosphorus(I) compound is the most accessible adduct to run further chemistry in order to investigate their reactivities.
In this chapter, in addition to the synthesis of 1,4-dialkyl-1,2,4-triazolylidene stabilized P(I) adducts where the carbene acts as a mono chelating reagent, we also tried to explore the ability of our 1,2,4-triazolylidenes as bis chelating reagents to stabilize P(I) centres. 1,1'-methylene-bis(4-methyl-1,2,4-triazolium) dibromide, 1,1'-methylene-bis(4-n-butyl-1,2,4-triazolium) dibromide and 1,1'-methylene-bis(4-benzyl-1,2,4-triazolium) dibromide were prepared according to the literature procedures\textsuperscript{70} for the methyl substituted adduct with some modifications and by following a similar manner for the other two salts with butyl and benzyl substituents.

In contrast to the work that was established in our lab to synthesize bis-NHC adducts using imidazoles, the procedure to obtain these products was not straightforward and their products are temperature-sensitive (decompose at room temperature). Since the synthesis of 1,2-dialky-1,2,4-
triazolylidene-stabilized P\textsuperscript{I} adducts are not straightforward, therefore; our attempts were all performed at low temperatures (-76°C). Deprotonation of 1,1'-methylene-bis(4-methyl-1,2,4-triazolium) dibromide with a base in dry THF solvent produced a yellow solution immediately and upon stirring for 10 min it turned to orange. A cold solution of triphosphenium salt in THF was added to this and left to stir for 1hr. \textsuperscript{31}P NMR spectra of the orange solution showed no peaks for the expected product. We decided to use ligands with larger alkyl groups such as butyl and benzyl as those exhibited excellent results with imidazoles. Thus, same method and under same conditions were applied to synthesize butyl and benzyl derivatives of the bis-chelating 1,2,4-triazoles in an attempt to produce the target products. Indeed, \textsuperscript{31}P NMR showed peaks of the targeted products at -87.8 and -86.8 ppm for 1,1'-methylene-bis(4-\textit{n}-butyl-1,2,4-triazolylidene-stabilized P\textsuperscript{I} and 1,1'-methylene-bis(4-benzyl-1,2,4-triazolylidene-stabilized P\textsuperscript{I} adducts respectively, however impurities of phosphonium salt and oxidized by-products were present which were difficult to remove and prevented further characterizations. The \textsuperscript{31}P NMR of these products are comparable with what was reported for the chelating bis-imidazole-stabilized P\textsuperscript{I} adducts at -83.1 and -81.8 ppm for butyl and benzyl substituted adducts respectively.

Compared to those isopropyl-substituted IMID-stabilized P\textsuperscript{I} ions, which we have already reported, the \textsuperscript{31}P NMR chemical shift of [(\textit{i}Pr\textit{TAZ})\textsubscript{2}P][B\textit{Ph}_4], \textbf{2.8} found at –126 ppm is identical to that of the cation [(\textit{i}Pr\textit{IMIDMe})\textsubscript{2}P]\textsuperscript{+}. This observation is interesting because \textsuperscript{31}P NMR spectroscopy is a powerful tool in predicting \(\pi\) acidity of carbenes.\textsuperscript{16} Because the recent publications on the correlation of \textsuperscript{31}P NMR and \textsuperscript{77}Se NMR chemical shifts of carbene-phosphinidene or selenium adducts to the \(\pi\) acidity of various carbenes did not feature systems with 1,4-dialkyl-1,2,4-triazolylidenes,\textsuperscript{16,43,71} we were interested to see how the TAZ framework differed from the IMID framework in the (bis)carbene-stabilized P\textsuperscript{I} systems. We reasoned that an IMID-stabilized phosphorus(I) ion
more similar to [(iPrTAZ)2P][BPh4], 2.8 would be ideal to compare the TAZ framework vs. the IMID framework. Thus, we synthesized [(iPrIMIDH)2P][BPh4], 2.9, Figure 2.7 in a related fashion (see Experimental Section) since the only difference between this salt and [(iPrTAZ2)P][BPh4], 2.8 is the replacement of one backbone methine “CH” group by the isolobal “N:” fragment.

The first significant difference between the two salts is observed with respect to their solubilities. Whereas [(iPrTAZ)2P][BPh4], 2.8 is very soluble in MeCN, THF, and DCM, [(iPrIMIDH)2P][BPh4], 2.9 is only sparingly soluble in THF and MeCN. We also observed that the 31P NMR resonance for [(iPrIMIDH)2P][BPh4], 2.9 in [D3]MeCN appears at −134 ppm, suggesting that TAZs are better π acceptors than IMIDs, in accord with the lower LUMO energy of TAZ ligands as compared to IMID ligands.72

As we have previously remarked, the π accepting ability of the carbene plays a large role in the structural characteristics of the carbene-stabilized PI cation (and in turn the electronic environment of the phosphorus atom).27,28,38 Crystals suitable for scXRD were obtained for both salts in order to prove this hypothesis. While one might have anticipated that the two salts may crystallize in an isostructural fashion, we found that they pack very differently in the solid state. Whereas [(iPrIMIDH)2P][BPh4], 2.9 crystallizes in the space group Pī, [(iPrTAZ2)P][BPh4], 2.8 crystallizes in the chiral space group C2221. As with the methyl-substituted analog, the triazolyl fragments are oriented with the NN unit approximately anti to the σ-type lone pair on phosphorus. Further examination reveals that there are distinct structural differences between the metrical parameters of both cations, which are best seen in an overlaid plot viewed normal to one of the carbene planes (Figure 2.7). The structure of [(iPrIMIDH)2P]⁺, 2.9 contains long P–C bonds [1.8208(8) Å and 1.8174 (8) Å], a small C–P–C angle [95.73(4)°] and a high degree of twisting of the heterocycles from the C–P–C plane (56.1° and 59.3°). In contrast, the structure of [(iPrTAZ2)P]⁺, 2.8 contains
significantly shorter (and crystallographically identical) P–C bond lengths [1.799(2) Å] and a significantly larger C–P–C angle [99.72(12)°].

Figure 2.7: Thermal ellipsoid plot (50% probability surface) of [(iPrIMID)₂]₂[BPH₄] 2.9 (hydrogen atoms are omitted for clarity), and overlay of the crystal structures of the cations [(iPrTAZ)₂]⁺, 2.8 (violet) and [(iPrIMID)₂]⁺, 2.9 (green) as [BPH₄] salts (anions omitted)

Table 2.4: Selected bond lengths /Å and angles /° of the (IMID and TAZ)-stabilized PI cations

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<th>[(EtTAZ)₂]⁺, 2.10</th>
<th>[(MeTAZ)₂]⁺, 2.11</th>
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Table 2.5: Summary of crystallographic data for the (IMID and TAZ)-stabilized PI cations

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</table>

Table 2.6(a) shows \(^{31}\text{P}\) NMR records of different TAZ-stabilized phosphorus(I) adducts ranges from -116 to -126 ppm in addition to \(^{\text{Pr}}\text{IMID}\text{H}^+\text{P}(\text{I})\) at -134 ppm. The \(^{31}\text{P}\) NMR chemical
shifts of both TAZs and IMID exhibit an interesting trend where the methyl-substituted adducts bear higher chemical shifts whereas the isopropyl-substituted adducts shows lower chemical shifts. In other words, the chemical shifts increase from the adducts with methyl groups to the adducts having secondary alkyl groups as the following: $^{\text{Me}}\text{TAZ} > ^{\text{Bzl}}\text{TAZ} > ^{\text{Et}}\text{TAZ} > ^{\text{Et,Pr}}\text{TAZ} > ^{\text{iPr}}\text{TAZ} > ^{\text{iPr}}\text{IMID}^H$. By comparing our TAZs with the previously reported IMIDs$^{38}$ Table 2.6(b), the chemical shifts for the $^{\text{Me}}\text{IMID}^{\text{Me}}$ (-114.7ppm) and $^{\text{iPr}}\text{IMID}^{\text{Me}}$ (-126ppm) are very similar to our TAZs, $^{\text{Me}}\text{TAZ}$ (-116 ppm) and $^{\text{iPr}}\text{TAZ}$(-125 ppm), however; $^{\text{Et}}\text{IMID}^{\text{Me}}$ (-129 ppm) is slightly different from our $^{\text{Et}}\text{TAZ}$(-121.2 ppm) Table 2.6(b).

The chemical shifts of the chelating bis-TAZs and reported bis-IMIDs$^{27}$ are quite similar and more shifted downfield than non-chelating analogues which could be due to the presence of the methylene bridge that enforce the molecules to be more planar and thus increases the $\pi$-delocalization system Table 2.6(a), (b).
Table 2.6 (a): $^{31}$P NMR analysis of di-substituted-TAZ-stabilized P(I) compounds

<table>
<thead>
<tr>
<th>TAZ-P(^{I}) Compound</th>
<th>Structure</th>
<th>$^{31}$P (ppm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(^{t})TAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-116.0</td>
<td>this work</td>
</tr>
<tr>
<td>Bz(^{t})TAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-118.3</td>
<td>this work</td>
</tr>
<tr>
<td>Et(^{t})TAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-121.2</td>
<td>this work</td>
</tr>
<tr>
<td>Et(_{2})Pr(^{t})TAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-121.7</td>
<td>this work</td>
</tr>
<tr>
<td>Compound</td>
<td>Structure</td>
<td>E [kcal/mol]</td>
<td>Source</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------</td>
<td>--------------</td>
<td>---------</td>
</tr>
<tr>
<td>$^3$PrTAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-125.9</td>
<td>this work</td>
</tr>
<tr>
<td>$^3$PrIMID$^\text{H}$</td>
<td><img src="image" alt="Structure" /></td>
<td>-133.7</td>
<td>this work</td>
</tr>
<tr>
<td>$^\text{NBu}$Bis-TAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-87.8</td>
<td>this work</td>
</tr>
<tr>
<td>$^\text{Bz}$Bis-TAZ</td>
<td><img src="image" alt="Structure" /></td>
<td>-86.8</td>
<td>this work</td>
</tr>
</tbody>
</table>
Table 6 (b): $^{31}$P NMR analysis of reported substituted-IMID-stabilized P(I) compounds

<table>
<thead>
<tr>
<th>NHC-P&lt;sup&gt;I&lt;/sup&gt; Compound</th>
<th>Structure</th>
<th>$^{31}$P(ppm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\text{Me}^{\text{IMID}}\text{Me}$</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>-114.7</td>
<td>38</td>
</tr>
<tr>
<td>$^\text{iPr}^{\text{IMID}}\text{Me}$</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>-126</td>
<td>38</td>
</tr>
<tr>
<td>$^\text{Et}^{\text{IMID}}\text{Me}$</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>-129</td>
<td>38</td>
</tr>
<tr>
<td>$^\text{nBu}^{\text{Bis-IMID}}$</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>-83.1</td>
<td>27</td>
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<tr>
<td>$^\text{Bz}^{\text{Bis-IMID}}$</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>-81.8</td>
<td>27</td>
</tr>
</tbody>
</table>
2.4 Computational Studies

In an effort to determine if the differences between the solid state structures of \([\text{(iPrTAZ)}_2\text{P}]^+\) and \([\text{(iPrIMID)}_2\text{P}]^+\) are inherent or if they are caused by packing effects in the solid state, gas phase structures of complete models were optimized at the PBE1PBE/TZVP level of theory, Figure 2.8(a,b). We find that the structural differences between the ions are reproduced in the gas phase models: the model structure of \([\text{(iPrIMID)}_2\text{P}]^+\) is much more twisted than that of the \([\text{(iPrTAZ)}_2\text{P}]^+\) model and the same distortions of the isopropyl fragments are observed in the later cation (overlapped pictures of the calculated models are shown in Figure 2.8 (c).

![Geometry-optimized structures](image)

**Figure 2.8:** a) and b) Geometry-optimized structures for model cations \([\text{(iPrTAZ)}_2\text{P}]^+\) and \([\text{(iPrTAZ)}_2\text{P}]^+\) respectively. (c) Overlay of the optimized gas-phase models of cations \([\text{(iPrTAZ)}_2\text{P}]^+\) (black) and \([\text{(iPrIMID)}_2\text{P}]^+\) (white).
As anticipated, the Natural Bond Orbital (NBO) analyses of the models identifies two lone pairs on phosphorus in each case (Table 2.7), and the π-type lone pair is found to be engaged in a considerably greater amount of hyperconjugation with the C–N antibonding orbitals of the TAZ fragments in [(iPrTAZ)2P]+ (ca. 50 kcal mol⁻¹) than the IMID fragments in [(iPrIMIDH)2P]+ (ca. 33 kcal mol⁻¹). The calculated HOMO energy of [(iPrTAZ)2P]+ (–8.73 eV) is also significantly lower than that of [(iPrIMIDH)2 P]+ (–8.22 eV). These computational results agree well with the crystallographic and spectroscopic data, all of which imply that the TAZ fragments are superior π acceptors than IMID fragments. We also conducted an investigation of a simple model system featuring only hydrogen atom substituents [(iHTAZ)2P]+ in order to probe the cause of the anti-orientation of the triazole rings that we observed in the solid state. As indicated in Table 2.6, the relative Gibbs’ energies of three models are very similar (with the anti, anti isomer being the most favorable) and the most notable difference between the properties of the models is the magnitude of the dipole moment. In light of the small energy differences between the isomers, it is possible that crystal or ionic packing effects and secondary bonding interactions are responsible for the experimental observations in the solid state.
Table 2.7: Summary of the calculated results

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_{H}$/eV</th>
<th>$E_{L}$/eV</th>
<th>$E_{H-L}$/eV</th>
<th>$\text{LP}_{(p)}$ (NBO)$^a$</th>
<th>$E_{\text{deloc.}}$ $^b$</th>
<th>$R(\text{C-P})$ / Å</th>
<th>$\text{C-P-C}$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>($^{iPr}$TAZ)$_2$P$^+$</td>
<td>-8.73</td>
<td>-4.30</td>
<td>4.43</td>
<td>1.59</td>
<td>45.50</td>
<td>1.816</td>
<td>99.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>53.29</td>
<td>1.813</td>
<td></td>
</tr>
<tr>
<td>($^{iPr}$IMID$^{ll}$)$_2$P$^+$</td>
<td>-8.22</td>
<td>-3.73</td>
<td>4.49</td>
<td>1.63</td>
<td>33.26</td>
<td>1.824</td>
<td>98.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33.24</td>
<td>1.824</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Delta G_{\text{relative}}$ /kJ.mol$^{-1}$</th>
<th>Dipole moment (Debye)</th>
<th>$R(\text{C-P})$ / Å</th>
<th>$\text{C-P-C}$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>($^{iPr}$TAZ)$_2$P$^+$ syn,syn</td>
<td>7.2</td>
<td>3.43</td>
<td>1.798</td>
<td>97.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.798</td>
<td></td>
</tr>
<tr>
<td>($^{iPr}$TAZ)$_2$P$^+$ syn,anti</td>
<td>3.1</td>
<td>3.18</td>
<td>1.793</td>
<td>97.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.800</td>
<td></td>
</tr>
<tr>
<td>($^{iPr}$TAZ)$_2$P$^+$ anti,anti</td>
<td>0.0</td>
<td>1.08</td>
<td>1.796</td>
<td>97.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.796</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Population of the $\pi$-type lone pair the phosphorus atom in the lowest energy configuration determined by the NBO analysis. $^b$ Stabilization energy associated with delocalization of the $\pi$ lone pair on P with the adjacent $\pi$ bonds as determined by the NBO analysis.

