Building New Low Valent Phosphorus Molecules by P+ Transfer

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Building New Low Valent Phosphorus Molecules by P+ Transfer

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December 8, 2017
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: Chapter 2 contains results published in the journal article entitled “Low Valent Chemistry: An Alternative Approach to Phosphorus-Containing Oligomers” (Kosnik, S.C., Farrar, G.J., Norton, E.L., Cooper, B.F.T., Ellis, B.D., Macdonald, C.L.B., Inorg. Chem. 2014, 53, 13061-13069.) I prepared the manuscript and synthesized and characterized three of the five reported compounds in this work, Gregory J. Farrar synthesized and characterized the molecule \([\text{C}_5\text{H}_3(\text{PPh}_2)_2\text{P}]_2\) and optimized the literature preparations of the ligand. Erin L. Norton first synthesized the molecule \([\text{Ph}_2\text{P}_2\text{NP}]_2\), whos work-up I optimized. Benjamin F.T. Cooper performed the X-ray crystallography experiments for the molecules: \([\text{N(Ph}_2\text{P)}_2\text{P}]_2\) and \([\text{C}_5\text{H}_3(\text{PPh}_2)_2\text{P}]_2\). My supervisor, Dr. Charles L.B. Macdonald provided significant edits to the article.

I was the sole researcher for the results presented in Chapter 3, which are based on the publication entitled “A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor” (Kosnik, S.C., Macdonald, C.L.B., Dalton. Trans. 2016, 45, 6251-6258). My supervisor, Charles L.B. Macdonald performed the computational studies for this work and wrote the computational section of this manuscript, and provided edits for the entire manuscript.

The work in contained in Chapter 4 has been published in the journal article entitled “Accessing Multimetallic Complexes with a Phosphorus (I) Zwitterion” (Kosnik, S.C., Nascimento, M. C., Binder, J.F., Macdonald, C.L.B., Dalton Trans., 2017, 46, 17080-17092) and was co-authored by Maxemilian C. Nascimento, Justin F. Binder and Charles L.B. Macdonald. I prepared and fully characterized all the
molecules reported in this work. I also fully prepared the manuscript, with the assistance of my supervisor, Dr. Charles L.B. Macdonald, who provided edits to the article. Maxemilian Nascimento carried out the synthesis of some of the metal carbonyl complexes under my supervision, and Justin Binder provided the computational investigations reported in this work.

Chapter 6 contains results published in the journal article “Synthesis of bis(trithio)phosphines by oxidative transfer of phosphorus(I)” (Kosnik, S.C., Nascimento, M. C., Rawson, J. M., Macdonald, C.L.B., Dalton Trans. 2017, 46, 9769-9776.) I did the initial reactivity studies of the tetrathiocin and disulfide ligands with [dppeP][Br], provided supervision to my undergraduate student, Maxemilian Nascimento, who carried out the preparation of the molecules presented in the work. I did the characterization of all of the molecules and prepared the manuscript. Jeremy M. Rawson and Charles L.B. Macdonald provided significant edits for the manuscript.

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II. Previous Publications

This thesis includes 4 original papers that have been previously published/submitted for publication in peer reviewed journals, as follows:
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<td>Published</td>
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III. General

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Abstract

$P^+$ transfer was achieved through ligand metathesis and oxidative addition reactions from an air- and moisture- stable triphosphenium cation, [dppeP$^+$][Br], to generate new molecules containing low valent phosphorus. This protocol, involving the transfer of $P^+$, allows for the generation of these molecules without the use of harsh reagents, in high yields, and is often achieved in few synthetic steps.

This protocol has allowed for the synthesis of new phosphorus containing oligomers, including a phosphorus-rich analogue to polyphosphazenes, which can act as a bidentate donor to late transition metals.

Further, neutral triphosphenium analogues can be synthesized through ligand exchange reactions, leading to the production of two different multidentate donors. These molecules, which feature a low oxidation state phosphorus center have the ability to act as multidentate donors. The molecule [Cp(PPh$_2$)$_3$P$^+$] selectively generates complexes at the phosphine fragment on the backbone of the ligand, and this reactivity is rationalized based on computational studies. In contrast, the molecule [tBuCp(PPh$_2$)$_3$P$^+$] generates multimetallic complexes with metal carbonyls through either the P$^+$ fragment or the Cp and P$^+$ fragments simultaneously. The reactivity of this ligand changes dramatically with mid- and late- transition metals, which insert into the P-P bond of the triphosphenium fragment.

Finally, the addition of disulfide based ligands to [dppeP$^+$][Br] result in the oxidative transfer of the P$^+$ moiety, generating trithiophosphines in one step. We postulate that the formation of these molecules proceeds through a P$^{III}$ dimer, to which an additional fragment of disulfide adds, to generate the final thiophosphines.
Acknowledgments

During the last five years while speaking to friends and family about graduate school, the two most common questions I’ve asked are: “Why?” and “Well, what are you going to do with that?” The latter is easiest to answer of course, it is simply: I’ll be a chemist. The former, is much more difficult. I like to think that everything fell into place as it should, I often reply: “it felt like the right thing to do.”. In many ways, this adventure has been guided by my supervisor, committee members, colleagues, friends and family, all of whom I would like to thank here.

Chuck Macdonald has been my supervisor from the beginning of my undergraduate thesis project until the end of my Ph.D. He has provided me with an enormous amount of assistance and guidance throughout the years, and most valuably, with creative freedom in each of my projects. Chuck has given me a vast amount of opportunities throughout grad school, which have greatly enhanced my overall experience. I’ve learnt an extraordinary amount of chemistry from him, for which I am sincerely thankful for. I also feel extremely privileged to great committee members: Jeremy Rawson and Steve Loeb. Jeremy has been an intricate part of my studies at the University of Windsor, both as a lecturer and researcher; He invited me to his own research group’s meetings, allowed me to “pop” by his office whenever I had a question, comment, or concern, and provided significant direction and support in the completion of one of my last projects (Chapter 6). I have been fortunate enough that both Jeremy and Steve have always been extremely accommodating with their busy schedules, and have always taken the time to ask insightful questions or to give advice.

In my six years in the Macdonald research group, I have spent every day working with some great colleagues. I would like to thank all the past and present members of the group for the good company, lending me NMR tubes, or P\textsuperscript{1} salt, and
occasionally cleaning up the lab after I’ve reminded them several times. I would like to
first thank Dr. Greg Farrar who got me started in the group, provided tremendous
training for all my eventual projects, and for his support and advice throughout grad
school. I’d also give my sincerest gratitude to my former undergrad and now co-Ph.D
student: Justin Binder, for his daily support throughout the last four years, particularly
for great conversations about main group chemistry, new reactions to try, new projects
to start, and sometimes just to rant. Most of all, I am thankful for all the laughs and
great times throughout the past couple years. I think we have ridiculous stories from
every single conference we’ve been to, from hobbling down the cobblestone streets of
Montreal (on crutches) to get a late-night poutine, to belting out the theme song to Game
of Thrones in the residential area of downtown Halifax at 2am on a Tuesday. It should
be noted here that it’s likely that we set a record for beer consumed at a conference
while still attending every single talk, at the IRIS conference in Germany, a great
accomplishment given the lack of still water. It’s been a pleasure to have you around
throughout these past couple years. I’d also like to thank Ala, for his companionship in
the office and lab over the past couple years. I couldn’t have obtained that white board
for the office without your help. (By the way, I still want you to clean your fume hood,
and don’t pawn it off on your undergrad!) On the subject of undergrads, I’d like to give
my deepest gratitude to Max Nascimento for all his help on various projects, most of
which are contained in this thesis. Max helped me work on multiple projects
simultaneously and never really complained when I asked to “quickly do ___” or “Can
you check___”, at least I didn’t hear him complain. Max has been a fantastic co-worker
and I am indebted to him for his assistance in the lab. To Brad, Emily, Louae, and
Blake, thanks for all the laughs, conversations, and memes in the last two months during
which time I spent more time in the office than I wanted to while writing this thesis.
The Department of Chemistry has been an extremely supportive environment to work in. Thank you to all the friends I’ve made other research groups: Dr. Karen Johnston, Dr. John Hayward, Chris O’Keefe (My first chem-prom date), Mike Jaroszewicz, Akhil Vohra, Pablo Bulit, Manar (Jafar) Shoshani, Hi Taing, Dr. Meghan Doster (Djurdjevic), Mitch Nascimento, Elodie Heyer, Konstantina Pringouri, and Ronan San Juan. There are too many good memories to recount, between conferences, beer festivals, (keg) parties, and weekends in the lab. Aside from that, I would like to especially thank Manar for his help with his consultation with complicated NMR coupling patterns, simulating spectra, and general questions about organometallic chemistry.

To all the staff in the department: Una, Janeen Auld, Matt Revington, Beth Kickham, Cathy & Marlene, thank you for your patience and help throughout the last couple years; particularly to Una for being patient when I was “running late” for GA-ing every week because I have experiments to finish up, and to the office staff for letting us use the smart TV to watch Game of Thrones on Sunday nights in the conference room. I’d also like to thank other faculty members in the department: Dr. Rob Schurko, for allowing me to loiter in his student office almost every day, and always inviting me to his research group’s outings and parties. To Dr. Jim Green, for constant guidance and questions regarding synthesis and everything else chemistry related, and to Dr. Holger Eicchorn for his help in translating German publications, and in setting up the soxhlet extractor, which ended up being a vital technique for the purification of my starting materials.

Finally, and most importantly, I’ve like to thank my family and friends for all their incredible support over the last five years. I had the good fortune of meeting my fiancé, David, at the beginning of graduate school, and it has made the past five years
have been absolutely amazing. I am eternally grateful for his constant patience when I had to go into the lab to mount a crystal at midnight, or when I said I was almost done in the lab, only to spend the next hour setting up crystallizations or getting a “quick” NMR spectrum. Most of all thanks for your support when we were both stressed about comprehensive exams, conference talks, writing publications, or projects that weren’t working, I truly feel that I couldn’t have completed this thesis without you. Thank you to my good friends, for making me take breaks from chemistry: Sylvia (lab partner for life), Katie, Saskia, Christiana, Chris, Sydney, and Mel; and to Michael, for stimulating discussions about philosophy, especially when I was no longer able to take classes in that area.

Certainly, not least, I would like to deepest gratitude to my parents for their support and patience throughout the years, and always pushing me to accomplish my goals.
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List of Abbreviations

A⁻ Non-descript anion
Å Angstrom
Ar-BIAN bis(arylimino)acenaphthene
BIPY 2,2’-bipyridine
Bu butyl
CSD Cambridge Structural Database
COD cyclooctadiene
Cp cyclopentadienyl
δ chemical shift (NMR)
d doublet (NMR)
DCM dichloromethane
DFT density functional theory
Do donor
dppe diphenylphosphinoethane
E element
ERO Electron Rich Olefin
Et₂O diethyl ether
FLP Frustrated Lewis Pair
HOMO highest occupied molecular orbital
HRMS high-resolution mass spectrometry
iPr iso-propyl
IUPAC International Union of Pure and Applied Chemistry
Jₓᵧ coupling constant between nuclei x and y
L ligand
LUMO lowest unoccupied molecular orbital
m multiplet (NMR)
Me methyl
Mes Mesityl - 1,3,5-trimethylbenzene
mmol millimole
NHC N-heterocyclic carbene
NHP N-heterocyclic phosphine
NMR Nuclear Magnetic Resonance
OTf triflate, trifluoromethanesulfonate
P¹ phosphorus in the +1 oxidation state
Ph phenyl
Pn Pnictogen- an element in group 15
ppm parts per million
q quartet (NMR)
R organic substituent
Redox reduction-oxidation
s singlet (NMR)
t triplet (NMR)
<table>
<thead>
<tr>
<th>THF</th>
<th>tetrohydrofuran</th>
</tr>
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<tbody>
<tr>
<td>X</td>
<td>halogen</td>
</tr>
<tr>
<td>Xs</td>
<td>excess</td>
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Philosophy stands in need of a science which shall determine the possibility, principles, and extent of human knowledge *a priori*.

— Immanuel Kant
Chapter 1: Introduction

1.1 General Introduction

The elements that make up the main group – the ones organized in the s- and p-blocks – are the most diverse and abundant elements within the periodic table. They exist as metals, metalloids and non-metals, and as solids, liquids and gases. This diversity of properties allows these elements and their compounds to be used for a tremendous array of applications across all sub-disciplines in chemistry.

In 1963 W.E Dasent published an article (and later a book) entitled “Non-existent Compounds”; the purpose of the report was to outline some of the shortcomings in valence bond theory, the octet rule, and other models that rationalize chemical interactions and bonding, and to draw attention to some of the reasons why molecules might be unstable despite “obeying” these standard rules. The educational aspect of this work had strong merit, however, it’s also conceivable that this editorial inadvertently challenged a community of main group chemists to explore new directions in synthesizing and stabilizing main group compounds in unusual bonding motifs. A perfect example of this is Dasent’s assertion that third row elements are reluctant to form multiple bonds involving $\pi$-$\pi$ overlap. There is of course, nothing fallacious about this statement but nevertheless some two decades later, Yoshifuji and co-workers reported the first diphosphene complex, flanked by bulky tri-tertbutylphenyl groups and complete with a double bond between two second row elements. This was achieved through the use of large, bulky groups which provide both kinetic and in some cases, electronic stabilization for these otherwise highly reactive species. Subsequently, there have been many more examples of heavy main group elements having multiple bonds, some of which have been useful for transition-metal free
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catalysis.3–7 One of the most notable aspects in the recent main group chemistry8 has been the continued development and investigation of compounds containing elements in low coordination environments. An important category of such compounds are those that contain main group elements in unusually low oxidation states.9

1.1.1 Oxidation States

The idea of oxidation states is one of the most fundamental concepts in chemistry because it allows for an assessment of the number of electrons associated with an individual atom. Since the oxidation state of an atom provides a description of the electron distribution surrounding that atom, it subsequently provides significant insight into the physical and chemical properties of the molecule or material in which the atom is found, and thus allows for predictive reactivity of molecules. The oxidation state of a given atom can be assigned in many ways; commonly, oxidation states are determined using a series of axiomatic rules that are generally based on relative electronegativities of the atoms in a molecule or ion.10 Such counting models are sufficient for some purposes, such as balancing redox equations, but the formal oxidation states determined in this manner provide no information as to the actual distribution of electrons within the molecule.11 Because of this deficiency, formal oxidation states do not offer direct insight into the nature of the bonding or structure within a molecule or much guidance in regard to its physical properties or chemical reactivity.

For p-block compounds, the conclusion associated with the assignment of formal oxidation states can often be ambiguous, counter-intuitive or even misleading. For example, consider the following general metathesis reaction: 3 LiR + PCl3 → 3 LiCl + PR3 and the products illustrated in Figure 1.1. When R = H, the typical counting rule in traditional oxidation state formalism requires that this reaction be considered a redox
process in which the phosphorus has gone from a $+3$ to $-3$ oxidation state. In contrast, when $R = NR'_2$, the identical salt-elimination reaction would never be considered to involve a redox process because there are no changes in oxidation states, When $R$ is a carbon-based substituent, the interpretation of the reaction is ambiguous (at best) and is dependent on the nature of the groups bound to the carbon atom. Finally, if $R$ is a phosphinyl fragment ($PR'_2$), the fractional formal oxidation states for the phosphorus atoms in the product would require a redox process. Regardless of the interpretation, in every instance, the product of the reaction $PR_3$ is a compound with a pyramidal geometry at the phosphorus that features one non-bonding pair of electrons.

![Figure 1.1 Salt metathesis reactions involving a phosphorus trihalide and various organolithium reagents to demonstrate the change in oxidation states of the phosphorus center determined by traditional counting rules.](image)

Clearly, the formal oxidation states resulting from counting rule approaches should not be over interpreted. The shortcomings in the assignment of oxidation states can make the use of valence states of the element in question more useful. Although the valence state is similar to the concept of an oxidation state, there are some important differences between
the two. A valence state corresponds to the number of electrons that an atom uses in bonding (or charges), while the oxidation state describes the charge remaining on an atom when all ligands are removed.\textsuperscript{11} Thus, the actual electron distribution within a compound must be known to determine the valence state of an atom, which may sometimes be undeterminable without experimental evidence. A rational approach to elucidate the electronic and structural features of a molecule is ultimately unification of both these ideas.

Our research group, amongst others, has employed a model in which the number of non-bonding electrons of an atom are used to assign an oxidation state of that atom. The success of this model also depends on an assumption: the atom in question must be considered less electronegative than any bonded atoms\textsuperscript{9,12}. While this is obviously unrealistic, this assumption eliminates anomalies in the assignment of oxidation states. For example, the assignment of the phosphorus center in the previously examined phosphines: PH\textsubscript{3}, P(CH\textsubscript{3})\textsubscript{3}, and P(NMe\textsubscript{2})\textsubscript{3} would all be +3 rather than -3, ± 3, and +3 respectively. We note that phosphorus is most commonly found in the +5 and +3 oxidation states; molecules P(V) often behave as Lewis acids, and have been extensively studied recently because of their applicability to the area of Frustrated Lewis Pair (FLP) chemistry.\textsuperscript{13} While compounds containing P(III) typically behave as Lewis bases, and represent the most ubiquitous class of ligands: phosphines. Phosphorus in the +1 oxidation state, in which the phosphorus center has two lone pairs, is commonly thought of as a reactive intermediate, and there are significantly less examples of stable molecules containing a P(I) center when compared to its higher oxidation state counterparts (\textbf{Figure 1.2}).
Figure 1.2 Oxidation states of phosphorus assigned based on number of lone pairs, and how the bonding arrangements might differ to variety the overall charge of the molecule.

It is the low valent, +1 oxidation state that intrigues us; this electron-rich phosphorus center proves to have different and sometimes unexpected reactivities in comparison to more common P(V) or P(III) analogues.\(^8\)

It is well known that low valent phosphorus centers display chemistry similar to group 14 compounds and phosphorus has often been labeled the “carbon copy.”\(^14\) Thus, many of the same considerations of bonding and stabilization of these elements have been applied to the other. In fact, alternative diagonal\(^15\) and isolobal\(^16,17\) relationships have extended these ideas of low valent- stabilization to different groups across the p-block and subsequently generated some truly remarkable compounds.\(^18,19\) It is these ideas that have made vast contributions to main group chemistry over the past few years.

1.1.2 Bonding Models

The depiction of molecular structures and bonding is the most critical aspect of chemistry, and it is most important when new complexes are first reported. Many of the new molecules that have been synthesized within the field of main group chemistry contain low valent main group elements, as such, it is pertinent that the distribution of electrons – \(i.e.\) bonding motifs – be described and depicted accurately, so as to best describe the
electronic structure and ultimately, the reactivity of these molecules. There are two frequently used models for drawing molecules: (1) **The Lewis bonding model**, first suggested in 1916 by G.N. Lewis, which uses a set of rules to determine both the number of bonds and number of unpaired electrons that should be drawn between atoms in a molecule. When drawing molecules using this model, relative electronegativities, valence electrons and formal charges are all considered to produce depiction of the molecule in question. Generally, this bonding model works well to describe the bonding arrangement in most molecules. However, in some circumstances this model provides an insufficient or inaccurate depiction of where the electrons might be located as a consequence of the protocols to minimize the number of formal charges drawn in a molecule. In many cases, it is would be more accurate to depict molecules as a multitude of canonical structures or resonance structures.

In 1923 Lewis published a follow-up chapter to this original work, introducing the idea of what we now term to be Lewis acids and bases. With this, also came the idea of (2) **The dative bond**, describing the donation of electrons from a Lewis acid to a Lewis base. Dewar, Chatt, and Duncanson later demonstrated the utility of dative bonds to describe bonding in transition metal and organometallic complexes, but this concept was underutilized by main group chemists at the time. More recently, the dative model has been used to describe main group complexes containing unusual bonding motifs, and/ or low valent main group atoms, sometimes with supporting evidence for its use from X-ray diffraction and computational studies. The increased use of dative bonds in main group chemistry has caused some controversy however, and individuals have been accused of
using dative bonds as a marketing ploy to increase the impact of new main group complexes.\textsuperscript{24}

“Bonding models are not right or wrong but they are more or less useful.”\textsuperscript{25}

Throughout this dissertation, a combination of these models will be used to best describe the bonding and electronics of the molecules presented. For example, Figure 1.3 shows the possible depictions of a triphosphenium cation using both Lewis structures and the dative bonding model.

![Figure 1.3 Depictions of a triphosphenium cation](image)

Experimental data suggests that the canonical form (III) in Figure 1.3 is likely the best depiction of the triphosphenium molecule. There are no examples of triphospheniums with a linear geometry within the R\textsubscript{3}P-P\textsuperscript{I}-PR\textsubscript{3} framework, whether the bis(phosphines) are chelating or not, so form (I) is an unreasonable depiction. Canonical form (II) is a common depiction of the triphosphenium fragment, as it satisfies Lewis drawing rules, but the inability of d orbitals to participate in bonding for p-block compounds does not allow for a true, P=P double bond in even a canonical structure. However, another type of $\pi$-interaction can allow some multiple bonding character but it should be noted that the P-P distances for triphosphenium cations usually fall into the range of single and double bonds.\textsuperscript{26} Computational and reactivity studies indicate that canonical form (III) is the best representation of the bonding and electron distribution in this molecule.\textsuperscript{27,28}
1.2 Stabilization of Low Valent Phosphorus

The first examples of low coordinate organophosphorus molecules came in the in the early 1960s, first with the highly reactive phosphaalkyne \((\text{HC≡P})\)\(^{29}\) and then with Dimroth’s phosphacyanine,\(^{30}\) and Märkl’s 2,4,5-triphenylphosphinine.\(^{31}\) These three molecules, which contradicted the double-bond rule, encompassed new electronic properties and subsequently new reactivities that were previously unknown for P(III) molecules at that time. Within the last two decades, accessing compounds that contain a low valent main group center has been topic of great interest to many main group chemists. Recent discoveries of great significance are the report of the first examples of heavy analogues of alkenes by Power\(^3\) as well as stable carbenes by Arduengo\(^{32}\) and Bertrand.\(^{33}\) These discoveries and many others, shaped current main group chemistry. In the cases of heavy alkenes and the first reports of stable carbenes, the use of sterically encumbering ligands became one of the key components in the isolation of what would otherwise be highly reactive or transient species. In this sense, while the designation of low oxidation state main group centers can be easily described by the presence of non-bonding electron “pairs”, the ancillary ligands play a vital role in understanding the chemistry of the low valent fragment as it dictates the electronic distribution and reactivity of the low valent center. This idea is well understood in organic functional groups: for example, a tricoordinate nitrogen center maybe classified as an amine or amide, depending on the presence of an adjacent carbonyl fragment and the chemistry of these tri-coordinate nitrogen compounds is very different. There are many ways to stabilize low valent centers\(^{12,19}\) and for low-valent phosphorus, there are three general classifications of ligands that help to stabilize these molecules: (1): ligands that act as relatively weak \(\pi\) acceptors
and provide stabilization via $\pi$-backbonding interactions into antibonding orbitals. (2): ligands which are excellent $\pi$ acceptors and provide stabilization by formal electron transfer on to the backbone of the ligand; and finally, (3): poor $\pi$ acceptors such as NHCs which maintain electron density on the main group center (Figure 1.4).

![Orbital depictions of low valent P\(^{I}\) centers; right a diimine fragment which accepts electron density from the phosphorus center to the ligand backbone. Middle, a triphosphenium fragment with arrows indicating negative hyperconjugation of one of the $\pi$-type lone pairs to available anti-bonding orbitals of the diphosphine backbone. Left, carbene stabilized phosphorus fragment, a weak $\pi$ acceptor](image)

**Figure 1.4** Orbital depictions of low valent P\(^{I}\) centers; right a diimine fragment which accepts electron density from the phosphorus center to the ligand backbone. Middle, a triphosphenium fragment with arrows indicating negative hyperconjugation of one of the $\pi$-type lone pairs to available anti-bonding orbitals of the diphosphine backbone. Left, carbene stabilized phosphorus fragment, a weak $\pi$ acceptor

### 1.2.1 P\((+1)\) Stabilized by Phosphines

Over the last few decades, phosphorus in the +1 oxidation state has become an attractive area of research; it has led to atypical compounds with alternative reactivities that are normally not observed in the more common oxidation states. The first report of a molecule containing a low valent phosphorus center bound between two phosphine fragments was reported in the late 1970’s by Fluck\(^{34}\), and remains one of the few examples of an anionic analogue to what was later referred to as triphosphenium cations. Schmidpeter and coworkers pioneered much of the work in this area during the 1980’s and synthesized the first examples of triphosphenium cations. Such ions can be thought of as having a P\(^{I}\) center flanked by phosphonio moieties, as described earlier. Early syntheses of these compounds typically involved addition of PCl\(_3\) to a chelating bis(phosphine) in the
presence of a reducing agent (for example SnCl₂) to produce the cationic P⁺ moiety (Figure 1.5, I). Later, Schmidpeter would employ excess phosphine to act as the reducing agent, however this only mildly improved the synthesis and yield and also generated reactive complex anions.35,36

In 2003, our group reported an improved synthesis to produce analogous triphosphenium salts by employing PI₃ in the absence of a reducing agent (Figure 1.5, II).37 This synthesis was an improvement in many ways on the original, as the number of complex byproducts was eliminated and reaction conditions were mild. Furthermore, this synthesis produced a by-product (I₂) that can be easily removed from the reaction mixture.

Figure 1.5 Protocols for the synthesis of cyclic triphosphenium cations from phosphorus trihalides.

Despite these improvements, one drawback to the PI₃ protocol is that the work up to remove I₂ decreases the overall yields of the reaction. Nevertheless, the Woollins group extended this protocol to peri-substituted bis(phosphine) naphthalene, to generate a P⁺ stabilized triphosphenium analogue with a rigid backbone;38 and subsequently a related molecule, a phosphanylidene phosphorene, which is an example of a compound featuring
a stabilized $P^I$ fragment (similar to a triphosphenium moiety) stabilized by a neighbouring phosphine. These types of phosphine-phosphinidene donor-acceptor complexes were shown to accommodate two equivalents of a Lewis acid at the univalent phosphorus center\textsuperscript{39} and the synthetic protocol was extended to heavier analogues.\textsuperscript{40}

The development of new synthetic protocols to generate stable compounds containing a low valent phosphorus center lead to a renewed interest in triphosphenium species as useful reagents, perhaps because of their stability as $P^I$ sources. In 2007, the Dillon group reported an NMR study of the proposed mechanism of formation of these triphosphenium salts. They demonstrated that the bis-phosphine ligand attacks the phosphorus trihalide to produce a cyclic “trapped” $P^{\text{III}}$-X fragment and $X_2$. The final halide atom is removed via the reducing agent, be it SnCl\textsubscript{2}, or a sacrificial bis-phosphine ligand, and this is the rate determining step of the reaction.\textsuperscript{41} In 2008, our group reported an improved synthesis to obtain these triphospheniums by employing a halogen scavenging agent (cyclohexene) and PBr\textsubscript{3} (\textbf{Figure 1.5, III}). Utilization of a halogen sequestering agent resulted in higher yields and fewer by-products than anything previously reported, we also found that this method was highly scalable without any complications.\textsuperscript{42}

In spite of their positive charge, cations containing one or more $P^I$ center can behave as electron donors (Lewis bases). For example, the acyclic \([(\text{Ph}_3\text{P})_2P]^+\) and \([(\text{N(Me}_2)_3\text{P})_2P]^+\) cations have shown to coordinate to AlCl\textsubscript{3} in a typical Lewis acid/base manner.\textsuperscript{43} Cyclic triphospheniums have been shown to undergo a limited number of oxidation reactions with more electrophilic reagents such as triflic acid or methyl triflate (\textbf{Figure 1.6, I}), however there has been limited success in the coordination of these salts to other metals. With respect to the cyclic triphospheniums, the Dillon group has shown
that some cyclic triphospheniums can undergo coordination of platinum (II) complexes to the P$^\text{I}$ center, though the coordination of the transition metal is largely influenced by the substitution of the ancillary phosphine ligands, and these complexes are only stable in solution, and decompose upon attempted isolation (Figure 1.6, III). Driess reported that acyclic triphosphenium cations, and their analogous arsenium cations, undergo a type of ligand exchange with Schwartz’s Reagent to produce square planar phosphonium and arsonium salts (Figure 1.6 I). Despite these reports, the chemistry involving these molecules remains underdeveloped, and it is postulated that the triphosphenium cations in particular are hindered in this respect because of the positive charge delocalized across the P-P-P fragment or the presence of nucleophilic anions (in some cases).

**Figure 1.6** The reactivity of triphosphenium cations with transition metals (I, III) and alkylating agents (II)

Recently, the Ragogna group reported the generation of a novel triphosphenium employing the PBr$_3$/cyclohexene methodology; resulting in a neutral species that features
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an anionic borate backbone. The zwitterionic nature of this molecule both enhances the solubility of these compounds and allowed them to exploit the donor abilities of the P\textsuperscript{I} center by increasing the electron density of the system.\textsuperscript{47} The zwitterions could coordinate one or even two AuCl fragments simultaneously and can ligate a variety of other transition metals (Figure 1.7).\textsuperscript{48}

![Diagram](image-url)

**Figure 1.7** Some reactions of Ragogna’s zwitterionic triphosphenium analogue with various transition metals.

1.2.2 Stabilization with diimine ligands

In contrast to bisphosphine ligands, diimine based ligands act as excellent π-acceptors such that they participate in a formal electron transfer (non-innocent behaviour) from the low valent phosphorus center resulting in a P\textsuperscript{III} center rather than a P\textsuperscript{I} center. Thus, some researchers noticed that the synthetic approaches developed for triphosphenium salts could be applied to obtain novel P\textsuperscript{III} compounds: specifically, N-heterocyclic
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phospheniums (NHPs). NHPs are the isovalent and isoelectronic analogues of the Arduengo-type carbene, but their discovery and isolation predate that of the carbene by about 20 years. Much of the modern progress towards NHPs was established by the groups of Cowley\textsuperscript{49} and more recently Gudat\textsuperscript{50}.

In 2006 the Cowley group reported the use of diimine ligands to produce Pn\textsuperscript{III} cations by employing Schmidpeter’s PCl\textsubscript{3}/SnCl\textsubscript{2} and our PI\textsubscript{3} method- reporting the first synthesis of these heterocycles;\textsuperscript{49} their study was supported by computational experiments done our research group at the same time.\textsuperscript{51} They had also observed similar results with aryl-BIAN ligands and noted that the “PCI” fragment causes the 2-electron reduction of the ligand due to the presence of an available low lying LUMO.\textsuperscript{52}

With Cowley’s work and our previous success employing PBr\textsubscript{3} and cyclohexene to synthesize triphospheniums, we were interested in applying this to some α-diimine ligands. We were able to synthesize the N-heterocyclic bromophosphane \textit{(p-bromo-diaazaphospholenes)}, an analogue of the N-heterocyclic phosphonium, by reacting a diimine ligand in the presence of PBr\textsubscript{3} and excess cyclohexene. We found that the bond length of the P-Br bond was about 0.2 Å longer than that of a standard bromophosphine bond, which is consistent with the observed bond lengths for various NHP-X bonds such as chlorine. The increased length is attributable to partial population of the antibonding σ*-orbital for P-Br (by the non-bonding electrons on N) which increases the non-bonding character in the phosphorus-bromine bond and makes it more easily ionized.