2.5 Conclusions

We have synthesized and characterized a series of 1,4-dialkyl-1,2,4-triazolium iodide salts. This was achieved by a ligand replacement reaction where the stronger carbene replaced the weaker dppe ligand. We find that while the synthesis TAZ-stabilized phosphorus(I) ions from these precursors is not straightforward, anion exchange to BPh$_4$ and the reacting excess of carbene with [(dppe)$^+$][BPh$_4$] improve the synthesis significantly and allows for the isolation of TAZ-stabilized phosphorus(I) cations. We have also directly compared the properties of TAZ- and IMID-stabilized phosphorus(I) cations using NMR, scXRD and computational analyses and found
that the TAZ groups are greater $\pi$-acceptors than IMIDs and serve to increase $\pi$-bonding across the C–P–C fragment in these systems.
2.7 References


(56) Gaussview 3.0, Gaussian Inc., Pittsburgh, PA, U. **2003**.


(58) NBO 3.0, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, University of Wisconsin, Madison, WI, USA, **1990**.

(59) APEX II, Bruker AXS Inc., Madison, WI, USA, **2012**.

(60) SADABS, Bruker AXS Inc., Madison, WI, USA, **2008**.


Chapter 3: Coordination Chemistry of 1,2,4-Triazol-5-ylidenes-Stabilized Phosphorus(I) Cations

3.1 Introduction

Phosphorus is one of the most important elements which play a significant role in the growth of the main group chemistry.\(^1\) The synthesis of phosphamethine cyanine cations was among the earliest dicoordinate containing phosphorus species which have led to the development of the chemistry of the low coordinate phosphorus compounds. These compounds have shown notable applications in various fields such as coordination chemistry and catalysis.\(^2\,3\) In 1973, Dimroth stated that complexes of benzimidazolylphosphamethine with silver and mercury were isolated as crystalline materials.\(^4\) The coordination chemistry of phosphorus compounds such as phosphides,\(^5\,6\,7\,8\) phosphinidenes,\(^9\,10\,11\,12\,13\,14\,15\) phosphaalkenes\(^16\,17\,18\,19\,20\) and phospheniums\(^21\,22\,23\,24\,25\,26\) have received intensive growth throughout the previous years, in contrast; the coordination chemistry of phosphamethine cyanine cations has received less attention since the year 1973. The poor development of these compounds could be due to the weak ability of these ligands to donate electrons to the transition metals. For example, triphosphenium cation requires an involvement of an anion to be isolated as a solid.\(^27\,28\,29\) The counter ion is usually more reactive than the phosphorus(I) centre which in turn impact the investigation of the donor ability of the designated phosphorus atom. The electronic structure of the phosphorus(I) centre displays the presence of two pairs of electrons in which the π-type lone pair is located in HOMO and the σ-type lone pair in a more stable orbital. These electrons could participate in π-back bonding (negative hyperconjugation) with the other two phosphorus atoms which subsequently decreases the donor ability of the central phosphorus. In addition, the positive charge of the cation could show some effect on the participation of the electron pairs on the central phosphorus atom. Also, the electronic nature of the central phosphorus atom...
could be affected by the flanking ligands\textsuperscript{28}. Carbons (carbon(0) compounds) on the other hand, such as carbondicarbenes and carbodiphosphoranes display substantial electron donor abilities and well-known as ligands for transition metal chemistry. It was illustrated that the carbodicarbene compounds display better nucleophilic character than carbodiphosphorane compounds (Figure 3.1) as the NHC ligands are significantly less π-acidic than that of the phosphane groups\textsuperscript{30–36}.

Macdonald's group have synthesized a variety of NHC-stabilized P\textsuperscript{I} compounds which are known as canonical structures of phosphamethine cyanine through the diminishing of the delocalization of the π-type lone pair on phosphorus atom (Figure 3.1).

![Figure 3.1: Representations of triphosphenium cation and its isolobal carbon(0) compounds and phosphorus(I) compounds.\textsuperscript{29}](image)

The reactivity of the phosphorus centre in the acyclic and cyclic NHC and their analogues SNHC were tested through the reaction with some oxidizing agents such as sulfur, triflic acid and methyl triflate that produced the thionated, protonated and methylated compounds respectively. The group has reported the isolation and full characterization of a series of NHC-stabilized P\textsuperscript{I} derivatives coordinating to several transition metals. It was shown that, NHC-stabilized P\textsuperscript{I} cations

\(\begin{align*}
\text{Triphosphenium} & \quad \text{NHC-Stabilized P}\textsuperscript{I} \text{ Cation } [\text{L}]^+ \\
\text{Carbodiphosphorane} & \quad \text{Carbodicarbene} \\
\text{Phosphamethine Cyanine} & \quad \text{Bent Allene}
\end{align*}\)
were able to bind one or two equivalents of gold(I) chloride. Recently, the group has reported the synthesis of the first crystallographically characterized cationic metal–carbonyl derivatives of a PI-centred ligand. These derivatives include mononuclear coordination complexes [LM(CO)₅][BPh₄], (M = Cr, Mo, W), [LFe(CO)₄][BPh₄] and the dinuclear complexes [LMn₂(CO)₈][BPh₄] and [LCo₂(CO)₆][BPh₄], in which L = [bis(1,3,4,5-tetramethylimidazol-2-ylidene)phosphanide]+. The dicationic platinum complex trans-[L₂PtCl₂][BPh₄]₂ was reported and fully characterized as well. The donor ability of NHC-stabilized PI cations as ligands has been investigated by IR spectroscopy and theoretical studies of its metal–carbonyl complexes. The results suggest that the ligands are weak π-acceptors with moderate donor strengths and as a result they exhibit donor abilities in the range between phosphines and amines. In a manner analogous to carbondicarbene compounds, and the reported compounds by Macdonald et al., it was considered worthwhile to use 1,4-dialkyl-1,2,4-triazol-5-ylidene phosphorus(I) compounds and investigate their behavior towards p-block elements and transition metals.³⁷,³⁸,³⁹

3.2 Experimental

Reagents and General Procedures. All manipulations were carried out using standard inert atmosphere techniques. Gold(I) chloride (AuCl) and Fe₂(CO)₉ were purchased from Strem Chemicals Inc. and all other chemicals and reagents were obtained from Aldrich. All reagents were used without further purification. CD₃CN was dried over calcium hydride or phosphorus pentoxide and stored over molecular sieves under nitrogen. All other solvents were dried on a series of Grubbs’ type columns and were degassed prior to use.
**Instrumentation.** NMR spectra were recorded at room temperature on Bruker Advance Ultrashield 300 MHz or Bruker Advance DPX 300 MHz spectrometers. Chemical shifts are reported in ppm relative to internal standards for $^1$H and $^{13}$C (the given deuterated solvent) and external standards for $^{31}$P (85% H$_3$PO$_4$), and $^{11}$B (Et$_2$O·BF$_3$).

**Theoretical Methods.** Calculations were performed with the Gaussian 09 suite of programs using Compute Canada’s Shared Hierarchical Academic Research Computing Network (SHARCnet). Model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method$^{53,54,55}$ in conjunction with the TZVP basis sets for all atoms.$^{56,57}$ Geometry optimizations were started using models in which the relevant atoms were placed in geometrically appropriate positions using Gaussview.$^{46}$ Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical information. Natural bond orbital (NBO) analyses$^{58}$ to determine orbital contributions, Wiberg Bond Indicies and orbital energies$^{60}$ were obtained using the routine included in the Gaussian distributions. Summaries of the calculated results are presented in the sections below.

**Preparation of [(iPrTAZ)$_2$PH][OTf]$_2$**

To a yellow solution of [(iPrTAZ)$_2$P][OTf] (0.050 g, 0.104 mmol) in DCM (5 mL) was added 0.01 mL triflic acid (0.016 g, 0.104 mmol), and the mixture was allowed to stir for 24 h producing a lighter yellow colour. The solution was filtered and left to crystalize. $^{31}$P{$_1$H} NMR (300 MHz, DCM, 25 °C): $\delta = -127, -134$
Preparation of [(iPrTAZ)_2PH][OTf]_2 by Addition of 2 equivalents of HOTf

To a yellow solution of [(iPrTAZ)_2P][OTf] (0.050 g, 0.104 mmol) in DCM (5 mL) was added 0.02 mL triflic acid (0.032 g, 0.208 mmol), and the mixture was allowed to stir for 3 days producing a lighter yellow colour. The solution was filtered and left to crystalize. $^{31}\text{P}\{^1\text{H}\}$ NMR (300 MHz, DCM, 25 °C): $\delta = -127, -134$

Preparation of [(iPrTAZ)_2PCH_3][OTf]_2

To a yellow solution of [(iPrTAZ)_2P][OTf] (0.050 g, 0.104 mmol) in DCM (5 mL) was added 0.01 mL methyl triflate (0.015 g, 0.104 mmol), and the mixture was allowed to stir for 24 h with no change in colour. The solution was filtered and left to crystalize. $^{31}\text{P}\{^1\text{H}\}$ NMR (300 MHz, DCM, 25 °C): $\delta = -127, -58$

Note: Another 0.01 mL of Methyl Triflate was added to the solution and left to stir for 24h. The solution turned very pale yellow colour. The solution was filtered and left to crystalize. $^{31}\text{P}\{^1\text{H}\}$ NMR (300 MHz, DCM, 25 °C): $\delta = -127, -58$

Preparation of [(iPrTAZ)_2PS_2][BPh_4]

Trial 1:

A yellow solution of [(iPrTAZ)_2P][BPh_4] (0.050 g, 0.076 mmol) in THF (2 mL) was added to a suspension of sulfur (0.005 g, 0.152 mmol) in THF (2 mL), and the mixture was allowed to stir for 24 h. A pale yellow colour with precipitate formed. All volatiles were removed under reduced pressure to produce yellow solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (300 MHz, THF, 25 °C): $\delta = 24.5, 29.9, 36, 40.5, 56.4, 84.5$
**Trial 2:**

\[ [(\text{PrTAZ})_2\text{P}][\text{BPh}_4] \ (0.050 \text{ g}, 0.076 \text{ mmol}) \text{ and sulfur (0.005 g, 0.152 mmol)} \] were dissolved in THF \((\approx 10 \text{ mL})\). The mixture was allowed to reflux for 2 h. A white colour with precipitate formed. All volatiles were removed under reduced pressure to produce white solid. \(^{31}\text{P}\{^1\text{H}\} \text{ NMR (300 MHz, THF, 25 °C):} \ \delta = 29.5, 55.9, 84.5

**Preparation of \([(\text{PrTAZ})_2\text{P(BH}_3)_n][\text{BPh}_4]\)**

**Trial 1:** Addition of one equivalent of BH\(_3\)-THF

To a yellow solution of \([(\text{PrTAZ})_2\text{P}][\text{BPh}_4] \ (0.040 \text{ g}, 0.061 \text{ mmol}) \) in THF (5 mL) was added \((61 \mu\text{L}, 1.0 \text{ M}) \text{ BH}_3\cdot\text{THF} \ (0.005 \text{ g}, 0.061 \text{ mmol})\), and the yellow mixture was allowed to stir for 24 h forming lighter yellow colour. \(^{31}\text{P}\{^1\text{H}\} \text{ NMR (300 MHz, DCM, 25 °C):} \ \delta = -125, -116

**Trial 2:** Addition of 4 equivalents of BH\(_3\)-THF

To the solution of trial 1, \(\approx 0.3 \text{ mL}\) of BH\(_3\)-THF was added and left to stir for 3 days. \(^{31}\text{P}\{^1\text{H}\} \text{ NMR (300 MHz, DCM, 25 °C):} \ \delta = -125, -116

**Trial 3:** Addition of one equivalent of BH\(_3\)-DMS

To a yellow solution of \([(\text{PrTAZ})_2\text{P}][\text{BPh}_4] \ (0.040 \text{ g}, 0.061 \text{ mmol}) \) in DCM (5 mL) was added 5.78 \(\mu\text{L}\) borane dimethylsulfide \((0.005 \text{ g}, 0.061 \text{ mmol})\), and the yellow mixture was allowed to stir for 24 h with no change in colour. \(^{31}\text{P}\{^1\text{H}\} \text{ NMR (300 MHz, DCM, 25 °C):} \ \delta = -125, -66, -63.5, 6.8, 61.5
**Trial 4:** Addition of 4 equivalents of BH$_3$·DMS

To the solution of trial 3, 23.12 µL of borane dimethylsulfide was added and left to stir for 24 h. $^{31}$P$\{^1$H$\}$ NMR (300 MHz, DCM, 25 °C): $\delta = -125, -66, -63.0, 7.2, 40.2, 61.1$

**Trial 5:** Heat

The solution in trial 4 was heated to 40 °C under flow of N$_2$ for ≈ 20 min. $^{31}$P$\{^1$H$\}$ NMR (300 MHz, DCM, 25 °C): $\delta = -125, -66, -63.0, 7.2, 40.2, 61.1$

**Trial 6:** Addition of 10 equivalents of BH$_3$·DMS

To a yellow solution of [(iPrTAZ)$_2$P][BPh$_4$] (0.050 g, 0.076 mmol) in THF (5 mL) was added 0.072 mL borane dimethylsulfide (0.058 g, 0.761 mmol), and the yellow mixture was allowed to stir for 24 h with no change in colour. $^{31}$P$\{^1$H$\}$ NMR (300 MHz, CD$_3$CN, 25 °C): $\delta = -126, -68$

**Preparation of [(MeTAZ)$_2$PAuCl][BPh$_4$]**

A solution of [(MeTAZ)$_2$P][BPh$_4$] (0.050 g, 0.092 mmol) in DCM (2 mL) was added to a suspension of AuCl (0.021 g, 0.092 mmol) in DCM (1 mL), and the mixture was allowed to stir for 24 h. A gray colour with dark precipitate formed. All volatiles were removed under reduced pressure to produce dark solid. $^{31}$P$\{^1$H$\}$ NMR (300 MHz, DCM, 25 °C): $\delta = -116, 34, 84$