Similarly, the group of Gudat was interested in these types of ligands as candidates for the generation of phosphinidines through release of the P\textsuperscript{III} from the diimine fragment via retro cycloaddition. For this, they targeted pyrido-annulated variants, utilizing PI\textsubscript{3} to
generate the anticipated phosphonium in good yields; unfortunately there has been no report of release of the target phosphinidene fragment.\textsuperscript{53}

\begin{center}
\textbf{Figure 1.8} Protocols for the generation of N-heterocyclic phosphoniums and precursors.
\end{center}

\textit{N}-heterocyclic halo-phosphanes are ideal precursors for access to a variety of complexes including the \textit{N}-heterocyclic phosphonium via halide abstraction.\textsuperscript{54} The \textit{N}-heterocyclic bromo-phosphaene and the related chlorophosphaene are convenient starting materials for a variety of reactions including but not limited to: 1 electron reduction to generate the subsequent radical and dimer,\textsuperscript{55} electrophilic substitution\textsuperscript{56–58}, as well as halide displacement in the presence of nucleophiles, as demonstrated by Grutzmacher with phosphaethynolate.\textsuperscript{59} It should be noted that when auxiliary reagents are not employed (e.g. cyclohexene, NEt\textsubscript{3}) the result is a mixture of bromophosphine product as well as the 2,4-dibromo-substituted analogue; whereas for the analogous reaction using PCl\textsubscript{3} results in the formation of only the 2,4-dihalo product.\textsuperscript{60}
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When diiminopyridine ligands ($^8$DIMPY) ligands were employed, the result is a trapped $^1$ complex, as the ligand is not capable of reduction.\textsuperscript{61} The Ragogna group reported both heavy pnictogen analogues of these heterocycles as well as chalcogen analogues, generating intriguing examples of chalcogen dications.\textsuperscript{62–64} Diimine based ligands have also proven to be useful for the stabilization of heavy pnictogen cations. Gudat \textit{et al.} had shown that diimine ligands perform in much of the same way to produce diazastibolenes (antimony analogue of Arduengo’s carbene).\textsuperscript{65} In a similar fashion, diketimines have been shown to stabilize bismuth(III) cations\textsuperscript{66} while both $^8$DIMPY type ligands stabilize antimony and bismuth(I) due to both steric bulk of these ligands as well as their poor electron accepting ability in comparison to their diimine derivatives.\textsuperscript{67,68} Recently, it was shown that DIMPY-stabilized bismuth could facilitate C-H activation\textsuperscript{69} as well as two electron donors in the stabilization of metal carbonyl complexes.\textsuperscript{70} In comparison to their phosphine stabilized analogues, NHPs have proven to act as excellent ligands to a variety of transition metal complexes.\textsuperscript{71}

1.2.3 Stabilization with Strong Donors: Carbenes

The analogy between phosphines and carbenes is well-appreciated by many main group chemists. Although the latter were perhaps initially considered merely as phosphine mimics, they now represent a vast and diverse class of ligands whose transition metal and main-group element complexes often display properties which are more desirable than those of analogous phosphine complexes. When drawn in the $^1$ canonical form, it is apparent that triphosphenium ions may be described as (bis)phosphate-stabilized $^+ \mathrm{ion}$s, and thus should be susceptible to ligand displacement reactions. Indeed, we found that treatment of [dppeP][X] with two equivalents of carbene results in the quantitative...
formation of (bis)carbene-stabilized P\textsuperscript{I} cations.\textsuperscript{72,73} We have now been able to extend this strategy to a myriad of carbenes, with varying heteroatom composition, wingtip groups, and backbone types including: chelating NHCs,\textsuperscript{74} thiazol-2-ylidenes,\textsuperscript{75} and triazol-5-ylidenes.\textsuperscript{76}

It should of course be noted that the ligand displacement reactivity of triphosphenium ions had been seen nearly 20 years before us by Schmidpeter,\textsuperscript{77} who was able to synthesize a carbene-stabilized P\textsuperscript{+} salt by the reaction of a triphosphenium salt with an electron-rich olefin (ERO), likely in an attempt to reduce the triphosphenium cation. He proposed the formal insertion of the P\textsuperscript{+} fragment into the C=C bond of a tetraazafulvalene \textit{via} a phosphiranylphosphonium intermediate, although this was never observed directly.\textsuperscript{78} It was not until the remarkable advances in the chemistry of “bottle-able” carbenes\textsuperscript{32,33} that one could envision displacement of the phosphines by the more strongly donating carbene ligands, generated by thermolysis of the ERO at the elevated temperatures to which those reactions were subjected (\textit{via} the Wanzlick equilibrium).\textsuperscript{79–82}

Our group coined the name “NHC-stabilized phosphorus(I) cation” to describe the cations produced from these reactions, but these compounds were historically called phosphamethine cyanines.\textsuperscript{83} As an important class of inorganic dyes, they are among the first examples of molecules containing a dicoordinate phosphorus atom and the crystal structure of one of these furnished the first concrete evidence of multiple bonding between carbon and a heavier element.\textsuperscript{84} Notwithstanding this historical significance, they were not extensively investigated in the four decades following their initial reports. The P(III) canonical form – which would imply a nearly planar cation – was used to describe all of these species (presumably due to the previous lack of crystallographically characterized
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examples). However, with the many examples which we have been able to synthesize and crystallographically characterize, we have shown that this structural depiction (and the phosphamethine cyanine nomenclature associated with it) only holds when more \( \pi \)-acidic carbenes are used (thiazol-2-ylidenes for example).\textsuperscript{75} In other cases where the \( \pi \)-type lone pair on phosphorus is less able to engage in negative hyperconjugation with the carbene fragments (as is the case with weakly \( \pi \)-accepting carbenes or cases where planarity is hindered by bulky N-R groups), the P(I) canonical form more accurately depicts these species and the “NHC-stabilized phosphorus(I)” most accurately describe its structure (Figure 1.9, A).\textsuperscript{73,85,86} That description is also consistent with the “inverse” \( \pi \)-electron distribution about the P-C fragments (often inferred by highly shielded \(^{31}\text{P}\) NMR shifts observed for many of these species).\textsuperscript{87–90}

Figure 1.9. Some representative reactions of carbenes with various phosphorus sources.
The many recent reports of carbone-stabilized diatomic p-block allotropes (Figure 1.9 B, C), and mononuclear p-block “atoms” have renewed interest in low-valent species like NHC-stabilized $P^+$ cations. Traditionally, these types of cations were synthesized from phosphorus sources such as reduction of $\text{PCl}_3$ (D-F), $\text{P(CH}_2\text{OH)}_3$, or P(SiMe$_3$)$_3$ (G). More recent synthetic routes involve either the use of white phosphorus ($\text{P}_4$) or strong reducing agents, which are also pyrophoric. These types of starting materials, when treated with carbenes result in the production of activated polyphosphorus carbene adducts (for example, $K$, $L$) reported by Bertrand et. al including functionalized $\text{P}_4$ and $\text{P}_8$ cages with carbenes of various size and steric demands.

In this context, the triphosphenium $\text{P}^+$ transfer protocol represents a safe, controlled, and scalable synthetic procedure which is preferred in many circumstances. It is also very versatile, and we have found it to work well with many types of carbenes as long as the N-R groups are not overly bulky (e.g. tert-butyl and large aryl groups on nitrogen destabilize the P-C bond and no products of these reactions have been isolated in our hands).

The reactivity of NHC-stabilized $P^+$ cations has been explored by our group and by others, and it typically involves the oxidation of the electron rich phosphorus center. Treatment with sulfur oxidizes the cations fully ($P^V$) resulting in dithiophosphinium salts, which may alternatively be thought of as carbene-stabilized $\text{PS}_2^+$ ions. Protonation and methylation generates dicationic secondary and tertiary phosphines respectively, which have been proven their worth as ligands supporting $\pi$-acidic transition metal-mediated catalysis. Weigand and coworkers were able to generate a remarkable
phosphanyl radical dication by the one electron oxidation of their abnormally substituted NHC-stabilized P\(^{I}\) cation.\(^{110}\)

While the P\(^{I}\) center of the triphosphenium cations tend to act as poor ligands towards transition metals, it has been demonstrated from their use in transition metal chemistry that the replacement of phosphines with carbenes generally makes for a more electron-rich metal center (which helps to promote oxidative addition of substrates). It appears that this trend of increased electron-richness also holds for P\(^{I}\) cations and it is manifested in their increased ligand ability. A handful of group 11 complexes of NHC-stabilized P\(^{I}\) cations have now been reported, and these range from homoleptic complexes to bimetallic complexes in which both formal lone pairs on phosphorus are engaged in bonding.\(^{73,85,111}\)

### 1.3 Other Low Valent Phosphorus Molecules

#### 1.3.1 Phosphinidenes

There are some examples of stable low valent phosphorus molecules that fall outside of the three classifications of ligands which stabilize low valent phosphorus described above. These molecules are worth discussing in this chapter because of their extensive use in the areas of coordination chemistry.

Phosphinidenes (R-P, Figure 1.10, I) are the phosphorus analogue to nitrenes, silylenes, and carbenes, and now represent an extensively studied class of compounds containing low valent phosphorus.\(^{112}\) Much of the interest in synthesizing these compounds was for use as phospha-Wittig reagents, and indeed, this type of chemistry was shown by many.\(^{113}\) The reactivity of phosphinidene fragments predates their isolation; typically via thermolysis reactions involving (PhP)\(_3\) and subsequent trapping by conjugated dienes.
Later, phosphinidene species were first observed in solution through the coordination of 7-phosphanobornadienes with group 6 carbonyls\textsuperscript{114} and then as “terminal” phosphinidenes (\textit{i.e} RP=ML\textsubscript{n} \textbf{Figure 1.10, II}),\textsuperscript{115} which can exist as either electrophilic or nucleophilic species, and have been extensively reviewed.\textsuperscript{113,115–117}

\textbf{Figure 1.10} Some phosphinidene frameworks depicted as both Lewis structure and with the dative bonding model. Pictured are: free phosphinidenes (I), terminal phosphinidenes (II) and carbene-stabilized phosphinidenes (III)

In spite of all of these reports, the use of phosphinidenes as 4e- donors had remained unexploited as they remained as either transient species, or as stable molecules in the shadows of the transition metals to which they are coordinated. However, recently there have been several reports of metal-free phosphinidenes, with the use of strong σ-donors such as carbenes (\textbf{Figure 1.10, III}), allowing the electron rich phosphorus center to act as a 4 e- donor.\textsuperscript{106,118–120} After this breakthrough, it was realized that analogous molecules could synthesized by replacing the carbene fragments with phosphines, and subsequently, these stable phosphino-phosphinidenes were shown to be excellent donors to a variety of main group and transition metal compounds (\textbf{Figure 1.11}).\textsuperscript{39,118,119,121,122}
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Figure 1.11 Phosphinidenes stabilized carbenes and phosphines.

1.4 Dissertation Overview

To date, the foremost building blocks in organophosphorus chemistry are predominantly phosphorus halides (PX₃, PX₅) or one of its allotropes, (red, white, or black phosphorus). These starting materials often require harsh transformation reagents, such as strong reducing agents to form phosphorus-carbon bonds. Only recently has there been interest in the use of other pathways of building phosphorus molecules with other synthetic methodologies; one strategy might be to start from low coordinate phosphorus and build upwards via coordination or oxidation. Our significant experience in the field of the stabilization of low valent main group chemistry, outlined throughout this chapter, has led us to the development of a P⁺ transfer protocol, where the low valent phosphorus center of an air- and moisture-stable triphosphenium cation can be transferred to another suitable ligand to generate new molecules containing low coordinate phosphorus. This triphosphenium cation, [P⁺dppe][Br], is most easily synthesized by PBr₃ and cyclohexene—which acts as a bromine scavenging agent—in the presence of 1,2-bis(diphenylphosphino)ethane, or any chelating diphosphine ligand. The P⁺ transfer strategy can be exploited in several ways; either by ligand substitution by stronger or more appropriate donors (than dppe), by salt metathesis with the anion of the triphosphenium...
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salt, or by oxidative addition. These methods do not require harsh reagents, and in all conditions, the transformations are P atom efficient, meaning 100% of the starting $\text{P}^I$ is transferred to generate the new molecule, without the formation of unnecessary by-products. In fact, in almost all cases, the dppe which is liberated in the process can be recovered under standard work-up procedures and used again to generate more of the starting material, $[\text{P}^I\text{dppe}][\text{Br}]$.

The idea of P+ transfer is not new; Schmidpeter had discovered this type of transformation in 1983 shortly after his initial report of the first example of a triphosphonium cation,$^{124}$ and described it as an insertion of P+ into a carbon-carbon double bond of an electron rich olefin.$^{78}$ It is now well appreciated that these electron-rich olefins are in fact sources of carbene, and the reaction likely takes place via ligand displacement of the auxiliary phosphine (PR$_3$) by the carbene, rather than electrophilic attack at the C=C bond. Prior to our efforts in this area, there was only one other example in the literature of transformations involving the transfer of P+; Driess reported that acyclic triphosphonium cations and their analogous arsenium cations undergo ligand exchange with Schwartz’s Reagent to produce square planar phosphonium and arsenium salts.$^{45,46}$

Our recent ventures towards a more convenient synthesis of cyclic triphosphonium cations via PI$_3$, initially, and then eventually PBr$_3$ and cyclohexene,$^{125}$ eventually led us to re-visit Schmidpeter’s proposal of P+ transfer. Indeed, we discovered that not only does this transfer technique work very well for many types of carbenes,$^{73-76,86}$ but also anionic phosphines$^{126,127}$ and even disulfide ligands.$^{128}$ The multiple reports of coordination chemistry with neutral triphosphonium analogues by the group of Ragogna has given great
precedence for the coordination studies involving zwiterionic triphosphenium species \(^{47,48,129}\) and has bolstered our efforts in this area.

In chapter 2, \(P^+\) is utilized to as a convenient preparative approach to low valent phosphorus-rich oligomers. Ligand substitution reactions involving anionic diphosphine ligands of the form \([(PR_2)_2N]^−\) and \([(PPh_2)_2C_5H_3]^−\) and the triphosphenium bromide \(P^I\) precursor result in the formation of phosphorus(I)-containing heterocycles. The methodology described also allows for the preparation of the heterocycle \(\text{cyclo-}[P(PPh_2)N(PPh_2)]_2\) in better yields and purity than the synthetic approach reported previously.\(^{130}\) Preliminary reactivity studies demonstrate the viability of such zwiterionic oligomers as multi-dentate ligands for transition metals.

Chapter 3 details the preparation of a triphosphenium zwitterion featuring di-, tri-, and tetra-coordinate phosphorus centers derived from a 1,2,4-tris-(diphenylphosphinyl) cyclopentadienyl framework. The reactivity of this multidentate donor with various main group and transition metal centers is described, and the experimental results are rationalized on the basis of density functional theory investigations.

In Chapter 4, a related zwiterionic triphosphonium molecule is described, \(\text{^tBu(C_5H_2)(PPh_2)_2P}^I(L)\), which can act as a single- or multidentate ligand with group 6, 7, 8 and 9 metal carbonyl complexes. Group 6, \([\text{M(CO)}_3L]\) complexes are formed under photolytic conditions, where the metal is bound at the \(P(I)\) center. In the case of \(\text{Mo(CO)}_6\), the bimetallic complex \([\text{M(CO)}_3L\text{Mo(CO)}_3]\) is generated, which features bonds to both the phosphorus(I) center and the cyclopentadienyl moiety of the molecule. Interestingly, Group 7 and 9 metal carbonyl dimers generate bimetallic complexes in the form \([\text{M}_2(\text{CO})_nL]\), where both metal centers are bound at the bridging phosphorus(I) center.
Chapter 5 describes the interesting reactivity of this ligand (L) with late transition metals. Rather than the simple coordination complexes described above for in case of zero-valent metal carbonyls, these transition metals insert into the P-P bond to generate complexes in which the former P(I) center has dimerized between two molecules, generating diphosphine fragments. This type of chemistry has been observed once before in the case of Kilan’s phosphino-phosphinidene molecule, but this type of reactivity is unprecedented in the area of triphosphonium chemistry.

Finally, in Chapter 6, the synthesis of various trithiobisphosphines by oxidative addition of disulfide ligands to the phosphorus(I) reagent, [Pdppe][Br], is described. This method provides an alternative synthetic pathway to this class of molecules, with good yields and less synthetic steps. The synthesis of these trithiobisphosphines and the proposed intermediate diphosphine species are characterized by X-ray diffraction and multinuclear NMR and a mechanism is proposed for the formation of these molecules.
1.5 References

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Chapter 2: \( P^+ \) Transfer as An Alternative Approach to Phosphorus-Containing Oligomers

2.1 Introduction

Phosphorus-containing oligomers and macromolecules have been and continue to be materials of tremendous investigation, both from academic and industrial perspectives. The interest in such molecules stems primarily from the different properties that are engendered in these species by the presence of the phosphorus atoms in comparison to their "carbon copy" analogues. For example, the sometimes unique and often improved performance of phosphorus-containing polymers renders them useful for a very large number of applications, including: biomedical applications, catalysis, light-harvesting, sensing lubrication, flame-retardant materials, and much more.\(^1\)\(^-\)\(^5\) In this context, the development of new or improved methods to produce phosphorus-containing macromolecules is desirable.

Triphosphenium salts are a remarkable class of compounds first prepared by Schmidpeter and co-workers in the 1980's\(^6\)\(^,\)\(^7\) that feature a dicoordinate and low valent \( P^1 \) atom but are unusually stable (Figure 2.1, A, B). More recently, our development of a facile approach to cyclic triphosphenium iodide and bromide salts (cf. Figure 2.1, C)\(^8\) provided materials that are particularly amenable to anion exchange metathesis reactions\(^9\). The availability of a convenient and high-purity route to such compounds is important because it had already been demonstrated that triphosphenium salts may be used as reagents for the preparation of other poly-phosphorus compounds\(^9\)\(^,\)\(^10\) or as convenient \( P^1 \) sources.\(^7\) In particular, access to other triphosphenium \( P^1 \) salts is possible via ligand exchange reactions\(^10\) in which a relatively poor phosphine donor is replaced with a more strongly donating phosphine. In this sense, the low valent \( P(\text{I}) \) center is effectively
transferred to another ligand system. The use of monodentate phosphine ligands to form acyclic P\(^{i}\) complexes has also been reported\(^7,11\) (Figure 2.1, A) although only a handful of these have been characterized comprehensively.

![Figure 2.1 Triphosphenium species: a general depiction (A) and reported compounds (B-C), zwitterionic compounds (D, E, 1) featuring at least one P\(^{i}\) fragment](image)

Given the foregoing, anionic phosphinous ligands are particularly good ligands for generating P\(^{i}\) containing compounds as they can readily displace neutral phosphine ligands from the triphosphenium transfer reagent, [dppeP\(^{i}\)][Br]. Importantly, the resultant zwitterionic products (e.g. Figure 2.1, D)\(^12,13\) are soluble in most organic solvents and they can act as excellent ligands to various transition metals\(^12-14\) with the capacity to bind one or two metal fragments simultaneously.\(^12\)

In the context of larger molecules, we reasoned that the use of anionic, non-chelating linkers with P\(^{i}\) ions should lead to phosphorus-containing oligomers that are neutral overall. In fact, Schmidpeter and co-workers had previously reported compounds of this type, (Figure 2.1, E) that they had isolated from reactions of a phosphinous amide
Chapter 2: $P^+$ Transfer as An Alternative Approach to Phosphorus-Containing Oligomers

with $P_4$. Notably, the heterocycle $E$ is a phosphorus-rich isovalent analog of phosphazenes, which are arguably the most useful class of phosphorus-nitrogen compounds and which are precursors for polymers. Although phosphazenes are usually drawn with alternating single and double bonds to satisfy the rules of formal Lewis structures (Figure 2.2, I), the more justifiable zwitterionic Lewis-type description of the electron distribution (Figure 2.2, II) highlights the electron-rich nature of the dicoordinate atom. In this canonical form, the di-coordinate nitrogen atom bearing two lone pairs of electrons is clearly isovalent with the univalent phosphorus centers in triphosphenium species. Given our experience in the development of methods for the preparation of triphosphenium ions and our interest in the exploitation of the unique reactivity of this functional group, we reasoned that triphosphenium chemistry could provide a convenient route to make phosphorus-containing oligomers and perhaps polymers (Scheme 2.1).

Figure 2.2 Lewis-type drawings structures of some phosphazene analogues. The typical depiction (I), a more justifiable depiction (II), and a related isolobal analogue in which one nitrogen fragment has been replaced by a $P^+$ centre.

In this chapter, it is demonstrated that the approach outlined in Scheme 2.1 can indeed be used to generate oligomers containing multiple $P^+$ centers, and the structural characterization of these heterocycles is reported. Further, the utility of one of the macrocycles as a zwitterionic bis-phosphanide-type ligand for noble metals is detailed.
2.2 Results & Discussion

2.2.1 Synthesis and Reactivity of [Ph₄P₃N]₂

In the 1980's, Schmidpeter and co-workers were able to isolate the neutral, 8-membered ring compound \( \text{E} \) through the reaction of a phosphinous amide with elemental phosphorus.\(^{15}\) However, the material was isolated in low yield (20%) and the reaction is complicated by the use of the highly-toxic and pyrophoric \( P_4 \) reagent and by the formation of several poly-phosphorus byproducts. Our experience with triphosphenium salts led us to posit that ligand exchange using a readily-prepared, air-stable \( P^I \) precursor might provide a more convenient and generalizable route to such species.

In order to prove that hypothesis, we investigated the reaction of our easily prepared \( P^I \) source \([\text{dppeP}^I][\text{Br}]\) (dppe = 1,2-bis(diphenylphosphino)ethane) with \([\text{Li}][\text{N(PPh}_2)_2]\) in THF in an effort to make 2.1. It should be noted that metallated phosphinous amide is notoriously difficult to isolate so the lithiated amide was prepared and used \textit{in situ} by adding excess butyl lithium to the amine precursor at 78°C. The resultant mixture was left to stir for an hour and then added to a solution of \([\text{dppeP}][\text{Br}]\) in THF at 78°C to produce compound 2.1 in very good isolated yield (79%). It should be noted that \([\text{dppeP}][\text{Br}]\) has proven to be stable in the presence of many strong bases – at least for brief periods – so the reaction can also be done in one-pot.
Scheme 2.2 Reaction of a triphosphenium bromide reagent with a salt containing an anionic, non-chelating bis(diphenylphosphino)amide proligand to produce 2.1

Surprisingly, the $^{31}$P NMR spectrum of the compound we obtained was not consistent with the values reported originally for 1 by Schmidpeter and co-workers: they had noted that the spectrum of heterocycle E is indicative of an AA’A’’A’’’BB’ spin system using a spectrometer with a $^{31}$P NMR frequency of 40.48 MHz (35.0 ppm, -141.5 ppm, $^{1}J_{PP} = 429$ Hz). In contrast, we observe a spectrum consistent with an (A$_2$X)$_2$ spin system with signals at 35.5 (d, $^{1}J_{PP} = 423$ Hz) and -140.2 (t, $^{1}J_{PP} = 422$ Hz) using a spectrometer with a $^{31}$P NMR frequency of 121.5 MHz. (Figure 2.3)

Figure 2.3 $^{31}$P{$^{1}$H} NMR of 2.1

Thus, in order to confirm that we had indeed produced the same compound given the differences in the spectral data, we crystallized our compound from a concentrated dichloromethane solution and performed X-ray diffraction experiments on the resultant material. The single-crystal structure (Figure 2.4) is indistinguishable from that reported
previously and confirms the identity of the product and validates our synthetic approach. Powder XRD experiments on the bulk recrystallized material indicate that the only crystalline material is consistent with the single-crystal structure and the reason for the difference in appearance of the $^{31}$P NMR spectra remains unanswered. We had postulated that Schmidpeter and co-workers may have unintentionally collected the spectrum with $^1$H coupling but when we conducted our own $^1$H coupled $^{31}$P NMR experiments to test this hypothesis, we were unable to obtain a spectrum similar to the reported one.

![Thermal ellipsoid plot (30% probability surface) of the molecular structure of 2.1. The hydrogen atoms and dichloromethane solvent of crystallization have been removed for clarity. Selected metrical parameters are listed in Table 2.1.](image)

Figure 2.4 Thermal ellipsoid plot (30% probability surface) of the molecular structure of 2.1. The hydrogen atoms and dichloromethane solvent of crystallization have been removed for clarity. Selected metrical parameters are listed in Table 2.1.

The convenient and clean preparation of 2.1 (and analogous P-rich phosphazenes) allows for the investigation and development of such species as poly-dentate ligands or supramolecular building blocks. In fact, Schmidpeter had shown that 2.1 could form bidentate $P,P'$-complexes to Pd and Pt but further investigations do not appear to have been
pursued.\textsuperscript{15} Thus, in order to probe the utility of 2.1 for other catalytically relevant species, we treated the zwitterion with some univalent group 11 halides.

NMR investigations indicate that the reaction of 2.1 with one equivalent of CuBr, results in the immediate formation of a complex featuring a different AX\textsubscript{2} spin system with chemical shifts at 28.6 (d, \textsuperscript{1}J\textsubscript{P,p} = 371.1 Hz) and -162.6 (t, \textsuperscript{1}J\textsubscript{P,p} = 369.0 Hz) consistent with the formation of a bidentate \textit{P,P'}-complex. For the compound \textbf{1·CuBr (2.2)}, we were able to grow crystals suitable for single crystal X-ray diffraction from a concentrated solution in dichloromethane. The complex crystallizes in the space group C\textsubscript{2} with half a molecule and one disordered CH\textsubscript{2}Cl\textsubscript{2} solvent molecule in the asymmetric unit. The molecular structure of the compound is illustrated in Figure 2.5 and confirms the formation of a $\kappa\text{\textsuperscript{2}}$-$\textit{P,P'}$ bidentate complex of 2.1 with CuBr. The Cu-Br distance of 2.3427(8) Å is consistent with those reported in the Cambridge Structural Database (CSD)\textsuperscript{17} for compounds containing copper(I) bromide coordinated by two phosphorus atoms. Perhaps expectedly given the zwitterionic nature and geometric constraints of the ligand, the unique P-Cu distance of 2.2953(10) Å is at the long end of the range of distances reported for phosphanido P-Cu bonds and is most comparable to the 2.286(2) Å phosphanido P-Cu distance observed in cyclo-(P3\text{\textsuperscript{5}}Bu4)Cu(PPh3)\textsubscript{2}.\textsuperscript{18} The P-Cu-P angle of 120.17(5)° is much wider than those observed in most other complexes of chelating diphosphine donors however it is on the smaller side of trans-spanning diphosphines and wide-bite angle diphosphines.\textsuperscript{10–21} This is almost certainly a consequence of the geometric constraints of the heterocyclic donor. It is perhaps worth noting that the P\textsuperscript{1}⋯P\textsuperscript{1} distance of 3.979(3) Å in 2.2 is shorter than the corresponding value of 4.1101(7) Å in 2.1. Consequently, the N⋯N distance of 3.449(1) in 2.2 is longer than the N⋯N distance of 3.3018(6) Å in 2.1. The
molecules of 2.2 pack in a manner reminiscent to the packing badminton shuttle cocks: the Cu-Br fragment of one molecule is "cupped" by the aromatic substituents on an adjacent molecule (featuring six C_aryl-H···Br contacts under 3.3 Å with a closest pair being 3.1421(2) Å).

![Figure 2.5](image)

**Figure 2.5** Thermal ellipsoid (30% probability) plots of 2.2 (right) and 2.3 (left). Hydrogen atoms and the CH_2Cl_2 of crystallization for 2.2 have been removed. Selected metrical parameters are listed in Table 2.1.

The related compound 2.3 is generated upon the treatment of 2.1 with a suspension of silver(I) bromide in dichloromethane as evidenced by the signals at 30.5 (d, ^1^J_p,p = 376), -157.3 (dt, ^1^J_p,p = 383 Hz, ^1^J_Ag-p = 113 Hz) in the ^31^P NMR spectrum. Crystals of the complex 2.3 were obtained from acetonitrile solution and the material crystallizes in the space group C2; there is no solvent of crystallization but the structure of the metal complex is roughly isostructural with that of 2.2 (Figure 2.5). Both the Ag-Br distance (2.5000(12) Å) and P-Ag distance (2.4907(12) Å) are within, but toward the short end, of the range of bond lengths for reported compounds in the CSD containing a phosphine ligand coordinated to a terminal Ag-Br fragment. The P-Ag-P bond angle of 2.3 (114.26(6)°) is
considerably narrower than that of the lighter copper analogue (120.17(5)°); this is a consequence of the larger size of the Ag\(^{+}\) ion and it results in a much larger P\(^{1}\)···P\(^{1}\) separation (4.183(2) Å) within the ligand. The N···N separation in 2.3 (3.3699(1) Å) is also more similar to the value in the free ligand (2.1) rather than that seen in 2.2 so it appears as if the binding to silver(I) requires considerably less distortion of the ligand. However, it is worth noting that both coordination compounds feature longer P-P\(^{1}\) bond lengths and wider P-P\(^{1}\)-P angles than proligand 2.1 (Table 2.1) as one would anticipate considering the necessary decrease in negative hyperconguation (i.e. P\(^{1}\)→PR\(_2\) backbonding) upon metal binding.

2.2.2 Synthesis of \([iPr_4P_4N]_2\)

Although the ligand exchange methodology outlined in Scheme 2.2 clearly works for the generation 2.1, we wish to emphasize that the stability of the resultant heterocycles is substituent-dependent and this can affect the nature of the product obtained. For example, attempts to prepare the isopropyl-substituted analogue of 2.1 consistently produced the linked two-ring compound 2.4 (Scheme 2.3) rather than the analogous 8-membered ring. Even at low temperatures, \(^{31}\)P NMR experiments reveal the initial formation of an intermediate that exhibits a spectrum consistent with an AX\(_2\) spin system with shifts at 78.9 (d, \(^1J_{PP} = 271.7\) Hz) and -162.6 (t, \(^1J_{PP} = 271.7\) Hz) – this could be either a 4-membered triphosphenium zwitterion or the 8-membered ring analogue of 2.1 – but the compound rapidly transforms into a material that exhibits four chemically-distinct phosphorus environments and generates byproducts including both the protonated proligand (\(^{i}Pr_2P\)_2NH and the anticipated dppe (Figure 2.6)
Figure 2.6 $^{31}$P{$^1$H} stackplot of the reaction between [dppeP$^1$][Br] and bis(isopropyl)phosphinoamide ligand, showing the presence of an intermediate molecule (bottom, $\delta$ 82 ppm, $d$ and -142 ppm, $t$) and resulting rearrangement product, 2.4 (top, $\delta$: 123 ppm, $d$, 104 ppm, $d$, 23 ppm, $m$, -150 ppm, $m$). Also present in both specta are dppe (-11 ppm) and HN(P$^i$Pr$_2$)$_2$ (70 ppm).

The identity of the product (2.4) was elucidated using single-crystal X-ray diffraction on a crystalline sample obtained at low temperature. The compound crystallizes in the space group $P2_1/n$ with one molecule in the asymmetric unit. The molecular structure of 2.4 (Figure 2.7) features two 5-membered $P_4N$ rings that are linked by a P-P bond to make an approximately centro-symmetric $[P_2(PC_2)N]_2$ dimer core. Although there are no examples of any $P_4N$ rings in the CSD, the overall structure is clearly similar to that of the isolobal As$_2P_2C$ dimer reported by Karsch and co-workers$^{22,23}$ and many other polyphosphorus compounds$^{24}$ Each ring in 2.4 contains one dicoordinate P$^i$ center featuring a short P-P bond distance (Table 2.1) to the adjacent tetracoordinate phosphorus atom.
(2.1435(7) Å and 2.1417 (7) Å) and a marginally longer bond to the tricoordinate phosphorus atom that links the two heterocycles (2.1635(7) Å and 2.1651(7) Å). Such short P-P bonds are consistent with those observed for other cyclic triphosphenium ions and related species\(^9,25\) In contrast, the 2.2647(7) Å P-P bond linking the two heterocycles lies at the long end of the range of P-P bonds reported in the CSD for tetraorganodiphosphines\(^17\) and is considerably longer than the distances of 2.200 Å and 2.187 Å reported by Fritz and co-workers for two tetraphosphinodiphosphines.\(^26,27\) The P-P-P angles for the dicoordinate phosphorus atoms of 95.72(3)° and 94.96(3)° are, as one would anticipate given the larger size of phosphorus, somewhat larger than those observed for 5-membered ring triphosphenium cations of the type [dppeP]\(^+\) and are more comparable to those observed in 6-membered ring triphosphenium species.\(^9,10,12,25\)

**Figure 2.7.** Thermal ellipsoid plots (30% probability) of 2.4. Hydrogen atoms have been removed for clarity. The top view presents ellipsoids for all atoms and the bottom view illustrates the step-like dimeric arrangement. Selected metrical parameters are listed in Table 2.1.

The formation of 2.4 from its intermediate involves the formal extrusion of one (\(^i\)Pr\(_2\)P)\(_2\)N fragment for each 5-membered ring and the oxidative coupling of two P\(^i\) centers
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(Scheme 2.3). Although the mechanistic details of the process remain unclear, examination of putative models of the \(^{1}\text{Pr}\)-substituted 8-membered ring (using the \(\text{P}_6\text{N}_2\) core from 2.1) suggest that the steric requirements of the isopropyl groups would engender considerable repulsion. DFT geometry optimization (Ch.2 Supplementary Information) suggests that the 8-membered ring is stable but only with a much more planar \(\text{P}_6\text{N}_2\) core structure featuring a considerably longer \(\text{P}^\cdots\text{P}\) distance (4.90Å vs. 4.10Å in 2.1). Moreover, the nearly complete absence of bis(isopropyl)-substituted phosphazenes from the literature is noteworthy: in fact, there appears to be only one structurally characterized compound containing the repeat unit \([^{1}\text{Pr}_2\text{PN}]_2\) in the CSD and it is not a simple phosphazene.

Low temperature \(^{31}\text{P}\) NMR experiments only exhibit peaks attributable to 2.4 (Figure 2.6) and there is no indication of an anion of the form \([\text{P}((^{1}\text{Pr}_2\text{P})_2\text{N}_2)_2]\). Taken together, the evidence suggests that 2.4 is likely formed via the 4-membered ring intermediate analogous to the compound \(\text{P}(\text{PPh}_2)_2\text{CSiMe}_3\) reported by Karsch and co-workers\(^{23,29}\) rather than the 8-membered alternative.

### Scheme 2.3

Reaction of the triphosphenium bromide precursor and bis(isopropyl)phosphinoamide ligand, generating the intermediate molecule (which may be either a 4-membered or 8-membered ring) and resulting rearrangement product 2.4

We conducted a series of experiments in which the stoichiometry of the reagents were altered in an effort to optimize the yield of 2.4. Interestingly, the unidentified
intermediate is always observed regardless of the stoichiometric ratio of [Na][\(\text{Pr}_2\text{P}_2\text{N}\)] and [dppeP\(^1\)][Br] used, but compound 2.4 is formed only when the ratio is 1:1. We postulate that the extrusion of \(\text{HN(P(Pr)}_2\)\ is essential in the formation of 2.4 and is not particularly surprising as this type of extrusion has been reported for compounds featuring similar ligands.\(^{30}\) Unfortunately, efforts to characterize or identify reaction intermediates using NMR and EPR spectroscopy have not yet been successful.