**Preparation of [(MeTAZ)$_2$P(AuCl)$_2$][BPh$_4$]**

A solution of [(MeTAZ)$_2$P][BPh$_4$] (0.050 g, 0.092 mmol) in DCM (2 mL) was added to a suspension of AuCl (0.042 g, 0.184 mmol) in DCM (1 mL), and the mixture was allowed to stir for 24 h. A gray colour with dark precipitate formed. All volatiles were removed under reduced pressure to produce a dark solid. $^{31}$P$\{^1$H$\}$ NMR (300 MHz, DCM, 25 °C): $\delta = 34, 164, 221$
Preparation of [(iPrTAZ)₂PAuCl][OTf]

A solution of [(iPrTAZ)₂P][OTf] (0.050 g, 0.010 mmol) in DCM (2 mL) was added to a suspension of Me₂SAuCl (0.031 g, 0.010 mmol) in DCM (1 mL), and the mixture was allowed to stir for 24 h. A red colour with precipitate formed. All volatiles were removed under reduced pressure to produce dark solid. $^{31}$P{$^1$H} NMR (300 MHz, DCM, 25 °C): $\delta = 34$

Preparation of [(iPrTAZ)₂PFe(CO)₄][BPh₄]

**Trial 1:** Addition of 1:1 equivalent

A solution of [(iPrTAZ)₂P][BPh₄] (0.020 g, 0.030 mmol) in THF (2 mL) was added to a suspension of Fe₂(CO)₉ (0.011 g, 0.030 mmol) in THF (1 mL), and the mixture was allowed to stir for 24 h. A dark red colour with precipitate formed. All volatiles were removed under reduced pressure to produce dark red solid. $^{31}$P{$^1$H} NMR (300 MHz, DCM, 25 °C): $\delta = -126$

**Trial 2:** Addition of 1:3 equivalents

A solution of [(iPrTAZ)₂P][BPh₄] (0.020 g, 0.030 mmol) in THF (2 mL) was added to a suspension of Fe₂(CO)₉ (0.033 g, 0.091 mmol) in THF (2 mL), and the mixture was allowed to stir for 48 h. A dark red colour with precipitate formed. All volatiles were removed under reduced pressure to produce dark red solid. $^{31}$P{$^1$H} NMR (300 MHz, DCM, 25 °C): $\delta = -126, -60.8$

**Trial 3:** Addition of 1:4 equivalents

A solution of [(iPrTAZ)₂P][BPh₄] (0.020 g, 0.030 mmol) in THF (2 mL) was added to a suspension of Fe₂(CO)₉ (0.044 g, 0.120 mmol) in THF (2 mL), and the mixture was allowed to stir for 24 h. A dark red colour with precipitate formed. All volatiles were removed under reduced pressure to produce dark red solid. $^{31}$P{$^1$H} NMR (300 MHz, DCM, 25 °C): $\delta = -60.8$
Preparation of [(iPrTAZ)$_2$PCo$_2$(CO)$_6$][BPh$_4$]

**Trial 1**: Addition of 1:1 equivalent

A solution of [(iPrTAZ)$_2$P][BPh$_4$] (0.020 g, 0.030 mmol) in THF (2 mL) was added to a suspension of Co$_2$(CO)$_8$ (0.010 g, 0.030 mmol) in THF (1 mL), and the mixture was allowed to stir for 24 h. A dark purple colour with precipitate formed. All volatiles were removed under reduced pressure to produce dark solid. $^{31}$P{$^1$H} NMR (300 MHz, DCM, 25 °C): $\delta = -126$

**Trial 2**: Addition of 1:3 equivalents

A solution of [(iPrTAZ)$_2$P][BPh$_4$] (0.020 g, 0.030 mmol) in THF (2 mL) was added to a suspension of Co$_2$(CO)$_8$ (0.0312 g, 0.091 mmol) in THF (2 mL), and the mixture was allowed to stir for 48 h. A dark purple colour with precipitate formed. All volatiles were removed under reduced pressure to produce dark solid. $^{31}$P{$^1$H} NMR (300 MHz, DCM, 25 °C): $\delta = 48.46$(br).

3.3 Results and Discussion

As reported in an early work of Macdonald et al.$^{49,37}$, the NHC-stabilized P$^I$ cations (NHC = IMID) exhibit a remarkable reactivity towards various main group elements and transition metals. The availability of two lone pairs of electrons on the P$^I$ centre increases the nucleophilicity and electron donor properties of the IMID$_2$P$^I$ cations. As demonstrated in Chapter 2, TAZ$_2$P$^I$ cations have two pairs of electrons potentially available for reactivity, and thus should respond similarly to other P$^I$ compounds in the presence of electron acceptor species. Inspired by our observations in Chapter 2 that TAZ$_2$P$^I$ cations are more acidic than IMID$_2$P$^I$ cations, and the presence of a third nitrogen atom on the TAZ ring, we decided to examine to what extent the reactivity of the TAZs in comparison to the IMIDs could be by employing similar reactions reported for IMIDs by Macdonald and coworkers.
Reactions with Oxidizing Agents

The IMID$_2$P$^{I}$ cations were reacted with triflic acid and methyl triflate to assess their behavior towards protonation and methylation respectively. In these reactions it is more convenient to use the P(I) salts having triflate as an anion to minimize complications that leads to products with mixed anions. Accordingly, we have prepared triazolium triflate salts and triphosphenium salts through metathesis reactions using trimethylsilyl triflate or potassium triflate in order to synthesize the desired TAZ$_2$P$^{I}$ triflate salts Scheme 3.1.

![Scheme 3.1: a) and b) Preparation of triazolium and triphosphenium triflate salts via metathesis reactions. c) Preparation of TAZ$_2$P$^{I}$ triflate](image)

In both protonation and methylation of the reported IMID$_2$P$^{I}$ triflate salts produced white product as a good sign that the oxidation of the phosphorus did indeed take place. The $^{31}$P NMR
signals of the protonated and methylated IMID were shifted to -128 and -55 ppm respectively compared to the parent cation at -112.3 ppm. In our lab, the treatment of the TAZ₂Pᵢ triflate with triflic acid in DCM solvent (Scheme 3.2) under similar conditions produced impure products as the starting material still visible in the ³¹P NMR at -127 ppm. In addition to the signal at -127 ppm, the protonation salt showed a ³¹P NMR signal at -134 ppm (doublet) which is close to the chemical shift of the protonated IMID adduct (-128 ppm) suggesting that this peak corresponds to the protonated TAZ adduct. The doublet peak with ¹J₂₃ of 285.85 Hz could refers to the coupling of the phosphorus to the proton which is similar to that was reported for the protonated imidazoles (¹J₂₃ = 282.22 Hz). Similarly, the methylation reaction of TAZ₂Pᵢ triflate (Scheme 3.3) produced two peaks in ³¹P NMR spectrum, at -127 ppm which corresponds to the starting material and -58 ppm which presumably presents the methylated product as it is very close to the chemical shift of the methylated IMID₂Pᵢ₃ adduct (-55 ppm). Since the starting materials were still present according to the ³¹P NMR, two equivalents of the oxidizing agent were added, however; the attempts to complete oxidation of the phosphorus failed. As well, attempts to obtain crystals of the product were unsuccessful.

Scheme 3.2: Protonation of TAZ₂Pᵢ triflate
Macdonald et al. also reacted the IMID$_2$P$^+$ cations with two equivalents of elemental sulfur producing dithionophosphonium cations of colorless to pale yellow solids. The $^{31}$P NMR showed a signal at 25 ppm which is more deshielded than the chemical shift of the parent cation at -114 ppm. We reacted TAZ$_2$P$^+$ tetraphenyl borate salt in THF with two equivalents of elemental sulfur in THF in order to obtain similar results, (Scheme 3.4). After one hour of the reaction, $^{31}$P NMR of the yellow suspension showed multiple peaks which include the starting material and other peaks that were difficult to identify. The reaction was left to proceed for 24 hours, however; multiple peaks were still visible in the $^{31}$P NMR.

In the second trial where we refluxed the reaction solution for 2 hours in order to drive the reaction to the desired product, we were able to obtain a cleaner $^{31}$P NMR spectrum and only two peaks observed at 29.5 and 55.9 ppm. According to the $^{31}$P NMR chemical shift shown for the dithionated IMID cation at 25 ppm, we believe that the peak at 29.5 corresponds to our dithionated product. The crystals we obtained from this reaction mixture in THF based on the X-ray diffraction were elemental sulfur.
The BH$_3$ molecule was shown by Arduengo et al.$^{50}$ to react rapidly with carbene-phosphinidene compounds where the P$^1$ centre has two pairs of electrons available for interaction with Lewis acids. Two equivalents of BH$_3$ were added to the corresponding carbene and the product bis(borane) was obtained which showed a $^{31}$P NMR chemical shift at 4 ppm, however; they were not able to produce mono(borane) adduct. In 2001, Hanh et al.$^{51}$ reacted azaphospholine with two equivalents of BH$_3$·THF forming colorless crystals of the product with two coordinated BH$_3$ molecules. The product showed $^{31}$P NMR chemical shift at 2.8 ppm which is more deshielded than the chemical shift of the parent compound (-64.2 ppm).
In contrast, in our lab, the treatment of the TAZ$_2$P$^i$ tetraphenylborate under similar conditions even with a four-fold excess of BH$_3$·THF complex does not result in adduct formation as evidenced by $^{31}$P NMR spectrum which showed only two peaks at -125 and -116 ppm even upon adding excess of the BH$_3$·THF complex and stirring for a long period of time. The chemical shift at -125 ppm corresponds to the TAZ$_2$P$^i$ tetraphenylborate precursor while the chemical shift at -116 could indicate an isomer of the same precursor where phosphorus atom possibly binds to C3 instead of C5 of the TAZ ring as this case has been seen during the synthesis of TAZ$_2$P$^i$ cations.

Scheme 3.5: Reaction of TAZ$_2$P$^i$ cation with Borane (BH$_3$·THF or BH$_3$·DMS)

Since the complex BH$_3$·DMS is more stable than BH$_3$·THF, we decided to try this complex with our TAZ$_2$P$^i$ as well. Unfortunately, multiple peaks appeared in the $^{31}$P NMR spectrum (Figure 3.3) including the P$^i$ cation even after addition of four-fold excess of the complex. We thought that an equilibrium state might be involved through dissociation of the P—B bond and forming back the complex BH$_3$·DMS. Based on that, we decided to warm the reaction solution to remove the volatile DMS under flow of N$_2$ and thus force the equilibrium towards the targeted product. $^{31}$P NMR showed an increase in the peak intensity at -65.4 ppm and decrease in the other peaks. The proton-coupled $^{31}$P NMR spectrum showed splitting in the peak at -65.4 ppm which indicates a coordination of BH$_3$ to the phosphorus centre.
As the $^{31}$P NMR resonance indicates some evidence of the possibility of BH$_3$ molecule to coordinate to phosphorus centre, $^{11}$B NMR also presents proof that coordination took place on the phosphorus atom of the TAZ ring. From Figure 3.4, the $^{11}$B NMR shows peaks at -6.0, -20.3 and -33.3 ppm. The chemical shifts of -6.0 and -20.3 ppm are corresponding to BPh$_4$ anion in the TAZ$_2$P$_i$ compound and the neat BH$_3$·DMS respectively. However, the peak at -33.3 possibly corresponds to BH$_3$ coordinated to the phosphorus of the TAZ$_2$P$_i$ compound. In the literature, compounds 1,1'-Bis(3-borane-4,5dimethylimidazolyl) methane and [1,1'-Methylene-(3-borane-4,5-dimethylimidazolyl)-2-diylidene]dicyclopenta-dienyltitanium where the borane molecules are binding to the nitrogen atoms displayed broad $^{11}$B NMR signals at -20.3 and -22.3 ppm respectively$^{52}$ which is very close to the chemical shift of BH$_3$·DMS which was not straightforward for us to confirm that this peak whether it refers to coordinated boron to nitrogen atom or it is residue from the reagent BH$_3$·DMS. Attempts to obtain crystals of the aimed product were unsuccessful.
In an effort to obtain better insight to the coordination of borane to TAZ$_2$P$^\text{I}$ cation, we decided to add an excess of ten-fold of BH$_3$·DMS in THF solvent to (iPrTAZ)$_2$P$^\text{I}$ cation in THF at room temperature, however similar results to our previous observations were detected according to the spectra of $^{31}\text{P}$ NMR, $^1\text{H}$ NMR and $^{11}\text{B}$ NMR. Figure 3.5, $^{31}\text{P}$ NMR shows two singlet peaks at -126 and -68 ppm which again is most likely related to (iPrTAZ)$_2$P$^\text{I}$ cation and BH$_3$ coordinated to phosphorus atom respectively. The proton-coupled $^{31}\text{P}$ NMR spectrum Figure 3.5 (red spectrum) displays a broad multiplet at -68 ppm which indeed confirms bonding between borane and phosphorus atom. The $^1\text{H}$ NMR spectrum, Figure 3.6, (blue), shows multiplets at 4.4 and 4.6 ppm (CH(CH$_3$)$_2$) and a singlet at 8.5 ppm (NCH), these peaks are same as those of the starting material TAZ$_2$P$^\text{I}$ cation (green spectrum). However, new peaks appear at (5.3 and 4.9 ppm, multiplets) and (8.8 ppm, singlet) which most likely correspond to (CH(CH$_3$)$_2$) and (NCH) respectively of the proposed product in which borane coordinated to phosphorus centre as was detected by $^{31}\text{P}$ NMR. Also, if we look at the integration ratio between the multiplets (ca.1:8) matches that of the singlets.
(ca. 1:8) which indicated that the peaks at (5.3 and 4.9 ppm, multiplets) and (8.8 ppm, singlet) are related. The red spectrum shows $^1$H NMR of the solid collected after a few days as it shows disappearance of the new peak at 8.8 ppm and smaller multiplets at 5.3 and 4.9 ppm. Same observation was noted in $^{31}$P NMR as the peak at -68 ppm disappeared as well. The $^{11}$B NMR spectrum could indicate an interaction have taken place by the appearance of a new peak at -24.9 ppm, Figure 3.7. According to our observations from the attempts to coordinate TAZ$_2$P$^+$ cation to borane, BH$_3$, we conclude that the TAZ$_2$P$^+$ cation has a relatively poor electron donor ability to coordinate to borane as Lewis acid and that the stability of these complexes are low which in turn prevented us from performing further characterizations.

![Figure 3.5: $^{31}$P NMR of a reaction between TAZ$_2$P$^+$ compound and BH$_3$·DMS complex (1:10 equivalents)](image)
Figure 3.6: $^1$H NMR of a reaction between TAZ-P(I) compound and BH$_3$·DMS complex (1:10 equivalents)

Figure 3.7: $^{11}$B NMR of a reaction between TAZ$_2$P(I) compound and BH$_3$·DMS complex (1:10 equivalents)
Reactions with Transition Metals

In 2017, Macdonald et al. isolated and fully characterized a series of cationic metal carbonyl complexes bearing an N-heterocyclic carbene- stabilized phosphorus(I) ligand. Among these complexes were the mononuclear complexes \([\text{LFe(CO)}_4][\text{BPh}_4]\) and dinuclear complex \([\text{LCo}_2(\text{CO})_6][\text{BPh}_4]\), where \(L = \text{[bis(1,3,4,5- tetramethylimidazol-2-ylidene)phosphanide]}^+\). They reacted \(\text{IMID}_2\text{P}^\text{I}\) and one equivalent of \(\text{Fe}_2(\text{CO})_9\) in THF at room temperature for 12 hrs which resulted in the emergence of a new signal at -57.5 ppm which is more downfield than the parent ligand at -113.4 ppm. In this vein, I reacted the \(\text{TAZ}_2\text{P}^\text{I}\) cation with one equivalent of \(\text{Fe}_2(\text{CO})_9\) in THF at room temperature for 24 h and the \(^{31}\text{P NMR}\) showed a peak at -60.8 ppm which is presumably attributable to the target product and another peak at -126 ppm which corresponds to the \(\text{TAZ}_2\text{P}^\text{I}\) cation (Figure 3.8). An excess of 3 equivalents of \(\text{Fe}_2(\text{CO})_9\) in THF was added to the \(\text{TAZ}_2\text{P}^\text{I}\) cation and left to react for 48 h, this led to a decrease in the signal related to starting \(\text{P}^\text{I}\) cation and a relative increase in the product signal. By adding 4-fold excess of the iron complex, we were indeed able to consume all the \(\text{P}^\text{I}\) cation and only obtain the product. Unexpectedly, in an effort to fully characterize the product by dissolving it in [D\(_3\)]\text{MeCN}, \(^{31}\text{P NMR}\) showed no signals. In another attempt to prepare the complex under same condition but using [D\(_8\)]THF for full NMR characterization, the attempt was not successful as well. These observations suggest the complex has limited stability in solutions.
Figure 3.8: $^{31}$P NMR of reactions between TAZ-P$^I$ compound and Fe$_2$(CO)$_9$ complex.

1:1 (blue); 1:3 (red); 1:4 (green)

Similar conditions were applied in an effort to coordinate Co$_2$(CO)$_8$ complex to TAZ$_2$P$^I$. Reaction of 1:1 ratio led to a color change from yellow to dark purple but did not convert the TAZ$_2$P$^I$ salt completely to the target complex. Addition of three-fold excess led to a complete disappearance of TAZ$_2$P$^I$ salt and emergence of a new broad $^{31}$P NMR signal at 48.4 ppm, Figure 3.9, which was shifted more downfield similar to the broad peak observed by Macdonald et al. for IMID$_2$P$^I$ adducts at 70.8 ppm. Attempts to obtain crystals of this adduct were unsuccessful.
3.4 Computational Studies

We sought to employ computational investigations in order to provide insight to the bonding, electronic and structural features, and reactivity patterns for the TAZ-based phosphorus(I) compounds and to rationalize why our attempts to synthesize the target complexes were not completely successful. We used DFT calculations to optimize the geometries of series of compounds. We chose as our model to investigate: [(R\text{TAZ})_2P]^+, [(R\text{TAZ})_2P\text{ W(CO)}_5]^+, [(i^{Pr}\text{IMID}^H)_2P\text{ W(CO)}_5]^+, [(i^{Pr}\text{TAZ})_2P\text{AuCl}]^+, [(\text{Me}\text{TAZ})_2P\text{BH}_3]^+, [(i^{Pr}\text{TAZ})_2P\text{BH}_3]^+ and [(R\text{TAZ})_2\text{PH}]^{2+} where R = \text{Me, Et and iPr}. The optimized geometry structures of the uncoordinated models are shown in Figure 3.10 and relevant data are presented in Table 3.1

As anticipated, the Natural Bond Orbital (NBO) analyses of the models identifies two lone pairs on phosphorus in each case (Table 3.1), and the π-type lone pair is found to be engaged in a considerably greater amount of hyperconjugation with the C–N antibonding orbitals of the TAZ fragments in [(R\text{TAZ})_2P]^+ (> 40 kcal mol\(^{-1}\)) than the IMID fragments in [(i^{Pr}\text{IMID}^H)_2P]^+ (ca. 33
kcal mol$^{-1}$). The calculated HOMO energies of $[(^9\text{TAZ})_2\text{P}]^+$ (−8.73, −9.01, −9.31 eV) is also significantly lower than that of $[(^\text{iPrIMID}^\text{H})_2\text{P}]^+$ (−8.22 eV). These computational results agree well with the crystallographic and spectroscopic data, all of which imply that the TAZ fragments are superior π acceptors compared with IMID fragments.

3.1

3.2
Proton affinity is a method used to rank the donor ability of both phosphorus and nitrogen centres and determine the more favorable positions (P or N atoms) to get readily protonated over the other in the model compounds (Figure 3.11). The proton affinity is calculated as the difference in $E_{\text{total}}$ between the protonated species and that of the original model. From Table 3.2, all compounds; 3.1, 3.2 and 3.3, are favored to protonate at the phosphorus atom more than nitrogen atoms, as the proton affinities are (ca. $\geq$600 kJ mol$^{-1}$) and ($\leq$600 kJ mol$^{-1}$) respectively. The difference in proton affinity between two positions (P and N) is the least in the case of dimethyl substituted TAZ model (41 kJ mol$^{-1}$) and the highest in the case of diisopropyl substituted TAZ (ca. 54
kJ mol$^{-1}$), however the diethyl substituted TAZ model (ca. 53 kJ mol$^{-1}$) is slightly less than diisopropyl substituted TAZ. This small difference between protonation of the two different positions could lead to the presence of two different isomers in solution at the same time the possibility would be higher in the case of dimethyl substituted model than that of diisopropyl substituted one. The Natural Bond Orbital (NBO) analysis of the models identifies two lone pairs on phosphorus in all models and small involvement of the $\pi$-type lone pair to the C-N antibonding orbitals is found in all models specially the ones protonated on the phosphorus centre which could indicate that an interaction between the models 3.1 to 3.3 with the proton is possible. The protonation on the nitrogen centres shows more delocalization of the $\pi$-type lone pair (ca. 14 kJmol$^{-1}$) than that of protonated phosphorus (ca. 10 kJmol$^{-1}$) which is anticipated since the positive charge on the protonated nitrogen would increase the engagement of these electrons in the $\pi$-system. Additionally, the HOMO-LUMO energy gap is higher when protonation occurs on phosphorus atom than that when it occurs on nitrogen atom. This again reveals that the possibility of the presence of the phosphorus protonated form and its stability is higher than the nitrogen protonated form. These results agree well with what we experimentally have found, as we observed from $^{31}$P NMR spectra peaks refer to starting materials (disubstituted-TAZ$_2$P$^+$ cations) and new less intense peaks of the expected products.
3.1-P-H
3.1-N-H
3.2-P-H
3.2-N-H
Figure 3.11: Optimized Geometry Structures of Protonated Model Compounds 3.1 to 3.3

Table 3.2: Summary of Proton Affinity Computational Results of Compounds 3.1 to 3.3

<table>
<thead>
<tr>
<th>Model</th>
<th>Corrected Energy$^a$ (au)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_{\text{H}}-E_{\text{L}}$ (eV)</th>
<th>LP$_{(p)}$ (NBO)</th>
<th>Q$(P)^b$ (au)</th>
<th>$E_{\text{deloc}}$</th>
<th>Proton Affinity (PA)/kJ mol$^{-1}$</th>
<th>PA(P)-PA(N)/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1-P-H</td>
<td>-982.5187</td>
<td>-0.577</td>
<td>-0.346</td>
<td>0.231</td>
<td>1.916</td>
<td>0.59</td>
<td>6.96</td>
<td>9.28</td>
<td>587.0</td>
</tr>
<tr>
<td>3.1-P-N-H</td>
<td>-982.1952</td>
<td>-0.495</td>
<td>-0.337</td>
<td>0.158</td>
<td>1.918</td>
<td>0.39</td>
<td>5.02</td>
<td>14.56</td>
<td>546.0</td>
</tr>
<tr>
<td>3.2-P-H</td>
<td>-1139.2338</td>
<td>-0.562</td>
<td>-0.330</td>
<td>0.232</td>
<td>1.918</td>
<td>0.58</td>
<td>6.34</td>
<td>9.78</td>
<td>626.0</td>
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<tr>
<td>3.2-P-N-H</td>
<td>-1139.2139</td>
<td>-0.479</td>
<td>-0.322</td>
<td>0.157</td>
<td>1.918</td>
<td>0.36</td>
<td>5.31</td>
<td>14.30</td>
<td>573.0</td>
</tr>
<tr>
<td>3.3-P-H</td>
<td>-1296.2535</td>
<td>-0.549</td>
<td>-0.317</td>
<td>0.232</td>
<td>1.918</td>
<td>0.58</td>
<td>6.12</td>
<td>9.66</td>
<td>656.0</td>
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<tr>
<td>3.3-P-N-H</td>
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<td>0.153</td>
<td>1.916</td>
<td>0.36</td>
<td>5.41</td>
<td>14.94</td>
<td>602.0</td>
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</table>

$^a$) Corrected Energy = $E_{\text{total}}$ + ZPVE; $^b$) Q = Charge on P atom.
Another way to understanding the different reactivities of di-substituted-TAZ$_2$P$^i$ cations is may be by examining the relative energies of the molecules compared to those of isomeric forms or alternative products. Some calculations have been performed on models 3.1 and 3.3 coordinated to either BH$_3$ or AuCl molecules to illustrate the more favorable position that possibility the base-acid interactions would take place and forms the corresponding complexes. The results as shown in Table 3.3 indicate that phosphorus centre is more favorable to coordinate to BH$_3$ or AuCl species than nitrogen centre. The difference in the energy for interaction with two positions in case of diisopropyl-substituted-TAZ models (3.3-P-BH$_3$ and 3.3-N-BH$_3$) and (3.3-P-AuCl and 3.3- N-AuCl) are (27 and 91 kJ mol$^{-1}$) respectively. This is more apparent when the substituents are bulkier (isopropyl groups) as the relative energy of these molecules (ca. 8250.60 x 10$^2$ and 23196.54x 10$^2$ kJ mol$^{-1}$) respectively is less than that of dimethyl-substituted-TAZ models which results in a higher stability of the corresponding molecule. It is worth noting that, the key factor in the stability of these model compounds could be the electronic effect and not the steric effect. In other words, since the presence of the isopropyl group on compound 3.3 leads to a twisting in the two TAZ rings plane, it seems that the electron density is more present on the phosphorus atom than involving in a conjugation with the $\pi$-system of the ring. However, in case of smaller substituents (methyl groups), TAZ$_2$P$^i$ molecule is less twisted and thus the lone pairs of electrons are more involved in conjugation leading to less stability.
Figure 3.12: Optimized Geometry Structures of Model Compounds 3.1 to 3.3 coordinated with BH$_3$ and Au(I)Cl

Table 3.3: Summary of Computational Results of Reactions Involving BH$_3$ and Au(I)Cl

<table>
<thead>
<tr>
<th>Model</th>
<th>P-bound 3.1-P-BH$_3$</th>
<th>N-bound 3.1-N-BH$_3$</th>
<th>P-bound 3.3-P-BH$_3$</th>
<th>N-bound 3.3-N-BH$_3$</th>
<th>P-bound 3.3-P-Au(I)Cl</th>
<th>N-bound 3.3-N-Au(I)Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (kJ mol$^{-1}$)</td>
<td>-26486.80 X 10$^2$</td>
<td>-26486.79 X 10$^2$</td>
<td>-34737.40 X 10$^2$</td>
<td>-34737.13 X 10$^2$</td>
<td>-49683.34 X 10$^2$</td>
<td>-49682.43 X 10$^2$</td>
</tr>
<tr>
<td>Relative Energy (kJ mol$^{-1}$)</td>
<td>0/+1</td>
<td>0/+27</td>
<td>0/+91</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Relative Energy = Difference between P-bound and N-bound energies of each model compound.
To assess the metal-ligand bond strength, snapping energy of the L-W(CO)₅ bond of a series of models; 3.1-W(CO)₅, 3.2-W(CO)₅, 3.3-W(CO)₅ and iPrIMID₅P-W(CO)₅ was calculated and compared with that reported for MeIMID₅P-W(CO)₅, as shown in Figure 3.13 and Table 3.4. All models optimized at the same level of theory. Snapping energy is calculated by taking the optimized bound structure (Ligand-W(CO)₅) and run single point energy calculations on the fragments, Ligand and W(CO)₅ separately. Bond energy then calculated by the summation of the energy of the optimized fragments and then taking the difference between this energy and the energy of the optimized bound structure. The calculated bond snapping energies of all substituted TAZ₅P-W(CO)₅ bonds are 125.1, 130.0 and 133.7 kJ mol⁻¹ less than 139.4 kJ mol⁻¹ and 190.6 kJ mol⁻¹ of MeIMID₅P-W(CO)₅ and iPrIMID₅P-W(CO)₅ complexes. These calculated results indicate that the metal-ligand bond of the imidazole complex is stronger than that of the triazole complexes and thus it supports the conclusions provided in chapter 2 in which the TAZ ligands showed higher acidic properties than the IMID ligands. This also rationalizes the experimental results obtained by attempting to coordinate metals to the diisopropyl-TAZ₅P⁺ cations. The calculated snapping energy of the metal-ligand bond of TAZ-W(CO)₅ complexes increases as the size of alkyl groups increases leading to a stronger metal-ligand bond when the alkyl group is bulkier (isopropyl) and this agrees with our previous observations from the calculated energy for the coordinated ligands with BH₃ and AuCl bases.