### 2.2.3 Synthesis of [\(\text{Ph}_2\text{P}_3(\text{C}_5\text{H}_3)\)]\(^2\)

Considering the successful generation of 2.1, we wished to probe the applicability of the method to other diphosphines bridged by anionic linkers to produce larger neutral heterocycles containing multiple P\(^1\) centers. Toward this end we targeted the heterocycles derived from non-chelating 1,3-bis(diorganophosphine)cyclopentadienide ligands.

Although there are two reported syntheses of lithium 1,3-bis(diphenylphosphino)cyclopentadienide,\(^{31,32}\) we were unable to isolate material of sufficient purity for further use with either of those methods so we undertook the development of an improved approach to the preparation of such proligands. The method described by Brasse \textit{et al.} had produced the most promising results in our hands so we used this as a starting point.\(^{31}\) Our modified synthesis (\textbf{Scheme 2.4}) is a step-wise approach that produces potassium 1,3-bis(diphenylphosphino)cyclopentadienide (2.5) in excellent yield with no unanticipated side-products.
Scheme 2.4 Synthesis of potassium 1,3 (diphenylphosphino)cyclopentadienide, 2.5

With a pure salt of the anionic diphosphine ligand 2.5 in hand, the ligand substitution reaction with [dppeP][Br] was investigated. $^{31}$P NMR spectroscopy reveals that when a THF solution of 2.5 is mixed with a THF solution of [dppeP][Br], the heterocycle subsequently characterized as 2.6 is produced in quantitative yield (Scheme 2.5) with the concomitant generation of the anticipated dppe product.

Scheme 2.5 Synthesis of the heterocyclic dimer 2.6 from 2.5 and the triphosphenium bromide P$I$ precursor.

We discovered that is possible to precipitate the dimeric product 2.6 selectively by exposing a diethylether solution of the crude product mixture (containing a mixture of 2.6 and dppe) to sonication; the oligomer may be collected as a pure product by filtration. It is worth noting however that the sonication of the mixture for a longer period (more than a few hours) results in the precipitation of mixtures containing some dppe in addition to 2.6.

Crystals of 2.6 suitable for examination by single-crystal X-ray diffraction were obtained by the slow vapor diffusion of diethylether into a concentrated CH$_2$Cl$_2$ solution of the heterocycle. The compound crystallizes in the space group $P-1$ with half of the
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molecule present in the asymmetric unit; the complete molecular structure is depicted in Figure 2.7. The P-P bond distances (Table 2.1) in macrocycle 2.6 fall within the ranges of distances (2.113(2)-2.184(2) Å) for cyclic triphosphonium complexes reported in the CSD, but the P-P-P angle of 100.82(4)° is considerably larger and is more consistent with those of acyclic triphosphonium cations. The centroid-to-centroid distance between the two cyclopentadiene rings is 3.590 Å and the inter-planar spacing of the rings is 3.195 Å. Thus, it would appear as if the heterocycle should be capable of generating endocyclic sandwich-type complexes. The powder XRD pattern of the bulk material isolated by this recrystallization method is in excellent agreement with the pattern simulated on the basis of the single crystal structure and confirms that sample contains only a single crystalline product. However, it should be noted that on one occasion we obtained a polymorph of this compound in which the asymmetric unit contains an entire heterocycle and more than one diethyl ether molecule; data are of low quality but the non-parallel arrangement of the Cp fragments in the molecule suggests that macrocycle 2.6 can exhibit considerable conformational flexibility.
Figure 2.7. Thermal ellipsoid plot (30% probability plot) of the contents the unit cell for 2.8. Selected metrical parameters are listed in Table 2.1.

Table 2.1 Selected bond lengths (Å), angles (°) and $^{31}$P NMR data for structurally-characterized molecules in this chapter.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>2.1</th>
<th>2.2</th>
<th>2.3</th>
<th>2.4</th>
<th>2.6</th>
</tr>
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<tr>
<td>P-P$^1$ (Å)</td>
<td>2.1390(6)</td>
<td>2.1654(12)</td>
<td>2.1625(16)</td>
<td>2.1635(7)</td>
<td>2.1259(11)</td>
</tr>
<tr>
<td></td>
<td>2.1310(6)</td>
<td>2.1672(12)</td>
<td>2.1546(16)</td>
<td>2.2097(7)</td>
<td>2.1259(11)</td>
</tr>
<tr>
<td>P-P$^1$-P (°)</td>
<td>95.44(2)</td>
<td>98.15(5)</td>
<td>98.50(6)</td>
<td>95.72(3)</td>
<td>100.82(4)</td>
</tr>
<tr>
<td>P-A$^2$ (Å)</td>
<td>1.5957(14)</td>
<td>1.595(3)</td>
<td>1.596(4)</td>
<td>1.6009(16)</td>
<td>1.746(3)</td>
</tr>
<tr>
<td></td>
<td>1.6019(14)</td>
<td>1.600(3)</td>
<td>1.596(4)</td>
<td>1.6629(16)</td>
<td>1.758(3)</td>
</tr>
<tr>
<td>P-M (Å)</td>
<td>2.2952(10)</td>
<td>2.4906(12)</td>
<td>2.4907(12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2953(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta^{31}$P (ppm)</td>
<td>35 (d), -140(t)</td>
<td>28, d; -162, t</td>
<td>31, d; -157, t</td>
<td>123*(d), 104**(d), -23(m), 150(m)</td>
<td>19, d; -148, t</td>
</tr>
<tr>
<td>$^{1}$J$_{p-p}$ (Hz)</td>
<td>423</td>
<td>373</td>
<td>376</td>
<td>510*, 332**</td>
<td>459</td>
</tr>
</tbody>
</table>

$^a$Where $A$ represents the bridging functionality: nitrogen for compounds 2.1, 2.2, 2.3 and 2.4; and carbon for compound 2.6.
2.3 Conclusion

We have demonstrated that ligand exchange using stable P\textsuperscript{3} reagents is a viable synthetic approach for the preparation of electron-rich phosphorus-rich oligomers. The use of this protocol for the generation of such heterocycles appears only to be constrained by the preparation of suitable diphosphine ligands. We are currently evaluating a variety of methods for the reliable production of larger oligomers and the related polymeric species. Furthermore, the macrocycles presented herein are also being studied to examine in order to assess their abilities to serve as multifunctional donors using both the dicoordinate P atoms and the bridging functionality (i.e. N or Cp).

2.4 Experimental

2.4.1 General Procedures.

All manipulations were carried out using standard inert atmosphere techniques. Phosphorus (III) bromide, sodium cyclopentadienide, and all other chemicals and reagents were purchased from Aldrich. Phosphorus(III) bromide was distilled before use, and all other reagents were used without further purification. All solvents were dried using a series of Grubbs’-type columns and were degassed prior to use. THF-d\textsubscript{8} was dried over sodium and benzophenone. The precursors HN\{P(\textit{t}Pr\textsubscript{2})\}_\textsubscript{2} and NaN\{P(\textit{t}Pr\textsubscript{2})\}_\textsubscript{2} were synthesized based on modified literature procedures\textsuperscript{37}, and Cu(I)Cl was purified by a literature procedure.\textsuperscript{38} NMR spectra were recorded at room temperature in THF-d\textsubscript{8} or CD\textsubscript{2}Cl\textsubscript{2} solutions on a Bruker Advance 300-MHz spectrometer or Bruker Advance III 500 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe\textsubscript{4} for \textsuperscript{1}H and \textsuperscript{13}C, 85% H\textsubscript{3}PO\textsubscript{4} for \textsuperscript{31}P). Coupling constant magnitudes, |J|, are given in Hz. The high-resolution mass spectra (HRMS) were obtained using electro-spray ionization of
acetonitrile solutions of species either by The McMaster Regional Centre for Mass Spectrometry, Hamilton, Canada or in house; calculated and reported mass:charge ratios are reported for the most intense signal of the isotopic pattern. Melting points were obtained on samples sealed in glass capillaries under dry nitrogen using an Electrothermal® Melting Point Apparatus. Elemental analysis was performed by Atlantic Microlabs, Norcross, Georgia, USA or at the University of Windsor.

2.4.2 Specific Procedures

[-N-PPh₂-P-PPh₂]₂, (2.1)

To a flask containing NH(PPh₂)₂ (1.000 g, 2.59 mmol) in THF (50 mL) was added 1.3 equivalents of n-BuLi (1.62 mL, 3.37 mmol) via syringe at -78°C. The reaction mixture was stirred for 2 hours and was then added to a -78°C solution of [dppeP][Br] (1.321 g, 2.59 mmol) in THF (20 mL). The reaction was allowed to stir overnight before the resulting solid was filtered and washed with hexane, which yielded a yellow solution containing dppe. The solvent was removed under reduced pressure and the subsequent paste was then sonicated for 1 hour in hexane and was filtered and washed with hot hexane (100 mL) to give the pale yellow solid 1, 79% (0.850 g). n.b. Although this is a known compound, the NMR data are not consistent with those previously reported so they are presented here:

³¹P{¹H} NMR (THF-d₈): δ 35.5 (d, ¹JPP = 423 Hz), -140.2 (t, ¹JPP = 422 Hz); ¹H NMR (THF-d₈): δ 7.66-7.59 (m, 2H, Ph-meta); 7.12-7.09 (m, 1H, Ph-para); 7.10-6.98 (m, 2H, Ph-ortho); ¹³C{¹H} NMR (CD₂Cl₂) δ 135.3 (d, JPC = 93.98 Hz, Ph-ipso); 131.3 (s, Ph-meta); 129.7 (s, Ph-para); 129.7 (m, JPC = 5.9 Hz, Ph-ortho).
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[-N-P(Ph)$_2$-P(Ph)$_2$-]$_2$CuBr, (2.2)

To an orange solution of 1 (0.085g, 0.102 mmol) in dichloromethane was slowly added a suspension of white Cu(I)Br (0.0146g, 0.102 mmol) in dichloromethane, over the course of 5 minutes. The mixture was allowed to stir for two hours, yielding a dark red mixture. The solution was centrifuged and the resulting yellow-orange precipitate was collected. The solid was washed with cold dichloromethane twice to yield a golden-orange powder. Gold-colored crystals were obtained from dichloromethane. Yield: 60% (0.061g)

$^{31}$P{$_{^1}$H} NMR (CD$_2$Cl$_2$): $\delta$ 28.6 (d, $^{1}J_{PP}$ = 373 Hz), -162.5 (t, $^{1}J_{PP}$ = 373 Hz)  

$^{1}$H NMR (DMSO-d$_6$): $\delta$ 7.43 (m, 2H, Ph-meta); $\delta$ 7.56-7.59 (m, 1H, Ph-para); $\delta$ 7.71 (m, 2H, Ph-ortho).  

Anal. calcd for C$_{48}$H$_{40}$BrCuP$_6$N$_2$·(CH$_2$Cl)$_2$: C, 55.57; H, 4.00; N, 2.65; found: C, 53.57; H, 4.23; N, 2.04.

[-N-P(Ph)$_2$-P(Ph)$_2$-]$_2$AgBr, (2.3)

As AgBr is light sensitive, the reaction was performed in a dark room to avoid any degradation of the starting material. A suspension of AgBr (0.0137g, 0.734 mmol) in dichloromethane was added to a stirring orange solution of 1 (0.061g, 0.734 mmol) in dichloromethane over 10 minutes. The mixture was stirred for thirty minutes thereafter, yielding a light orange suspension. Solvent was removed under reduced pressure and the resulting powder was washed with THF and the orange powder was collected using a frit. The product does not appear to be light sensitive. Yield: 81% (0.061g)  

$^{31}$P{$_{^1}$H} NMR (CD$_2$Cl$_2$): $\delta$ 30.5 (d, $^{1}J_{PP}$ = 376), -157.3 (dt, $^{1}J_{PP} =$ 383 Hz, $^{1}J_{Ag-P}$ $\approx$ 113 Hz; due to a broadening of the triplet peaks, individual coupling to $^{107}$Ag and $^{109}$Ag could not be resolved).  

$^{1}$H NMR (DMSO-d$_6$): $\delta$ 6.97 (m, Ph-meta, 1H), 7.04 (m, Ph-meta, 1H), 7.15 (m, Ph-para, 1H), 7.36 (m, Ph-ortho, 1H), 7.56 (m, Ph-ortho, 1H)
Reaction of NaN(P(iPr)₂)₂ and [dppeP][Br] (2.4)

The white solids, [Na][N(P(iPr)₂)₂] (0.184 g, 0.677 mmol) and [dppeP][Br] (0.379 g, 0.745 mmol) were added to a Schlenk flask and cooled to -78°C in a dry ice-acetone bath. Approximately 40 mL of cold dichloromethane was added to the flask. The solution turned yellow immediately and was allowed to stir for 6 hours at -78°C. $^{31}$P{$^1$H} NMR spectroscopy was performed on an aliquot of this stirring solution, showing evidence of the formation of an intermediate ($^{31}$P{$^1$H} NMR: $\delta$ 82.0 (d, $^1J_{PP} = 273$ Hz), $\delta$ -142.5 (t, $^1J_{PP} = 267$ Hz)); The dichloromethane was removed from the resulting yellow-orange solution under reduced pressure, while maintaining a temperature of approximately 0°C. To the resulting precipitate was added cold pentane, yielding a pale yellow solution. The solution was decanted and stored in a Schlenk flask under reduced pressure at -10°C, yielding pale yellow crystals. Due to similarities in solubility, the isolated product, 3, and the by-product, HN[P(iPr)₂]₂, were not able to be separated in our hands. $^{31}$P{$^1$H} NMR of the product mixture (CD₂Cl₂):

$67.7$ (s, HN[P(iPr)₂]₂), $-11.2$ (s, dppe), $123.8$ (d, $^1J_{PP} = 510$ Hz, (Pr)₂P-N-P(Pr)₂-P-P), $104.77$ (d, $^1J_{PP} = 332.7$ Hz), (Pr)₂P-N-P(Pr)₂-P-P), $-23.3$ (m, (Pr)₂P-N-P(Pr)₂-P-P), $-150.6$ (m, (Pr)₂P-N-P(Pr)₂-P-P).

Potassium (diphenylphosphino)cyclopentadienide, [K][C₅H₄(PPh₂)].

NaCp in diethylether (5.0 ml, 10.0 mmol) was added to a stirring solution of ClPPh₂ (2.251 g, 10.2 mmol) in diethylether (ca. 15 mL) at 30°C. Upon additional the reaction mixture turns red and gradually became orange after stirring for 2 hours at which point the mixture was filtered through Celite© to remove NaCl. The filtrate was washed
with diethylether and volatiles were removed under reduced pressure. The resulting oil was
dissolved in toluene, cooled to -78°C and a solution of KN(SiMe₃)₂ (2.074 g, 10.4 mmol) in
toluene was added. A white precipitate appeared upon the addition was isolated after
stirring for 3 hours and subsequently washed with diethyl ether yielding a white solid
powder characterized as [K][C₅H₄(PPh₂)]. 94% (2.800 g, 0.97 mmol). ³¹P{¹H} NMR
(THF-d₈): δ -17.6; ¹H NMR (THF-d₈): δ 7.33-7.29 (m, 4H, Ph-ortho); 7.14-7.07 (m, 8H, Ph-
meta/para); 5.97-5.87 (m, 4H, C₅H₄); ¹³C{¹H} NMR (THF-d₈): δ 147.26 (d, Jₚₛₛ = 13.2
Hz, Ph-ipso); 133.72 (d, Jₚₛₛ = 18.3 Hz, Ph-ortho); 127.98 (d, Jₚₛₛ = 6.2 Hz, Ph-meta); 126.70
(s, Ph-para); 114.44 (d, Jₚₛₛ = 22.7 Hz, C₅H₄P); 109.1 (d, Jₚₛₛ = 10.1 Hz, C₅H₄P); 104.78 (d,
Jₚₛₛ = 4.2 Hz, C₅H₄P). HRMS: calcd for C₁₇H₁₄P² 249.0840, found 249.0833 (-2.8 ppm).

Potassium 1,3-bis(diphenylphosphino)cyclopentadienide, (2.5)

A solution of chlorodiphenylphosphine (2.306 g, 10.05 mmol) in toluene (ca. 80
mL) was added by cannula to a solution containing the previously prepared
[K][C₅H₄(PPh₂)] (2.955 g, 10.2 mmol) in toluene (ca. 20 mL) at -78°C. Upon addition,
the solution underwent a color change to orange and gradually became yellow over time.
The resulting solution was allowed to stir for 2 hours and filtered through Celite to remove
the potassium chloride precipitate, which was subsequently washed with additional toluene
(ca. 10 mL). The filtrate was cooled to -78°C and then a solution of KN(SiMe₃)₂ (2.125 g,
10.7 mmol) in toluene (ca. 30 mL) was slowly added. The resultant mixture immediately
produced a white precipitate and was refluxed for 3 hours. Diethyl ether (ca. 50 mL) was
then added to the mixture, which was stirred for an additional hour. The resulting solid was
collected by filtration and washed with diethyl ether (ca. 50 mL). Any remaining volatile
components were removed from the solid under reduced pressure to afford a white powder
Chapter 2: \( P^+ \) Transfer as An Alternative Approach to Phosphorus-Containing Oligomers

characterized as 2.5, 93% (4.200 g, 10.2 mmol). \(^{31}P\{^1H\} NMR\) (THF-\(d_8\)): \( \delta \) -18.2; \(^1H\) NMR (THF-\(d_8\)): \( \delta \) 7.36-7.30 (m, 4H, Ph-ortho); 7.17-7.10 (m, 8H, Ph-meta/para); 7.36-7.30 (m, 1H, C\(_3\)H\(_3\)); 7.17-7.10 (m, 2H, C\(_3\)H\(_3\)); \(^{13}C\{^1H\} NMR\) (THF-\(d_8\)): \( \delta \) 146.0 (d, \( J_{PC} = 13.1 \text{ Hz} \), Ph-ipso); 133.8 (d, \( J_{PC} = 19.2 \text{ Hz} \), Ph-ortho); 128.2 (d, \( J_{PC} = 5.7 \text{ Hz} \), Ph-meta); 127.1 (s, Ph-para); 124.0 (t, \( J_{PC} = 20.1 \text{ Hz} \), C in C\(_3\)H\(_3\)P\(_2\)); 117.1 (dd, \( J_{PC} = 18.5 \text{ Hz} \), \( J_{PC} = 8.5 \text{ Hz} \), C\(_5\)H\(_3\)P\(_2\)); 110.4 (d, \( J_{PC} = 9.0 \text{ Hz} \), C in C\(_3\)H\(_3\)P\(_2\)). \text{HRMS: calcd for } C\(_{29}\)H\(_{23}\)P\(_2\) \( -433.1283 \), found 433.1275 (-1.8 ppm). \text{Anal. calcd for } C\(_{29}\)H\(_{23}\)P\(_2\): C, 73.7; H, 4.91; found: 71.2; H, 4.94.

\([-C_5H_3-PPh_2-P-PPh_2-]_2\), (2.6)

To a flask containing [dppeP][Br] (1.500 g, 2.95 mmol) in THF (20 mL) was added a solution of 2.5 (1.391 g, 2.95 mmol) in THF (30 mL) at -78°C. The reaction mixture was stirred for 2 hours before the resulting KBr was removed by filtration. The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in ether and subjected to ultrasonic agitation for 1h. The product precipitated from the ether and was collected by filtration; removal of the volatile components provided a pale-yellow solid characterized as 6. 95% (1.300 g, 1.4 mmol). Crystals suitable for X-ray diffraction were obtained by dissolving the powder in CH\(_2\)Cl\(_2\) followed by vapor diffusion with Et\(_2\)O. \(^{31}P\{^1H\} NMR\) (THF-\(d_8\)): \( \delta \) 19.71 (d, \( J_{pp} = 459 \text{ Hz} \), -148.40 (t, \( J_{pp} = 459 \text{ Hz} \)); \(^1H\) NMR (THF-\(d_8\)): \( \delta \) 7.74-7.68 (m, 8H, Ph-ortho); 7.34-7.20 (m, 12H, Ph-meta/para); 6.21 (s, 1H, C\(_3\)H\(_3\)); 5.84 (s, 2H, C\(_3\)H\(_3\)); \(^{13}C\{^1H\} NMR\) (THF-\(d_8\)): \( \delta \) 134.9 (d, \( J_{PC} = 16.3 \text{ Hz} \), Ph-ipso); 133.6 (d, \( J_{PC} = 3.5 \text{ Hz} \), Ph-ortho); 131.2 (s, Ph-meta); 128.6 (s, Ph-para); 119.2 (broad singlet, C\(_5\)H\(_3\)P\(_2\)); 97.6 (broad singlet, C\(_5\)H\(_3\)P\(_2\)); (C\(_1\)

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2.4.3 X-Ray Crystallography.

Each crystal was covered in Nujol and placed rapidly into a cold N₂ stream of the Oxford Cyrostream low temperature device. The data were collected using the SMART software package on a Bruker APEX CCD diffractometer employing a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) source or using the APEX2 software on a Bruker D8 Venture diffractometer with a Photon 100 CCD detector using a Mo Kα radiation (λ = 0.71073 Å) source. Hemispheres of data were collected using counting times of 10-30 seconds per frame at -100 °C. The details of crystal data, data collection, and structure refinement are listed in Table 2.1. Data reductions were performed using the SAINT implementations in the SMART or APEX2 software packages and the data were corrected for absorption using SADABS. The structures were solved by direct methods using SIR97 and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2012 and the WinGX software package; thermal ellipsoid plots were produced using SHELXTL. Please note that for the metal complexes 2.2 and 2.3, although only the predominant enantiomeric form within each experimental chiral crystal is depicted, both enantiomers should have an equal probability of formation. Powder X-ray diffraction (pXRD) experiments were performed with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using Cu Kα radiation (λ = 1.54186 Å).
Table 2.2 Summary of X-ray Diffraction Collection and Refinement Details for the Feature Compounds Reported in This Chapter

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<td>173(2)</td>
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<td>15.4287(13)</td>
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<td>b (Å)</td>
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### Chapter 2: \( P^+ \) Transfer as An Alternative Approach to Phosphorus-Containing Oligomers

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<td>0.387, -0.698</td>
<td>0.551, -0.249</td>
<td>0.484, -0.488</td>
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</table>

\[
R_1 = \frac{\sum |F_o| - |F_c|}{\sum F_o}, \quad wR_2 = \frac{\sum (w(F_o^2 - F_c^2)^2)}{\sum (wF_o^4)}, \quad GOF = \frac{\sum (w(F_o^2 - F_c^2)^2)}{(\text{No. of reflns.} - \text{No. of params.})^{1/2}}.
\]
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2.5 References

(2) Allcock, H. R. Chemistry and Applications of Polyphosphazenes; John Wiley & Sons, Inc.
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49, 1198–1205.


(39) SMART. *Bruker AXS, Madison, Wi 2001*.

(40) SAINTPlus. *Bruker AXS, Madison, Wi 2001*.

(41) SADABS. *Bruker AXS, Madison, Wi 2001*.


Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

3.1 Introduction

One of the principal areas of investigation during this time has been the development of stable compounds containing elements in low valence states or low oxidation states.\(^1,2\) One of the landmark classes of molecules containing low-valent phosphorus atoms are triphosphenium cations, which are stable molecules containing a dicooordinate phosphorus atom in the +1 oxidation state, stabilized by two phosphonio substituents.\(^3,4\) Because of the electron-rich nature of the P\(^{I}\) fragment, these molecules were initially proposed to be good candidates for coordination chemistry as ligands for transition metals. However, despite several reports of improved syntheses\(^5,6\) and some reports of complex formation,\(^7\) the coordination chemistry of these molecules remains underdeveloped – particularly in comparison to their isoelectronic carbon(0) analogues known as carbodiphosphoranes.\(^8-11\) The relatively poor ligating ability of triphosphenium cations is likely a consequence of the positive charge on the moiety containing the P\(^{I}\) center in addition to the presence of reactive anions. For example, it has been postulated that the bromide ion of (Figure 3.1, A) preferentially reacts with transition metals, leading to degradation of the triphosphenium fragment.\(^12\) To overcome these deficiencies, Ragogna and co-workers recently reported a zwitterionic cyclic triphosphenium species – constructed using anionic phosphine ligands – and demonstrated that the donor ability of these molecules is significantly increased with respect to their cationic analogues (Figure 3.1, B).\(^12,1\)
Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

Figure 3.1 Selected molecules featuring a triphosphenium fragment, including: triphosphenium cations (A) and neutral triphosphenium analogues (B and C).

As described in chapter 2, we have also had success in generating neutral triphosphenium analogues with the initial aim of targeting the generation of macrocycles and oligomers for use as multidentate donors, and demonstrated their utility as ligands for coinage metals (Figure 3.1, C). In this chapter, we explore the possibility of engaging the negatively charged bridging moiety for additional coordination. In particular, we postulate that the differing electronic behavior of the potential donor sites in such molecules could allow for different binding and specificity (e.g. the sites feature both hard and soft donors). Such design elements would permit for the potential generation of multi-metallic systems in which various metals can be selectively coordinated in a controlled manner.

As such, the anionic linker we employed was cyclopentadienyl (Cp). Cp ligands are one of the most ubiquitous and coordinatively-flexible anionic ligands for transition metals owing to its ability to bind metals in different modes (σ, and η₁ to η₅) and its significant capacity for functionalization. Of particular relevance to the work in this chapter, it has been demonstrated recently that ferrocene derivatives featuring multiple pendant phosphine groups can bind up to two additional transition metals to generate trimetallic systems which could prove useful for multi-metallic oligomers or
polymers.15 With the foregoing design elements in mind, we targeted cyclopentadiene as the backbone of our neutral triphosphenium, with an appended, uncoordinated phosphine at the back. This could allow for the molecule to function as a 2 e−, 4 e− or up to 6 e− donor, depending on the requirements of the metal to which it binds. The multi-functional nature of the system, which also features a phosphine and a phosphide-like triphosphenium moiety, should also permit for site-specific modification of the parent ligand (e.g. via oxidation, protonation and alkylation) for the generation of analogues with different donor abilities. We wish to note that Stradiotto and co-workers demonstrated the practicality of this method in the generation of substituted $P,N$-indene ligands for transition metals.16,17 Thus, in this chapter, we report a simple method to generate this molecule using our $P^I$ transfer agent and we probe some of the surprising chemistry associated with this multifunctional molecule containing a $P^I$ center.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization of [(Ph$_2$P)$_5$H$_2$(Ph$_2$P)$_2$P$^I$]

The synthesis of our target $P^I$ molecule was inspired by a ligand we have previously commissioned to generate $P^I$ containing macrocycles, namely the potassium salt of 1,3-bis(diphenylphosphino)cyclopentadienide. To produce a chelating analogue of these types of molecules, we appended an additional diphenylphosphine fragment to provide 1,2,4-tris(diphenylphosphino) cyclo pentadiene, which was deprotonated with potassium hexamethyldisilazide to generate the potassium salt in good yield. The reaction of this potassium tris(diphenylphosphino)cyclopentadiene in a 1:1 stoichiometric ratio with [dppeP][Br] yields (3.1) in quantitative yield (Scheme 3.1).
Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

As anticipated, the presence of two phosphines alpha to each other favors the generation of a monomeric, chelated triphosphenium analogue rather than producing dimers (or higher oligomers). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture features doublet, singlet and triplet resonances indicative of 3.1 ($\delta$ 32.4, -16.9, -174.2 ppm respectively, Fig. 3.2) in addition to a singlet for the dppe that is liberated in the process. The crude mixture was filtered to remove KBr and the filtrate was collected and washed with hexanes via Soxhlet extraction overnight to remove the diphenylphosphinoethane.

Scheme 3.1 Synthetic route to a neutral triphosphenium, 3.1 via ligand metathesis

Figure 3.2 $^{31}\text{P}$ NMR of 3.1, showing distinctive shifts for the P(I) center (-174 ppm), the pendant phosphine (-16 ppm) and the chelating phosphines (32 ppm)

Crystals of the air-sensitive compound 3.1 suitable for X-ray diffraction were obtained from the slow evaporation of a concentrated dichloromethane solution. The molecular structure (Figure 3.3) reveals a zwitterionic triphosphenium analogue,
crystallizing in the space group P2₁/c with one molecule present in the asymmetric unit. The P–P bond lengths of the triphosphenium fragment, 2.1418(12) and 2.1467(12) Å are relatively long—falling outside of the range of distances reported for cationic cyclic triphosphenium cations (2.11–2.13 Å)⁴—and are most similar to those in Ragogna’s zwitterionic triphospheniums (2.1328(9) to 2.1371(9) Å). Similarly, the P–P₁–P angle of 90.39 (4) ° is obtuse in comparison to typical angles for reported 5-membered ring triphosphenium cations (86–88°). As anticipated, the P–CCp bond length of the free phosphine (1.802(3) Å) is significantly longer than the P–C^Cp distances (1.749(3)–1.750(3) Å) to the chelating phosphine groups.

**Figure 3.3** Thermal ellipsoid plot of 3.1. Ellipsoids are drawn at 50% probability and hydrogen atoms are removed for clarity. Selected bond distances (Å) and angles (°): P1–P3: 2.1418(12), P2–P3: 2.1467(12), P1–C1:1.750(3), P2–C2: 1.749(3), P4–C4: 1.802(3), P1–P3–P2: 90.39(4).

We conducted cyclic voltammetry (CV) experiments as a preliminary probe for the reactivity of the three potential sites of this ligand. The groups of Alcarazo,18
Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

Weigand and ourselves have previously employed this technique to attempt to quantify the donating ability of ligands containing a low valent phosphorus atom. The voltammogram for compound 3.1 shows both quasi-reversible and irreversible oxidation peaks at potentials of +0.227 V and +0.817 V (versus Fc/Fc'). Based on the CV data obtained for both starting materials we postulate that the potentials correspond to two oxidations; the lower one likely being attributable to the cyclopentadienyl ring and the higher one being attributable to the P^I center (cf. the oxidation potential of [(dppe)P]^+ at 1.066 V) (Figure 3.4). The latter assignment suggests that 3.1 should be a better donor than the triphosphenium cation found in the starting material and investigated previously.

![Figure 3.4 Cyclic voltammograms of 3.1 and its reactants ([K][(Ph2P)3Cp], A and [dppeP][Br], B). The CV of 3.1, C, shows an irreversible and quasi-reversible oxidation peaks (C); the potential illustrated is with respect to Ag/AgCl (1 M).](image)

3.2.2 Coordination of AuCl to [(Ph2P)C5H2(Ph2P)2P]^+

In order to probe the ligand properties of our zwitterionic triphosphenium with transition metals, we selected to conduct our initial investigation using d10 coinage metals as these have been found to coordinate to various low valent centers and the linear structures minimize steric complications. We found that the addition of an orange suspension of gold(I) chloride to a stirring bright yellow solution of 3.1 resulted...
in an immediate colour change from yellow to gold. The reaction was monitored by $^{31}\text{P}{{\{^{1}\text{H}}}}$ NMR, and the most obvious change in the spectrum of the reaction mixture is a significant desheilding of the singlet signal corresponding to the terminal phosphine to 25 ppm (cf. $-16.9$ ppm in 3.1). This observation suggested that the gold chloride coordinates through the appended phosphine rather than at the P(I) center (Scheme 3.3).

![Figure 3.5](image)

**Figure 3.5** $^{31}\text{P}{{\{^{1}\text{H}}}}$ NMR stack plot illustrating of 3.1 (grey, top), and the spectrum obtained after the addition of gold(I) chloride to generate 3.2 (black, bottom).

This perhaps unanticipated result is confirmed by the molecular structure obtained from crystals grown from a concentrated solution of dichloromethane. The molecule crystallizes in the space group P 21/c with one molecule present in the asymmetric unit (Figure 3.6). Notably, the P–Au distance of 2.2336(7) Å falls within the typical range of AuCl fragments bound to phosphine ligands in the Cambridge Structural Database (CSD). Additionally, there is a significant decrease in the bond length of the phosphine to the carbon of the cyclopentadienyl group to 1.780(3) Å (cf. 1.802 Å in 3.1). Preliminary NMR studies of reactions with 2:1 stoichiometric ratio of gold suggest that the second equivalent of gold is indeed bound at the P(I) center.
Figure 3.6 Thermal ellipsoid plot of 3.2, hydrogen atoms omitted for clarity and ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): P1–P2: 2.1377(10), P2–P3: 2.1378(10), P1–C1: 1.760(3), P3–C2: 1.767(3), P4–C4: 1.7808(3), P1–P3–P2: 91.09(4).

3.2.3 Protonation reactions of [(Ph₂P)C₅H₂(Ph₂P)₂P]⁻

Considering the perhaps surprising result with gold(I), we investigated reactions with a strong main group acceptor – a proton – to further probe the reactivity of this molecule. Again, to our surprise, the addition of trifluoromethanesulfonic (triflic) acid protonates selectively, at the pendant phosphine when added in a 1:1 ratio (Scheme 3.2). This is indicated by a significant, downfield shift of the singlet corresponding to the terminal phosphine from −17 ppm to −4 ppm while the doublet and triplet signals corresponding to the triphosphenium fragment remain at the nearly the same shifts. (Figure 3.7, B). Thus, it appears as if not only soft Lewis acids, such as gold(I) chloride, selectively react at the terminal phosphine, but so do harder acids. Based on ³¹P NMR investigations, the addition of a further equivalent of triflic acid protonates the P⁺ center,
Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

shifting the corresponding triplet peak from -178 ppm to ca -80 ppm (Figure 3.7, C).

Unfortunately, we have been unsuccessful in obtaining high-quality single crystals for the protonated products.