The resultant bond energies follow the same trend as the snapping energies of all three models. The model 3.3-W(CO)₅ contains the highest bond energy and the 3.1-W(CO)₅ the lest bond energy. Model 3.2-W(CO)₅ contains bond energy that falls between these and slightly similar to that of 3.1-W(CO)₅. This result indicates that the diisopropyl-TAZ₅P⁺ cation has higher donor properties than the others. In terms of energies the metal-ligand bond is stronger in case of model
3.3-W(CO)₅ which is most likely due to the electronic effect having higher impact than the steric effect. In contrast, in terms of metal-ligand bond length the model 3.3-W(CO)₅ shows slightly longer bond than 3.1-W(CO)₅ which again could refer to the availability of the lone pairs to coordinate with metals more than the case of the dimethyl substituted models. It is also could be due to the fact that the steric effect exhibits certain contribution to the stability of the metal-ligand bond. Accordingly, both electronic and steric effects might play an important role in affinity of TAZ ligands towards electron acceptor species. Additionally, more energy is released by the relaxation of 3.3-W(CO)₅ than 3.1-W(CO)₅ which is a consequence of increasing the strength of metal-ligand bond respectively.
Figure 3.13: Optimized Geometry Structures of Model Compounds 3.1 to 3.3 coordinated with W(CO)$_5$

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_{\text{Snap}}$ (kJ mol$^{-1}$)</th>
<th>$E_{\text{Bond}}$ (kJ mol$^{-1}$)</th>
<th>$E_{\text{Relax}}$ (kJ mol$^{-1}$)</th>
<th>P-WBond Length /Å</th>
</tr>
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<tbody>
<tr>
<td>3.1-W(CO)$_5$</td>
<td>125.1</td>
<td>107.3</td>
<td>-17.8</td>
<td>2.592</td>
</tr>
<tr>
<td>3.2-W(CO)$_5$</td>
<td>130.0</td>
<td>107.4</td>
<td>-22.6</td>
<td>2.604</td>
</tr>
<tr>
<td>3.3-W(CO)$_5$</td>
<td>133.7</td>
<td>114.4</td>
<td>-19.3</td>
<td>2.603</td>
</tr>
<tr>
<td>MeIMIDMeP-W(CO)$_5$</td>
<td>139.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
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<td>119.3</td>
<td>-71.3</td>
<td>2.619</td>
</tr>
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</table>
3.5 Conclusions

While the reported complexes of substituted imidazole-stabilized phosphorus(I) cations with both main group and transition metal Lewis acids were stable under air and moisture free conditions and readily isolated and fully characterized, coordination of disubstituted triazole-stabilized phosphorus(I) cations with both main group and transition Lewis acids under same conditions resulted in unstable complexes that are prone to dissociate over short time preventing us from isolation and characterization of these complexes. Theoretical calculations were performed to models of some of disubstituted triazole-stabilized phosphorus(I) and their targeted complexes and then compared to their analogous of the reported substituted imidazole-stabilized phosphorus(I) complexes revealed that disubstituted triazole-stabilized phosphorus(I) complexes are less stable as they have higher snapping energy than the IMIDs and possess higher π-accepting properties and less σ-donor abilities. Also, since the TAZs have nitrogen atom on each ring backbone that might show possibility to coordinate to Lewis acids, calculations indicated that the phosphorus atom is more favorable than the nitrogen centre and this behavior agrees well with the experimental findings.
3.6 References


(4) Prof, S.; Dimroth, K. *Phosphorus-Carbon Double Bonds*, Springer-Verlag, Berlin/Heidelberg, **1973**.


(22) Gudat, D.; Haghverdi, a; Hupfer, H.; Nieger, M. Chemistry 2000, 6 (18), 3414.


Chapter 4: 1,4-Dialkyl-1,2,4-Triazol-5-Selenones

4.1 Introduction

The chemistry of N-heterocyclic carbenes plays a major role in a variety fields of chemistry, and particularly in organometallic, main group synthesis, and catalysis. Various methods have been used to investigate their steric and electronic properties such as the Tolman Electronic Parameter (TEP)\textsuperscript{6,7} and Percent Buried Volume (\%V\textsubscript{bur}).\textsuperscript{8,9} These methods have led to the exploration and comparison of their electronic and steric properties.\textsuperscript{10,11} The TEP is the most common method utilized to test the electronic properties of NHCs with transition metals such as [Ni(CO)\textsubscript{3}L] complexes based on the weakening of the bond C-O as a result of d→π* back bonding which then vibrates at different region in the infra-red range according to how electron rich the metal is.\textsuperscript{12,13} NHCs were initially considered to be pure σ-donor ligands, however; subsequent reports showed that NHCs can exhibit π-donor and π-acceptor characters.\textsuperscript{14,15}

Other methods were reported to investigate the electronic properties of NHCs in compounds that do not involve CO groups in their structures. In complexes [PtCl\textsubscript{2}(DMSO)(NHC)], Nolan assessed π-acceptor properties of NHCs by using \textsuperscript{1}J\textsubscript{Pt-C} coupling constants.\textsuperscript{16} In phosphinidenes, which form from a reaction between free NHC carbene and PPhCl\textsubscript{2}, Bertrand\textsuperscript{17} used \textsuperscript{31}P NMR spectroscopy and then Ganter\textsuperscript{18} used \textsuperscript{77}Se NMR spectroscopy for his selenourea compounds to assess the π-acceptor properties of the carbene, see Figure 4.1.
The majority of studies and experiments reported were those using for phosphinidene and selenourea compounds as well as their chemical shifts trends. However, selenium compounds have shown advantages over the phosphinidene adducts since the preparation of these compounds are straightforward and can be obtained in one step at room temperature. In light of the study of electronic properties of NHCs, we have synthesized and characterize series of selenone compounds based on the reaction of triazolium salts with selenium powder in presence of a base. We will report their $^{77}$Se NMR spectroscopy and their chemical shifts trends. We also will present our investigations by commencing some DFT studies for our synthesized compounds.
4.2 Experimental

Reagents and General Procedures. All manipulations were carried out using standard inert atmosphere techniques. Selenium powder, elemental sulfur, K\(_t\)BuO, K\(_2\)CO\(_3\) and Ni(II)Cl·dme were purchased from Sigma Aldrich. Anhydrous ethanol was used as received. Hexanes was dried with molecular sieves. [D]chloroform was dried with phosphorus pentoxide or calcium hydride. All other solvents were dried on a series of Grubbs’ type columns and were degassed prior to use. 1,4-dimethyl-1,2,4- triazolium iodide, 1,4-diethyl-1,2,4- triazolium iodide\(^{56}\), 1,4-diisopropyl-1,2,4-triazolium iodide\(^{56}\) and 1,4-dibenzyl-1,2,4-triazolium bromide were all synthesized according to literature methods.

Instrumentation. NMR spectra were recorded at room temperature with Bruker Advance Ultrashield 300 MHz, or Bruker Advance DPX 300 MHz spectrometers. Chemical shifts are reported in ppm relative to internal standards for \(^1\)H and \(^{13}\)C (the given deuterated solvent) and external standards for \(^{31}\)P (85% H\(_3\)PO\(_4\)) and \(^{77}\)Se (Me\(_2\)Se in Et\(_2\)O or CHCl\(_3\)). Elemental Analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a Perkin Elmer 2400 combustion CHN analyzer. High-resolution electrospray ionization mass spectrometry was performed at the McMaster Regional Centre for Mass Spectrometry.

Theoretical Methods. Calculations were performed with the Gaussian 09 suite of programs\(^{20}\) using Compute Canada’s Shared Hierarchical Academic Research Computing Network (SHARCnet). Model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method\(^{21,22,23}\) in conjunction with the TZVP basis sets for all atoms.\(^{24,25}\) Geometry optimizations were started using models in which the relevant selenium, nitrogen, and carbon atoms were placed at the positions found experimentally using X-ray
crystallography and the hydrogen atoms were placed in geometrically appropriate positions using Gaussview. Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical information. Natural bond orbital (NBO) analyses to determine orbital contributions, Wiberg Bond Indices and orbital energies were obtained using the routine included in the Gaussian distributions. Summaries of the calculated results, including Cartesian coordinates are presented in the sections below.

**X-ray Crystallography.** Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N$_2$ of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were collected using the APEXIII software suite with a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with Mo-$\text{K}\alpha$ ($\lambda = 0.71073$ Å) or Cu-$\text{K}\alpha$ ($\lambda = 1.54178$ Å) radiation. For each sample, data were collected at low temperature. APEXIII software was used for data reductions and SADABS was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX software suite as implemented in the WinGX or OLEX2 program suites. Validation of the structures was conducted using PLATON.

**Preparation of 1,4-Dimethyl-1,2,4-Triazol-5-Selenone**

A flask containing $[^{35}\text{MeTAZ}][\text{I}]$ (0.500 g, 2.223 mmol), Selenium powder (0.176 g, 2.223 mmol), K$_2$CO$_3$ (0.615 g, 4.446 mmol) and anhydrous EtOH (15 mL) heated to 77°C for 5 hours. After cooling to room temperature, the suspension was centrifuged, and colorless solution was separated. All volatiles were removed under reduced pressure to give a white solid. Solid was
dissolved in ether or hexanes and filtered and then pure solid collected by removing solvent under reduced pressure. Yield: 81% (0.316 g, 1.794 mmol). Crystals suitable for scXRD were obtained by slow evaporation of Et₂O solution. **¹H NMR** (300 MHz, CDCl₃, 25 °C): δ = 3.66 (s, 3 H, NCH₃), 3.87 (s, 3 H, NNCH₃), 7.87 (s, 1 H, NCH). **¹³C NMR** (300 MHz, CDCl₃, 25 °C): δ = 34.8 (s, NCH₃), 38.6 (s, NNCH₃), 140.9 (s, C3), 161.3 (s, C5). **⁷⁷Se NMR** (300 MHz, CDCl₃, 25 °C): δ = 24.50 (s, CSe).

**HR-ESI-MS**: calcd. for C₄H₇N₃Se [M⁺] m/z = 176.98, found: 176.9799. C₄H₇N₃Se (176.08): C 27.85 (calcd. 27.28); H 3.82 (4.01); N 23.85 (23.86) %.

**Preparation of 1,4-Diethyl-1,2,4-Triazol-5-Selenone**

A flask containing [EtTAZ][I] (0.5 g, 1.976 mmol), Selenium powder (0.156 g, 1.98 mmol), K₂CO₃ (0.546 g, 3.95 mmol) and anhydrous EtOH (15 mL) heated to 60°C for 5 hours. After cooling to room temperature, the suspension was centrifuged, and very pale solution was separated. All volatiles were removed under reduced pressure to give yellow oil. Light yellow oil was extracted using ether. Yield: 63% (0.253 g, 1.240 mmol). **¹H NMR** (300 MHz, CDCl₃, 25 °C): δ = 1.35 (t, ³J_H,H = 7.2, 3 H, NCH₂CH₃), 1.38 (t, ³J_H,H = 7.5, 3 H, NNCH₂CH₃), 4.09 (q, ³J_H,H = 7.5, 2 H, CH₂CH₃), 4.27 [q, ³J_H,H = 7.2, 2 H, CH₂CH₃], 7.89 (s, 1 H, NCH). **¹³C NMR** (300 MHz, CDCl₃, 25 °C): δ = 13.5 (s, NCH₂CH₃), 14.4 (s, NNCH₂CH₃), 42.9 (s, NCH₂CH₃), 46.1 (s, CH₂CH₃), 140.1 (s, C3), 159.1 (s, C5). **⁷⁷Se NMR** (300 MHz, CDCl₃, 25 °C): δ = 2.31 (s, CSe). **HR-ESI-MS**: calcd. for C₆H₁₁N₃Se [M+H⁺] m/z = 205.0113, found: 205.0106. C₆H₁₁N₃Se (204.13): C 35.87 (calcd. 35.3); H 5.33 (5.43); N 19.91 (20.58) %.
Preparation of 1,4-Diisopropyl-1,2,4-Triazol-5-Selenone

A flask containing [^PrTAZ][I] (0.500 g, 1.778 mmol), Selenium powder (0.140 g, 1.778 mmol), K₂CO₃ (0.491 g, 3.556 mmol) and anhydrous EtOH (15 mL) heated to 77°C for 6 hours. After cooling to room temperature, the suspension was centrifuged, and colorless solution was separated. All volatiles were removed under reduced pressure to give a white solid. Solid was dissolved in ether or hexanes and filtered and then pure solid collected by removing solvent under reduced pressure Yield: 46% (0.192 g, 0.820 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a hexanes solution. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.41 [d, ³J_H, H = 6.7, 6 H, NCH(CH₃)₂], 1.48 [d, ³J_H, H = 6.8, 6 H, NNCH(CH₃)₂], 5.05 [p, ³J_H,H = 6.8, 1 H, NCH(CH₃)₂], 5.33 [p, ³J_H,H = 6.7, 1 H, CH(CH₃)₂], 7.89 (s, 1 H, NCH). ¹³C NMR (300 MHz, CDCl₃, 25 °C): δ = 20.9 [s, NCH(CH₃)₂], 22.2 [s, NNCH(CH₃)₂], 50.2 [s, NCH(CH₃)₂], 52.1 [s, NNCH(CH₃)₂], 138.0 (s, C₃), 158.5 (s, C₅). ⁷⁷Se NMR (300 MHz, CDCl₃, 25 °C): δ = 5.96 (s, C₅Se) HR-ESI-MS: calcd. for C₈H₁₅N₃Se [M + H]⁺ m/z = 233.0426, found: 233.0427. C₈H₁₅N₃Se (232.09): C 41.43 (calcd. 41.38); H 6.13 (6.51); N 17.97 (18.1) %.

Preparation of 4-Isopropyl-1-Ethyl-1,2,4-Triazol-5-Selenone

THF solvent (5mL) was added to a flask containing [^PrEtTAZ][I] (0.500 g, 1.872 mmol), Selenium powder (0.147 g, 1.872 mmol), KtBuO (0.252 g, 2.246 mmol). The mixture was left to stir over night at room temperature. The suspension was centrifuged, and colorless solution was separated. All volatiles were removed under reduced pressure to give a pale yellow oil. Ether or hexanes was added to the oil and filtered and then pure oil collected by removing solvent under reduced pressure Yield: 79% (0.324 g, 1.485 mmol). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.43 (t, ³J_H,H = 7.2, 3 H, CH₂CH₃), 1.46 [d, ³J_H,H = 6.8, 6 H, CH(CH₃)₂], 4.35 (q, ³J_H,H = 7.26, 2 H,
\( \text{CH}_2\text{CH}_3 \), 5.00 \([p, J_{\text{H,H}} = 6.81, 1 \text{ H, CH(CH}_3\text{)_2}]\), 7.89 \((s, 1 \text{ H, NCH})\). \(^{13}\text{C}\) NMR \((300 \text{ MHz, CDCl}_3, 25 \, ^{\circ}\text{C})\): \(\delta = 13.5 \,(s, \text{ CH}_2\text{CH}_3), 22.2 \,[s, \text{ CH(CH}_3\text{)_2}], 46.0 \,(s, \text{ CH}_2\text{CH}_3), 50.5 \,[s, \text{ CH(CH}_3\text{)_2}], 137.9 \,(s, \text{ C}_3), 185.8 \,(s, \text{ C}_5)\). \(^{77}\text{Se}\) NMR \((300 \text{ MHz, CDCl}_3, 25 \, ^{\circ}\text{C})\): \(\delta = 4.49 \,(s, \text{ CSe})\).

HR-ESI-MS: calcd. for \(\text{C}_7\text{H}_{13}\text{N}_3\text{Se}\) [M + H] \(+ m/z = 219.0269\), found: 219.0264. \(\text{C}_7\text{H}_{13}\text{N}_3\text{Se}\) \((218.16\)): C 40.30 (calcd. 38.54); H 6.13 (6.01); N 19.38 (19.26)

**Preparation of 1,4-Dibenzyl-1,2,4-Triazol-5-Selenone**

THF solvent \((10\text{mL})\) was added to a flask containing \([^{\text{Btz}}\text{TAZ)][\text{Br}]\) \((0.100 \text{ g, 0.303 mmol})\), Selenium powder \((0.024 \text{ g, 0.303 mmol})\), KtBuO \((0.041 \text{ g, 0.363 mmol})\). The yellow mixture was left to stir over night at room temperature. The suspension was filtered and all volatiles were removed from the filtrate under reduced pressure to give an orange solid. Solid was dissolved in ether or hexanes and filtered and then pure orange solid collected by removing solvent under reduced pressure. Yield: 73\% \((0.072 \text{ g, 0.219 mmol})\). \(^1\text{H}\) NMR \((300 \text{ MHz, CDCl}_3, 25 \, ^{\circ}\text{C})\): \(\delta = 1.91 \,(s, 2 \text{ H, NCH}_2\text{C}_6\text{H}_5), 5.46 \,(s, 2 \text{ H, NNCH}_2\text{C}_6\text{H}_5), 7.26 \,(m, 4 \text{ H, C}_6\text{H}_5), 7.30 \,(m, 4 \text{ H, C}_6\text{H}_5), 7.42 \,(m, 2 \text{ H, C}_6\text{H}_5), 7.59 \,(s, 1\text{ H, NCH})\). \(^{13}\text{C}\) NMR \((300 \text{ MHz, CDCl}_3, 25 \, ^{\circ}\text{C})\): \(\delta = 51.7 \,(s, \text{ NCH}_2\text{C}_6\text{H}_5), 54.4 \,(s, \text{ NNCH}_2\text{C}_6\text{H}_5), 128.5 \,(s, \text{ C}_6\text{H}_5), 128.9 \,(m, \text{ C}_6\text{H}_5), 129.4 \,(s, \text{ C}_6\text{H}_5), 140.8 \,(s, \text{ C}_3), 161.8 \,(s, \text{ C}_5)\). \(^{77}\text{Se}\) NMR \((300 \text{ MHz, CDCl}_3, 25 \, ^{\circ}\text{C})\): \(\delta = 31.46 \,(s, \text{ CSe})\).

HR-ESI-MS: calcd. for \(\text{C}_{16}\text{H}_{15}\text{N}_3\text{Se}\) [M + H] \(+ m/z = 329.09\), found: not observed. \(\text{C}_{16}\text{H}_{15}\text{N}_3\text{Se}\) \((328.27\)): C 61.19 (calcd. 58.54); H 5.10 (4.61); N 13.06 (12.8) %.

**Preparation of 1,4-Diisopropyl-1,2,4-Triazol-5-thione**

THF solvent \((10\text{mL})\) was added to a flask containing \([^{\text{iPr}}\text{TAZ}][\text{BPh}_4]\) \((1.000 \text{ g, 2.112 mmol})\), KtBuO \((0.284 \text{ g, 2.535 mmol})\). After stirring for 15 minutes, elemental sulfur \((0.068 \text{ g,}...\))
2.112 mmol) in THF was added to the mixture. The yellow mixture was left to stir overnight at room temperature. All volatiles were removed from the mixture under reduced pressure to give yellow solid. Solid was dissolved in ether or hexanes and filtered and then pure pale-yellow solid collected by removing solvent under reduced pressure. Yield: 51% (0.198 g, 1.068 mmol). Crystals suitable for scXRD were obtained by slow evaporation of a hexanes solution. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 1.37 [d, $^3$J$_{H,H}$ = 6.7, 6 H, NCH(CH$_3$)$_2$], 1.42 [d, $^3$J$_{H,H}$ = 5.9, 6 H, NNCH(CH$_3$)$_2$], 4.89 [p, $^3$J$_{H,H}$ = 6.1, 1 H, NCH(CH$_3$)$_2$], 5.17 [p, $^3$J$_{H,H}$ = 6.1, 1 H, CH(CH$_3$)$_2$], 7.77 (s, 1 H, NCH). $^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 20.8 [s, NCH(CH$_3$)$_2$], 22.0 [s, NNCH(CH$_3$)$_2$], 48.3 [s, NCH(CH$_3$)$_2$], 50.1 [s, NNCH(CH$_3$)$_2$], 136.2 (s, C3), 164.0 (s, C5). HR-ESI-MS: calcd. for C$_8$H$_{15}$N$_3$S [M + H]$^+$ m/z = 186.10, found: not observed. C$_8$H$_{15}$N$_3$S (185.10): C 52.60 (calcd. 51.86%); H 8.15 (8.16%); N 22.14 (22.68)%.

Preparation of Bis(1,4-Diisopropyl-1,2,4-Triazol-5-Selenone)Nickel(II) Chloride

Acetonitrile (5mL) was added to a flask containing $^{i}$PrTAZ-Se (0.050 g, 0.215 mmol), NiCl$_2$·dme (0.024 g, 0.107 mmol). The yellow-bluish mixture was left to stir overnight at room temperature. All volatiles were removed from the mixture under reduced pressure to give a green solid. Yield: 47% (0.030 g, 0.051 mmol). Green crystals suitable for scXRD were obtained by slow evaporation of a MeCN solution. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 1.42 [d, $^3$J$_{H,H}$ = 6.7, 6 H, NCH(CH$_3$)$_2$], 1.46 [d, $^3$J$_{H,H}$ = 6.7, 6 H, NNCH(CH$_3$)$_2$], 5.08 [p, 1 H, NCH(CH$_3$)$_2$], 5.36 [p, 1 H, CH(CH$_3$)$_2$], 7.88 (s, 1 H, NCH). $^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 21.0 [s, NCH(CH$_3$)$_2$], 22.2 [s, NNCH(CH$_3$)$_2$], 50.1 [s, NCH(CH$_3$)$_2$], 52.1 [s, NNCH(CH$_3$)$_2$], 137.8 (s, C3), not observed (C5). $^{77}$Se NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 5.77 (d, CSe) C$_{16}$H$_{36}$Cl$_2$N$_6$NiSe$_2$ (593.77): C 33.97 (calcd. 32.34); H 4.8 (5.09); N 14.02 (14.15) %.
Preparation of Bis(1,4-Diisopropyl-1,2,4-Triazol-5-Thione)Nickel(II) Chloride

Acetonitrile (5mL) was added to a flask containing \(^{iPr}\)TAZ-S (0.050 g, 0.270 mmol), NiCl\(_2\)-dme (0.029 g, 0.135 mmol). The yellow-bluish mixture was left to stir overnight at room temperature. All volatiles were removed from the mixture under reduced pressure to give a blue solid. Yield: 75% (0.050 g, 0.100 mmol). \(^1\)H NMR (300 MHz, CDCl\(_3\), 25 °C): \(\delta = 1.43\) [s(br), 24 H, NCH(CH\(_3\))\(_2\)], 4.93 [br, 2 H, NCH(CH\(_3\))\(_2\)], 5.21 [br, 2 H, CH(CH\(_3\))\(_2\)], 7.76 (s, 2 H, NCH). \(^{13}\)C NMR (300 MHz, CDCl\(_3\), 25 °C): \(\delta = 20.9\) [s, NCH(CH\(_3\))\(_2\)], 22.0 [s, NNCH(CH\(_3\))\(_2\)], 48.3 [s, NCH(CH\(_3\))\(_2\)], 50.3 [s, NNCH(CH\(_3\))\(_2\)], 136.2 (s, C3), not observed (C5). C\(_{16}\)H\(_{30}\)Cl\(_2\)N\(_6\)NiS\(_2\) (593.77): C 38.06 (calcd. 38.42); H 5.08 (6.05); N 13.91 (16.81)%.

4.3 Results and Discussion

Inspired by the previous work has been established on phosphinidene adducts\(^{35,36,37}\) and substituted imidazole-containing selenium compounds\(^{38,19,39}\) to explore the correlation between their \(\pi\)-acceptor properties and the chemical shift of phosphorus and selenium atom respectively, we decided to follow the same insight and investigate these characters for our substituted triazole compounds.

We attempted to synthesize phosphinidene adducts in situ by deprotonation of five equivalents of the corresponding triazolium salt and then followed by addition of one equivalent of pentaphenylcyclopentaphosphane in dry THF under inert atmosphere producing yellow colour which turned to white upon stirring overnight. \(^{31}\)P NMR spectrum of the reaction solution showed multiple peaks amongst these peaks are related to cyclic oligophosphines P\(_4\)Ph\(_4\), P\(_5\)Ph\(_5\) and P\(_6\)Ph\(_6\) at -48, -3.1, -21.9 respectively. Even addition of 10 equivalents of triazolium cation did not show
any improvement. In addition, reactions with dichlorophenylphosphine followed by reduction using either Mg or KC\textsubscript{8} did not show any promising results. Consequently, we decided to study the acidity properties of our TAZs through the synthesis of selenium adducts using the approach that was reported in the literature.\textsuperscript{38,19,39}

A range of new 1,4-dialkyl-1,2,4-triazol-5-selenone compounds (4.4,4.6-4.9) were prepared from the corresponding triazolium salts (Figure 4.2). The compounds were prepared either by the deprotonation of the triazolium salts in the presence of K\textsubscript{2}CO\textsubscript{3} in anhydrous ethanol with heating to ca. 70 °C or by the deprotonation of the triazolium salts in the presence of KtBuO in dry THF at room temperature. In 2014, Tian and coworkers reported the investigation of an efficient method for the synthesis of dialkyl imidazole-containing selenium compounds (IMID-Se) in several solvents. According to their results, the deprotonation of the imidazole produced higher yield percentage by the use of ethanol as a solvent of the reaction.\textsuperscript{39} We have followed their procedure in order to prepare dialkyl triazole-containing selenium compounds (TAZ-Se) and this method partially succeeded and produced the target compounds with some of the triazoles, however; it failed to work with others. In comparison to imidazole-containing compounds which are air and moisture stable, we have noticed that triazole-containing selenium compounds are air and moisture sensitive as they decompose upon exposing to air and the white solid turns pink and chemical shifts of $^{77}$Se NMR spectroscopy of the triazoles disappear. An alternative and more efficient synthetic method was used to obtain the target compounds which involved the use of KtBuO in dry THF and then work up the reactions under inert atmosphere and subsequently, the targeted compounds were obtained without complication. All compounds (4.4,4.6-4.9) were fully characterized $^1$H, $^{13}$C, and $^{77}$Se NMR spectroscopy in chloroform-$d$. Elemental analysis and mass spectroscopy were performed on all compounds.
Figure 4.2: Proposed routes to dialkyl-1,2,4-triazol-5-selenone

In Figure 4.3, the structure A illustrates the extreme of a low acceptor ability causing the selenium atom to be more shielded and consequently it shifts to higher field resonance. In contrast, the structure B illustrates the extreme with higher acceptor properties leading to less shielding for the selenium atom and thus it appears at lower field resonance.

Figure 4.3: Canonical structures of NHC-containing selenium compounds

Table 4.1 represents data records of $^{77}$Se NMR and $^{13}$C NMR for our new compounds (4.4,4.6-4.9) which are a part of this dissertation and the data for the other compounds (4.1-4.3,4.5) are from the literature and are only for comparison. All $^{77}$Se NMR spectra were recorded in Chloroform-$d$ solution with dimethyl selenide in ether or in chloroform as the external standard reference. It should be noted that the natural abundance of $^{77}$Se is very low (7.5%), so the solutions needed to be very concentrated in order to obtain a good signal within a short time. Also, attempts
to determine $^1J_{\text{CSe}}$ coupling constant from the selenium satellites in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were not successful. Again, this is because the very low natural abundance of $^{77}\text{Se}$ and $^{13}\text{C}$ (7.5 and 1.1% respectively), as the probability of a $^{13}\text{C}$ atom adjacent to a $^{77}\text{Se}$ atom is approximately 0.08%. Another key point that has to be considered is that the chemical shifts of $^{77}\text{Se}$ NMR are very sensitive to concentration, temperature, pH and the solvent.

The $^{77}\text{Se}$ NMR of dialkyl triazole-containing selenium compounds covers a range from 2.31 to 31.46 ppm versus the reported dialkyl imidazole-containing selenium compounds which covers a range from -6 to 3 ppm. Our TAZ-Se adducts display higher chemical shifts than the previously reported IMID-Se compounds. Accordingly, our TAZ-Se compounds bear higher $\pi$-acceptor properties than the reported IMID-Se analogues. The $^{77}\text{Se}$ NMR of TAZ-Se compounds show some interesting trends. The chemical shifts of the three adducts $\text{EtTAZ-Se}$ (4.4), $\text{EtIPTAZ-Se}$ (4.6) and $\text{iPTAZ-Se}$ (4.7) are in order in which $\text{EtTAZ-Se}$ has the lowest chemical shift while the chemical shift of $\text{iPTAZ-Se}$ is the highest. The notable thing about these three compounds is that, all of them have either ethyl, isopropyl or both groups. In other words, the TAZ-Se compound that bears primary alkyl N-substituents exhibit a lower chemical shift, whereas; the one with secondary N-substituents exhibit a higher chemical shift. This appealing trend has been observed by Cavallo et al. and Ganter et al.\textsuperscript{19, 38} Compound 4.9 ($^{\text{Bzl}}\text{TAZ-Se}$) shows the highest chemical shift comparing to the other TAZ-Se adducts and this trend is similar to the IMID-Se compound (4.3) which exhibit the higher chemical shift among the other IMID-Se compounds shown in the table.
Table 4.1: NMR spectroscopic data for the new substituted 1,2,4-triazol-5-selenone compounds (4.4,4.6-4.9) and the reported substituted 1,3-imidazol-3-selenone compounds (4.1- 4.3,4.5).\textsuperscript{38}

<table>
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<th>Compound Number</th>
<th>NHC-Se Compound</th>
<th>$\delta^{77}$Se (ppm)</th>
<th>$\delta^{13}$C (ppm)</th>
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<td>38</td>
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<td>159.1</td>
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<td>38</td>
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<tr>
<td>4.6</td>
<td><img src="4.6" alt="NHC-Se Compound 4.6" /></td>
<td>4.4</td>
<td>158.8</td>
<td>this work</td>
</tr>
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<td>4.7</td>
<td><img src="4.7" alt="NHC-Se Compound 4.7" /></td>
<td>5.9</td>
<td>158.5</td>
<td>this work</td>
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<tr>
<td>4.8</td>
<td><img src="4.8" alt="NHC-Se Compound 4.8" /></td>
<td>24.5</td>
<td>161.3</td>
<td>this work</td>
</tr>
<tr>
<td>4.9</td>
<td><img src="4.9" alt="NHC-Se Compound 4.9" /></td>
<td>31.4</td>
<td>161.8</td>
<td>this work</td>
</tr>
</tbody>
</table>
Finally, $^{125}\text{MeTAZ-Se}$ (4.8) compound locates among the highest chemical shifts resulting in higher acidic properties. It has a chemical shift of 24.5 ppm closer to $^{125}\text{BzTAZ-Te}$ adduct (31.46 ppm) which reasonable since the structural difference between two compounds is the presence of phenyl group in $^{125}\text{BzTAZ-Te}$ as an electron-withdrawing which could be a reason to increase the acidity of this compound comparing to $^{125}\text{MeTAZ-Se}$ analogues. Interestingly, The acidity trend observed for TAZs and IMIDs through the study of $^{77}\text{Se}$ NMR resonance of TAZ-Se and IMID-Se compounds in Table 4.1 in which TAZ-Se indicated higher $\pi$-acceptor properties than IMID-Se analogues have been proven in chapter 2 in this dissertation by the investigation accomplished on isopropyl-substituted TAZ-stabilized $^{31}\text{P}$ ($^{p}\text{TAZ-P}^{\dagger}$) against isopropyl-substituted IMID-stabilized $^{31}\text{P}$ ($^{p}\text{IMID-P}^{\dagger}$) ions. The $^{p}\text{TAZ-P}^{\dagger}$ and $^{p}\text{IMID-P}^{\dagger}$ have $^{31}\text{P}$ NMR chemical shifts of -126 ppm and -134 ppm respectively suggesting that the TAZs are better $\pi$ acceptors than the IMIDs.