![Scheme 3.2 Reaction of 3.1 with 1 and 2 eq. triflic acid, and proposed products.](image)

Scheme 3.2 Reaction of 3.1 with 1 and 2 eq. triflic acid, and proposed products.

![Figure 3.7 31P{1H} NMR spectra of 3.1 (A) and reactions with HOTf (B), 2 eq HOTf, (C).](image)

Figure 3.7 31P{1H} NMR spectra of 3.1 (A) and reactions with HOTf (B), 2 eq HOTf, (C).

3.2.4 Computational Investigations

The observation that 3.1 binds at the tricoordinate phosphine (P(III)) site rather than the dicoordinate phosphide-like (P(I)) site suggested that an overly simple model of electron density – i.e. one based on canonical forms of Lewis-type drawings such as in Figure 3.1 – does not provide accurate predictions of reactivity for this molecule. In order to obtain a more accurate understanding of the electronic structure and reactivity
of compounds such as 3.1, we conducted a series of density functional theory (DFT) calculations using the M062X/TZVP approach. The results of these calculations are particularly enlightening. Geometry optimization of a complete model of 3.1 bearing phenyl substituents accurately reproduces all of the structural features observed experimentally but the calculations are computationally expensive. We found that a model complex in which all the phenyl substituents are modelled with hydrogen atoms ([H$_2$P$_3$(C$_5$H$_2$)P$_3$]), 3.1', also provides excellent agreement with the experimental observations at a much lower computational cost; this model was used for the more in-depth computational reactivity investigations.

Interestingly, examination of the frontier molecular orbitals for 3.1' (Figure 3.8) reveals that the three highest energy occupied molecular orbitals (HOMO to HOMO-2) are all primarily based on either the triphosphenium fragment or the cyclopentadienyl fragment! In fact, the HOMO (and LUMO) is very similar in composition to those of other cyclic triphosphenium ions. Thus, one might predict that 3.1' should function as a donor either via the P\(^{\text{i}}\) center or the Cp fragment. In fact, the orbital corresponding to the “lone pair” on the free phosphine fragment- the fragment that actually appears to react in the experimental observations-is HOMO-3 and is around 1 eV more stable than the HOMO.
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Figure 3.8 Depictions of the frontier orbitals of 3.1′.

Given that the simple frontier MO analysis also did not appear to provide a rationale for the experimental results, we examine the electrostatic potential (ESP) of 3.1’. A plot of the ESP of 3.1′ mapped onto the electron density, illustrated in Figure 3.8 (top) does indeed provide insight into the regiochemistry observed experimentally. The highest potential (depicted in red) on 3.1′ is localized on the free phosphine fragment; there is a somewhat smaller potential localized on the Cp ring and a considerably decreased potential on the P¹ fragment. This observation suggests that, perhaps in contrast to simple chemical intuition, the phosphine fragment should indeed be the most reactive part of the molecule.

Calculations of the proton affinities for 3.1′ for binding a proton at either the P¹ or P³ sites reveal that the binding of one proton at the tricoordinate phosphine site is 36 kJ/mol more favourable than is binding a proton at the dicoordinate P¹ site. Interestingly, the calculations predict that protonation at the Cp ring is even more
favourable (but by less than 3 kJ/mol) for this model but we see no evidence of such chemistry experimentally. Thus, the proton binding calculations corroborate the conclusions drawn from the ESP calculation and the experimental observations in terms of the preference of the site of phosphorus reactivity.

Importantly, examination of the ESP of the most stable protonated variant of 3.1' (i.e. [P(H2P)2C5H2PH3]+) reveals that protonation of the phosphine results in a cation in which the P° center and the Cp ring have a high potential (Figure 3.9, bottom). This observation suggests that the ligand properties of 3.1, should indeed be tunable using acids.

Similarly, calculations of the electrostatic potentials of derivatives of 3.1' in which the phosphine is protected with oxygen, sulfur, borane, and methyl groups (Figure 3.9) suggest that the binding properties and preferences of these variants may be easily modified.
Figure 3.9 Electrostatic potential map of 3.1′ (left, above) and protonated variant (left, below); regions colored red exhibit the highest potentials and regions in violet have the lowest potentials.

3.2.5 Reaction of [(Ph₂P) C₅H₂(Ph₂P)₂P] with Main Group Acceptors

With the results of our computational investigation in hand, we sought to selectively react the terminal phosphine with main group acceptors to evaluate how the properties of the compound change, with regards to the cyclopentadienyl or P⁺ moiety. The addition of a yellow solution of 3.1 in dichloromethane to a suspension of one
equivalent of elemental sulfur in dichloromethane results in immediate reaction that yields a cloudy yellow solution. The reaction is complete after 10 minutes and can be monitored by $^{31}$P NMR spectroscopy: once again, there was a significant shielding (from $\delta -16.9$ ppm to $\delta 35.4$ ppm) of the singlet corresponding to the terminal phosphine while the doublet and triplet (at $\delta 35$ ppm, $-173$ ppm) attributable to the triphosphenium fragment, are virtually unchanged from their original shifts (cf. $\delta 34$ ppm, $-175$ ppm). (Figure 3.10). $^{31}$P NMR spectroscopy is again consistent with the reaction having occurred at the appended phosphine moiety (Scheme 3.3).

![Figure 3.10](image)

The product can be obtained from simply removing the reaction solvent (dichloromethane), as the product is generated in quantitative yield. The moderately air sensitive solid can be stored indefinitely in an inert atmosphere and is stable for several hours on the bench top without decomposition.
Scheme 3.3 Reaction of 3.1 gold chloride (right) to generate 3.2 and with elemental sulfur (left) to generate 3.3.

The regiochemistry of the reaction to generate the sulfide 3.3 inferred based on the NMR spectroscopy was confirmed by the molecular structure obtained from crystals grown from dichloromethane. The molecule crystallizes in the space group P2\(_1\)/c with one molecule present in the asymmetric unit (Figure 3.11). The P–S bond length is 1.9618(10) Å and is well within the range of phosphine sulfide bond lengths reported in the CSD.\(^{22}\) As anticipated, there is a significant shorting of the P–C\(^{\text{Cp}}\) bond distance to 1.778(3) Å (cf. 1.802(3) Å) in comparison to the parent ligand. The bond lengths within the triphosphenium moiety virtually unchanged in the thionated ligand.
Figure 3.11 Thermal ellipsoid plot of 3.3, hydrogen atoms omitted for clarity and ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): P1–P2: 2.1477(10), P2–P3: 2.1393(10), P1–C1: 1.763(3), P3–C2: 1.757(3), P4–C4: 1.778(3), P4–S: 1.9618(10), P1–P3–P2: 90.8(4).

To evaluate the changes in the redox properties, we also conducted cyclic voltammetry experiments on 3.3 to compare the potentials to those of the parent molecule (Figure 3.12). We found that there is only one clear oxidation potential present, which corresponds to an irreversible oxidation appearing at 0.662 V (versus Fc/Fc+) which appears to overlap with an oxidation at higher potential (ca. 0.9 V).

Thus, it appears as if the alteration of the relatively electron-donating PPh₂ fragment in 3.1 to a much more electron-withdrawing P(S)Ph₂ fragment in 3.3 to results in a significant increase in the oxidation potential of the Cp ring, as one would anticipate.
Figure 3.12 Cyclic voltammogram of 3.4 showing two overlapping oxidation peaks; the potential illustrated is with respect to Ag/AgCl (1 M).

In addition to sulfur, the calculations described earlier indicated that “blocking” the pendant phosphine with methyl or borane groups can also increase the magnitude of the negative electrostatic potential of both the Cp⁻ and P(I) sites. Additionally, the addition of a methyl group to the backbone of the molecule could generate an interesting molecule where the formal cationic charge is located on the back of the molecule, with an anion present that could be used for metathesis. Thus, we employed iodomethane in hopes of generating 3.4 (Scheme 3.4).

Scheme 3.4 The reaction of 3.1 with 1 eq and 2 eq of iodomethane to produce 3.4, and 3.5 respectively.
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The dropwise addition of MeI to a stirring solution of 3.1 in dichloromethane results in the immediate generation of orange-yellow solution, and the reaction appears to be complete by $^{31}$P NMR. As anticipated, NMR spectroscopy suggests that the methylation occurs at the pendant phosphine group (rather than the P(I) center), as the singlet corresponding to that moiety shifts from -17 ppm to 13 ppm (Figure 3.14). The reaction solvent was removed and the material was washed with Et$_2$O. Single crystals were grown from a cold, layered solution of pentane and dichloromethane. The molecular structure confirms the generation of 3.4 (Fig 3.13), with one molecule in the asymmetric unit accompanied by a THF solvent molecule.

![Figure 3.13](image)

Figure 3.13. Two orientations of the thermal ellipsoid plot of 3.4, ellipsoids are depicted at 50% probability, THF molecule and hydrogens removed for clarity. Selected bond distances (Å) and angles (°): P1–P2: 2.136(2), P2–P3: 2.135(2), P1–C1:1.777(5), P3–C2: 1.7774(5), P4–C4: 1.765(6), P4–C6: 1.777(15), P1–P3–P2: 90.78(4).

The bond lengths of 3.4 show similar effects to the other coordination molecules reported in this chapter: a slight shortening of the P-P bonds within the triphosphenium fragment, from 2.1467(12)-2.1418(12) Å to 2.135(2)-2.136(2) Å, while maintaining a similar P-P-P angle (90.76(8))° to what is observed in the
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proligand \((90.39(4))\)°. The P-CH\(_3\) of the methylated phosphine within the backbone is \(1.777(5)\) Å, which is in good agreement with average P-C bond length of phosphoniums reported in the CSD \((1.794(32)\) Å). There is also a slight shortening of the P-C\(_{CP}\) bond, from \(1.802(3)\) Å to \(1.765(6)\) Å.

Interestingly, the reaction of \(3.1\) with two equivalents of methyl iodide partakes in a similar reactivity to our experiments described above when two equivalents of triflic acid were added to \(3.1\) – that is, the formation of the dimethylated variant (Scheme 3.4), based on \(^{31}\)P NMR. For this reaction, there is a dramatic shift of the triplet corresponding to the P(I) center from -178 ppm to -35 ppm. (Figure 3.14)

![Figure 3.14](image)

**Figure 3.14** \(^{31}\)P\(_{\{^1\}H}\) NMR stack plot illustrating of \(3.1\) (A, bottom, 300 Mz spectrometer), \(3.4\) (B, middle, 500 Mhz spectrometer), and the spectrum obtained after the addition of 2 eq. of MeI to \(3.1\), generated a dimethylated species (C, top, 500 Mhz spectrometer).

Unfortunately, the resulting material has only been isolated as an oil and thus far we have been unable to obtain single crystals of this material. However, \(^{31}\)P, \(^1\)H and \(^{13}\)C NMR experiments corroborate our hypothesis.
Finally, the addition of borane (BH₃) to 3.1 yields the now-anticipated phosphine-borane complex utilizing the pendant phosphine on the backbone of the ligand (Scheme 3.5). The reaction proceeds quickly and with a high yield to generate the complex 3.5. As described earlier for the previous complexes, the $^{31}$P NMR of this reaction shows a distinctive shift of the singlet signal from -20 ppm to +10 ppm (Figure 3.15)

Scheme 3.5 Reaction of 3.1 with BH₃ to generate 3.5

Figure 3.15 $^{31}$P{$^1$H} NMR stack plot illustrating of 3.1 (grey, top, acquired on a 300 Mhz spectrometer), and the spectrum obtained after the addition of BH₃ to generate 3.5 (black, bottom, acquired on a 500 Mhz spectrometer)
Single crystals of this material were obtained from slow evaporation of dichloromethane, and X-ray diffraction confirms the anticipated structure described above (Figure 3.16). Structural details are anticipated; The P-P bonds within the triphosphenium fragment remain virtually unchanged (2.1357(8)-2.1434(8) Å), and the same can be said of the P-\( \text{C}^\text{Cp} \) bonds (1.755(2)-1.760(2) Å, as well as the P-P-P angle (90.84(3)°). However, there is a slight shortening of the P-\( \text{C}^\text{Cp} \) bond of the pendant phosphine-borane group, from 1.802(3) Å to 1.916(3) Å upon complexation. The P-B bond length of this Lewis pair is 1.916(3) Å is a typical \( \text{R}_3\text{P}^-\text{BH}_3 \) bond length, and is very close to the average length reported for this type of complex in the CSD (1.919(20) Å).

**Figure 3.16** Molecular structure of 3.5, thermal ellipsoids depicted at 50% probability, hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P1–P2: 2.1434(8), P2–P3: 2.1357(8), P1–C1: 1.760(2), P3–C2: 1.755(2), P4–C4: 1.780(2), P4–B: 1.916(3), P1–P3–P2: 90.84(3).
3.3 Conclusions & Future Work

This chapter describes the synthesis of a new multifunctional zwitterionic triphosphenium and provides some insight into its reactivity. Both reactivity studies and calculations reveal that this molecule is most reactive at the phosphine fragment rather than at the P(I) fragment within the triphosphenium moiety. Experimental investigations reveal that the reaction of the ligand with gold(I), protons, methyl, borane or sulfur all result in selective binding at the free phosphine initially. Computational investigations suggest that this ligand can easily be modified to preferentially bind at either the cyclopentadienyl ring or the P(I) moiety, by blocking the terminal phosphine.

The use of 3.1 with other transition metal fragments should be investigated; particularly metal carbonyl fragments which could bind at the pendant phosphine, cyclopentadienyl, or P(I) center. Utilization of the main group adducts described in this chapter (3.3, 3.5) might lead to the generation of transition metals at the P(I) (for example, Au(I), Rh(II), Pt(II), Ni(0)). Further, the methylated (3.4) or protonated variants of 3.1 might provide access to transition metal complexes via metathesis reactions, this type of reactivity has been demonstrated for N-heterocyclic phospheniums by Gudat et al. 37 (Figure 3.17)

![Figure 3.17 Potential reactivity of 3.4 towards metal carbonyl complexes](image)
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3.4 Experimental

3.4.1 General Procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried according to literature procedure when necessary, and all other solvents were dried over a series of Grubbs’-type columns and degassed prior to use. The ligand, [K][((Ph₂P)₃C₅H₂] was synthesized according to modified literature procedures.14,15 NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz or Bruker Avance Ultrashield 300 MHz spectrometer. Chemical shifts are reported in ppm, relative to internal standards for ¹H and ¹³C (the given deuterated solvent) and external standards for and ³¹P (85% H₃PO₄). Coupling constants, |J|, are given in Hz. Elemental Analysis was performed at the University of Windsor using a Perkin Elmer 2400 combustion CHN. Cyclic voltammetry was performed in dry CH₂Cl₂ solutions using [NBu₄][PF₆] (0.1 M) as the electrolyte with an analyte concentration of approximately 0.01 M. A glassy carbon electrode, a platinum wire, and 1.0 M Ag/AgCl electrode were used as the working, auxiliary, and reference electrodes, respectively. The experiments were run with a scan rate of 100 mV s⁻¹ and a sensitivity of 100 μAV⁻¹, and the potentials reported are referenced to ferrocene/ferrocenium (E₁/₂ = 0.0 V).

3.4.2 Crystallographic Details

Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N₂ of the low-temperature
apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXII software suite\textsuperscript{32} on a Bruker D8 Venture diffractometer with a Photon 100 CCD detector with MoK\textsubscript{\textalpha} radiation ($\lambda = 0.71073$ Å). For each sample, data were collected at low temperature. APEXII software was used for data reductions and SADABS\textsuperscript{33} 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{34} software suite as implemented in the WinGX\textsuperscript{35} program suites. Validation of the structures was conducted using PLATON.\textsuperscript{36} Details are provided in Table 3.1

3.4.3 Crystallographic Details

All the computational investigations were performed using the Compute Canada Shared Hierarchical Academic Research Computing Network (SHARCNET) facilities (http://www.sharc-net.ca) with the Gaussian09\textsuperscript{24} program suites. Geometry optimizations have been calculated using density functional theory (DFT), specifically implementing the M062X method\textsuperscript{25} in conjunction with the TZVP basis set\textsuperscript{26} for all atoms. The geometry optimizations were not subjected to any symmetry restrictions and each stationary point was confirmed to be a minimum having zero imaginary vibrational frequencies. Pictures of the optimized structures were prepared using Gaussview 3.0.\textsuperscript{27} Population analyses were conducted using the Natural Bond Orbital (NBO)\textsuperscript{28} implementation included with the Gaussian package. Plots of molecular orbitals and electrostatic potentials were generated at the M062X\textbackslashTZVP level of optimized structures, including electronic energies and Cartesian components for each of the atoms, are detailed in the appendix.
3.4.4 Specific Procedures

**Synthesis of [(Ph₂P)₅C₅H₂(Ph₂P)₂P] (3.1)**

To a cold, stirring white suspension of [dppeP][Br] (1.939 g, 3.8 mmol) in THF, was added a THF solution of [K][(Ph₂P)₅C₅H₂] (2.50 g, 3.8 mmol). Upon addition, the solution was allowed to warm to room temperature and a yellow colour appeared with the production of a white precipitate. The solution was subsequently filtered through Celite® and washed with THF (10 mL) to remove KBr and the yellow filtrate was collected. The THF was removed from the filtrate in vacuo to obtain a bright yellow powder. This powder was washed via soxhlet extraction with hexanes overnight to remove the dppe and the subsequent bright yellow precipitate was collected as 3.1.

(2.24 g 91%) Crystals were obtained from slow evaporation of a concentrated solution of dichloromethane. ³¹P{¹H} NMR (CD₂Cl₂) δ(ppm): -174.2 (t, Jₚₚ = 426 Hz), -16.9 (s), 32.4 (d, Jₚₚ = 426 Hz). ¹H NMR (CD₂Cl₂) δ(ppm): 6.57 (pseudo-q, 2H, 2JₚH @ 3.5 Hz, 3JₚH @ 3.5 Hz, C₅H₂), 7.2-7.7 (m, 30H, Ar); ¹³C{¹H} NMR (CD₂Cl₂) δ(ppm): δ 141.7 (d, Jₚ₉ = 10.4 Hz, Ph), 133.5 (d, Jₚ₉ = 7 Hz, P–C₉), 133.0 (d, Jₚ₉ = 18.6 Hz, Ph), 132.5 (d, Jₚ₉ = 7.3 Hz, P–C₉); 131.9 (d, Jₚ₉ = 10.7 Hz, Ph), 131.4 (s, para-Ph); 128.7 (d, 12 Hz, Ph); 127.9 (d, 3Jₚ₉ = 5.6 Hz, Ph); 127.5 (s, para-Ph); 121.5 (m, Jₚ₉ ≥ 5 Hz, C₉–H).  

**Anal. Calcd (%) for:** C₄₃H₃₄P₄: C, 75.92; H, 4.97; N, 0; found: C, 75.61; H, 4.93, N, -0.05. **HR-ESI-MS:** Calcd for [C₄₁H₃₂P₄]⁺ m/z = 648.1460, found: 648.1455
Synthesis of [AuCl (Ph₂P)C₅H₂(Ph₂P)₂P⁺] (3.2)

To a stirring pale yellow solution of 3.1 (0.110 g, 0.169 mmol) was added a dichloromethane suspension of AuCl (0.039 g, 0.169 mmol). Upon addition, the solution turned a golden yellow colour and was left to stir for 10 minutes. The dichloromethane was removed and the subsequent yellow powder was washed with diethyl ether (5 mL) and then collected as 3.2. (0.141 g, 94.6%) Crystals were obtained from slow evaporation of a concentrated solution in dichloromethane. ³¹P{¹H} NMR (CDCl₃) δ (ppm): -175.0 (t, ¹Jₚₚ = 432 Hz), 18.7 (s), 34.1 (d, ¹Jₚₚ = 432 Hz). ¹H NMR (CDCl₃) δ (ppm): 6.67 (pseudo-q, 2H, ²Jₚₖ ≥ 3.5Hz, ³Jₚₖ ≅ 3.5 Hz, C₅H₂), 7.3-7.7 (m, 30H, Ar); ¹³C{¹H} NMR (CDCl₃) δ (ppm): δ 139 (s, Ph), 135 (s, Ph) (133.0 (d, 18.6 Hz, Ph), 132.5 (br, 7.3 Hz, P–CCp); 132 (br, Ph-P), 131.4 (s, para-Ph); 128.7 (d, 12 Hz, Ph); 127.9 (d, 5.6 Hz, Ph); 127.5 (s, para-Ph); 121.5 (m, ²Jₚₖ ≥ 5 Hz, C₅–H). Anal. Calcd (%) for: C₄₁H₃₂P₄AuCl: C, 55.9; H, 3.66; N, 0; found: C, 55.77; H, 3.70, N, -0.05.

Synthesis of [(Ph₂P(S)) C₅H₂(Ph₂P)₂P⁺] (3.3).

To a stirring pale yellow solution of 3.1 (0.189 g, 0.29 mmol) was added a dichloromethane suspension of elemental sulfur (0.009 g, 0.036 mmol). There was no colour change upon addition and the solution was allowed to stir for 1 hour at which point the solution was centrifuged to ensure no unreacted sulfur remained, and the resulting solution was collected. Dichloromethane was removed and the subsequent pale yellow powder was collected. (0.191 g, 97%) Single crystals were obtained via slow evaporation from a concentrated solution of dichloromethane. ³¹P{¹H} NMR (CD₂Cl₂)
\( \delta (\text{ppm}) : -173.3 \ (t, J_{\text{PP}} = 431 \text{ Hz}), 35.38 \ (s), 35.3 \ (d, J_{\text{PP}} = 431 \text{ Hz}) \). \(^1\text{H} \text{ NMR (CD}_2\text{Cl}_2)\)

\( \delta (\text{ppm}) : 6.57 \ (\text{pseudo-}q, 2H, 2J_{\text{PH}} \approx 4.75 \text{ Hz, } 3J_{\text{PH}} \approx 4.75 \text{ Hz, C}_5\text{H}_2), 7.3-7.7 \ (m, 30H, Ar); \)

\(^{13}\text{C}\{^1\text{H} \} \text{ NMR (CD}_2\text{Cl}_2) \delta (\text{ppm}) : \delta 137.2 \ (s, \text{Ph}); 136.1 \ (s, \text{Ph}); 132.60 \ (d, \text{unresolved, } C_{\text{CP}}-\text{P}), 132.6-131.75 \ (m, 2J_{\text{PC}}=7.3 \text{ Hz, Ph}); 130.5 \ (s, C_{\text{CP}}-\text{H, Ph}); 129-128 \ (m, \text{Ph}); 120.5 \ (m, 2J_{\text{PC}} \text{ unresolved, } C_{\text{CP}}-\text{P}); \text{Anal. Calcd (%) for: } C_{41}\text{H}_{32}\text{P}_4\text{S: } C, 72.35; H, 4.74; N, 0; \text{found: } C, 72.05; H, 4.61, N, 0.1. \)

**Synthesis of \([\text{Me(Ph}_2\text{P)C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{P}][\text{I}] \) (3.4)**

To a stirring solution of 3.1 (0.204g, 0.314 mmol) in 10 mL of THF was added MeI (0.019mL, 0.314 mmol) via syringe, dropwise. The formerly pale yellow solution turns golden yellow in colour and the reaction is complete after 5 minutes. \(^{31}\text{P} \text{NMR indicated quantitative formation of the product and can be isolated via removal of the reaction solvent. Crystals were obtained from tetrahydrofuran layered with pentane which was placed in a freezer overnight or for several days. (0.239g, 96%) \(^{31}\text{P}\{^1\text{H} \} \text{NMR (CD}_2\text{Cl}_2) : \delta 36.5 \ (d, J_{\text{PP}} = 442 \text{ Hz}), 12.9 \ (s), -178.6 \ (t, J_{\text{PP}} = 441 \text{ Hz}); \(^1\text{H} \text{ NMR (CD}_2\text{Cl}_2) : \delta : 7.4-7.7 \ (m, \text{Ar, 30 H}), 6.7 \ (\text{pseudo-}q, 2J_{\text{PH}} = 3.5 \text{ Hz, } 3J_{\text{PH}} = 3.5 \text{ Hz, C}_5\text{H}_2, 2H, ) 2.6 \ (d, 2J_{\text{PH}} = 13.2 \text{ Hz, P-CH}_2, 3H); \(^{13}\text{C}\{^1\text{H} \} \text{ NMR (CD}_2\text{Cl}_2) : \delta : 134.5 \ (br, P-\text{C}_\text{CP}); 132.6-132.0 \ (m, \text{Ph}), 129.8 \ (d, 7.5 \text{ Hz, Ph}); 129.1 \ (m, \text{Ph}); 123.5 \ (s, \text{para-Ph}); 120.5 \ (br, \text{ C}_\text{CP}-\text{H}); 12.5 \ (d, \text{P-CH}_3, 1J_{\text{CP}} = 50 \text{ Hz}) \text{Anal. Calcd for } C_{41}\text{H}_{35}\text{P}_4\text{I: } C, 63.81; H, 4.46; N, 0; \text{found: } C, 63.50; H, 4.87; N, -0.02%. \)

**Synthesis of \([\text{Me(Ph}_2\text{P)C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{PMe}[\text{I}] \) \text{2}**

To a stirring solution of 3.1 (0.149g, 0.231 mmol) in 10 mL of MeCN was added MeI (0.028mL, 0.462 mmol) via syringe, dropwise. The formerly pale yellow solution turns golden yellow in colour and the reaction is complete after 5 minutes based on \(^{31}\text{P} \)
NMR. The product was isolated as a yellow oil, and is soluble in MeCN, THF and DCM. Despite repeated washing with non-polar solvents (hexanes, pentane) and a variety of crystallization methods, single crystals were not isolated from this reaction.

\[ ^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\}: \delta 24.8 (d, J_{P-H}=262 \text{ Hz}), 12.8 (s), -35.3 (t, J_{P-H}= 263 \text{ Hz}); \]

\[ ^1\text{H NMR (CD}_2\text{Cl}_2\): \delta: 7.5-7.8 (m, Ar, 30 H), 7.1 (pseudo-q J_{P,H}= 4 \text{ Hz, } C_5H_2, 2H), 2.8 (d, J_{P-H}= 13.5 \text{ Hz, } P-C_5H_2, 3H); 1.51 (dt, J_{P,H}=16 \text{ Hz, } J_{P,H}=8.5 \text{ Hz, } 3H). \]

**Synthesis of \([\text{BH}(\text{Ph}P)\text{C}_5\text{H}_2(\text{Ph}P)\text{P}]\text{OTf}\) 3.5**

To a stirring solution yellow solution of 3.1 (0.150g, 0.231 mmol) in THF was added BH$_3$SMe$_2$, via syringe, dropwise (0.022 mL, 0.231 mmol). The reaction stirred for 1hr at room temperature and then the reaction solvent was removed and the resulting precipitate was washed with diethyl ether and then collected. (0.111g, 73%)

\[ ^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\): \delta: 33.5 (d, J_{P-H}= 431 \text{ Hz}), -8.9 (s), -175.5 (t, J_{P-H}= 431 \text{ Hz}); \]

\[ ^1\text{H NMR (CD}_2\text{Cl}_2\): \delta: 7.77-7.2 (m, 30 H, Ar), 6.57 (pseudo-q J_{P,H}= 3.5 \text{ Hz, } C_5H_2, 2H), 1.2, (br, BH$_3$, 3H); \]

**Synthesis of \([\text{BH}(\text{Ph}P)\text{C}_5\text{H}_2(\text{Ph}P)\text{P}]\text{OTf}\) 3.5**

To a stirring solution yellow solution of 3.1 (0.150g, 0.231 mmol) in THF was added BH$_3$SMe$_2$, via syringe, dropwise (0.022 mL, 0.231 mmol). The reaction stirred for 1hr at room temperature and then the reaction solvent was removed and the resulting precipitate was washed with diethyl ether and then collected. (0.111g, 73%)

\[ ^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\): \delta: 33.5 (d, J_{P-H}= 431 \text{ Hz}), -8.9 (s), -175.5 (t, J_{P-H}= 431 \text{ Hz}); \]

\[ ^1\text{H NMR (CD}_2\text{Cl}_2\): \delta: 7.77-7.2 (m, 30 H, Ar), 6.57 (pseudo-q J_{P,H}= 3.5 \text{ Hz, } C_5H_2, 2H), 1.2, (br, BH$_3$, 3H); \]

\[ ^1\text{B}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\) \delta-37.3 (s, br) \]

\[ ^{13}\text{C}\{^1\text{H}\} \text{NMR(CD}_2\text{Cl}_2\): \delta: 133 (br, P-C$_{5}$); 132.1-131.0 (m, Ph), 128.5 (d, 7.2 Hz, Ph); 127.1 (m, Ph); 123.5 (s, para-Ph); 120.5 (br, C$_{5}$-H). \]

**Anal. Calcd for C$_{41}$H$_{35}$P$_4$B: C, 74.34; H, 5.33; N, 0; found: C, 74.61; H, 5.03; N, 0.15%.**

**Synthesis of \([(\text{Ph}P)\text{C}_5\text{H}_2(\text{Ph}P)\text{P}]\text{OTf}\) 3.5**

To a stirring solution yellow solution of 3.1 (0.150g, 0.231 mmol) in THF was added BH$_3$SMe$_2$, via syringe, dropwise (0.022 mL, 0.231 mmol). The reaction stirred for 1hr at room temperature and then the reaction solvent was removed and the resulting precipitate was washed with diethyl ether and then collected. (0.111g, 73%)

\[ ^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\): \delta: 33.5 (d, J_{P-H}= 431 \text{ Hz}), -8.9 (s), -175.5 (t, J_{P-H}= 431 \text{ Hz}); \]

\[ ^1\text{H NMR (CD}_2\text{Cl}_2\): \delta: 7.77-7.2 (m, 30 H, Ar), 6.57 (pseudo-q J_{P,H}= 3.5 \text{ Hz, } C_5H_2, 2H), 1.2, (br, BH$_3$, 3H); \]

\[ ^1\text{B}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2\) \delta-37.3 (s, br) \]

\[ ^{13}\text{C}\{^1\text{H}\} \text{NMR(CD}_2\text{Cl}_2\): \delta: 133 (br, P-C$_{5}$); 132.1-131.0 (m, Ph), 128.5 (d, 7.2 Hz, Ph); 127.1 (m, Ph); 123.5 (s, para-Ph); 120.5 (br, C$_{5}$-H). \]

**Anal. Calcd for C$_{41}$H$_{35}$P$_4$B: C, 74.34; H, 5.33; N, 0; found: C, 74.61; H, 5.03; N, 0.15%.**
oil and we have been unable to obtain amorphous or single crystalline material. $^{31}$P{$^1$H} NMR: $\delta$ 35.17 (d, $^{1}J_{PP}$=443 Hz), -4.2 (s), -178.0 (t, $^{1}J_{PP}$= 437 Hz). $^{31}$P NMR: $\delta$ 35.2 (d, $^{1}J_{PP}$= 445 Hz), -4.15 (d, $^{1}J_{PH}$= 500 Hz), -178.0 (t, $^{1}J_{PP}$= 445 Hz). $^1$H NMR: $\delta$ 8.60 (d, $^{1}J_{PH}$= 498 Hz, 1H, P-H), 8.8-7.4 (m, 30H, Ph), 6.82 (pseudo-q, $^{2}J_{PH}$= 3.5 Hz, $^{3}J_{PH}$=3.5 Hz, 2H, C$_5$H$_2$).

**Synthesis of [(Ph$\_2$PH)C$_5$H$_2$(Ph$\_2$P)$\_2$P$I$H) OTf$_2$]**

To a vial containing 3.1 (0.200g, 0.39 mmol) in dichloromethane was added triflic acid 2 stoichometric equivalents of triflic acid via syringe (0.106g, 0.78 mmol). After stirring the yellow solution for 5 minutes, $^{31}$P NMR confirmed the complete consumption of 3.1. The resulting product is an oil and we have been unable to obtain amorphous or single crystalline material. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 35.17 (d, $^{1}J_{PP}$=443 Hz), -4.2 (s), -178.0 (t, $^{1}J_{PP}$= 437 Hz). $^{31}$P NMR (CD$_2$Cl$_2$): $\delta$ 35.2 (d, $^{1}J_{PP}$= 445 Hz), -4.15 (d, $^{1}J_{PH}$= 500 Hz), -178.0 (t, $^{1}J_{PP}$= 445 Hz). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 11.2 (b, $^{1}J_{PH}$ unresolved, 1H, P-H), 8.60 (d, $^{1}J_{PH}$= 500 Hz, 1H, P-H), 8.8-7.1 (m, 30H, Ph), 6.82 (pseudo-q, $^{2}J_{PH}$= 3.5 Hz, $^{3}J_{PH}$=3.5 Hz, 2H, C$_5$H$_2$).
Table 3.1: Summary of Crystallographic Data

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R₁ = Σ(|Fo| - |Fc|) / Σ|Fo|, wR₂ = [Σ(w(|Fₒ|² - |F_c|²)) / Σ(w|Fₒ|²)] × 100, GOF = [Σ(w(Fₒ² - F_c²))² / (No. of reflns. - No. of params.)]¹/²
Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

3.5 References

Chapter 3: A Zwitterionic Triphosphene Compound as a Tunable Multifunctional Donor


Chapter 3: A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion

4.1 Introduction

The synthesis of multimetallic complexes has been an important topic in organometallic chemistry, both in the areas of catalysis\textsuperscript{1,2} and in ligand design\textsuperscript{3,4}. Typically, bulky, pincer-type ligands or macrocycles are used for these applications, often featuring various main group donors or acceptors (B, C, N, P, S, O).\textsuperscript{3,5-8} An alternative approach to generate multimetallic species is to employ ligands containing low valent main group centers, which may bind multiple metal centers at one atom due to the increased electron density and low coordination number about the low valent main group center. The low valent ligand approach may reduce the steric bulk in the system, and perhaps increase the activity of the transition metal center, or allow two metals in close proximity for cooperative catalysis.\textsuperscript{2,9} There are several classes of low valent or low coordinate phosphorus centers that have been used to coordinate transition metals, including phosphides,\textsuperscript{10-14} phospholides,\textsuperscript{15,16} phosphinines,\textsuperscript{17-24} phosphaalkenes,\textsuperscript{25-29} isophosphindoliums\textsuperscript{30-33} and even phosphanes,\textsuperscript{34} among others. One of the most extensively investigated classes of neutral ligands featuring low valent phosphorus centers are the phosphinidenes, the phosphorus analogue of carbenes or nitrenes. These ligands have been comprehensively studied by many, and have shown to create numerous stable mono- and bimetallic complexes with a variety of transition metals\textsuperscript{35-44} (Figure 4.1, A, B).