Another interesting prospective that we noticed for NHCs is the relation between the $^{77}\text{Se}$ resonance $^{13}\text{C}$ resonance of NHC-Se compounds. From Table 4.1 we have observed that, in addition to the trend we have previously discussed for $^{77}\text{Se}$ NMR chemical shifts, $^{13}\text{C}$ NMR chemical shifts exhibit a significant trend among TAZ-Se compounds in particular and among both TAZ-Se and IMID-Se compounds in general. Indeed, plotting $^{77}\text{Se}$ NMR versus $^{13}\text{C}$ NMR of TAZ-Se compounds resulted in a correlation of $R^2 = 0.9404$. Also, plotting $^{77}\text{Se}$ NMR against $^{13}\text{C}$ NMR of both TAZ-Se and IMID-Se compounds resulted in a correlation of $R^2 = 0.8883$. The plotting in Figure 4.4 is consistent with an approximately linear correlation between the two scales for TAZ-Se compounds; whereas, the plotting in Figure 4.5 confirms the linear correlation between the two scales for both TAZ-Se and IMID-Se compounds.
Figure 4.4: Plot of $^{77}$Se NMR chemical shifts versus $^{13}$C NMR chemical shifts of TAZ-Se compounds

Figure 4.5: Plot of $^{77}$Se NMR chemical shifts versus $^{13}$C NMR chemical shifts of TAZ-Se and IMID-Se compounds

X-ray crystal structure data were obtained for 1,4-dimethyl-1,2,4-triazol-5-selenone and 1,4-diisopropyl-1,2,4-triazol-5-selenone. Crystals of these two selenones were obtained via slow evaporation of hexanes solution at room temperature. For the compounds (1,4-diethyl-) and (1-ethyl-4-isopropyl)-1,2,4-triazol-5-selenones were oils and thus no X-ray structure was obtained. Figure 4.6 shows crystal structures of compounds $^{iPr}$TAZ-Se and $^{Me}$TAZ-Se. Crystallographic data and metrical parameters are listed Tables 4.2, 4.3 and 4.4. Comparing the Se—C bond distance in both compounds, the bond in $^{iPr}$TAZ-Se (1.830(4) Å) is slightly shorter than that in $^{Me}$TAZ-Se.
(1.842(9) Å) suggesting that ca. 0.01 Å bond length difference is not meaningful. In addition, comparing the Se—C bond lengths and the \( \delta_{\text{Se}} \), there is no correlation between them. However, Se—C5 bond length of ca. 1.8 Å is longer than that of Se═C double bond that seen in CSe\(_2\) (1.698) and shorter than a single bond distance as seen in cationic selenoether adducts of C\(_5\)H\(_3\)Fe(CO)\(_2\) (1.924 Å and 1.942 Å). A bond length of 1.884(9) Å was reported for dimethylimidazole selone adduct\(^{40}\) which is longer than that of our TAZ-Se suggesting that the donor properties of our TAZ-Se adducts are less than the reported IMID-Se. The bond angle of \(^{i\text{Pr}}\)TAZ-Se (104.4(3)°) is similar to that of \(^{Me}\)TAZ-Se (105.0(8)°) and both are less than that reported for \(^{Me}\)IMID-Se adduct (106.8(7)°).

In this chapter, attempts to explore the ability of triazole carbenes to react with other main group elements, such as Germanium (Ge), Gallium (Ga) and Sulfur (S). Deprotonation of diisopropyl triazolium salt by KtBuO in dry THF at room temperature then adding either GeCl\(_4\) or GaCl\(_3\) did not succeed, however; addition of elemental sulfur led to the formation of the thione product which is air and moisture stable. X-ray structure from the thione compound, diisopropylTAZ-S, was obtained. The crystals were formed via slow evaporation of a solution of the product in either in ether or hexane. The S—C5 distance of 1.6745(18) Å is slightly longer than C=S (1.61 Å) and is shorter than that of a C—S single bond (1.81 Å) suggesting that the bond C—S has more of double bond character than a single bond. Also, the S—C5 bond length in \(^{i\text{Pr}}\)TAZ-S is shorter than the Se—C5 of the analogues \(^{i\text{Pr}}\)TAZ-Se (1.830(4) Å). The S—C5 bond length in \(^{i\text{Pr}}\)TAZ-S is shorter than of S—C5 bond length in \(^{Me}\)IMID-S (1.688 Å) \(^{41}\) which indicates stronger \( \pi \)-acceptor properties of TAZs than IMIDs.

By obtaining selenium and sulfur compounds in our hands, their reactivities with transition metals were examined. Two equivalents of diisopropylTAZ-Se were added to one equivalent of
iron chloride but no reaction was occurred. Similar results were observed by using diisopropylTAZ-S. However, colour change from very pale yellow to greenish blue was observed upon trials to coordinate nickel chloride in acetonitrile with both selenone and thione compounds. A green solid was collected from the selenium complex and blue solid from the sulfur complex with yields of 47 and 75% respectively. Both complexes are air and moisture sensitive and both are slightly soluble in DCM, THF, MeCN and CHCl₃. The ¹H NMR spectra of both complexes did not show a good resolution as it is rarely to see coupling and the peaks appear as broad singlets which could be a consequence of the paramagnetic properties of these complexes as was reported for other nickel complexes with tetrahedral geometry.⁴² Green crystals were obtained by slow evaporation of selenone solution and the molecular crystal structure (TAZSe)₂NiCl₂ was determined by X-ray diffraction. The coordination geometry of the Ni centre could be seen as distorted tetrahedron with two chlorine atoms and two selenium atoms. Se₁-Ni-Se₁ = 111.26(5); Se₁-Ni-Cl₁ = 101.97(5); Se₁-Ni-Cl₁ = 103.78(4); Cl₁-Ni-Cl₁ = 133.52(11). This deviation of the ideal tetrahedral angle is probably due to a steric effect of the two large TAZSe fragments. The Ni-Se bond length = 2.4389(9)Å which is slightly longer than that reported of imidazole analogous NiBr₂mbis (2.3941(8)Å).⁴² The Se-C₅ bond length of (1.867(5) Å in (TAZSe)₂NiCl₂ is significantly longer than that of the corresponding ligand ³⁴²TAZSe 1.830(4) which could be indicative of increased electron back donation from metal to the selenone fragment.

It has been reported that some of nickel(II) complexes could display square planar geometry as well based on spectroscopic and crystallographic data. When the complex is considered a square planar, it possesses diamagnetic properties and results in a good resolution in the NMR spectroscopy, and it obtains a trans configuration in the solid state. In contrast, the structure could exhibit a distorted tetrahedral geometry when it displays paramagnetic properties that can be
known by a poor NMR spectra resolution. In addition, the paramagnetic isomer was reported to have a blue or green colour. Accordingly, our Ni-Se complex is a distorted tetrahedron and has paramagnetic properties in both solution and solid state.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>iPrTAZ-Se</th>
<th>MeTAZ-Se</th>
<th>iPrTAZ-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se1—C5</td>
<td>1.830(4)</td>
<td>1.842(9)</td>
<td>—</td>
</tr>
<tr>
<td>S1—C5</td>
<td>—</td>
<td>—</td>
<td>1.6745(18)</td>
</tr>
<tr>
<td>N1—N2</td>
<td>1.372(5)</td>
<td>1.369(11)</td>
<td>1.374(2)</td>
</tr>
<tr>
<td>N1—C5</td>
<td>1.339(5)</td>
<td>1.335(12)</td>
<td>1.349(2)</td>
</tr>
<tr>
<td>N1—C6</td>
<td>1.471(5)</td>
<td>1.450(11)</td>
<td>1.472(2)</td>
</tr>
<tr>
<td>N4—C5</td>
<td>1.368(5)</td>
<td>1.361(12)</td>
<td>1.374(2)</td>
</tr>
<tr>
<td>N4—C3</td>
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<td>1.357(12)</td>
<td>1.366(2)</td>
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<tr>
<td>N4—C9</td>
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<td>1.443(11)</td>
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<tr>
<td>N2—C3</td>
<td>1.308(6)</td>
<td>1.302(13)</td>
<td>1.296(3)</td>
</tr>
<tr>
<td>N1—C5—N4</td>
<td>104.4(3)</td>
<td>105.0(8)</td>
<td>103.96(14)</td>
</tr>
<tr>
<td>N1—C5—Se1</td>
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<td>128.1(7)</td>
<td>—</td>
</tr>
<tr>
<td>N4—C5—Se1</td>
<td>127.5(3)</td>
<td>126.9(7)</td>
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<tr>
<td>N1—C5—S1</td>
<td>—</td>
<td>—</td>
<td>128.33(14)</td>
</tr>
<tr>
<td>N4—C5—S1</td>
<td>—</td>
<td>—</td>
<td>127.71(14)</td>
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<tr>
<td>C5—N1—N2</td>
<td>112.7(3)</td>
<td>112.5(7)</td>
<td>112.62(14)</td>
</tr>
<tr>
<td>C3—N4—C5</td>
<td>107.5(3)</td>
<td>106.7(8)</td>
<td>107.26(15)</td>
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Table 4.3: Selected bond lengths /Å and angles /° of the (TAZSe)$_2$NiCl$_2$

<table>
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<tr>
<th>Bond lengths /Å</th>
<th>angles /°</th>
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<tr>
<td>Se1—Ni1</td>
<td>2.4389(9)</td>
</tr>
<tr>
<td>Se1—C5</td>
<td>1.867(5)</td>
</tr>
<tr>
<td>Ni1—Cl1</td>
<td>2.2345(16)</td>
</tr>
<tr>
<td>Ni1—Cl1$^1$</td>
<td>2.2345(16)</td>
</tr>
<tr>
<td>N1—C5</td>
<td>1.338(7)</td>
</tr>
<tr>
<td>N1—N2</td>
<td>1.371(7)</td>
</tr>
<tr>
<td>N1—C6</td>
<td>1.491(7)</td>
</tr>
<tr>
<td>N4—C5</td>
<td>1.366(7)</td>
</tr>
</tbody>
</table>

Table 4.4: Summary of crystallographic data for the 1,2,4-triazol-5-selenone compounds

<table>
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<tr>
<th>Compound</th>
<th>$^{iPr}$TAZ-Se</th>
<th>$^{Me}$TAZ-Se</th>
<th>$^{iPr}$TAZ-S</th>
<th>(TAZSe)$_2$NiCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>FE227_1_P21n</td>
<td>FE311_P21_new</td>
<td>twin4</td>
<td>FE341_C2c</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>8$H$</em>{15}$N$_3$Se</td>
<td>C$_4$H$_7$N$_3$Se</td>
<td>C$<em>8$H$</em>{15}$N$_3$S</td>
<td>C$<em>8$H$</em>{15}$ClN$<em>3$Ni$</em>{10.5}$Se</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>185.29</td>
<td>296.99</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
<td>monoclinic</td>
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<tr>
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<td>P21</td>
<td>P21/n</td>
<td>C2/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>5.6467(5)</td>
<td>4.2409(6)</td>
<td>5.6869(3)</td>
<td>17.8370(12)</td>
</tr>
<tr>
<td>b/Å</td>
<td>18.0801(17)</td>
<td>5.8566(7)</td>
<td>17.7886(8)</td>
<td>9.4407(7)</td>
</tr>
<tr>
<td>c/Å</td>
<td>10.8349(10)</td>
<td>13.0765(17)</td>
<td>10.6002(5)</td>
<td>14.8705(10)</td>
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<td>α/°</td>
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<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β/°</td>
<td>98.335(3)</td>
<td>94.531(6)</td>
<td>102.132(2)</td>
<td>106.846(2)</td>
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<tr>
<td>γ/°</td>
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<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>Volume/Å$^3$</td>
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<td>323.77(7)</td>
<td>1048.39(9)</td>
<td>2396.6(3)</td>
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<td>Value 1</td>
<td>Value 2</td>
<td>Value 3</td>
<td>Value 4</td>
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<td>---------</td>
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<tr>
<td>$\rho_{\text{calc}}$/cm$^3$</td>
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<td>1.8061</td>
<td>1.174</td>
<td>1.646</td>
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<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>1.474</td>
<td>7.031</td>
<td>2.372</td>
<td>4.083</td>
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<tr>
<td>$F(000)$</td>
<td>562.0</td>
<td>170.7</td>
<td>400.0</td>
<td>1192.0</td>
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<td>Crystal size/mm$^3$</td>
<td>0.2 x 0.165 x 0.07</td>
<td>0.22 x 0.22 x 0.08</td>
<td>0.5 x 0.22 x 0.1</td>
<td>0.7 x 0.4 x 0.2</td>
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<td>Cu K$\alpha$ ($\lambda = 1.54178$)</td>
<td>CuK$\alpha$ ($\lambda = 1.54178$)</td>
<td>MoK$\alpha$ ($\lambda = 0.71073$)</td>
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<tr>
<td>2$\theta$ range for data collection/$^\circ$</td>
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<td>9.878 to 144.964</td>
<td>6.04 to 58.36</td>
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<td>-24 $\leq$ h $\leq$ 24</td>
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<tr>
<td>Reflections collected</td>
<td>36247</td>
<td>4769</td>
<td>6002</td>
<td>17534</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3993 [Rint = 0.0498]</td>
<td>1172 [Rint = 0.0565]</td>
<td>6002 [Rint = 0.0519]</td>
<td>3138 [Rint = 0.0641]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
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<td>1172/49/76</td>
<td>6002/0/115</td>
<td>3138/0/127</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
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<td>1.035</td>
<td>1.056</td>
<td>1.196</td>
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<td>Final R indexes [I$\geq$2$\sigma$ (I)]</td>
<td>R1 = 0.0643</td>
<td>R1 = 0.0607</td>
<td>R1 = 0.0534</td>
<td>R1 = 0.0698</td>
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<tr>
<td></td>
<td>wR2 = 0.1606</td>
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<td>wR2 = 0.1416</td>
<td>wR2 = 0.1302</td>
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<td>R1 = 0.1110</td>
<td>R1 = 0.0609</td>
<td>R1 = 0.0558</td>
<td>R1 = 0.0896</td>
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<td>wR2 = 0.1814</td>
<td>wR2 = 0.1752</td>
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<tr>
<td>Largest diff. peak/hole / e Å$^{-3}$</td>
<td>1.90/-0.83</td>
<td>2.12/-1.09</td>
<td>0.26/-0.39</td>
<td>1.28/-0.91</td>
</tr>
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</table>
Figure 4.6: Thermal ellipsoid plot (50% probability surface) of 1,2,4-triazol-5-selenones. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /° are summarized in Table 4.2
4.4 Computational Studies

Table 4.5: Summary of the calculated results

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<th>Model</th>
<th>$E_{H}$/eV</th>
<th>$E_{L}$/eV</th>
<th>$E_{H-L}$/eV</th>
<th>LP$<em>{(p)}$ (NBO)$</em>{a)}$</th>
<th>$E_{deloc.}$_{b)}</th>
<th>R(C—Se) / Å</th>
<th>N—C—N / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{iPr}$TAZSe</td>
<td>-5.52</td>
<td>-0.11</td>
<td>5.41</td>
<td>1.69</td>
<td>72.72</td>
<td>1.83114</td>
<td>103.195</td>
</tr>
<tr>
<td>$^{Et}$TAZ$^{iPr}$Se</td>
<td>-5.58</td>
<td>-0.08</td>
<td>5.5</td>
<td>1.68</td>
<td>74.41</td>
<td>1.82490</td>
<td>103.390</td>
</tr>
<tr>
<td>$^{Et}$TAZSe</td>
<td>-5.61</td>
<td>-0.11</td>
<td>5.50</td>
<td>1.68</td>
<td>75.57</td>
<td>1.82356</td>
<td>103.260</td>
</tr>
<tr>
<td>$^{Me}$TAZSe</td>
<td>-5.66</td>
<td>-0.19</td>
<td>5.47</td>
<td>1.67</td>
<td>79.27</td>
<td>1.81996</td>
<td>103.090</td>
</tr>
<tr>
<td>$^{Bz}$TAZSe</td>
<td>-5.71</td>
<td>-0.68</td>
<td>5.03</td>
<td>1.69</td>
<td>73.16</td>
<td>1.82691</td>
<td>103.148</td>
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</tbody>
</table>

The Natural Bond Orbital (NBO) analysis of the models identifies two lone pairs on selenium in each case (Table 4.5). The π-type lone pair is found to be engaged in a great amount of hyperconjugation with the C—N antibonding orbitals of the TAZ fragment in each compound. The amount of the hyperconjugation in the compounds presents a significant order as follows: $^{Me}$TAZSe (ca. 80 Kcal mol$^{-1}$) > $^{Et}$TAZSe (ca. 75 Kcal mol$^{-1}$) > $^{iPr}$TAZSe (ca. 70 Kcal mol$^{-1}$). This
order indicates that the \( \text{iPrTAZSe} \) possesses less \( \pi \)-acceptor ability and the \( \text{MeTAZSe} \) exhibits the highest \( \pi \)-acceptor properties. The calculated HOMO energy of \( \text{MeTAZSe} \) (-5.66 eV) < \( \text{EtTAZSe} \) (-5.61 eV) < \( \text{iPrTAZSe} \) (-5.52 eV) supports the results that the \( \text{iPrTAZSe} \) is stronger donor than the \( \text{MeTAZSe} \). However, the LUMO energy in \( \text{EtTAZSe} \) and \( \text{iPrTAZSe} \) are the same (-0.11 eV) and is greater than that of \( \text{MeTAZSe} \) (-0.19 eV) suggesting that the \( \text{iPrTAZSe} \) has less \( \pi \)-acceptor properties than \( \text{MeTAZSe} \) which in turn causes the C—Se bond length of \( \text{MeTAZSe} \) (1.81996 Å) shorter than that of \( \text{iPrTAZSe} \) (1.83114 Å) as shown in Table 4.5. These computational results agree well with the observed \( ^{77}\text{Se} \) NMR spectroscopic data. The \( ^{77}\text{Se} \) NMR resonance of \( \text{MeTAZSe} \) (24.50 ppm) is greater than that of \( \text{iPrTAZSe} \) (5.96 ppm) indicating that the former is higher \( \pi \)-acceptors than the later.

### 4.5 Conclusions

TAZ-Se compounds have been synthesized and characterized by \( ^{77}\text{Se} \) NMR, \( ^{13}\text{C} \) NMR, \( ^{1}\text{H} \) NMR, EA and X-ray. \( ^{77}\text{Se} \) NMR, \( ^{13}\text{C} \) NMR showed a good correlation to the \( \pi \)-acceptor properties of the corresponding carbenes. According to the observed \( ^{77}\text{Se} \) NMR chemical shifts of the TAZ-Se compounds and that of reported IMID-Se compounds, TAZs have higher \( \pi \)-acceptor properties than IMIDs. In addition, \( \text{MeTAZ} \) and \( \text{BzlTAZ} \) have the highest acceptor properties and the \( \text{iPrTAZ} \) has the lowest \( \pi \)-acceptor abilities. DFT calculations were employed and the HOMO and LUMO energies revealed that \( \text{MeTAZ} \) and \( \text{BzlTAZ} \) have the highest acceptor properties and lowest donor properties in comparison with \( \text{iPrTAZ} \) that shows higher donor properties and lower \( \pi \)-acceptor abilities which agree well with the experimental results. \( \text{iPrTAZ-S} \) adduct was synthesized and fully characterized by \( ^{13}\text{C} \) NMR, \( ^{1}\text{H} \) NMR, EA and X-ray. Both adducts, \( \text{iPrTAZ-S} \) and \( \text{iPrTAZ-Se} \) were reacted with \( \text{NiCl}_2 \cdot \text{dme} \) and produced green and blue materials respectively. X-ray structure of the
complex \((^{1}PrTAZSe)_{2}NiCl_{2}\) was obtained and showed a distorted tetrahedral geometry around nickel centre. The NMR spectra of both complexes indicated the presence of paramagnetism as illustrated by the broad peaks and the poor coupling resolutions.
4.6 References


Chapter 5: Conclusions and Future Work

5.1 Conclusions

The aim of this research was the examination of the ability of triazole carbenes to stabilize phosphorus in a low oxidation state (+I) and to compare these compounds their imidazole analogues via the synthesis of 1,2-dialkyl-1,2,4-triazole-stabilized phosphorus(I) cations. The unique feature of P\textsuperscript{I} compounds is that the phosphorus(I) fragment is a very electron rich and low coordinate centre which allow for further studies such as examining their reactivity towards Lewis acids. The Macdonald group has reported the synthesis and isolation of various substituted imidazole-stabilized phosphorus(I) cations via a transfer of P\textsuperscript{I} fragment using the precursor [(dppe)P\textsuperscript{I}]\textsuperscript{+} cation.\textsuperscript{1–5}

Our initial work in this research began with the synthesis of various 1,2-dialkyl-1,2,4-triazolium salts which mainly contain small alkyl groups (Me, Et, iPr and Benzyl) and different counter ions (Iodide, triflate and tetraphenylborate). We noted that these salts are moisture sensitive except for isopropyl substituted salt and therefore the preparation of the salts was performed under inert atmosphere. 1,2-dialkyl-1,2,4-triazole-stabilized phosphorus(I) cations [(R\textsuperscript{TAZ}R')\textsubscript{2}P\textsuperscript{I}]\textsuperscript{+} were then prepared through deprotonation of trizolium salt using a suitable base and then followed by addition of [(dppe)P\textsuperscript{I}]\textsuperscript{+} as a source of P\textsuperscript{I} fragment in situ. Attempts to isolate free carbenes were unsuccessful as they decompose readily upon the typical isolation processes. Also, it is worth noting that the diisopropyl-TAZP\textsuperscript{I} is the most stable and the easiest to purify among the others. The acidity of TAZP\textsuperscript{I} adducts were studied by comparing their crystallographic and \textsuperscript{31}P NMR spectroscopic properties to those of their IMIDP\textsuperscript{I} analogues; the results indicated that TAZP\textsuperscript{I} adducts are superior acids comparing to the IMIDP\textsuperscript{I} adducts. Theoretical studies were accomplished by using
DFT theory suggested that TAZ$^{\text{I}}$ models have stronger $\pi$-acidic properties than that of IMID$^{\text{I}}$ models which agrees will with the observed results. Cyclic TAZ$^{\text{I}}$ adducts were synthesized as well and $^{31}\text{P}$ NMR spectroscopy results show that these compounds are stronger $\pi$-acceptors than both acyclic TAZ$^{\text{I}}$ and reported acyclic IMID$^{\text{I}}$ compounds.\textsuperscript{6}

In previous work by the Macdonald lab, the IMID$^{\text{I}}$ ions showed interesting reactivities towards Lewis acids through oxidation reactions and reactions with transition metals. We have examined the reactivity of TAZ$^{\text{I}}$ adducts by interactions with oxidizing reagents and transition metals using same conditions applied for the reported IMID$^{\text{I}}$ cations. Even though the $^{31}\text{P}$ NMR spectroscopy showed that the coordination does occur, the complexes were unstable and decompose in solutions. We have used computational studies to rationalize the low stability of these compounds and the results agreed well with the experimental observations. In addition, as the triazoles have the ability to show different coordination modes, we examined the possibility of the coordination to occur through nitrogen centres as alternative binding sites. The results for TAZ$^{\text{I}}$ compounds according to NMR spectroscopic data showed that the coordination only occurs through the phosphorus centre and not the nitrogen atoms even upon addition of an excess of the corresponding Lewis acid.

In accordance with our previous observations and computations, we chose to study the electronic properties of the TAZ carbenes. Some studies were reported on IMID carbenes in which the electronic properties were investigated according to the observed $^{31}\text{P}$ NMR chemical shifts of phosphinidene compounds and $^{77}\text{Se}$ NMR resonance of selenone compounds.\textsuperscript{7,8,9,10} We synthesized $^R\text{TAZ}^R \text{Se}$ adducts and according to the $^{77}\text{Se}$ NMR resonance, the TAZ carbenes are stronger $\pi$-acceptors than the well-known IMID carbenes. Computational studies were used to study the electronic properties of TAZ carbenes through using $^R\text{TAZ}^R \text{Se}$ models.
5.2 Future Work

Our work in this research provided us with valuable insights into the stabilization of the disubstituted-TAZP\textsuperscript{i} cations and their reactivities. We found from our study that as the alkyl group size increases the compounds shows less acceptor properties, as a result; bulkier alkyl groups could result in better electronic properties which enhances the stability of the Lewis base-acid adducts. For example, Ender’s carbnene\textsuperscript{11} (Scheme 5.1) which shows high stability in inert atmosphere, showed an interesting complexes with transition metals (Mo, Cr, W) as was reported by Frey et al. in 2006.\textsuperscript{12} This carbene could be reacted with the cyclic triphosphenium cation [(dppe)P\textsubscript{i}]\textsuperscript{+}, and investigates its ability to stabilize phosphorus in the +1 oxidation state and then further investigations on the complex reactivity could proceed as well. Same reaction could be applied on carbenes generated by Korotkikh el al. in 2003.\textsuperscript{13} In addition, triazole pyridinium salts could be prepared and then the carbene can be generated by using the suitable reagent followed by reaction with the precursor [(dppe)P\textsubscript{i}]\textsuperscript{+}.

\begin{center}
\textbf{Scheme 5.1: Proposed reaction between Ender's carbene and cyclic triphosphenium cation and Korotkikh’s Carbene; }R_1 = \text{C}_6\text{H}_5, \text{p-C}_6\text{H}_4\text{Br}; R_2 = \text{C}_6\text{H}_5, \text{α-C}_{10}\text{H}_{17}, \text{p-C}_6\text{H}_4\text{Br}
\end{center}
Our attempts to study the reactivity of triazole phosphorus(I) cations through reactions with Lewis acids were unsuccessful due to the high $\pi$-acceptor properties of triazole carbenes that reduces the basicity and donor ability of the P$^I$ fragment. For example, the oxidation of P$^I$ centre via methylation using methyl triflate did not lead to a complete methylation of the P$^I$ centre, therefore it could be worthwhile to try to force the methylation to completion by applying different conditions. Using a stronger methylation reagent could be one possible attempt such as trimethylloxonium tetrafluoroborate. Also, coordination of borane with triazole P(I) cation using BH$_3$·THF and BH$_3$·DMS resulted in unstable complexes as the bond between BH$_3$ and THF or DMS is stronger than that forms between BH$_3$ and P(I) centre, therefore; employing different source of BH$_3$ that is less stable could assist in isolation of TAZP-BH$_3$ complex. Weigand et al. reported a remarkable reactivity of imidazole phosphorus(I) cations as they can be oxidized by nitrosyl triflate NO(OTf) to form radicals.$^{14}$ The EPR spectroscopy and DFT studies revealed the synthesis of these radicals. Similar investigations can be applied to triazole phosphorus(I) cations to examine their ability to generate radicals.

Exploring the reactivity of triazole carbenes towards other main group elements would be of interest as it opens new classes of compounds. Reactions which are worth trying that between triazolium salts and the heavier pnictogens (As, Sb and Bi). By applying same approaches and conditions as the phosphorus analogues, low oxidation states of the heavier pnictogens can be obtained and then compare them with that has been reported for imidazoles.$^{15,16,17}$ These compounds can be further explored in the synthesis of the corresponding Lewis acid-base adducts. Triazoles with chalcogens (S and Se) showed remarkable results as we reported in Chapter 4. We were able to synthesize and fully characterize monocoordinated chalcogen atoms (S and Se). Further investigation on these adducts would be fruitful as these compounds display attractive features
in the medical field. Protonation and methylation of these compounds could produce dicooordinated chalcogen atoms similar to those reported for imidazole congeners. (TAZ)$_2$Ch dications is another example that is worth trying as dicooordinated chalcogenes which then leads to further investigations such as interactions with Lewis acids. Tetracoordinate chalcogens have been observed for imidazoles, thus triazoles could produce similar adducts as well.
5.3 References


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<tr>
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<tr>
<td>PLACE OF BIRTH:</td>
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<tr>
<td></td>
<td>Misurata University, B.Sc., Misurata, Libya, 1999</td>
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<tr>
<td></td>
<td>St. Francis Xavier University, M.Sc., Antigonish, NS, 2008</td>
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