Of particular relevance to the work presented herein are the bimetallic complexes with a low valent main group complexes reported by Frenking\textsuperscript{45} and Alcarazo using carbodiphosphorane (R\textsubscript{3}P-C-PR\textsubscript{3}) ligands. They demonstrated that these formally
carbon(0) compounds can accommodate up to two gold(I) fragments bound by a single carbon(0) center.$^{46}$ (Figure 4.1, C) Similar reactivity was demonstrated by Ragogna et al. using a zwitterionic triphosphenium$^{47}$ ligand that contains an isolobal phosphorus(I) center, (which was also able to coordinate up to two gold atoms on the $P^I$ center (Figure 4.1, D1 & D2).$^{48}$ The use of neutral zwitterionic analogues of triphosphenium cations for coordination chemistry is necessary because, in spite of the “phosphanide” fragment present in a triphosphenium cation, (e.g. Figure 4.1, E) these cations appear to be unsuitable for the generation of persistent metal complexes.$^{49,50}$

![Figure 4.1 Molecules containing a low valent phosphorus center which bind transition metals](image)

We have also been interested in the coordination chemistry of zwitterionic triphosphenium species, and in their potential use as multidentate donors, both in the form of macrocycles$^{51}$ and molecules which feature multiple coordination sites.$^{52}$ In the former case, we observed that the coordination of late transition metals occurs via both low coordinate phosphorus centers in a $\kappa-P,P'-$bidentate type fashion, while in the latter case we observed that the reactivity of the molecule is localized – surprisingly – on the pendant phosphine group rather than at the low coordinate phosphorus center or the
cyclopentadienyl fragment (Figure 4.1, F). We posited that we could better engage the
cyclopentadienyl fragment within the backbone by replacing the phosphine group with a
coordinately “inert” alkyl group instead. This would allow us to achieve bimetallic
complexes through either the P\textsuperscript{I} center alone or via both the Cp\textsuperscript{-} moiety and P\textsuperscript{I} center
together. The successful results of the improved ligand design are presented in this chapter.

4.2 Results & Discussion

4.2.1 Synthesis and characterization of [tBuC\textsubscript{5}H\textsubscript{2}(Ph\textsubscript{2}P)\textsubscript{2}P\textsuperscript{I}]

We previously reported the synthesis of a zwitterionic triphosphenium analogue
that featured three potential coordination sites. In our initial report, we had noted that the
reactivity of the molecule with occurred preferentially on the terminal phosphine group
attached to the cyclopentadienyl fragment rather than the phosphorus(I) center, and this
result was rationalized on the basis of electrostatic potential analysis derived from density
functional theory investigations.\textsuperscript{52} With this insight, we set out to modify the ligand so as to
enhance the reactivity of the phosphorus(I) moiety; one obvious modification was to
eliminate the terminal phosphine site and to utilize instead an alkyl-substituted
cyclopentadienyl backbone – we selected a tert-butyl substituted analogue – that would
still allow for the convenient preparation of the 1,2-diphosphine ligand. We were able to
generate the lithium 1,2-bis(diphenylphosphino) tert-butylcyclopentadienide ligand using
a literature method\textsuperscript{53} and we found that the reaction of this ligand with our P\textsuperscript{I} transfer agent,
[P\textsuperscript{I}dppe][Br], generates the desired product, 4.1, in good yields (Scheme 4.1).
Scheme 4.1 The reaction of [Li][tBuC₅H₅(Ph₂P)₂] with [P¹dppe][Br] to generate 4.1.

The removal of the two by-products (dppe and LiBr) was accomplished using a two-step process. The dppe was removed by Soxhlet extraction of the crude mixture in hexanes overnight, and then the remaining solid was dissolved in dichloromethane and filtered through a fritted flask to remove the LiBr. The pure material has distinctive $^{31}$P NMR shifts consistent with those reported for triphosphenium species: a shielded triplet (−174 ppm) and corresponding doublet, (34 ppm) with large $^1J_{PP}$ coupling (418 Hz). Single crystals were grown by the slow evaporation of a dichloromethane solution, and the molecular structure is depicted in Figure 4.2. The air-sensitive molecule crystallizes in the space group $P-1$ with one molecule present in the asymmetric unit. The P–P bond lengths of the triphosphenium fragment of 2.1260(9) and 2.1303(9) Å are within the range of distances reported for cationic cyclic triphosphenium cations (2.11–2.13 Å) – and are short in comparison to those of other zwitterionic triphospheniums that have been reported previously (2.1328(9) to 2.1467(12)Å). The P–P¹–P angle of 89.76(4)° falls in between the ranges of the typical angles observed for zwitterionic triphosphenium fragments, (90.39(4)–95.70(3)°) and triphosphenium cations (86–88°).
Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion

4.2.2 Reactions of Group 6 Metal Carbonyls with 4.1 \( [tBuC_5H_2(Ph_2P)_2P^I] \)

In light of some of the previous coordination chemistry of zwitterionic compounds containing \( P^I \) centers – and in light of the potential for compound 4.1 (indicated as \( L \) in the formulas of the complexes) to also support piano stool complexes – we began our studies with early zero-valent transition metal carbonyl complexes. The addition of excess \( M(CO)_6 \) (\( M = \) Cr, Mo, W) to 4.1 in THF under UV light for 1-3 hours generates the corresponding coordination complexes 4.2-4.3 (Scheme 4.2).
Scheme 4.2 The reaction of 4.1 with Cr(CO)$_6$ and W(CO)$_6$ under UV light.

Upon radiation, the light yellow coloured solutions gradually turn dark orange or dark gold in colour, and the progress of the reaction monitored by $^{31}$P NMR. All the complexes have dramatic deshielding of the triplet shift corresponding to the P$^I$ center upon complexation (-174 ppm to -51 ppm, -76 ppm, and -91 ppm for M=Cr, Mo, and W respectively), in addition to a significant decrease in the coupling constants by 50-70 Hz (Figure 4.3).

![Scheme 4.2](image)

Figure 4.3 $^{31}$P $\{^1$H$\}$ stack plot of complexes 4.1, 4.2, 4.3, 4.5, and 4.7

When the reaction had gone to completion, the reaction solvent was removed under reduced pressure and the excess M(CO)$_6$ can be removed via sublimation. The pure product was isolated by extraction into Et$_2$O, and the resultant solution was left to evaporate yielding large dark gold-coloured crystals. Single crystal X-ray diffraction experiments
reveal that the anticipated complexes $L(\text{Cr(CO)}_5)_2$ and $L(\text{W(CO)}_5)_3$ are isostructural (Figure 4.4). Both molecules crystallize in the space group $P-1$ with one molecule in the asymmetric unit. As anticipated, upon coordination of the $\text{P}^1$ center, there is a slight lengthening of the P–P bond within the triphosphenium fragment, from 2.1260(9)-2.1303(9) Å for 4.2 and 2.1656(13)-2.1696 (13) Å for 4.3. The phosphorus-metal bond lengths are 2.4420(5) Å, and 2.5799(7) Å for Cr and W respectively, and are similar length in comparison to the average bond length of related dicoordinate phosphorus atoms bound to Cr(CO)$_5$ or W(CO)$_5$ reported in the CSD, (2.489(26) Å for Cr and 2.612(30) Å for W).\textsuperscript{54} In each complex, the geometry about the coordinated phosphorus center is trigonal pyramidal, which is consistent with the presence of an additional pair of non-bonding electrons at the $\text{P}^1$ center; the sum of the angles around the $\text{P}^1$ center is 334.40(3)$^\circ$ and 333.38(8)$^\circ$ for the chromium and tungsten complexes, respectively.

Compound 4.2 exhibits an axial CO bond length of 1.146(2) Å which is similar in length to the average length of the equatorial CO ligands: 1.139(2) Å. The same is true of 4.3, which exhibits CO bond lengths of 1.138(6) Å (axial) and 1.132(6) Å (equatorial). The M-CO bonds range from 1.823(19)-1.9046(17) Å (Cr) and 1.989(5)-2.038(5) Å (W), with the axial M-CO bond being shorter than the equatorial bonds in all cases. The FT-IR spectra of both compounds (Figure 4.7) feature multiple carbonyl stretches between 1895 cm$^{-1}$ to 2055 cm$^{-1}$ (4.2) and 1913 cm$^{-1}$ to 2065 cm$^{-1}$ (4.3). The appearance of more peaks than what might be expected for a C$4v$ symmetric complex is due to the non-degeneracy of the usual E modes, which are split significantly due to the asymmetry introduced by the ligand; this also permits the appearance of the normally forbidden B1 mode, which gains some
intensity. To confirm the assignment of the peaks, frequency calculations were performed on a model of 4.5 optimized at the PBE1PBE/TZVP level of theory with an effective core potential basis set applied for the molybdenum atom (Ch.4 SI, Figure 10, 15).

**Figure 4.4** The thermal ellipsoid plot of 4.2 (left) and 4.3 (right), ellipsoids depicted at 50% probability, hydrogen atoms removed for clarity. Selected bond lengths and angles for 4.2: P1-P3: 2.1759(5), P2-P3:2.1711(5), P3-Cr: 2.4420(5) Å. P1-P3-P2: 91.081(19)°. Selected bond lengths and angles for 4.3: P1-P3: 2.1696(13), P2-P3: 2.1656(13), P3-W: 2.5601(10) Å. P1-P3-P2: 91.36(5)°.

The FT-IR spectrum of the material isolated from the reaction of 4.1 with excess Mo(CO)$_6$ under photolytic conditions, shows five similar carbonyl stretches (1896 cm$^{-1}$ to 2067 cm$^{-1}$) to that observed in the spectra of 4.2 and 4.3, however, there were three additional weaker stretches at 1804 cm$^{-1}$, 1814 cm$^{-1}$, and 1831 cm$^{-1}$ present in the spectrum for 4.4 which were not observed in the spectra for 4.2 and 4.3 (Figure 4.7). Additionally, the calculated frequencies for the complex L·Mo(CO)$_5$ do not account for the three additional stretches present in the spectrum (Ch.4 SI Figure 11).
Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion

The single crystals obtained from slow evaporation of the Mo(CO)$_6$ reaction revealed an unexpected result: a bimetallic molecule (4.4), featuring a Mo(CO)$_5$ fragment coordinated at the low valent phosphorus center and an additional Mo(CO)$_3$ fragment ligated through the cyclopentadienyl backbone in a piano-stool fashion (Figure 4.5). Despite using identical reaction conditions to those that produced 4.2 and 4.3, only the bimetallic species is observed based on the NMR and FT-IR spectra obtained, and from unit cell analysis of the resulting single crystals.

![Figure 4.5](image.png)

**Figure 4.5** The thermal ellipsoid plot of 4.4, ellipsoids depicted at 50% probability, hydrogen atoms and diethyl ether molecule removed for clarity. Selected bond lengths and distances: P1-P3: 2.1813(8), P2-P3: 2.1743(9), P3-Mo1: 2.5799(7), Mo2-Centroid 2.045 Å. P1-P3-P2: 91.65(3)°

Complex 4.4 crystallizes in the space group $Pbca$, with one molecule in the asymmetric unit, accompanied by a solvent molecule (Et$_2$O). The P–P bond lengths of the triphosphenium fragment, display a similar same lengthening upon complexation of the
metal center, in addition to an increase in the P–P–P angle to 91.65(3)°. Ligation of the additional metal center at the cyclopentadienyl fragment has similar effects; the C–C bonds within the five–membered ring increase in length from 1.398(3)-1.405(3) Å in 4.1 to 1.441(3)-1.420(3) Å in 4.4. The average M-C₅ bond length within the piano stool is 2.398(2) Å, which is a typical length compared to average length for molybdenum piano stool complexes reported in the CSD, (2.371(35) Å) and the same can be said about the M-CO bonds, which range from 1.940(3) to 1.951(3) Å, with the axial M-CO bond being shorter than the equatorial bonds, as might be expected. The three weaker frequency vibrations observed in the IR spectrum obtained for 4.4 (vide supra) are attributable to the E stretching modes of the Mo(CO)₃ fragment which is bound by the Cp- moiety (Figure 4.7) and are corroborated by calculations (Ch.4 SI, Figure 12).

In an effort to isolate the monometallic molybdenum carbonyl species, i.e. the molecule that contains only Mo(CO)₃ coordinated to the P⁺ center, we first reacted the ligand, 1 with Mo(CO)₆ in an equimolar (1:1) ratio, under photolytic conditions. The reaction proceeds quickly (within 1 hr), and the triplet in the ³¹P NMR corresponding to the P⁺ center in 1 shifts from −174 ppm, to −76 ppm, however some starting material remains, even after several hours in the UV reactor. Upon isolation of this reaction product, we confirmed via IR spectroscopy and single crystal diffraction that it was indeed 4.4, rather than the monometallic complex that we were targeting, so we attempted an alternative route to generate the molybdenum analogue of 4.2 and 4.3. Thus trimethylamine-N-oxide was added to Mo(CO)₆ in THF in the presence of 4.1 (Scheme 4.3). The reaction mixture became gold in colour and small bubbles were observed indicative of the loss of CO₂.
Scheme 4.3 Synthesis of molybdenum carbonyl complexes from 4.1.

$^{31}\text{P}$ NMR spectroscopy confirmed that all the starting material (4.1) was consumed in the reaction, and the new doublet and triplet shifts in the spectrum were indistinguishable from those observed for 4.4. The THF was removed under reduced pressure, and product extracted with Et$_2$O. FT-IR spectroscopic analysis of the resulting yellow solid provide a spectrum in which the three unique IR stretches corresponding to the Mo(CO)$_3$ fragment were absent; only the five stretches attributable to the Mo(CO)$_5$ fragment were present in the carbonyl region of this spectrum (1895-2067 cm$^{-1}$). Single crystals obtained from this reaction confirmed the molecular structure of L(Mo(CO)$_3$), 4.5 (Figure 4.6), which is isostructural to 4.2 and 4.3. The molecule, which crystallizes in the space group $P$-1, shows similar lengthening of the P–P bonds and P–P–P angle within the triphosphonium fragment, observed in the other metal complexes described above.
Figure 4.6 The thermal ellipsoid plot of 4.5, ellipsoids depicted at 50% probability, hydrogen atoms removed for clarity. Selected bond lengths and distances: P1-P3: 2.1635(4), P2-P3: 2.1677(4), P3-Mo1: 2.5734(4) Å. P1-P3-P2: 91.344(7)°

A summary of the IR data is depicted in Figure 4.7, the IR stretching frequencies observed for molecules 4.2-4.5 places the donor ability of this ligand between that of amines and phosphines.55–60
Figure 4.7 FT-IR spectrum of 4.1, 4.2, 4.3, 4.4, and 4.5. The dashed lines indicate the symmetry modes that are assigned to each stretching frequency. The * label indicates the stretches that correspond to the piano-stool moiety in 4.4, which are E stretching modes.

Orbital depictions of optimized LM(CO)$_5$ models show significant contributions from the Cp′ fragment on the three highest energy MOs (Figure 4.8). The relative energies of these orbitals are also very similar which suggests that the difference in observed reactivity between the Mo and two other carbonyl complexes is more likely caused by the increased photoactivity of Mo(CO)$_6$ and the larger kinetic lability of the CO ligands on Mo.

Thus far, our efforts towards the generation of bimetallic W$_2$(CO)$_8$ and Cr$_2$(CO)$_8$ analogues to 4.4 have been unsuccessful. Even under harsher conditions – UV radiation
for 48 h, and large excesses of metal carbonyl (10 equivalents) – there is no evidence for the formation of any bimetallic complexes in these cases.†

Interestingly, the addition of Mo(CO)$_6$ to the complex LCr(CO)$_5$ under UV conditions to make the bimetallic complex containing a molybdenum piano-stool moiety resulted in the production of single crystals of LMo(CO). This agrees well with other experiments not reported in this work, where the complex LCr(CO)$_5$, when placed under photolytic conditions on its own, produces free ligand (L).
Figure 4.8 Frontier orbitals of geometry optimized structure of 4.4.
Table 4.1 Summary of Bond Lengths, angles, and $^{31}$P NMR shifts for 4.1 and its complexes with its Group 6 Metal Carbonyls.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1 (L)</th>
<th>2 [LCr(CO)$_5$]</th>
<th>3 [LW(CO)$_5$]</th>
<th>4[LMo$_2$(CO)$_8$]</th>
<th>5 [LMo(CO)$_5$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-P$^I$ (Å)</td>
<td>2.1303(9)</td>
<td>2.1759(5)</td>
<td>2.1696(13)</td>
<td>2.1813(8)</td>
<td>2.1635(4)</td>
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<td>2.1260(9)</td>
<td>2.1711(5)</td>
<td>2.1656(13)</td>
<td>2.1743(9)</td>
<td>2.1677(4)</td>
</tr>
<tr>
<td>P-P$^I$-P (°)</td>
<td>89.76(4)</td>
<td>91.081(19)</td>
<td>91.37(5)</td>
<td>9.15(3)</td>
<td>91.344(17)</td>
</tr>
<tr>
<td>P$^I$-M</td>
<td>---</td>
<td>2.4420(5)</td>
<td>2.5601(10)</td>
<td>2.5799(7)</td>
<td>2.5734(4)</td>
</tr>
<tr>
<td>$\Sigma P^I$ (°)</td>
<td>---</td>
<td>334.40(3)</td>
<td>333.38(8)</td>
<td>325.05(5)</td>
<td>334.69(2)</td>
</tr>
<tr>
<td>$\delta^{31}$P (ppm)</td>
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<td>-51 (t), 28.8 (d)</td>
<td>-91 (t), 25.9 (d)</td>
<td>-77 (t), 28.2 (d)</td>
<td>-76 (t), 28.8 (d)</td>
</tr>
<tr>
<td>$^{1}J_{P-P}$ (Hz)</td>
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<td>376</td>
<td>356</td>
<td>356</td>
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<td>M-CO$_{eq}$ (Å)</td>
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<td>1.8996(18)</td>
<td>2.038(6)</td>
<td>2.0455(3)</td>
<td>2.4555(17)</td>
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<tr>
<td>M-CO$_{ax}$ (Å)</td>
<td>---</td>
<td>1.8523(19)</td>
<td>1.989(5)</td>
<td>1.9873(3)</td>
<td>1.9849(17)</td>
</tr>
</tbody>
</table>

4.2.3 Reactions of Group 7, 8, and 9 Metal Carbonyls with [tBuC$_5$H$_2$(Ph$_2$P)$_2$P$^I$]

We were curious about how the reactivity of this multidentate ligand might change to accommodate different zero-valent metal carbonyls moving across the first row of the periodic table. The equimolar reaction with manganese, Mn$_2$(CO)$_{10}$, did not proceed after stirring under standard conditions overnight. However, there was a significant colour change from pale yellow to bright red upon stirring under UV radiation for 3 hours. The reaction progressed to completion after stirring under photolytic conditions for 6 hours, and the THF was removed from the solution. The $^{31}$P spectrum of the resulting red solution showed a significant change from that of the proligand: the triplet corresponding to the P$^I$ center shifts from −178 ppm to +183 ppm, along with a significant decrease in $^{1}J_{P-P}$ coupling (418 Hz to 283 Hz). Broadening of the triplet resonances, along with a dramatic change of the triplet corresponding to the P$^I$ center by more than 200 ppm, and a decrease in $^{1}J_{P-P}$ coupling was our first indication that both manganese metal centers were bound by the P$^I$ center. The product was extracted with Et$_2$O and left to evaporate slowly, which lead to the deposition of large red crystals. The bimetallic complex L(Mn$_2$(CO)$_8$), 4.6 crystallizes in the space group $P$-$I$ with one molecule in the asymmetric unit (Figure 4.9).
Figure 4.9 The thermal ellipsoid plot of 4.6, ellipsoids depicted at 50% probability, hydrogen atoms and diethyl ether molecule removed for clarity. Selected bond lengths and angles: P1-P3: 2.2322(6), P2-P3: 2.2410(6), P3-Mn1: 2.2720(5), P3-Mn2: 2.2604(5) Å. P1-P3-P2: 88.88(2)°.

The P\textsuperscript{I} center of 4.1 acts as an µ-ligand across two Mn atoms, utilizing both available pairs of electrons on the low valent phosphorus center. Both the Mn-Mn bond length, (2.803(2) Å) and the P-Mn bond lengths (2.2604(5) and 2.2720(5) Å) are within the range of the average bond lengths (Mn-Mn 2.881(11) Å and P-Mn (2.297(60) Å) of complexes reported featuring Mn\textsubscript{2}(µ-PR\textsubscript{2}) fragments reported in the CSD. As anticipated, there is a substantial lengthening of the P-P bonds within the triphosphenium fragment upon complexation of the metal: from 2.1260(9)-2.1303(9) in 4.1 to 2.2322(2)-2.2410(6) – these distances are considerably longer than any of the other metal complexes reported in this work. The FT-IR spectrum of 4.6 has five frequencies corresponding to carbonyl stretches ranging from 1911 to 2050 cm\textsuperscript{-1}. 
In contrast to the reaction to generate 4.6, the addition of Fe$_2$(CO)$_9$ to 4.1 and the subsequent reaction under photolytic conditions yielded many species observable by $^{31}$P NMR in the form of an intractable mixture. In contrast, the reaction between the less reactive iron(0) source, Fe(CO)$_5$, lead to no reaction under both standard, thermolytic and photolytic conditions. The use of the trimethylamine-$N$-oxide protocol described earlier to generate 4.5 generated three different phosphorus-containing products based on $^{31}$P NMR spectroscopic investigations (as evidenced by three unique sets of triplets and doublets); all of these products have similar solubilities which rendered their separation and isolation difficult. Finally, we found that the reaction of 4.1 and Fe$_2$(CO)$_9$ under ambient conditions did generate only one product based $^{31}$P NMR experiments, but the reaction proceeded slowly. After 3 days stirring in THF, all of 4.1 was consumed and the distinctive triplet from the proligand (−174 ppm) shifts significantly downfield to −16 ppm. It should be noted that there is an additional singlet present in the spectrum at 77 ppm, which we suspect is $^t$BuCp(PPh$_2$)$_2$Fe(CO)$_4$ – i.e. the iron diphosphine complex derived from the formal extrusion of the phosphorus(I) fragment from 4.1. The formation of a similar complex was observed in the reaction of an analogous arsenic species with Co$_2$(CO)$_8$, as reported by Ragogna et al. (The $^{31}$P NMR shift for their complex resided at 43 ppm). Nevertheless, work up of the reaction by centrifugation and extraction with pentane yields the coordination complex L(Fe(CO)$_4$)$_4$ 4.7. Slow evaporation of hexanes yielded yellow single crystals of the material. X-ray diffraction experiments reveal the molecular structure of 4.7, (Figure 4.10) which crystalizes in the space group P2$_1$/c with one molecule in the asymmetric unit.
Figure 4.10 The thermal ellipsoid plot of 4.7, ellipsoids depicted at 50% probability, hydrogen atoms and diethyl ether molecule removed for clarity. Selected bond lengths and angles: P1-P3: 2.1982(6), P2-P3: 2.1871(6), P3-Fe1: 2.2869(5) Å. P1-P3-P2: 90.17(2)°.

As with the group 6 complexes described earlier in this work, the bond lengths and angles of complex 4.7 exhibit similar features: there is a slight shortening of the P-P bond lengths (2.1982(6)- 2.1871(6) Å), there is a small increase in the P-P-P bond angle (90.17(2)°), and the complex features a P-Fe bond length of 2.2869(5) Å that is in good agreement with the reported average for R₂P-Fe complexes in the CSD (2.314(59) Å). A summary of these parameters can be found in Table 4.2. Complex 4.7 has a FT-IR spectrum that is consistent with the mononuclear complex and features frequencies in the carbonyl region between 1930 and 2033 cm⁻¹.

In contrast to the iron carbonyl reactions, the 1:1 stoichiometric reaction between 4.1 and Co₂(CO)₈ proceeds immediately, yielding a dark red solution in dichloromethane. The ³¹P spectrum of this reaction after stirring for 5 mins shows complete consumption of the proligand and a new set of broadened peaks at +178 ppm (triplet), and 19 ppm (doublet).
Similarities in the $^{31}$P NMR spectrum between this reaction and the spectrum corresponding to 4.6 suggested an analogous dinuclear complex $L(CO_2(CO)_6)$ 4.8, (Scheme 4.4); these observations are also consistent with those of Ragogna et al. for their zwitterionic systems. The FT-IR spectrum of 4.8 (Figure 4.12, C) shows five distinct frequencies that correspond to the carbonyl ligands on each of the cobalt centers. The resulting solution was centrifuged to remove a dark brown precipitate and the reaction solvent evaporated, depositing dark red crystals.

Scheme 4.4 Synthesis of the bimetallic manganese (4.6) and cobalt (4.8) complexes from 4.1.

X-ray diffraction experiments performed on these single crystals confirmed the synthesis of the bimetallic cobalt carbonyl complex 4.8, in which both cobalt centers are bound by the single phosphorus(I) center in a manner that is analogous to 4.6 (Figure 4.11).
Figure 4.11 The thermal ellipsoid plot of 4.6, ellipsoids depicted at 50% probability, hydrogen atoms and diethyl ether molecule removed for clarity. Selected bond lengths and angles: P1-P3: 2.214(2), P2-P3: 2.2166(19), P3-Co1: 2.2720(5), P3-Co2: 2.2604(5) Å, P1-P3-P2: 91.14(7)°.

In light of the structural similarities between 4.6 and 4.8 it is unsurprising that the metrical parameters within the ligand are similar. A significant lengthening of the P-P bond lengths within the triphosphenium fragment upon complexation (to 2.214(2)-2.2166(19) Å) is observed. This longer distance is consistent with the decreased magnitude in $^1J_{PP}$ coupling (from 418 to 242 Hz); together, these results suggest significant donation of electrons from the phosphorus(I) center to the metal centers and decreased backbonding interaction within the triphosphenium core. The Co-Co bond length is 2.6675(13) Å which is somewhat longer than the average reported length (2.613(80) Å) of phosphine cobalt complexes. The FT-IR spectrum of 4.8 is similar to that of 4.6 and contains five frequencies corresponding to the C-O stretches from 1932 to 2032 cm$^{-1}$. A full list of the relevant
crystallographic details for all molecules reported in this work can be found in Tables 4.3 and 4.4.

**Table 4.2** Summary of Bond Lengths, angles, and $^{31}$P NMR shifts for 4.1, 4.6-4.8 and its complexes with Group 7, 8, and 9 metal carbonyls

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<tr>
<th>Parameter</th>
<th>4.1 (L)</th>
<th>4.6 [LMn$_2$(CO)$_8$]</th>
<th>4.7 [LFe(CO)$_4$]</th>
<th>4.8 [LCo$_2$(CO)$_8$]</th>
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<tr>
<td>P-P$_{\text{I}}$ (Å)</td>
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<td>2.2322(6)</td>
<td>2.1982(6)</td>
<td>2.214(2)</td>
</tr>
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<td>2.1260(9)</td>
<td>2.2410(6)</td>
<td>2.187(6)</td>
<td>2.2166(19)</td>
</tr>
<tr>
<td>P-P$_{\text{I}}$-$\text{P}$ (°)</td>
<td>89.76(4)</td>
<td>88.88(2)</td>
<td>90.17(2)</td>
<td>91.37(5)</td>
</tr>
<tr>
<td>P$_{\text{I}}$-$\text{M}$</td>
<td>---</td>
<td>2.2604(5),</td>
<td>2.2869(5)</td>
<td>2.1306(19)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2720(5)</td>
<td></td>
<td>2.1413(16)</td>
</tr>
<tr>
<td>$\Sigma$ P$_{\text{I}}$ (°)</td>
<td>---</td>
<td>---</td>
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<td>---</td>
</tr>
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<td>δ-P$_{\text{I}}$ (ppm)</td>
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<td>183.7 (t)</td>
<td>-16 (t),</td>
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</tr>
<tr>
<td></td>
<td>34 (d)</td>
<td>19(d)</td>
<td>22 (d)</td>
<td>6 (d)</td>
</tr>
<tr>
<td>$^{1}$J$_{p,p}$ (Hz)</td>
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<td>242</td>
</tr>
<tr>
<td>M-CO$_{\text{eq}}$ (Å)</td>
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<td>1.795(2)</td>
<td>1.795(7)</td>
</tr>
<tr>
<td>M-CO$_{\text{ax}}$ (Å)</td>
<td>---</td>
<td>1.831(2)</td>
<td>1.784(2)</td>
<td>1.775(6)</td>
</tr>
</tbody>
</table>

**4.3 Conclusion**

In this chapter, we report a neutral triphosphenium analogue for use as a multifunctional donor to zero-valent transition metals. Photolytic reactions with Group 6 metal carbonyls as well as Fe$_2$(CO)$_9$, result in the formation of monometallic complexes in which the low valent phosphorus(I) center within the triphosphenium fragment acts as a donor to the metal carbonyl moiety. For Mo(CO)$_6$, under photolytic conditions, a bimetallic complex is formed selectively, as the ligand is able to bind two molybdenum fragments through both the P$_{\text{I}}$ center and the cyclopentadienyl moiety within the ligand backbone. Similarly, the reaction of the zwitterionic triphosphenium with Co$_2$(CO)$_8$ and Mn$_2$(CO)$_{10}$ generate bimetallic complexes, however in this case both metal centers are bound through the phosphorus(I) center.
4.4 Experimental

4.4.1 General Procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich except for Fe$_2$(CO)$_9$ which was purchased from Strem Chemicals. The group 6 metal carbonyl complexes were sublimed prior to use, and all other materials were used as received, without further purification. Deuterated solvents were dried over activated 3Å sieves. All other solvents were dried over a series of Grubbs’-type columns and degassed prior to use. The reagents, [P$_1$dppe][Br],$^{62}$ and [Li][BuC$_5$H$_2$(Ph$_2$P)$_2$]$^{53}$ were synthesized according to literature procedures. NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz or Bruker Avance Ultrasound 300 MHz spectrometer. Chemical shifts are reported in ppm relative to internal standards for $^1$H and $^{13}$C (for the given deuterated solvent) and external standard for $^{31}$P (85% H$_3$PO$_4$ = 0 ppm). Elemental Analysis performed using a Perkin Elmer 2400 combustion CHN analyser. FT-IR was performed on a Bruker ALPHA FT-IR spectrometer using a platinum ATP sampling module; stretching frequencies are reported in cm$^{-1}$. Photolysis reactions were performed in a Luzchem Photoreactor (Model: LZC-ICH2) using UVA lamps under conditions listed in the experimental section. High-resolution electrospray-ionization mass spectrometry was performed at the McMaster Regional Center for Mass Spectrometry.

4.4.2 Crystallographic Details

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 then collected using the
APEXIII software suite on Bruker D8 Venture diffractometer with a Photon 100 CCD detector using a Mo Kα radiation (λ = 0.71073 Å) source. For each sample, data were collected at low temperature. APEX-III software was used for data collection and reduction 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 program suites. Validation of the structures was conducted using PLATON. The diethyl ether molecule in 6 was modelled using the DSR method implemented in ShelXle. Further details are provided in Table 2.

4.4.3 Computational Details

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 in conjunction with the TZVP basis sets for all atoms. The default Stuttgart-Dresden (SDD) quasi-relativistic effective core potentials were used for transition element atoms. Geometry optimizations were started using models in which the relevant non-hydrogen atoms were placed in 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 and vibrational 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. Visualizations of the Kohn-Sham orbitals and optimized geometries were made using Visual Molecular Dynamics (VMD). Summaries of the calculated results, including Cartesian coordinates are presented in the supplementary material.

4.4.4 Specific Procedures

Synthesis of $^t$BuCp(PPh$_2$)$_2$PI (4.1)

To a stirring, cold suspension of [P$^i$dppe][Br] (1.85g, 3.6 mol, 1 eq) in THF, was added 1.81g, 3.6 mmol, 1 eq) of [Li]$^t$BuCp(PPh$_2$)$_2$] in THF. The resulting cloudy yellow suspension was allowed to warm to room temperature immediately after addition, during which time a golden yellow solution with white precipitate appeared. The THF was removed under reduced pressure and the resulting solid was collected and placed in a soxhlet apparatus on a glass frit. The solid was washed overnight with hexanes (95°C) to remove the dppe. The resulting solid was collected and redissolved into DCM, producing a dark yellow solution with white precipitate. This mixture was filtered through Celite® to remove the LiBr and the solution was collected. The final product was collected as a yellow powder upon removal of DCM. Single crystals were grown from the slow evaporation of the product dissolved in dichloromethane. (Isolated Yield 1.35g, 74%). $^{31}$P{$^1$H} NMR (CDCl$_3$) δ(ppm): -174.7 (t, $^1$J$_{pp}$ = 418.3 Hz), 34.7 (d, $^1$J$_{pp}$ = 418.5 Hz). $^1$H NMR (CDCl$_3$) δ(ppm): 1.3 (s, 9H, $^t$Bu), 6.4 (t, $^3$J$_{Hp}$ = 7.5 Hz, 2H, Cp-H), 7.3-7.7 (m, 20H, Ar); $^{13}$C{$^1$H} NMR (CDCl$_3$) δ(ppm): 32.7 (s, $^1$Bu), 33.1 (s, $\sim$(CH$_3$)$_3$), 106.8, 105.6 (dd, $^1$J$_{pc}$=34.7 Hz, $^2$J$_{pc}$=7.31 Hz, Cp$\sim$(PPh$_2$), 111.6 (m, Cp$\sim$H), 128.5 (d, $^2$J$_{pc}$=13.2 Hz, o-Ph), 131.0 (s, p-Ph), 132.0 (d, $^3$J$_{pc}$=10.7 Hz, m-Ph), 134 (dd, $^1$J$_{pc}$=75 Hz, $^4$J$_{pc}$= 7 Hz, i-Ph). Anal. Calcd (%) for:
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\[ \text{C}_{33}\text{H}_{31}\text{P}_3: \text{C}, 76.15; \text{H}, 6.0; \text{N}, 0; \text{found: C}, 75.68; \text{H} 6.23, \text{N}, 0.04. \text{ HR-ESI-MS: calcd for } [\text{C}_{33}\text{H}_{31}\text{P}_3]^+ \text{ m/z= 521.1639, found: 521.1711} \]

Synthesis of \((\text{tBuCp(PPh}_2\text{P})_2\text{P})\text{Cr(CO)}_5\) (4.2)

\((\text{tBuCp(PPh}_2\text{P})_2\text{P})\text{Cr(CO)}_5\text{I}(0.048g, 0.092 mmol, 1 eq) and \text{Cr(CO)}_6 (0.061 g, 0.277 mmol, 3 eq) were added together to a vial in THF. The reaction solution was placed in a UV reactor under (315–400 nm) and was stirred for 3 hrs (the progress of the reaction can be monitored by \(^{31}\text{P} \text{NMR}). Upon completion of the reaction, the THF was removed under reduced pressure and the resulting solid was collected and any excess \text{Cr(CO)}_6 was removed by sublimation (1-2 hrs, static vacuum, 80°). \text{Et}_2\text{O} was added to the remaining solid to generate suspension which was centrifuged. The \text{Et}_2\text{O} solution was collected and left to slow evaporate to deposit yellow crystalline material. (Yield 0.055g, 84%). \(^{31}\text{P}\{^1\text{H}\} \text{NMR (CDCl}_3\) δ(ppm): -51.0 (t, \(^1J_{pp}= 376 \text{ Hz}, 28.8 \text{ (d, } ^1J_{pp}= 376 \text{ Hz).} \ ^1\text{H NMR (CDCl}_3\) δ(ppm): 1.3 (s, 9H, \text{tBu}), 6.5 (t, \(^3J_{HH}= 4.0 \text{ Hz, 2H, Cp-H}), 7.3-7.7 \text{ (m, 20H, Ar);} \ ^{13}\text{C}\{^1\text{H}\} \text{NMR (CDCl}_3\) δ(ppm): 32.5 (s, \text{tBu}), 117.6 (m, \text{Cp(CH)}, 129 (d, \(^2J_{pp}=15.0 \text{ Hz, o-Ph}), 132.3 \text{ (s, p-Ph), 133.0 \text{ (s, m-Ph), 218 (s, } \text{Cr(CO)}_5\text{s) FT-IR (cm}^{-1}\text{): 2055 (s,CO), 1971 (w, CO), 1940 (s, CO), 1915 (vs, CO), 1895 (vs, CO).} \text{Anal. Calcd (%) for: } \text{C}_{38}\text{H}_{31}\text{P}_3\text{O}_5\text{Cr: C, 64.05; H, 4.38; N, 0; found: C, 63.40; H 4.77, N, 0.19. HR-ESI-MS: calcd for } [\text{C}_{38}\text{H}_{31}\text{P}_3\text{O}_5\text{Cr}]^+ \text{ m/z = 711.0918, found: 711.0915} \]

Synthesis of \((\text{tBuCp(PPh}_2\text{P})_2\text{P})\text{W(CO)}_5\) (4.3)

\((\text{tBuCp(PPh}_2\text{P})_2\text{P})\text{W(CO)}_5\text{I}(0.048g, 0.092 mmol, 1 eq) and \text{W(CO)}_6 (0.097 g, 0.277 mmol, 3 eq) were added together to a vial in THF. The reaction solution was placed in a UV reactor (315–400 nm) and was stirred for 3 hrs (the progress of the reaction can be monitored by
31P NMR). Upon completion of the reaction, the THF was removed under reduced pressure and the resulting solid was collected and any excess W(CO)₆ was removed by sublimation (1-2 hrs, static vacuum, 80°C). Et₂O was added to the remaining solid to generate suspension which was centrifuged. The Et₂O solution was collected and left to slow evaporate to deposit yellow crystalline material. (Yield 0.061g, 78%). 31P{¹H} NMR (CDCl₃) δ(ppm): -91.0 (t, ¹Jpp = 356 Hz), 25.9 (d, ¹Jpp = 356 Hz). ¹H NMR (CDCl₃) δ(ppm): 1.3 (s, 9H, 'Bu), 6.5 (t, ³JHP = 4.0 Hz, 2H, Cp-H), 7.5-7.8 (m, 20H, Ar); ¹³C{¹H} NMR (CDCl₃) δ(ppm): 32.5 (s, 'Bu), 33.1 (s, C(CH₃)₃), 111.6 (m, CpCH), 129 (s, o-Ph), 132.3 (s, p-Ph), 133.0 (s, m-Ph), 196 (s, W(CO)₅). FT-IR (cm⁻¹): 2065 (s, C=O), 2016 (w, C=O), 1980 (s, C=O), 1936 (vs, C=O), 1913 (vs, C=O), 1891(vs, C=O). Anal. Calcd (%) for: C₃₈H₃₁P₃O₅W: C, 54.05; H, 3.7; N, 0; found: C, 53.58; H 3.51, N, -0.02. HR-ESI-MS: calcd for [C₃₈H₃₁P₃O₅W]^+ m/z = 845.0972, found: 845.0993

Synthesis of (¹BuCp(PPh₂)₂P)Mo₂(CO)₈ (4.4)

¹BuCp(PPh₂)₂P (0.048g, 0.092 mmol, 1 eq) and Mo(CO)₆ (0.097 g, 0.277 mmol, 3 eq) were added together to a vial in THF. The reaction solution was placed in a UV reactor (315–400 nm) and was stirred for 3 hrs (the progress of the reaction can be monitored by 31P NMR). Upon completion of the reaction, the THF was removed under reduced pressure and the resulting solid was collected and any excess Mo(CO)₆ was removed by sublimation (1-2 hrs, static vacuum, 80°C). Et₂O was added to the remaining solid to generate suspension which was centrifuged. The Et₂O solution was collected and left to slow evaporate to deposit yellow crystalline material. (Yield 0.050g, 63%). 31P{¹H} NMR (CDCl₃) δ(ppm): -76.8 (t, ¹Jpp = 366 Hz), 28.2 (d, ¹Jpp = 360 Hz). ¹H NMR (CDCl₃) δ(ppm): 1.3 (s, 9H, 'Bu),
6.5 (t, 3\textsubscript{J}\textsubscript{HP} = 4.0 Hz, 2H, Cp-H), 7.5-7.6 (m, 20H, Ar); \textsuperscript{13}\textsuperscript{C}{\textsuperscript{1}\textsuperscript{H}} NMR (CDCl\textsubscript{3}) \delta(ppm): 32.4 (s, tBu), 33.1 (s, C(CH\textsubscript{3})\textsubscript{3}), 103.7 (m, C\textsubscript{p}C(PPh\textsubscript{2})), 113 (s, C\textsubscript{p}CH) 128.9 (s, o-Ph), 130.8 (s, p-Ph), 132.8 (s, m-Ph), 205 (s, Mo(CO)\textsubscript{5}), 211 (br, Mo(CO)\textsubscript{3}). 

FT-IR (cm\textsuperscript{-1}): 2067 (s, CO), 2020 (w, CO), 1981 (w, CO), 1917 (vs, CO), 1896 (vs, CO), 1831 (s, CO), 1814 (s, CO).

Anal. Calcd (%) for: C\textsubscript{41}H\textsubscript{24}P\textsubscript{3}Mo\textsubscript{2}O\textsubscript{8}: C, 52.58; H, 3.34; N, 0; found: C, 52.73; H 3.75, N, 0.23. HR-ESI-MS: calcd for [C\textsubscript{41}H\textsubscript{24}P\textsubscript{3}Mo\textsubscript{2}O\textsubscript{8}]\textsuperscript{+} m/z = 937.9418, found: 937.9419

**Synthesis of (tBuCp(PPh\textsubscript{2})\textsubscript{2}P)Mo(CO)\textsubscript{5} (4.5)**

\textsuperscript{1}BuCp(PPh\textsubscript{2})\textsubscript{2}P\textsuperscript{I} (0.070 g, 0.134 mmol, 1 eq), Mo(CO)\textsubscript{6} (0.036 g, 0.134 mmol, 1 eq) and Me\textsubscript{3}NO (0.015 g, 0.2 mmol, 1.5 eq) were added together to a vial in THF. The reaction was left to stir for 1 hr during which time bubbles could be seen forming with the evolution of CO\textsubscript{2}. The solvent was removed from the resulting gold solution, and Et\textsubscript{2}O was added to extract the product. Slow evaporation of the Et\textsubscript{2}O produced gold coloured single crystals of this material. (Yield 0.082g, 81%). \textsuperscript{31}\textsuperscript{P}{\textsuperscript{1}\textsuperscript{H}} NMR (CDCl\textsubscript{3}) \delta(ppm): -76.3 (t, 1\textsubscript{J}_{pp} = 355 Hz), 28.8 (d, 1\textsubscript{J}_{pp} = 356 Hz). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta(ppm): 1.3 (s, 9H, tBu), 6.5 (t, 3\textsubscript{J}HP = 4.0 Hz, 2H, Cp-H), 7.5-7.7 (m, 20H, Ar); \textsuperscript{13}\textsuperscript{C}{\textsuperscript{1}\textsuperscript{H}} NMR (CDCl\textsubscript{3}) \delta(ppm): 32.5 (s, tBu), 33.0 (s, C(CH\textsubscript{3})\textsubscript{3}), 103.7 (m, C\textsubscript{p}C(PPh\textsubscript{2})), 113 (m, C\textsubscript{p}CH), 128.9 (s, o-Ph), 129.0 (s, p-Ph), 132.8 (s, m-Ph), 205 (s, Mo(CO)\textsubscript{5}). FT-IR (cm\textsuperscript{-1}): 2067 (s, CO), 2019 (w, CO), 1977 (w, CO), 1948 (s, CO), 1922 (vs, CO), 1895 (vs, CO). **Anal. Calcd (%) for:** C\textsubscript{38}H\textsubscript{31}P\textsubscript{3}MoO\textsubscript{5}: C, 60.33; H, 4.13; N, 0; found: C, 60.7; H 4.42, N, 0.44. **HR-ESI-MS:** calcd for [C\textsubscript{38}H\textsubscript{31}P\textsubscript{3}MoO\textsubscript{5}]\textsuperscript{+} m/z = 759.052, found: 759.0556
Synthesis of (t-BuCp(PPh$_2$)$_2$P)Mn$_2$(CO)$_8$ (4.6)

$t$-BuCp(PPh$_2$)$_2$P (0.053 g, 0.1 mmol, 1 eq) and Mn$_2$(CO)$_{10}$ (0.039 g, 0.1 mmol, 1 eq) were added together to a vial in THF to generate a pale-yellow solution. The reaction mixture was left to stir overnight, but no reaction was observed by $^{31}$P NMR. The solution was then placed in a UV reactor (315–400 nm) and stirred for 6 hrs to produce a red solution. The THF was removed under reduced pressure and Et$_2$O was added to the remaining solid to generate suspension which was centrifuged. The Et$_2$O solution was collected and left to slow evaporate, which produced large red single crystals. (Yield 0.058 g, 67%). $^{31}$P{$_1^H$} NMR (CDCl$_3$) δ(ppm): 183.7 (t, $^1$J$_{pp}$= 283 Hz), 19 (d, $^1$J$_{pp}$= 283 Hz).

$^1$H NMR (CDCl$_3$) δ(ppm): 1.28 (s, 9H, t-Bu), 6.5 (t, $^3$J$_{HP}$= 4.2 Hz, 2H, Cp-H), 7.3-7.8 (m, 20H, Ar); $^{13}$C{$_1^H$} NMR (CDCl$_3$) δ(ppm): 29.8 (s, $^1$Bu), 32.4 (s, C(CH$_3$)$_3$), 117 (s, C=CH), 129 (m, o-Ph), 133 (s, p-Ph), 134.2 (s, m-Ph), 219 (br, Mn(CO)$_3$). FT-IR (cm$^{-1}$): 2050 (s, CO), 1988 (s, CO), 1946 (vs, CO), 1930 (vs, CO), 1911 (vs, CO). Anal. Calcd (%) for: C$_{41}$H$_{24}$P$_3$Mn$_2$O$_8$: C, 57.63; H, 3.66; N, 0; found: C, 57.1; H 3.71, N, 0.26. HR-ESI-MS: calcd for [C$_{41}$H$_{24}$P$_3$Mn$_2$O$_8$]$^+$ m/z = 855.0069, found: 855.0066

Synthesis of (t-BuCp(PPh$_2$)$_2$P)Fe(CO)$_4$ (4.7)

$t$-BuCp(PPh$_2$)$_2$P (0.052 g, 0.099 mmol, 1 eq.) and Fe$_2$(CO)$_9$ (0.072 g, 0.199 mmol, 2 eq.) were added together to a vial in THF. The reaction was left to stir for 4 days. The resulting solution was centrifuged and the THF was removed in vacuo along with Fe(CO)$_5$ that may have formed because of the excess Fe$_2$(CO)$_9$ which was used in the reaction. Hexanes was then added to the precipitate to extract the product. A small impurity remains in the extracted solution, and has the same solubility as the product (both are soluble in
both polar and non-polar solvents), thus far we have been unsuccessful in the separation of the bulk material. Single crystalline material of 4.7 was obtained from the slow evaporation of the product in hexanes. $^{31}\text{P}^{1\text{H}}\text{NMR (CD}_2\text{Cl}_2)$ δ (ppm): -16 (t, $^1J_{pp}= 374$ Hz), 22 (d, $^1J_{pp}= 374$ Hz). $^1\text{H NMR (CD}_2\text{Cl}_2$ δ (ppm): 1.30 (s, 9H, t-Bu), 6.4 (t, $^3J_{HP}= 5$ Hz, 2H, Cp-H), 7.4-7.7 (m, 20H, Ar); $^{13}\text{C}^{1\text{H}}\text{NMR (CD}_2\text{Cl}_2$ δ (ppm): 29 (s, t-Bu), 30 (s, C(CH$_3$)$_3$), 114 (s, C$_p$CH), 128 (m, o-Ph), 132 (m, p-Ph), 133 (m, m-Ph), 214 (br, Fe(CO)).

**FT-IR (cm$^{-1}$):** 2033 (s, C-O), 2007 (s, C-O), 1981 (s, C-O), 1959 (vs, C-O), 1930 (vs, C-O).

**Synthesis of (t-BuCp(PPh$_2$)$_2$P)Co$_2$(CO)$_6$ (4.8)**

$^1\text{BuCp(PPh}_2$)$_2$P$^1$ (0.018g, 0.0345 mmol, 1 eq) and Co$_2$(CO)$_8$ (0.014g, 0.0345 mmol, 1.1 eq) were added together to a vial in MeCN, and the solution immediately turns dark red in colour and bubbles are formed, signifying the loss of CO. The proligand was completely consumed after 5 mins, as confirmed by $^{31}\text{P}$ NMR. The solution was then centrifuged to remove black precipitate that had formed and the MeCN was left to slowly evaporate to generate red single crystals. Unfortunately, we have been unable to obtain elemental analysis or mass spectroscopy on this material; we postulate that the complex eventually decomplexes, which has inhibited our ability to obtain sufficient microanalysis. (Yield 0.015g, 56%). $^{31}\text{P}^{1\text{H}}\text{NMR (CD}_3\text{CN$δ$ (ppm): 177.0 (t, $^1J_{pp}= 242$ Hz), 6.0 (d, $^1J_{pp}= 235$ Hz). $^1\text{H NMR (CD}_3\text{CN$δ (ppm): 1.4 (s, 9H, t-Bu), 6.9 (t, $^1J_{HP}=4$ Hz, 2H, Cp-H), 7.4-7.4 (m, 20H, Ar); $^{13}\text{C}^{1\text{H}}\text{NMR (CD}_2\text{Cl}_2$ δ (ppm): 32.0 (s, t-Bu), 32.9 (s, C(CH$_3$)$_3$), 117 (t, $^2J_{PC}=8.75$ Hz, C$_p$CH), 126 (m, C$_p$C(PPh$_2$), (128 (m, o-Ph), 129 (s, p-Ph), 133 (s, m-Ph), 205

123
Table 4.3 Summary of Crystallographic Data for compounds 4.1-4.4

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$R_1 = \Sigma |F_o| - |F_c| / \Sigma F_o$, $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (wF_o^2)]^{1/2}$, $GOF = [\Sigma (w(F_o^2 - F_c^2)^2) / \text{(No. of reflns. - No. of params.)}]^{1/2}$
Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion

4.5 References

Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion

Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion


Chapter 4: Accessing Multimetallic Complexes with a Phosphorus(I) Zwitterion


(75) NBO 3.0; Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphenium Fragment

5.1 Introduction

In the previous chapters, the use of triphosphenium cations as sources of “P+” was demonstrated, however the use of this class of molecules as electron-rich ligands remains underdeveloped in comparison to other stable molecules containing a low valent phosphorus center such as phosphinidenes.\(^1\)\(^{-}\)\(^{10}\) Furthermore, in comparison to analogous frameworks containing related main group elements, such as carbodiphosphoranes (\(R_3P-C-PR_3\), Figure 5.1, II),\(^{11}\)\(^{-}\)\(^{16}\) there are substantially fewer examples of the use of triphosphenium fragments (Figure 5.1, I) acting as robust ligand frameworks in a similar manner. Further, the isovalent and the ubiquitous “PNP” cations have been extremely well studied (Figure 5.1, III).\(^{17}\)\(^{-}\)\(^{21}\)

![Figure 5.1](image)

**Figure 5.1** The depiction of a triphosphenium fragment (I), and related carbodiphosphorane (II), and the isovalent “PNP” cation (III)

While the reports of reactivity between triphosphenium cations and transition metals have been limited, the few reported examples exemplify the interesting reactivity involving this molecule. Driess demonstrated the ability of an acyclic triphosphenium to undergo oxidation at the P(I) center upon the addition of Schwartz’s reagent: \(ZrCp_2HCl\) to generate an unprecedented square-planar phosphonium flanked by zirconocene “corners” which and bridged by hydrides.\(^{22}\)\(^{23}\)
In terms of the triphosphenium’s ligand ability, Dillon et al. reported strong NMR evidence for the formation of platinum complexes with these cations, however these molecules were only stable in solution, and could not be isolated.\(^{24}\) Some reactivity at the triphosphenium fragment was demonstrated by Schmidpeter,\(^{25}\) who showed that in the case of some acyclic triphospheniums, namely the tetrachloroaluminate salts ([R\(_3\)P-P-PR\(_3\)][AlCl\(_4\)]), these molecules could easily undergo protonation reactions with HCl, as well as a variety of alkylation reactions, all of which involve reactivity at the P(I) center.\(^{26}\) Interestingly, in the case of the cyclic triphosphenium, stronger acids (such as triflic acid) are required to generate analogous compounds, and there are significantly fewer examples of alkylation reactions.\(^{27}\)

It’s interesting to note that the phosphine ligands themselves can be substituted in the same type of ligand exchange reactions described previously. This provides a simple way to generate asymmetrically substituted or new triphosphenium cations by simple ligand displacement reactions. This reactivity was particularly well demonstrated by Schmidpeter in the case of the acyclic triphosphenium tetrachloroaluminate salts.\(^{28}\) We also found this this true in the case of cyclic triphosphenium halides, and the chelating bisphosphine ligand can be replaced with both chelating and non-chelating phosphines, the intermediate products can also sometimes be identified by NMR, where one of the chelating phosphines arms is attached and one is free, having been displaced by a PR\(_3\) fragment (Figure 5.2). Such exchange reactions are evident in the reaction of [dppeP\(^I\)][BPh\(_4\)] with Wilkinson’s catalyst, where the dppe molecule from [dppeP\(^I\)][BPh\(_4\)] is exchanged with two triphenylphosphine molecules from Rh(PPh\(_3\))Cl.
generating [(Ph₃P)₂P][BPh₄] and Rh(dppe)PPh₃Cl.‡ This reactivity is consistent with the description of the bonding in the triphosphenium cation being treated as a bisphosphine-stabilized P⁺ ion.

**Figure 5.2** Two canonical forms of a cyclic triphosphenium cation and examples of ligand displacement reactions with other phosphine molecules, which were observed in our laboratory.

### 5.2 Results & Discussion

In chapter 4, we established the coordination chemistry of ¹BuCp(PPh₂)₂P with various metal carbonyl starting materials, which make simple metal ligand complexes bound at the P(I) center of the molecule. The IR stretching frequencies of these complexes suggested that the donor ability of this molecule was between that of amines and phosphines. This observation is consistent with the observed phosphorus-metal bond lengths, which are slightly longer than analogous phosphine complexes. Cognizant of this, we wanted to probe the ligand chemistry of these molecules with more catalytically relevant transition metals: namely those within Groups 8-11.

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‡ Unpublished results
5.2.1 Reactions between $^1$BuCp(PPh$_2$I)$_2$ and Group 10 zero-valent Metals

There has been increased interest in the use of nickel complexes in catalysis, as a cost-effective alternative to its heavier group 10 elements, palladium and platinum. Nevertheless, group 11 catalysts remain the most prolific area of organometallic catalytic transformations, and in many cases set the standards to which new catalysts are held, in terms of catalytic efficiency. Of course, phosphines are used as ligands in many of these catalysts, and whereas carbenes form stronger metal complexes in this, we believe that more weakly binding electron-rich phosphorus (particularly P(I)) could play a useful role at the other end of the spectrum. Consequently, the aim of this project was to synthesize late transition metal complexes stabilized by P(I) and assess their potential for use in catalytic transformations.

The reaction between $^1$BuCp(PPh$_2$I)$_2$ and Ni(COD)$_2$ proceeds immediately, producing a dark golden-brown solution. The $^{31}$P{$^1$H} NMR spectrum obtained from an aliquot of solution produced a completely unexpected and complex spectrum (Figure 5.4). All of the starting material had been consumed and the signals present were second-order multiplets at -90ppm, 9 ppm, and 15 ppm. The solvent was removed from the solution and any cyclooctadiene (COD) that was produced was washed away with hexanes. The residual solid was extracted with diethyl ether, which upon slow evaporation, deposited gold-coloured crystals.

The molecular structure of 5.1 (Figure 5.3) revealed a result as surprising as the initial $^{31}$P NMR: the nickel metal had inserted into a P-P$^I$ bond, leading to the coupling of two P(I) fragments to form a diphosphene fragment across the metal center. (Figure 5.4, 1). This type of reactivity has only been observed once before with the somewhat related phosphanylidene phosphorene of Kilian (and could also be described as a phosphine-stabilized phosphinidene).
which undergoes an analogous insertion and subsequent dimerization to form a diphosphene fragment upon the addition of Pd(PPh₃)₄. They rationalize this result on the basis of the high reactivity of the phosphinidene fragment; however, triphosphonium species are not typically regarded as being examples of a (bis)phosphine stabilized phosphinidene (Figure 5.4, II).

![Molecular structure of 5.1](image)

**Figure 5.3** Molecular structure of 5.1, which crystallizes in the space group P-1, and is depicted with ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity. Selected bond lengths and angles: P12-P13: 2.188(4), P22-P23: 2.173(4), P13-P23: 2.162(4) Å. P-Ni-: 111.44(13) °.

The P=P has a bond length of 2.162(4) Å, which is similar to the length observed in Kilian’s coupled product (2.123(4) Å) and somewhat longer than the average reported lengths for R-P=P-R fragments (2.090(66) Å), although this is lengthening is undoubtedly a consequence of the metal coordination by this bond. The P₁₂-P₁₃ and P₂₂-P₂₃ are 2.188(4) Å and
2.173(4) Å, which are slightly longer than the P–P bond lengths of the triphosphenium fragment of the starting material (2.1260(9) and 2.1303(9) Å). The phosphine-Ni bonds of 2.174(3) and 2.187(3) Å are typical of bond lengths for nickel phosphine complexes reported in the CSD. The geometry around the Ni center is somewhat distorted from perfectly tetrahedral and the P-Ni-P bond angle is 111.44(13)°. Given the metrical parameters, and the lack of counterions in the crystal structure, we postulate that the Ni center maintains its oxidation state of zero and the formation of 5.1 is not based on and redox chemistry. The possible canonical forms are depicted in Figure 5.7. There are some other reports of bis(phosphino)nickel complexes that form diphosphene complexes across a nickel(0) center, and in all of these situations, the experimental data reported for that molecule are in good agreement with our observations.

![Figure 5.4](image)

**Figure 5.4** The synthesis of 5.1 (I), a related reaction molecules from Kilian (II), and an example of one reported synthesis of a nickel-diphosphene fragment.
The lack of symmetry within 5.1 explains the magnetic inequivalence that results in the AA′BB′XX′ spin system observed in the $^{31}$P NMR; The experimental and simulated spectra are depicted in Figure 5.5.

![Figure 5.5](image)

**Figure 5.5** $^{31}$P$\{^1$H$\}$ experimental (blue, bottom) and simulated (red, top) spectrum of 5.1.

To confirm that the unanticipated outcome of this reactivity is not a coincidence, we sought to make a Pd$^0$ variant which would be analogous to the example described by Kilian with the reaction between Pd$_2$(dba)$_3$CHCl$_3$ and ^1BuCp(PPh$_2$)$_2$P$. The addition of the palladium precursor to the ligand results in an immediate colour change from yellow to dark reddish-black. Fortuitously, the $^{31}$P NMR produces a similar spectrum to that which was observed for the nickel analogue (Scheme 5.1), as identified by $^{31}$P NMR.

![Scheme 5.1](image)

**Scheme 5.1** The reaction between $^1$BuCp(PPh$_2$)$_2$P$^1$ and Pd$_2$(dba)$_3$CHCl$_3$ to generate 5.2
After the reaction solvent is removed, the resulting precipitate was washed with hexanes to remove the dibenzylideneacetone (dba). The product was extracted from the remaining solid with diethyl ether and was collected as a dark red solid, 5.2. Unfortunately, we have been unable to obtain single crystals suitable for X-ray diffraction. The distinctive AA’BB’XX’ spin system in the $^{31}$P NMR of the material is nearly identical to that of 5.1, though the chemical shifts have subtle differences: the shifts corresponding to the diphosphene fragment appears at -60 ppm (ca. -90 ppm for 5.1), and the chemical shift for the phosphine fragment directly bound to the palladium atom (Figure 5.6) moves from 15 ppm in 5.1 to 13 ppm, upon changing the metal to which it is bound.

**Figure 5.6** $^{31}$P{$^1$H} NMR spectrum experimental (blue, bottom) and simulated (red, top) spectrum of 5.2.
5.2.2 Reactivity between 'BuCp(PPPh₂)₂P⁺ and Divalent Group 10 Metals

To determine what the difference would be, if any, on the reactivity of the ligand with higher oxidation state metal precursors within group 10. For this we targeted PtCl₂(COD) and PdCl₂(COD) starting materials. The reactions can be monitored by $^{31}$P NMR, and, in both cases, the starting material is consumed immediately. Both reactions undergo colour changes; in the case of platinum the resulting solution is dark orange, while reaction mixture containing palladium becomes red. The THF solutions were centrifuged and collected, and interestingly the resulting NMR spectra differ significantly. In the case of palladium, two singlets at 66.0 and 57.0 ppm represent the predominant peaks, with two smaller, broadened peaks in close proximity to each other. In contrast for platinum, the spectrum has many second-order peaks (Figure 5.8) indicating the likely formation of new P-P bonds.

Figure 5.7 Canonical structures of 5.1 and 5.2 depicting the bonding at the diphosphene fragment analogous to bonding depictions for metal alkene complexes.
Figure 5.8 $^{31}$P NMR spectra of the reaction between $^t$BuCp(PPh$_2$)$_2$P$I$ and PdCl$_2$COD (top) and PtCl$_2$COD (bottom)

Redissolution of the material from the reaction with PdCl$_2$(COD) in dichloromethane followed by slow evaporation yielded single crystals. The X-ray diffraction experiment produced the molecular structure of 5.3, depicted in Figure 5.9, of the resulting complex where the low valent center from $^t$BuCp(PPh$_2$)$_2$P$I$ has been replaced by the PdCl$_2$ fragment. While this accounts for the observed $^{31}$P NMR, this result is somewhat surprising in that the whereabouts of the P(I) ion remain unseen. It should be noted that upon assessment of the crystallization under a microscope that it is apparent that there are two separate materials present in the sample, the gold coloured crystals, and red amorphous material. Multiple attempts at separating or isolating this material as a crystalline solid have been unsuccessful.
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It is initially surprising that this square planar complex of palladium has two chloride substituents present since the \(^{t} \text{BuCp(PPh}_2\text{)}_2\) ligand is anionic itself, which would make the oxidation state of the metal center (+3). Since we were able to obtain an NMR spectrum of this reaction, we were not convinced that any paramagnetic material was being formed. However, after close evaluation of the crystal structure, we realized that the cyclopentadienyl fragment had been protonated, evidenced by longer C-C bond lengths on the protonated side of the Cp ring, (1.489(4) and 1.446(4) Å) than the other side of the ring (1.469(4), and 1.403(4) Å). Thus, we were able to assign a residual q-peak within the structure to this extra proton. Accordingly, the bisphosphine ligand in this complex is neutral, resulting in the palladium metal having a (+2) oxidation state.

Figure 5.9 Molecular structure of 5.3, which crystallizes in the space group \(P\ 2_12_12_1\). Ellipsoids drawn at 50% probability. The dichloromethane solvent molecule and hydrogen atoms removed for clarity except for those on the Cp ring. Selected bond lengths and angles: Pd-Cl: 2.3547(8), 2.3620(7), Pd-P: 2.2319(7), 2.2304(8), P1-Pd-P2: 87.36(3)°
Although this molecule has not yet been reported in the literature, there are many examples of bisphosphine complexes of PdCl₂. There are even a few closely related molecules to 5.3, synthesized by Hierso et al., all of which are based on a ferrocene framework built upon the 1BuCp(PPH₂)₂ ligand, (and the related (Ph₂P)₃Cp ligand).⁴⁸–⁵⁰ The ³¹P NMR chemical shifts reported in the literature were in good agreement with those observed for 5.3, and the P-Pd bond lengths are also very close, 2.2304(8) Å and 2.2319(7) Å in 5.3, in comparison to Hierso’s ferrocene-based molecules (2.305 and 2.349 Å).⁴⁹

For the analogous reaction between 1BuCp(PPH₂)₂Pᴵ and PdCl₂(COD), single crystals were obtained from the slow evaporation of acetonitrile, the molecular structure from this crystallization is isostructural to 5.3. In this situation, the crystal structure does not account for the ³¹P spectrum acquired for this material, and as was the case for the 5.3, other amorphous material was present in the crystallization. We believe that the “misplaced” P(I) center from the starting material produces this unidentified material.
**Figure 5.10** Molecular structure of 5.4, which crystallizes in the space group P 2\(_1\)/c. Ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity except for those on the Cp ring. Selected bond lengths and angles: Pt-Cl: 2.3560(15), 2.3570(15), Pt-P: 2.2138(15), 2.2257(15), P1-Pt-P2: 88.30(5)°

The reactivity of PtCl\(_2\)COD and \(^1\)BuCp(PPh\(_2\))\(_2\)P\(^I\) seem to have similar reactivities, despite their differences in \(^{31}\)P NMR. Again, the same type of protonation at the Cp ring occurs in this situation, leading to bond lengthening on one side of the ring (1.490(8), 1.495(8) Å compared to 1.428(8), 1.418(8) Å) producing a structure of 5.4 that is isostructural to 5.3 (Figure 5.10). There is only one closely related molecule, the ferrocene analogue and (Ph\(_2\)P)\(_3\)Cp ligand, in which the PtCl\(_2\) fragment is bound between the chelating bisphoshine ligand.\(^{51}\) The P-Pt bond lengths, 2.2137(15) and 2.2257(15) Å, are once again very similar to this reported example (2.2340(11), 2.2181(11) Å. In spite of the reported NMR data for Hierso’s analogues, we are unable to ascertain a shift for 5.4 in the \(^{31}\)P NMR spectrum acquired for this material. Further,
the complex 5.4 and the unidentified material have similar solubilities and we have been unsuccessful in the separation of these two materials.

Scheme 5.2 Synthesis of 5.3 (left) and 5.4 (right) from tBuCp(PPh₂)₂P⁺

The reactivity of tBuCp(PPh₂)₂P⁺ towards Pd(II) and Pt(II) (Scheme 5.2) is reminiscent of the reports from Dillon et al, with their reactions between Pt(PR₃)Cl₂ and cyclic triphosphenium cations. While some metal-ligand complexes were observed in solution, the complexes themselves were not isolable, and other molecules were generated as by-products: namely [dppe₂Pt]²⁺ and [dppePtCl(PR₃)], analogues of 5.3 and 5.4, where the P(I) center has been displaced by the transition metal.

5.2.3 Reaction between tBuCp(PPh₂)₂P⁺ and Iron(I)

In chapter 4 it was demonstrated that zero-valent metal carbonyl complexes form simple metal ligand complexes in the form L[M(CO)ₙ] in the case of chromium, molybdenum, tungsten and iron. During these studies, we noticed some peculiar shifts in the ³¹P NMR when (FeCp(CO)₂)₂ was employed as an alternative investigation to the reactions with Fe₂CO₉ that we were conducting. Upon addition and the mixture became dark brown in colour and occasionally bubbling, signalling the loss of CO. Large brown crystals grew throughout the reaction and X-ray diffraction experiments of the crystals that had deposited revealed the molecular structure of 5.5, where a FeCpCo fragment had inserted into the P-P⁺ bond of the
triphosphenium moiety, which likely causes dimerization between two P酚 fragments, generating the bimetallic species in Figure 5.11.

Figure 5.11 Molecular structure of 5.5 drawn at 50% probability. Hydrogen atoms and solvent molecule (MeCN) removed for clarity. In the bottom orientation phenyl substituents have been removed to show the core structure. Selected bond lengths: P12-P13: 2.2090(11), P13-P23: 2.2327(11), P21-P23: 2.1833(11) Å.

We were surprised that the (FeCp(CO)₂)₂ molecule participates in similar reactivity to the nickel(0) and palladium(0) complexes described above. The resulting dimerized P-P bond length is 2.2327(11) Å, which is in the range of typical P-P single bonds, with the average reported length in the CSD being 2.234(80) Å.⁴⁶ The R₃P-P bonds are 2.1833(11) and 2.2090(11) Å which fall in between the lengths of P-P single and double bonds, and these bonds
are also longer than the lengths within the proligand, (2.1260(9) and 2.1303(9) Å), but close to the lengths observed in 5.1. There are no examples in the literature of this type of reactivity involving a triphospheniums or their analogues, and during our studies involving iron carbonyl compounds, observed no indication of any breaking of P-P bonds within the triphosphenium fragment.

![Scheme 5.3](image)

**Scheme 5.3** The reaction between 1BuCp(PPh₂)₂P and (FeCp(CO)₂)₂ to generate 5.5

### 5.2.4 Reaction Between 1BuCp(PPh₂)₂P and AuCl

There are many examples of compounds containing low valent elements that have been shown to coordinate one or two gold(I) chloride molecules.³⁵²,⁵³ Univalent group 11 metal halides are soft acceptors and their linear geometry allow for coordination even in cases when the main group center might be crowded due to sterically demanding ligands. In an attempt to synthesize the gold(I) coordination complex with 1BuCp(PPh₂)₂P, one equivalent of AuCl was added to a stirring solution of the ligand in dichloromethane. The yellow solution darkens upon addition and the reaction was left to stir for 1 hour. The ³¹P NMR of the resulting solution showed that the starting material had been completely consumed and new shifts at 11 ppm, 22 ppm, and 30 ppm were present in the spectrum (Figure 5.12). The second-order multiplets suggest that the P-P bonds in the triphosphenium moiety of the ligand had been broken. The spectrum has no shifts in the low frequency (shielded) region of the spectrum, where shifts...
Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphениum Fragment

corresponding to phosphorus(I) or even the resonances for the P-P dimerization fragments in 5.1, 5.2 and 5.5 typically appear.

Figure 5.12 $^{31}$P{¹H} NMR of the reaction between $^t$BuCp(PPh$_2$)$_2$P$^t$ and AuCl.

The residual material from this reaction was oily, and was subsequently extracted with acetonitrile, leaving a precipitate which had no signal in its $^{31}$P NMR. Small single crystals were grown from the slow evaporation of the resulting acetonitrile solution. X-ray diffraction experiments revealed the molecular structure of 5.6, in which two $^t$BuCp(PPh$_2$)$_2$ ligands are bound to a gold atom in a tetrahedral geometry, and the chloride remains as an anion. (Figure 5.13).
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Figure 5.13 Molecular structure of 5.6 drawn at 50% probability. Hydrogen atoms removed for clarity except for those on the Cp ring. In the bottom orientation phenyl substituents have been removed to show the core structure. Selected bond lengths: P-Au: 2.393(2) and 2.411(2) Å. P1-Au-P2: 87.28(7)°.

The gold atom in this molecule is bound by two neutral bis(phosphino)cyclopentadienyl fragments, indicating protonation of the ligand had occurred as with the group 11 examples. The presence of chloride atom, suggests that the formal oxidation state of the gold center remains as +1. This suggests that the extrusion of the P¹ center, as in the reaction with Pd(II) and Pt(II), does not likely proceed through a redox reaction. The P-Au bond lengths are 2.393(2) and 2.411(2) Å, which are similar to P-Au lengths of the many reported examples of bisphosphine gold complexes in the CSD. Based on the molecular structure, this molecule should correspond to the singlet at 30 ppm present in the spectrum described above (Figure 5.9). Attempts to separate this product from the remaining, unidentified material have been
unsuccessful due to similar solubility characteristics, thus the fate of the P\textsuperscript{i} center from the proligand remains unclear.

5.3 Conclusion

The reaction between \textsuperscript{1}BuCp\((\text{PPh}_2)_2\)\textsuperscript{P}\textsuperscript{i} and zero-valent group 10 transition metals result in the insertion of the metal center into one of the P-P fragments within the triphosphenium fragment, leading to dimerization of two P\textsuperscript{i} fragments. In the case of higher oxidation state metals in the same group, there is some evidence for this same type of reactivity, however only complexes in which the P\textsuperscript{i} center has been displaced by the metal center were isolated. A necessary step in this reaction is the protonation of the cyclopentadienyl fragment producing a neutral bisphosphine ligand. Surprisingly, the reaction between \textsuperscript{1}BuCp\((\text{PPh}_2)_2\)\textsuperscript{P}\textsuperscript{i} and \((\text{FeCpCO}_2)_2\) results in a similar type of P-P insertion that was observed with Ni\textsuperscript{0} and Pd\textsuperscript{0}, resulting in a bimetallic iron complex with two \textsuperscript{1}BuCp\((\text{PPh}_2)_2\)P fragments dimerized through the former P\textsuperscript{i} centers. Finally, the reaction involving AuCl results in an analogous reaction to those observed with Pt(II) and Pd(II), as the P\textsuperscript{i} is displaced by the Au(I) center, and we have yet to determine the source of the protons or the fate of the P(I) center.

5.4 Experimental

5.4.1 General Procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. The reagent, \([\text{dppeP}\textsuperscript{i}][\text{Br}]\),\textsuperscript{54} was synthesized according to literature procedures. NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz or Bruker Avance Ultrashield 300 MHz spectrometer. Chemical shifts are reported in ppm relative to
internal standards for $^1$H and $^{13}$C (for the given deuterated solvent) and external standard for $^{31}$P (85% $\text{H}_3\text{PO}_4= 0$ ppm). High-resolution electrospray-ionization mass spectrometry was performed at the McMaster Regional Centre for Mass Spectrometry.

### 5.4.2 Crystallographic Details

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 then collected using the APEXIII software suite$^{56}$ on a Bruker D8 Venture diffractometer with a Photon 100 CCD detector using a Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) source. For each sample, data were collected at low temperature. APEX-III software was used for data collection and reduction and SADABS$^{57}$ 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$^{58}$ software suite as implemented in the WinGX$^{59}$ program suites. Validation of the structures was conducted using PLATON.$^{60}$ The diethyl ether molecule in 5.6 was modelled using the DSR method$^{55}$ implemented in ShelXle.$^{56}$ Further details are provided in Table 5.1.

### 5.4.3 Specific Procedures

**Synthesis of [tBuCp(PPh$_2$)$_2$P]$_2$Ni (5.1)**

To a stirring, yellow solution of tBuCp(PPh$_2$)$_2$P$_1$ (0.046g, 0.086 mmol) in THF, was added (0.012 g, 0.044 mmol) of Ni(COD)$_2$ in THF. The reaction immediately turns dark brown in colour and is stirred for 2 hrs. The solution was centrifuged and decanted from the black precipitate present. The THF was removed under reduced pressure and the resulting solid was washed and filtered with hexanes to remove the liberated COD and the dark reddish-brown precipitate was collected in a fritted filter. The resulting solid was collected and dissolved in
Et₂O and left to slow evaporate. The product was collected as an orange-brown crystalline material. (Isolated Yield 0.038 g, 79%).³¹P{¹H} NMR (CDCl₃) δ(ppm): -90.5 (AA’BB’MM’ apparent dp, 2P, RP=PR, ¹Jpp= 278 Hz, ²Jpp= 41 Hz, ⁴Jpp= 27 Hz), 9.51 (AA’BB’MM’ apparent dd, 2P, Ph₂P-P, ¹Jpp= 278 Hz, ²Jpp= 41 Hz, ³Jpp=30 Hz), 15.3 (AA’BB’MM’ apparent t, 2P, Ph₂P-Ni, ³Jpp= 30 Hz, ⁴Jpp= 27 Hz, ⁵Jpp=7 Hz).¹H NMR (CDCl₃) δ(ppm): 1.0 (s, 18H, tBu), 5.6 (br, 4H, Cp-H), 5.9 (br, 4H, Cp-H), 6.6-7.7 (m, 40H, Ar).¹³C{¹H} NMR (CDCl₃) δ(ppm): 32.2 (s, tBu), 118.2, 121.0, 125.3 (br, CpH), 127-129 (m, o-Ph), 131.0, 131.4 (s, p-Ph), 132.0-133.7 (m p-Ph). HR-ESI-MS: calcd for [C₆₆H₆₄NiP₆]⁺ m/z= 1099.2703, found: 1099.2723

Synthesis of [¹BuCp(PPh₂)₂P]₂Pd (5.2)

To a stirring, yellow solution of [¹BuCp(PPh₂)₂P]I (0.072g, 0.138 mmol) in THF, was added (0.036 g, 0.034 mmol) of Pd₂(dbta)₃CHCl₃ in THF. The reaction immediately turns dark red in colour and is stirred for 1 hr. The THF was removed under reduced pressure and the resulting solid was washed and filtered with hexanes to remove the liberated dba *and* the dark reddish-brown precipitate was collected in a fritted filter. Isolated Yield (0.049 g, 63%).³¹P{¹H} NMR (CDCl₃) δ(ppm): -60.0 (AA’BB’MM’ apparent dp, 2P, RP=PR, ¹Jpp= 305 Hz, ²Jpp= 55 Hz, ⁴Jpp=3.5 Hz), 11.2 (AA’BB’MM’ br, 2P, Ph₂P-Pd, ³Jpp= 35 Hz, ⁴Jpp= 3.5 Hz, ⁵Jpp=7 Hz), 13.1 (AA’BB’MM’ apparent dd, 2P, Ph₂P-P, ¹Jpp= 305 Hz, ²Jpp= 55 Hz, ³Jpp=35 Hz).¹H NMR (CDCl₃) δ(ppm): 0.99 (s, 18H, tBu), 5.44 (br, 4H, Cp-H), 6.15 (br, 4H, Cp-H), 6.4 (Fe-Cp) 6.4-7.7 (m, 40H, Ar).¹³C{¹H} NMR (CDCl₃) δ(ppm): 31.9 (s, tBu), 118.2, 121.0, 125.3 (br, CpH), 127-128.9 (m, o-Ph), 131.0, 131.8 (s, p-Ph), 132.0-133.5 (m, m-Ph).
Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphenium Fragment

**Reaction of $^{1}$BuCp(PPh$_2$)$_2$P and Pd(COD)Cl$_2$ to generate 5.3**

A yellow solution of $^{1}$BuCp(PPh$_2$)$_2$P (0.072g, 0.138 mmol) in THF, was added to PtCODCl$_2$ (0.036 g, 0.034 mmol) in THF. The mixture turns red immediately and is stirred for 1 Hr. The solution was then centrifuged to remove a precipitate, and the red solution was collected. $^{31}$P NMR (ppm): 66.0 (s, unidentified product), 57.6 (s, 5.3), 52.6 (d, $^{1}$J$_{pp}$ = 194 Hz, unidentified product), -20.9 (d, $^{1}$J$_{pp}$ = 194 Hz, unidentified product).

**Reaction of $^{1}$BuCp(PPh$_2$)$_2$P and Pt(COD)Cl$_2$ to generate 5.4**

A yellow solution of $^{1}$BuCp(PPh$_2$)$_2$P (0.072g, 0.138 mmol) in THF, was added to PtCODCl$_2$ (0.036 g, 0.034 mmol) in THF. The mixture turns red immediately and is stirred for 1 Hr. The solution was then centrifuged to remove a precipitate, and the red solution was collected. $^{31}$P NMR (ppm): 5.6 (m, unidentified product), 18.5 (d, unidentified product), 21.98 (s, 5.4), 24.2 (d, unidentified product).

**Synthesis of $[^{1}$BuCp(PPh$_2$)$_2$P]$_2$Fe(Cp)$_2$CO$_2$ (5.5)**

To a stirring, yellow solution of $^{1}$BuCp(PPh$_2$)$_2$P (0.075g, 0.143 mmol) in THF, was added (0.025 g, 0.072 mmol) of (FeCp(CO)$_2$)$_2$ in THF. The reaction immediately turns dark brown in colour, and bubbles form. The reaction was left to stir at room temperature for 4 days, under a flow of nitrogen to allow for release of CO. The THF was left to evaporate when the reaction was complete, and large brown crystals formed and collected. Isolated Yield (0.068 g, 71%). $^{31}$P$^{1}$H NMR (CD$_2$Cl$_2$) δ(ppm): -111.2 (dd, 2P, FeP=PR, $^{1}$J$_{pp}$ = 315 Hz, $^{2}$J$_{pp}$ = 300 Hz), 10.3 (dd, 2P, Ph$_2$P-P, $^{1}$J$_{pp}$ = 315 Hz, $^{2}$J$_{pp}$ = 300 Hz), 52 (br, Ph$_2$P-Fe). $^{1}$H NMR (CD$_2$Cl$_2$) δ(ppm): 1.12 (s, 18H, $^{1}$Bu), 5.9, 6.1 (br, 4H, Ph$_2$P=Cp-H), 6.7 (m, FeCp-H) 7.1-7.9 (m, 40H, Ar). $^{13}$C$^{1}$H NMR (CD$_2$Cl$_2$) δ(ppm): 32.2 (s, $^{1}$Bu), 86.9, 85.8 (s, FeCp(CH)), 115.4, 118.8 (br, Cp(CH)), 126.3-128.8 (m, o-Ph), 130.2, 131.8 (s, p-Ph), 132.7-132.9 (m m-Ph), 211.49 (CO)
Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphenium Fragment

Reaction of $^1$BuCp(PPh$_2$)$_2$P$^i$ and AuCl to generate 5.6

AuCl (0.013g, 0.057mmol suspended in DCM was added to a stirring solution of $^1$BuCp(PPh$_2$)$_2$P$^i$ (0.030g, 0.013 mmol). The mixture turns dark gold in colour and is left to stir for 1 Hr. The solvent was evaporated leaving a gold-coloured oil. Acetonitrile was added which resulted in a colourless precipitate and an orange solution. The solution was extracted and left for slow evaporation, which produced light yellow crystals and dark reddish-orange amorphous material. $^{31}$P NMR (ppm): 11.5 (2$^{nd}$ order multiplet, unidentified product), 22 (dt, unidentified product), 30.5 (s, 5.4)
**Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphonium Fragment**

**Table 5.1 Crystallographic details for molecules 5.1-5.6**

<table>
<thead>
<tr>
<th>Compound</th>
<th>5.1</th>
<th>5.3</th>
<th>5.4</th>
<th>5.5</th>
<th>5.6</th>
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<td>Empirical formula</td>
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<td>(\text{C}<em>{49}\text{H}</em>{73}\text{P}<em>{3}\text{ON}</em>{3}\text{Fe} )</td>
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<td>170(2)</td>
<td>170(2)</td>
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<td>Monoclinic</td>
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<td>(P 2\ 2\ 2\ 1)</td>
<td>(P 2\ 1/c)</td>
<td>(P - I)</td>
<td>(C 2/c)</td>
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<td>11.2656(6)</td>
<td>11.4424(3)</td>
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<td>(-14 \leq h \leq 14,)</td>
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<tr>
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<td>11883/0/826</td>
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<td>(R_1 = 0.0491)</td>
<td>(R_1 = 0.0488)</td>
<td>(R_1 = 0.0612)</td>
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<tr>
<td>([I \geq 2\sigma(I)])</td>
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<td>(wR_2 = 0.0674)</td>
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<td>0.998</td>
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\(R_1 = \Sigma|F_o| - |F_c|/\Sigma F_o\), \(wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_c^2)^2\), \(GOF = [\Sigma(w(F_o^2 - F_c^2)^2)]/\text{(No. of refinls. - No. of params.)}^{1/2}\)
Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphenium Fragment

5.5 References

Chapter 5: Insertion of Transition Metals into the P-P Bond of a Triphosphenium Fragment


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280, 560–564.


Chapter 6: Synthesis of Trithiobisphosphines by Oxidative Transfer of Phosphorus (I)

6.1 Introduction

Molecules containing elements in low valent and low oxidation states\(^{1,2}\) exhibit diverse, interesting, and sometimes unique patterns of reactivity\(^{3-8}\) and some of these compounds have proven useful in areas including: materials precursor chemistry, as ligands in coordination chemistry, organic synthesis, and catalysis.\(^{5,9-18}\) Our research group amongst others has been investigating the isolation of stable compounds featuring low valent and low oxidation state group 13, 14 and 15 environments over the past decade.\(^{19-21}\)

Typically, molecules containing low valent atoms are synthesized using protocols that include the use of harsh reagents such as strong reducing agents and bases. However, in several reports, we have described the facile generation of new molecules containing low-valent phosphorus(I) fragments \textit{via} the versatile “\(\text{P}^+\)” transfer agent \([\text{P}^\text{dppe}]\text{[Br]}\) (\textbf{Scheme 6.1}) through substitution of the diphenylphosphinoethane (dppe) molecule by a different set of ligands.\(^{22-24}\) This approach has proven to be “\(\text{P}\)” atom efficient in many cases – the transfer of \(\text{P}^\text{l}\) atoms from the starting material is often quantitative – and no unnecessary or unexpected by-products are generated.\(^{25}\)

\textbf{Scheme 6.1} Synthesis of molecules containing a low valent phosphorus center recently reported by our group using the \(\text{P}^+\) transfer agent, \([\text{P}^\text{dppe}]\text{[Br]}\).
Chapter 6: Synthesis of Trithiobisphosphines by Oxidative Transfer of Phosphorus(I)

One of the most obvious potential reactivity patterns of low valent elements exploits their ability to undergo oxidation. In this context, we had previously demonstrated the oxidation chemistry of some of these P\textsuperscript{I} molecules by employing oxidants such as sulfur, methylating agents and acids (Scheme 6.2). These reactions selectively oxidize phosphorus(I) ions to yield phosphorus(III)- or phosphorus(V)-containing species\textsuperscript{26,27}

![Scheme 6.2](image)

**Scheme 6.2** Selected examples of oxidation reactions of a phosphorus(I) compound reported by our group.

Cognizant of the reactivity of P\textsuperscript{I} fragments towards oxidation and the ligand exchange chemistry of the [P\textsuperscript{I}dppe][Br] molecule, we reasoned that this compound should be capable of undergoing other oxidative addition reactions with or without loss of the chelating phosphine. Indeed we have previously noted that the concepts of cycloaddition and electron transfer can be used to rationalize the formation of N-heterocyclic phosphines and phosphonium species\textsuperscript{28,29} in a formal sense, although the actual mechanism through which these compounds are actually formed does not likely involve any low-valent phosphorus intermediates.\textsuperscript{30}
Recent work by Rawson and co-workers has included the investigation of the oxidative addition chemistry of 1,2,5,6-tetrathiocins to zero-valent group 10 metal complexes to afford a range of monometallic metal dithiolate complexes\(^{21}\) (Scheme 6.3) as well as dimetallic and hexametallic clusters.\(^{22}\) The tetrathiocin precursors are readily formed in multi-gram quantities\(^ {31}\) and the oxidative addition chemistry often occurs quantitatively by NMR with recovered crystalline yields up to 89%.

![Scheme 6.3 Oxidative addition chemistry of tetrathiocins to zero valent group 10 metal complexes](image)

In a collaborative effort, our groups have commenced an examination of such tetrathiocins as reagents with which to explore the oxidative addition chemistry to a range of low oxidation state complexes of main group elements. In this chapter, we describe our first foray into this area where we examine the oxidative addition of tetrathiocins to the phosphorus(I) transfer agent, \([\text{P}^{\text{I}}\text{dppe}]\text{[Br]}\), to generate the benzo-dithiophosphinyl framework (Scheme 6.4, compound 6.1) containing formal phosphorus(II) centers in addition to compounds 6.2 and 6.3 which feature formal phosphorus(III) environments. It should be noted that work on such benzo-fused C\(_2\)S\(_2\)P heterocycles was initially reported by Baudler\(^ {32}\) and subsequent studies by Burford focused on the structure and Lewis acidity of divalent benzodithiaphosphenium cations derived.\(^ {33-36}\)
Chapter 6: Synthesis of Trithiobisphosphines by Oxidative Transfer of Phosphorus(I)

Related classes of thiophosphines have been shown to have many industrial applications such as antioxidants for lubricants and oils,\(^{37}\) and are traditionally synthesized from highly reactive and poisonous white phosphorus.\(^{38}\) We reasoned that the use of our easily handled, air- and moisture stable phosphorus(I) sources coupled with the readily prepared tetrathiocins might provide a more convenient and safer route to such compounds.

Scheme 6.4 Oxidative addition chemistry of tetrathiocins to \([\text{P}^{\text{I}}\text{dppe}][\text{Br}]\) to generate 6.1, 6.2, and 6.3.

6.2 Results & Discussion

The 1,2,5,6-tetrathiocin ring is a convenient source of 1,2-disulfides and can be prepared in multi-gram quantities from the treatment of electron-rich aromatics with \(\text{S}_2\text{Cl}_2\) in acetic acid. These molecules have proven successful in regard to oxidative addition reactions with various late transition metals.\(^{39-42}\) In this context, we suspected that these soft donors would be excellent candidates for oxidative addition reactions to the phosphorus(I) fragment in \([\text{P}^{\text{I}}\text{dppe}][\text{Br}]\).
The addition of bis(dimethoxybenzo)tetrathiocin (Scheme 6.4, I) with [P(dppe)[Br] was investigated initially using a stoichiometric ratio of 1:2, anticipating the formation of the P-bromo-benzo-1,3,2-dithiaphosphole. In spite of the low solubility of the tetrathiocins in most common laboratory solvents, the reactions proceeded smoothly within 1 – 2 hours in dichloromethane to produce a pale yellow solution. The progress of the reaction was followed using $^{31}$P NMR spectroscopy. In each case, the signals corresponding to the starting material, [P(dppe)[Br], (δ 64 ppm (doublet), and -220 ppm (triplet)) decreased as the reaction proceeded and singlets corresponding to dppe (-12 ppm) and trace amounts of dppeS (+32 ppm) appeared alongside two other products at ca. 50 ppm and 120 ppm. The singlet at ca. 50 ppm is comparable to those of other tetrathiodiphosphines reported by both Woollins$^{43}$ and Rawson$^{44}$ which feature $^{31}$P NMR resonances in the 40 – 70 ppm region and were tentatively assigned to the coupled product 6.1. The major product 6.2 at 120 ppm was more difficult to attribute. Post facto analysis, however, showed that the 120 ppm peak observed for 6.2 was in good agreement with that predicted based on $^{31}$P NMR chemicals shift correlations for C$_2$S$_2$P-X systems (ca. 161 ppm). Confirmation of the structure of 6.1 and unambiguous identification of 6.2 were made on the basis of single crystal X-ray diffraction studies of crystals grown from the slow evaporation of the dichloromethane reaction mixture.

Compound 6.1 crystalizes in the monoclinic space group $P2_1/c$ with half a molecule in the asymmetric unit (Figure 6.1). The P-P distance, 2.2350(16) Å is indicative of a single bond, and is well within the typical range (2.22 – 2.27 Å) observed for P-P bonds in other diphosphines.$^{45}$ It is indistinguishable from the only other reported dithiapophosphinyl dimer (2.2306(13) Å) and the only other example of a diphosphate bearing organosulfur
substituents.\(^4^3\) The P-S bond lengths [2.1017(11) Å and 2.1110(11) Å] fall in the range of reported bond lengths for P-S single bonds within the Cambridge Structural Database (CSD)\(^4^6\) (1.90 – 2.66 Å). The S-P-S angle of 95.90(4)° is also unexceptional. The C-C bond lengths within the carbocycles of the molecule range from 1.378(4)-1.411(4) Å and are consistent with the presence of an aromatic system, rather than a more diene-like system (which would suggest non-innocent behavior of the ligand). The heterocyclic ring in 6.1 is non-planar with a slight envelope effect observed such that the \(C_6S_2\) and \(S_2P\) mean planes form a fold angle of 31.1°, similar to that observed in the parent derivative, \((C_6H_4S_2P)_2\) (33.03°).\(^4^4\)

**Figure 6.1** Thermal ellipsoid plot of 6.1, hydrogen atoms omitted for clarity and ellipsoids drawn at 50% probability. The top down (top) and side on (bottom) views are depicted. Selected bond lengths (Å) and angles (°): P-P\(^1\): 2.2350(16), P-S\(^1\): 2.1017(11), P-S\(^2\): 2.1110(11), S1-P-S2: 95.90(4).

Based on the structure of 6.2 (*vide infra*), we repeated the reaction with the appropriate stoichiometry (tetrathiocin:[P\(^{I}\)dppe][Br] = 1.5:2) to prevent excess [P\(^{I}\)dppe][Br]
remaining in the reaction, and monitored the reaction by $^{31}$P NMR spectroscopy. In this case, the reaction proceeds to completion relatively quickly (within 1 – 2 hours depending on the amounts of the reagents used) and affords 6.2 as the major product. The $^{31}$P NMR spectrum of the reaction mixture contains a singlet at 120 ppm corresponding to 6.2, as well as a mixture of by-products, mainly [dppeBr][Br],47 dppeS$_2$(C$_6$H$_2$(OMe)$_2$), and dppe. The product was isolated by adding an equal volume of diethyl ether to the CH$_2$Cl$_2$ reaction mixture and cooling the mixture to -20°C overnight to precipitate by-products. The remaining CH$_2$Cl$_2$/Et$_2$O solution was decanted and left to crystalize by slow evaporation. This method was the only convenient protocol for the purification and isolation of 2 in analytically pure form and all characterization and further chemistry involving compound 2 was conducted with crystalline material obtained in that manner. We were able to confirm the formation of dppeS$_2$(C$_6$H$_2$(OMe)$_2$)- i.e the product of the addition of half an equivalent of tetrathiocin to one molecule of dppe- by adding the bis(dimethoxybenzo)tetrathiocin ligand to dppe as an NMR scale reaction. This reaction proceeds overnight to form dppeS$_2$(C$_6$H$_2$(OMe)$_2$) as the sole product observed apart from some remaining dppe.

Compound 6.2 crystallizes in the space group $P2_1/c$ with one molecule and two dichloromethane solvent molecules in the asymmetric unit. The structure of 2 comprises two C$_2$S$_2$P heterocycles linked via a 1,2-dithiolate bridge (Figure 6.2). The compound adopts a step-like structure featuring π-π stacking of the electron-rich dimethoxybenzo groups such that the centroid···centroid distances are 3.4490(18) Å. The P-S bond distances within the heterocycle range from 2.1095(10)-2.1152(10) Å and are essentially identical, within experimental error, to the lengths described above for 1. In contrast, the P-S bond lengths within the “bridging” thiocin moiety are significantly longer – ranging
from 2.1425(10) Å to 2.1527(10) Å – which might be a consequence of hyperconjugation within the terminal phosphine fragments of the kind that has been described for analogous phosphorus heterocycles.\textsuperscript{48} The S-P-S angles are similar to those in diphosphine, \textit{6.1} and range from 94.58(4)-94.43(4)°.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{6.2}
\caption{Thermal ellipsoid plot of \textit{6.2}, hydrogen atoms and solvent molecules omitted for clarity and ellipsoids drawn at 50\% probability. Selected bond lengths (Å) and angles (°): P1-S1: 2.1151(10), P1-S2: 2.1095(10), P-S3: 2.1527(10), P2-S4: 2.1425(10), P2-S5: 2.1152(10), P2-S6: 2.1112(10), S1-P1-S2: 94.58(4), S5-P2-S6: 94.43(4).}
\end{figure}

There is a single crystallographically characterized example analogous to \textit{6.2}, reported by Finder \textit{et al.} which features an ethylene dithiione linker between C\textsubscript{2}S\textsubscript{2}P heterocycles. The P-S bond lengths in that complex, which range from 2.102 to 2.126 Å, are consistent with those in \textit{6.2} and the S-P-S angle of 95.5° is also similar.\textsuperscript{49} Notably, a handful other examples of related structures in which P is replaced by heavier group 15 elements (As, Sb, Bi) have been described\textsuperscript{50,51,52} but this structural motif is surprisingly
rare. In fact, all the previous examples feature aliphatic dithiolate linkers and none of them exhibit step-like geometries in the solid state.

The reaction of \([\text{P}^1\text{dppe}][\text{Br}]\) with the dibenzo-15-crown-5-functionalized tetrathiocin (Scheme 6.4, II) under identical conditions (1.5:2 mole ratio) yielded the analogous molecule, 6.3. The \(^{31}\text{P}\) NMR spectrum of the reaction mixture features a dominant signal at a similar frequency (+119 ppm) to 6.2, and also features additional signals indicative of the anticipated by-products of the reaction. Product 6.3 can be isolated as crystalline material by washing the material with diethyl ether, using the same methodology employed for 6.2 (vide supra). Compound 6.3 crystallizes in the triclinic space group \(P\)-1 with one molecule in the asymmetric unit (Figure 6.3). The P-S bond distances within the structure are similar to the analogous distances in compound 2, and range from 2.111(2) – 2.133(2) Å, but in contrast to the methoxy-substituted variant, the P-S lengths \(exo\) to the heterocycle are not significantly longer than the heterocyclic P-S bonds.
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Figure 6.3 Thermal ellipsoid plot of 6.3, hydrogen atoms omitted for clarity and ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): P1-S1: 2.1117(2), P1-S2: 2.111(2), P-S3: 2.118(2), P2-S4: 2.133(2), P2-S5: 2.112(2), P2-S6: 2.116(2), S1-P1-S2: 94.24(8), S5-P2-S6: 94.44(9).

Our $^{31}$P NMR studies reveal that the diphosphine, 6.1, appears as an intermediate en route to 6.2 or 6.3. All of our attempts to isolate tetrathiodiphosphines such as 6.1 as the sole product, either by using the slow addition of tetrathiocin to $[P^I\text{dppe}]^{[Br]}$, by washing the reaction mixture containing excess $[P^I\text{dppe}]^{[Br]}$, or with decreased reaction temperatures have proven unsuccessful to date. Regardless of the stoichiometry or conditions employed in the reaction, we observe the selective formation of compound 6.2 or 6.3, while the appropriate intermediate diphosphine 6.1 can be identified while following the reaction progress by $^{31}$P NMR spectroscopy. In our hands, this diphosphine is only able to be isolated as single crystals grown from reactions containing excess $[P^I\text{dppe}]^{[Br]}$. This observation suggests that the tetrathiocin initially undergoes oxidative addition to the P$^I$ center followed by a dimerization with the formal elimination of Br$_2$ to generate the diphosphine 6.1. Although C$_6$H$_6$S$_2$PBr has been identified as a stable product from
oxidation of (C₆H₄S₂P)₂, the presence of electron donating alkoxy groups may promote such disproportionation reactions. The diphosphine can then react with additional tetrathiocin to form 6.2 (Scheme 6.5). Our inability to isolate intermediate 6.1 as the major product suggests that the kinetics of the subsequent addition process are at least comparable with the initial rate of formation of 6.1. In an effort to substantiate this mechanistic hypothesis, we treated half an equivalent of the bis(dimethoxybenzo)tetrathiocin with a sample of (MeC₆H₃S₂P)₂ (prepared using an alternative procedure) in dichloromethane. Previous studies indicate this diphosphine undergoes facile oxidation with even milder oxidants such as I₂.⁴⁴ The reaction mixture was left to stir for several hours until completion as identified by the disappearance of the solid reagent in the reaction flask. Analysis of the reaction mixture using ³¹P NMR revealed the absence of starting material (δ 40 ppm) and observation of a new singlet at ca. 115 ppm, consistent with formation of the bridged species 6.4 (Scheme 6.5).
Scheme 6.5 Reaction of [P(dppe)Br] and a substituted tetrathiocin to generate diphosphine 6.1. Subsequent addition of tetrathiocin generates the bis-trithiophosphines 6.2 – 6.4.

To further investigate the observed oxidative additions of disulfide ligands with [P(dppe)Br], we treated the “P” reagent with diphenyl disulfide in both 1:1 and 2:1 stoichiometric ratios of disulfide:[P(dppe)Br] in an effort to generate acyclic analogs of compounds 6.1-6.3. We posited that the 1:1 mixture would generate an analogous diphosphine (i.e. (PhS)2P-P(SPh)2) either selectively, or as an intermediate, however there was no evidence for the formation of this diphosphine during the reaction by 31P NMR. Instead, we observed exclusively the generation of the known tris(phenylthio)phosphine (132 ppm) and the by-product [dppe(SPh)][Br] (55 ppm). The observation of the former suggests that, assuming a similar mechanistic pathway, that the oxidative addition of the disulfide to the diphosphine (PhS)2P-P(SPh)2 is considerably more rapid than in the case of the tetrathiocin chemistry. One explanation might be the poor solubility of tetrathiocin which could potentially slow the final step to form the bridged compound.
Based on the required 2:1 (disulfide: [P^I(dppe)][Br]) stoichiometry to form (PhS)_3P, it was unsurprising that the 1:1 stoichiometric reaction left additional unreacted starting material -[P^I(dppe)][Br]- evidenced by the signals at 65 ppm (d) and -225 ppm (t). However, the reaction of a 2:1 ratio of disulfide to [P^I(dppe)][Br] results in the selective formation of tris(phenylthio)phosphine, and the by-product, [dppe(SPh)][Br]. During the progress of the reaction, the intermediate phosphonium salt [dppe(SPh)][Br] is visible in the ^{31}P NMR spectrum (doublets at -55 ppm and -11 ppm, ^3J_{p-p} = 95 Hz) (Figure 6.4). However, upon completion, only [dppe(SPh)_{2}][Br]_2 and dppe are observed. There are also small peaks at ca. 40 ppm and 85 ppm that appear upon consumption of [P^I(dppe)][Br], which do not correspond to the expected dimer, or the bromodithiophosphine, Ph_2S_2PBr, (150-180 ppm); to date, we have been unable to identify these minor products. Typically tris(phenylthio) phosphine is synthesized from the reaction of PhSPCl_2 and thiophenol, however we present this as an alternative synthetic approach to obtain thiophosphines, particularly where the corresponding disulfides are readily available. This phosphine can easily be isolated by extraction with non-polar solvents such as hexanes or pentane from the reaction mixture also containing dppe and [dppeSPh][Br].
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Figure 6.4 $^{31}$P NMR of the reaction of 1:1 (bottom) and 2:1 (top) diphenyl disulfide:[P'dppe][Br]. The product, tris(phenylthio)phosphine appears at 132 ppm, the by-product [dppeSPh][Br] at 53 ppm and dppe at -11 ppm. In the bottom spectrum, some of the starting material, [P'dppe][Br], remains (65 ppm (d) and -229 ppm (t)).

With our more convenient preparation of these types of phosphines, experiments are on-going to assess the donor ability of these molecules for the coordination of metals, as these (trithio)phosphine molecules can potentially be used as multidentate donors, featuring both hard and soft donor sites. In this context it is worth noting the bimetallic gold(I) complex in which the related ligand{(CH$_2$)$_2$S$_2$P}SCH$_2$CH$_2$S{PS$_2$(CH$_2$)$_2$} coordinates to two AuC$_6$F$_5$ groups through the two phosphine centers.$^{54}$

6.3 Conclusion

We have synthesized and characterized a new series of bis-trithiophosphines through the oxidative addition of tetrathiocins with the P$^+$ transfer agent, [P'dppe][Br]. The isolation of the intermediate- diphosphine (6.1)- during this reaction, coupled with the stoichiometric reaction of an isolated diphosphine with tetrathiocin to form the bis-trithiophosphine provides insight into the mechanistic pathway for formation of these bis-
trithiophosphines which therefore appears to progress through a formal sequence of oxidation steps from $\text{P}^\text{I}$ to $\text{P}^\text{II}$ to $\text{P}^\text{III}$. The use of $^{31}\text{P}$ NMR to track the progress of the reaction coupled with single crystal X-ray diffraction was used to characterize these unusual bis-trithiophosphine compounds, as well as identify the reaction intermediate. The analogous reactions of $[\text{P}^\text{I}\text{dppe}][\text{Br}]$ with acyclic disulfides leads directly to the useful phosphorus tris(thiolates) with no evidence for diphosphine intermediates. Further studies are on-going to evaluate the propensity of these molecule for the coordination of metals, or the generation of stable radicals.

6.4 Experimental

6.4.1 General Procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried according to literature procedures when necessary, and all other solvents were dried over a series of Grubbs’-type columns and degassed prior to use. The ligands, 1, 2- methoxy-tetrathiocin and benzo-15-crown-5-tetrathiocin were synthesized according to literature procedures.$^{55}$ NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz or Bruker Avance Ultrashield 300 MHz spectrometer. Chemical shifts are reported in ppm relative to internal standards for $^1\text{H}$ and $^{13}\text{C}$ (for the given deuterated solvent) and external standard for $^{31}\text{P}$ (85% $\text{H}_3\text{PO}_4 = 0$ ppm). Elemental Analysis was performed at the University of Windsor using a Perkin Elmer 2400 combustion CHN analyser.
6.4.2 Crystallographic Details

Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N₂ of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected on a Bruker D8 Venture diffractometer with a Photon 100 CCD detector using a Mo Kα radiation (λ = 0.71073 Å) source. 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 program suites. Validation of the structures was conducted using PLATON. Details are provided in Table 6.1.

6.4.3 Specific Procedures

**Isolation of the reaction Intermediate: 1**

1,2-dimethoxy-tetrathiocin (0.150 g, 0.374 mol, 1 eq) and [P(dppe)Br] (0.381 g, 0.749 mol, 2 eq) were added together in a Schlenk flask to which 15 mL of dichloromethane was added. Upon addition, a cloudy yellow solution appeared as the tetrathiocin is insoluble in DCM. The reaction was left to stir for several hours until a clear yellow solution was obtained. The solution was placed under reduced pressure until a yellow oil remained. Storage of a concentrated DCM solution of this mixture yielded pale yellow single crystals of 1 (in addition to colourless crystals of dppe and [P(dppe)Br]). As indicated in the text, we were fortunate enough to isolate this molecule as single crystals from a reaction mixture, and all our subsequent attempts to isolate this reaction intermediate have been unsuccessful.
**Synthesis of 6.2**

1,2-dimethoxybenzotetrathiocin (0.267g, 0.67 mol, 1.5 eq) and \([P^{1}\text{dppe}][\text{Br}]\) (0.438g, 0.86 mol, 2 eq) were loaded into a Schlenk flask, to which 25 mL of dichloromethane (DCM) was added. The resulting cloudy yellow was left to stir until a clear yellow solution was obtained after about 1hr. The DCM was removed under reduced pressure and the resulting oil was redissolved in 5 mL of DCM and 15 mL of diethyl ether was added. The solution was then left at -30 °C overnight to aid in the precipitation of by-products. This washing procedure was repeated until no by-products remained. The resulting pale yellow solution was collected and left for slow evaporation to afford yellow single crystals (Isolated Yield 0.170g, 60%). $\text{^3¹P\{^1\text{H}\} NMR } (\text{CD}_3\text{CN}):$ 120.9 (s) $^1\text{H NMR } (\text{CD}_3\text{CN})$: $\delta$ 6.92 (s, 3H, Ar), 6.83 (s, 3H, Ar), 3.76 (s, 18H OCH$_3$); $\text{^1³C\{¹H\} NMR } (\text{CD}_2\text{Cl}_2)$ $\delta$ 149.3-108 ppm (s, aromatic), 56.1 ppm (s, OCH$_3$). **Anal. Caled for:** C$_{24}$H$_{24}$O$_6$S$_6$P$_2$: C, 43.49; H, 3.65; N, 0; found: C, 43.0; H 3.73, N, -0.01.

**Synthesis of 6.3.**

Benzo 15-crown-5- tetrathiocin (0.100g, 0.151 mol) and \([P^{1}\text{dppe}][\text{Br}]\) (0.077g, 0.151 mol) were added together under an inert atmosphere and left to stir in approximately 15mL of dichloromethane. Upon addition of dichloromethane, a cloudy yellow solution initially appeared which cleared on stirring for approximately 1 hr to afford a clear yellow solution. The yellow solution was concentrated and 5 mL of diethyl ether was added. The solution was stored at -30 °C to form a white precipitate, a mixture of: [dppeS$_2$(O(C$_2$H$_4$O)$_4$)], and dppe, identified by $\text{^3¹P NMR}$. The remaining yellow solution was decanted and pale single crystals were obtained via slow evaporation of this concentrated solution. (Isolated Yield 0.083g 52%) $\delta$ $\text{^3¹P\{¹H\} NMR } (\text{CDCl}_3):$ 122.7ppm
(s). $^1$H NMR (CDCl$_3$): $\delta$ 6.9-7.1 (m, 2 H, Ar), 4.18 (m, 4H, C$_{10}$H$_{16}$O$_3$), 3.97 (s, 4H, C$_{10}$H$_{16}$O$_3$), 3.8 (s, 8 H, C$_{10}$H$_{16}$O$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 149 (s, Ar (C-O)), 121(s, Ar C-S), 114 (s, Ar C-H), 69-71 (s, C$_{10}$H$_{16}$O$_3$) 

Anal. Calcd for: C$_{42}$H$_{54}$O$_{15}$S$_6$P$_2$•$\frac{3}{2}$ CH$_2$Cl$_2$: C, 44.25; H, 4.87; N, 0; found: C, 43.99; H, 5.01; N, 0.03. The presence of CH$_2$Cl$_2$ was confirmed by $^1$H NMR.

**Synthesis of 6.4.**

To a Schlenk flask containing 4ʹ-methyl-1,3,2-benzodithiaphosphole (0.083g, 0.022 mol) was added half of an equivalent of 1,2-dimethoxybenzotetrathiocin (0.045g, 0.112 mol) suspended in 15 mL of dichloromethane. Upon addition of DCM, a cloudy yellow solution resulted which was left to stir for approximately 1 hr to afford a clear yellow solution. The reaction was quantitative by $^{31}$P NMR. (Isolated Yield 0.0436 g, 77%). $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 111, 113, 114 ppm (s) $^1$H NMR (CDCl$_3$): $\delta$ 128-136 ppm (Ar), 55.8 ppm (s, OCH$_3$), 20.5 (s, CH$_3$) $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 149 (s, Ar (C-O)), 137-111 (s, Ar), 56.1 ppm (s, OCH$_3$), 20.5 ppm (s, CH$_3$). 

**Anal. Calcd for:** C$_{20}$H$_{16}$O$_2$S$_6$P$_2$ C, 44.26; H, 2.97; N, 0; found: C, 44.69; H, 3.19; N, 0.05.

**Synthesis of Tris(phenylthio)phosphine**

To a dichloromethane solution of [P$^3$dppe][Br] (0.100 g, 0.196 mmol) was added diphenyl disulfide (0.085 g, 0.392 mmol). The mixture was left to stir for approximately 1 hr during which time it became pale yellow. $^{31}$P NMR confirmed the generation of tris(phenylthio)phosphine as well as the necessary by-product, [dppeSPh][Br]. The product was isolated by extraction with pentane. The pentane was removed to afford a white precipitate. (0.063g, 90%) $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 132.9 (s, P(SPh)$_3$), $^1$H NMR (CDCl$_3$): $\delta$ 7.05-8.17 (m, Ar), $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 128.5-136.9 (s, Ar)
### Table 6.1: Summary of Crystallographic Data

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\[
R₁ = \frac{\sum (|F_o| - |F_c|)}{\sum F_o}, \quad wR₂ = \left[ \frac{\sum (w(F_o^2 - F_c^2))}{\sum wF_o^2} \right]^{1/2}, \quad \text{GOF} = \frac{\sum (w(F_o^2 - F_c^2))}{(\text{No. of reflns. - No. of params.})^{1/2}}.
\]
6.5 References

Chapter 6: Synthesis of Trithiobisphosphines by Oxidative Transfer of Phosphorus(I)


Chapter 6: Synthesis of Trithiobisphosphines by Oxidative Transfer of Phosphorus(I)


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Chapter 7: Conclusions & Future Work

7.1 Dissertation Overview

Thus far, the chapters in this dissertation describe the use of P⁺ transfer as a valuable protocol to synthesis new low valent molecules, including macrocycles, oligomers, multidentate ligands, and thiophosphines. Additionally, the synthesis of molecules that are neutral overall were specifically targeted, as these molecules tend to be better donors, and their subsequent complexes have better solubilities and higher stabilities. Throughout chapters 2 through 5, the coordination chemistry of these compounds containing P(I) centers is explored. These molecules represent the some of the first examples of triphosphenium analogues acting as multidentate donors, and overall, some of the first examples that demonstrate the usefulness of triphospheniums themselves as ligands.

In chapters 2 and 6, it is demonstrated that P⁺ is a facile, high yielding, and P-atom efficient way to synthesize new phosphorus containing molecules, often in less synthetic steps, and minimum work-up steps to isolate the desired product. Finally, the P(I) starting material, [dppeP⁺][Br], is air- and moisture- stable, and also stable in the presence of strong bases and reducing agents, allowing for easy handling.

In this chapter, possibility of extending the P⁺ transfer protocol to the synthesis of anionic P(I) compounds is explored.

7.2 Phosphanides: Anionic P(I) Molecules

Organic phosphides (phosphanides) are compounds containing a phosphorus center that is univalent and has a P atom bearing a formal negative charge. Typically, the compounds can be thought of as phosphorus(I) bound by two anionic ligands. Since the only requirement for P⁺ transfer is displacement of the dppe fragment on [dppeP⁺][Br] by
a stronger donor (as depicted in Figure 7.1), this synthetic protocol could be useful in the
generation of phosphido type of molecules.

![Figure 7.1 General scheme for making phosphides using the P+ transfer agent, [P(dppe)]Br.](image)

However, in a more fundamental sense, these molecules could be useful as phosphination reagents, in organic transformations, or as electron rich donors to main group or transition metals, yielding polymetallic complexes in most instances. In this area, the auxiliary cation could also provide access to metathesis reactions involving the coupling reactions with the anionic fragment.

Phosphides are typically prepared either by reduction of a secondary phosphines, or by heating alkali metals with white or red phosphorus. Even in stoichiometric conditions, these reactions can sometimes produce polyphosphide materials, rather than discreet molecules, and can be tedious to work up. Worse, the heating of alkali metals together with one of the allotropes of phosphorus can be an explosive reaction, due to the nature of the starting materials, insufficient stirring, and uneven heating. As such, P+ transfer might provide a reliable way to access these types of materials in a facile manner.
Chapter 7: Conclusions & Future Work

7.3 Dicyanophosphide ([M][P(CN)₂])

7.3.1 Introduction

An interesting phosphide reported in the literature is the dicyanophosphide, [M][P(CN)₂], described originally by Schmidpeter. This molecule is actually the phosphorus analogue of metal dicyanamides ([N(CN)₂]), of which there are over 500 reported structure of in the CSD. The dicyanamides have been shown to make coordination polymers and have been prepared for many different applications ranging from ionic liquids to magnetic materials.3–5

The synthesis of this molecule phosphorus analogue was achieved in two different ways: by the reaction of white phosphorus with alkali metal cyanides, or by 2 e- reduction of a P(CN)₃.6,7 In both cases, it is reported that the molecules are only stable in solution so long as the alkali metal is contained within a crown ether.8

![Figure 7.2 Reported synthesis of a dicyanophosphide molecule by Schmidpeter.](image)

We have found that alkali metal salts of the form [M][P(CN)₃] can be readily prepared through the reaction of [dppeP][Br] with 2 eq. of [M][CN]. In this reaction, it is possible that the cyanide ligand forms a stronger bond to the P³ centre than dppe and the elimination of MBr salts could provide an additional thermodynamic driving force.
Additives such as glymes or crown ethers can be used to modify the solubility of the metal salts if needed or the use of organic-based cations of cyanide may increase the solubility.

![Proposed synthesis of [M][P(CN)₂] via ligand exchange reactions with [dppeP[I]]Br]

**Figure 7.3** Proposed synthesis of [M][P(CN)₂] via ligand exchange reactions with [dppeP[I]]Br

### 7.3.2 Preliminary Results

The reaction of either potassium cyanide and [dppeP[I]]Br or tetrabutylammonium cyanide and [dppeP[I]]Br proceeds immediately in dichloromethane, as evidenced by $^{31}$P NMR. (Figure 7.4)

![$^{31}$P{¹H} spectrum obtained for dicyanophosphide synthesized from the reaction of [dppeP[I]][Br] and two equivalents [nBu₄N][CN], and subsequent removal of dppe with Et₂O.]

**Figure 7.4** $^{31}$P{¹H} spectrum obtained for dicyanophosphide synthesized from the reaction of [dppeP[I]][Br] and two equivalents [nBu₄N][CN], and subsequent removal of dppe with Et₂O.

In the cases of the reactions using potassium cyanide or sodium cyanide the resulting reaction mixtures were centrifuged or filtered to remove the alkali metal bromide salt. The resultant powder was washed with diethyl ether to remove the dppe which had been liberated in the reaction. However, the precipitate obtained from this process is
sparingly soluble in most solvents; this problem could be resolved with the introduction of larger crown ethers, cryptands or polyether molecules to solubilize the cation, and alternatively, weakly coordinating cations could be used.

The reaction of tetrabutylammonium cyanide was more complicated, while the reaction proceeds immediately, the by-product from the metathesis reaction, tetrabutylammonium bromide, has similar solubility to that of the product. Unfortunately, this leads to difficulty in separation, and it’s difficult to determine if the by-product has been fully removed. Thus, it might be more practical to access these types of non-coordinating cations via ligand exchange reactions of $M[P(CN)_2]$ rather than from the cyanide starting material itself.

![Figure 7.5 FT-Raman spectrum of [nBu$_4$N][P(CN)$_2$]](image)

**Figure 7.5** FT-Raman spectrum of [nBu$_4$N][P(CN)$_2$]
7.3.3 Reactivity

Schmidpeter reported the crystal structures, of both the sodium and potassium salts of the dicyanophosphide featuring the bent C-P-C geometry, which suggests the presence of two lone pairs of electrons around the phosphorus atom.\textsuperscript{2,7} He also reported some preliminary reactivity studies; namely ability of this ligand to undergo methylation reactions as well as and oxidation. (\textbf{Figure 7.6}) In both situations, these reactions occur at the P(I) center, suggesting that the phosphorus atom appears to be the most reactive site. This was somewhat counterintuitive because the closest contacts to the alkali metal cation are with nitrogen atoms from the cyano groups: one might have posited that the contact implies that the negative charge is localized at nitrogen but the observation is likely a consequence of a hard-hard interaction from hard-soft acid base theory.\textsuperscript{7}

The softness of the phosphide site should lead to novel complexes with other soft metals, and the presence of the \textsuperscript{31}P NMR handle should make the study of such materials more convenient.

\textbf{Figure 7.6} Reactivity previously reported for P(CN)\textsubscript{2}. Both likely canonical structures are depicted for the dicyanophosphide (left).

Our initial reactivity studies commenced with the addition of copper(I) chloride, a soft, linear acceptor. Based on Schmidpeter’s previous results we anticipated reactivity
primarily at the central phosphorus atom. The addition CuCl to $[^6\text{Bu}_4\text{N}][\text{P(CN)}_2]$ results an immediate colour change from yellow to dark brown. $^{31}\text{P}$ NMR of the reaction solution indicated that the starting material had been consumed, and the copper had coordinated at the P(I) center, as the singlet corresponding to the starting material (-194 ppm) had shifted significantly downfield to -49 ppm. Unfortunately, we were not able to confirm our speculations by either $^{13}\text{C}$ NMR or by X-ray diffraction studies because of the insolubility of the material. However, our initial $^{31}\text{P}$ NMR results combined with the reactivity studies reported by Schmidpeter are consistent with a simple coordination complex of Cu at phosphorus. Because of the small size and potential flexibility of this ligand, together with two potential donor sites: (P and N) we believe that this could be an effective ligand for a variety of hard and soft metals spanning the periodic table.

7.4 $[\text{K}][\text{(R}_2\text{PCp)}_2\text{P}^\text{I}]$

7.4.1 Introduction

A ligand that had been highly successful in previous projects were the bisphosphino- and trisphosphino- cyclopentadienyl frameworks, thus we suspected that we might be able to access novel anionic triphosphonium analogues through the reaction of a related ligand: phosphinocyclopentadienide, $[\text{K}][\text{R}_2\text{PCp}]$, with our $\text{P}^+$ transfer agent, $[\text{dppeP}^\text{I}][\text{Br}]$ (Figure 7.7).
7.4.2 Preliminary Results

The reaction described above proceeds quickly and quantitatively by NMR. The anionic phosphine ligand is added to a cold, stirring solution of [dppeP][Br] in THF. After 20 minutes the reaction mixture is a dark orange solution, with precipitate present. The mixture can then be filtered to remove the KBr, and the dppe can be removed by Soxhlet extraction in hexanes. The product is a phosphide that is surprisingly soluble in most solvents – with the exception of hexanes and pentane – and is stable under inert atmosphere. The reaction is high yielding and does not generate any unexpected by-products. The $^{31}$P NMR of this molecule shows the characteristic doublet and triplet shifts typically seen for triphosphoeniums at (-212 (t) and 39 (d) ppm, along with strong $^1J_{PP}$ couplings, 487 Hz) (Figure 7.8).
Figure 7.8 $^{31}$P NMR of the reaction between [K][iPr$_2$PCp] and [dppeP]^+[Br] to form [K][(iPr$_2$PCp)$_2$P$^-$]

Single crystals of this material were grown from diethyl ether, and confirmed the anticipated molecular structure (Figure 7.9).
Figure 7.9 Molecular structure of [K] [(iPr₂PCp)₂P]⁴⁻, which crystallizes in the space group P2₁/n. Selected bond lengths and angles: P(1)-P(2):2.136(5) Å, P(2)-P(3): 2.1281(5) Å, K-Centroids: 2.769 and 2.791 Å P(1)-P(2)-P(3): 111.54(2)°

In this example, the cation of the salt is sandwiched by cyclopentadienyl rings. The K-Cp centroid distances are 2.769 and 2.791 Å. The flexibility of the ligand allows the Cp rings to accommodate the potassium atom in a non-linear packing arrangement. The P-P-P bond angle is 111.54(2)° and is a much larger angle than typical cyclic triphospheniums, which might be expected, but is interestingly also larger than those of acyclic triphosphenium cation that have been crystallographically characterized (90.67(4)-106.39(4)°). It is also even larger than the 8-membered rings containing triphosphenium analogues, such as the ones reported in Chapter 2. The P-P bond lengths within the triphosphenium fragment are 2.136(5) and 2.1281(5) Å which are similar to the lengths of typical triphosphenium cations, (2.113(2)-2.184(2) Å)⁹ and slightly shorter than
Chapter 7: Conclusions & Future Work

Zwitterionic triphospheniums reported in the literature and in the previous chapters of this dissertation.\textsuperscript{10,11}

The R groups on the pendant phosphines can be easily changed from isopropyl groups to phenyl, which could potentially change the bulkiness surrounding the P(I) center and the overall stability of this molecule. The phenyl variant was synthesized, and yielding a $^{31}$P NMR ($\delta$: -177 (t), -33 (d) ppm- \textbf{Figure 7.10}) that is slightly different that the isopropyl variant and is more similar to the spectra observed for other phenyl analogues, such as the trisphosphino- and bisphosphino- triphospheniums reported in chapters 3 and 4 respectively. The tunability of this molecule might have important effects on the coordination capabilities of this ligand in accommodating multiple metals, as was the observed for Ragogna’s zwitterionic triphosphenium.\textsuperscript{10}

\textbf{Figure 7.10} $^{31}$P NMR of the reaction between [K][Ph$_2$PCp] and [dppeP]$^\dagger$[Br] to form [K][(Ph$_2$PCp)$_2$P]$^\dagger$
7.4.3 Reactivity

The steric and electronic tunability of this molecule and the availability of multiple sites for metal complexation, make this particularly interesting as a ligand for transition metals as well as main group metals and metalloids. The presence of the potassium cation also provides access to the formation of these molecule through metathesis reactions. I envision that hard metals such as alkaline earth metals (Sr, Ba, Ca, Mg) could make interesting sandwich molecules or metallo-polymers through the Cp fragments of the molecule. Similarly, electron deficient metals-specifically early transition metals- could make similar sandwich molecules, where the electron rich P(I) center could have a close contact which might produce increased stability for these complexes (in spite of the hard-soft mismatch). These metal complexes can potentially be obtained through metathesis reactions of metal halide starting materials, of which there are many.

We might also be able to access sandwich and half-sandwich complexes by employing metal carbonyls, the reactivity of this molecule towards metal carbonyl complexes preferentially at the P(I) or at the cyclopentadienyl fragment would be an interesting study, and based on the work established in chapter 4, multimetallic complexes should be easily obtained with use of metal carbonyl starting materials. We postulate that mid- and late transition metals might complex through the P(I) center, and likely the same can be said for main group acceptors. The flexibility of this ligand framework might allow for facile synthesis of multi-metallic complexes at the P(I) center.

7.5 Conclusion

Overall, P+ transfer is a viable and effective way to synthesize new cationic, neutral, and anionic molecules containing low valent phosphorus. Low valent
phosphanides could be interesting ligands for a variety of different metals and main group acceptors, and represent a relatively unexploited area of low oxidation state phosphorus chemistry. In the case of the dicyanophosphide, this molecule represents the phosphorus analogue of the well-studied and very useful dicyanamide compounds, and could potentially have diverse applications in the fields of organometallic and materials chemistry. Meanwhile, the \([\text{K}][(\text{R}_2\text{PCp})_2\text{P}^+]\) molecule in an interesting example of a stable phosphanide that could be potentially exploited as a multidentate donor. In both cases, P⁺ transfer provides a simple and convenient way to access these types of molecules.

### 7.6 Experimental

#### 7.6.1 General Procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried according to literature procedures when necessary, and all other solvents were dried over a series of Grubbs’-type columns and degassed prior to use. The ligand, \([\text{K}][\text{Ph}_2\text{PCp}]\) was synthesized according to modified literature procedures.¹² NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz or Bruker Avance Ultrashield 300 MHz spectrometer. Chemical shifts are reported in ppm relative to internal standards for \(^1\text{H}\) and \(^{13}\text{C}\) (for the given deuterated solvent) and external standard for \(^{31}\text{P}\) (85% \(\text{H}_3\text{PO}_4 = 0\) ppm).

#### 7.6.2 Crystallographic Details

The single crystal for investigation was covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold \(\text{N}_2\) of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected...
using the APEXIII software suite\textsuperscript{13} on a Bruker D8 Venture diffractometer with a Photon 100 CCD detector using a Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at low temperature. APEXIII software was used for data reductions and SADABS\textsuperscript{14} 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{15} software suite as implemented in the WinGX\textsuperscript{16} program suites. Validation of the structures was conducted using PLATON.\textsuperscript{17} Details are provided in Table 7.1.

### 7.6.3 Specific Procedures

**Synthesis of \([n\text{Bu}_4\text{N}][\text{P(CN)}_2]$$**

\([n\text{Bu}_4\text{N}][\text{CN}] (0.300 \text{ g}, 1.11 \text{ mmol}, 2 \text{ eq})\) and \([\text{dppeP}^\text{I}][\text{Br}] (0.280 \text{ g}, 0.558 \text{ mmol}, 1 \text{ eq})\) were added together in a Schlenk flask to which 15 mL of dichloromethane was added, and the reaction was left to stir overnight. After stirring overnight, the pale yellow was washed with toluene to remove dppe. The \(n\text{Bu}_4\text{NBr}\) produced in the reaction has a similar solubility to the product, and the two were not successfully separated. \(^{31}\text{P}\{^1\text{H}\} \text{NMR} \delta (\text{CD}_3\text{CN}): -192.2 \text{ (s)}\)

\(^1\text{H} \text{NMR} \delta (\text{CD}_3\text{CN}): \delta 6.92 \text{ (s, 3H, Ar)}, 6.83 \text{ (s, 3H, Ar)}, 3.76 \text{ (s, 18H O-CH}_3); ^{13}\text{C}\{^1\text{H}\} \text{NMR} \delta (\text{CD}_2\text{Cl}_2) \delta 11.50 \text{ (s, Bu}_4\text{N), 18.02 \text{ (s, Bu}_4\text{N)}, 22.4 \text{ (s, Bu}_4\text{N)}, 56.1 \text{ (s, Bu}_4\text{N), 126.1 \text{ (d, J}_{\text{PC}} = 56 \text{ Hz, P-CN})}. \text{ FT-Raman (cm}^{-1}): 2700\text{-}3100 (\text{Bu}_4\text{N), 2100 (P-CN}_2)

**Synthesis of \([\text{Na 18-C-6}][\text{P(CN)}_2]$$**

Sodium cyanide (0.048g, 0.981mmol) and 18-crown-6 (0.259g, 0.981 mmol) were added together in THF and allowed to stir for several minutes before \([\text{dppeP}^\text{I}][\text{Br}] (0.250g, 0.490 \text{ mmol})\) was added to the same flask. The reaction was left to stir overnight and then the THF was removed from flask. The resulting precipitate was washed with diethyl ether
to remove the dppe and then dissolved in DCM to precipitate and remove the NaBr.

$^{31}$P{$_1$H} NMR $\delta$ (CD$_3$CN): -192.2 (s) $^{13}$C{$_1$H} NMR $\delta$ (CD$_2$Cl$_2$) $\delta$ 11.50 (s, Bu$_4$N), 18.02 (s, Bu$_4$N), 22.4 (s, Bu$_4$N), 56.1 (s, Bu$_4$N), 126.1 (d, $^1$J$_{PC}=$56 Hz, P-CN).

**Reaction of [nBu$_4$N][P(CN)$_2$] and CuCl**

To a solution of [nBu$_4$N][P(CN)$_2$] (0.200 g, 0.61 mmol) in THF was added CuCl (0.060 g, 0.61 mmol). The reaction turned from yellow to brown, and was left to stir for several hours, until no starting material remained, based on $^{31}$P NMR. The solvent was removed and the resulting brown material was collected. The product is insoluble in most solvents, and thus far, we have been unable to obtain single crystals from this reaction.

$^{31}$P{$_1$H} NMR $\delta$ (CD$_3$CN): -49 (s)

**Synthesis of [K][($i$Pr$_2$PCp)$_2$P]$^+$**

Two equivalents of [K][$i$Pr$_2$PCp] (0.638 g, 2.89 mmol) were transferred to a stirring solution of [dppeP]$^+$[Br] (0.737 g, 0.144 mmol) in THF at -78°. The reaction mixture turns yellow immediately, and once the addition is complete, the Schlenk flask was left to stir and slowly warm to room temperature over approximately 1 hour. The resulting orange solution was filtered through Cellite® and the THF was removed from the filtrate. The precipitate was collected and the dppe was removed via Soxhlet extraction with hexanes overnight. Single crystals were grown from a concentrated solution of the product in diethyl ether. (Isolated Yield 0.580 g, 93%) $^{31}$P{$_1$H} NMR $\delta$ (CD$_3$CN): -212 (t, $^1$J$_{pp}=$487 Hz), 39 (d, $^1$J$_{pp}=$487 Hz). $^1$H NMR $\delta$ (CD$_3$CN): $\delta$ 1.16 (m, 24H, CH$_3$), 2.29 (m, 4H, CH), 5.7 (dd, $^3$J$_{ph}=$ 5 Hz, $^3$J$_{HH}=$ 3 Hz 4H, Cp), 6.0 (dd, $^4$J$_{HH}=$ 2 Hz, $^3$J$_{HP}=$ 3Hz 4H, Cp); $^{13}$C{$_1$H} NMR $\delta$ (CD$_3$CN) $\delta$ 17.7 (m, CH$_3$), 26 (m, CH), 109 (t, $^2$J$_{cp}=$ 7 Hz, Cp), 113 (br, Cp)
Synthesis of $[\text{K}][(\text{Ph}_2\text{PCp})_2\text{P}]$

Two equivalents of $[\text{K}][\text{iPr}_2\text{PCp}]$ (0.638 g, 2.89 mmol) were transferred to a stirring solution of $[\text{dppeP}][\text{Br}]$ (0.737 g, 0.144 mmol) in THF at -78°. The reaction mixture turns yellow immediately, and once the addition is complete, the Schlenk flask was left to stir and slowly warm to room temperature over approximately 1 hour. The resulting orange solution was filtered through Cellite® and the THF was removed from the filtrate. The precipitate was collected and the dppe was removed via Soxhlet extraction with hexanes overnight. $^{31}\text{P}^{1\text{H}}\text{NMR}$ δ (CD$_3$CN): -177 (t, $^{1\text{pp}}_\text{P}=425$ Hz), 39 (d, $^{1\text{pp}}_\text{P}=425$ Hz).
## Table 7.1 Summary of Crystallographic Data

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$R_1 = \Sigma( |F_o| - |F_c| ) / \Sigma F_o$,  $wR_2 = [ \Sigma( w(F_o^2 - F_c^2)^2) / \Sigma(wF_o^4) ]^{1/2}$,  $\text{GOF} = [\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.  

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7.7 References


(13) APEX II. Bruker AXS Inc. APEX II, Madison, WI, 2012.


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