SYNTHESIS AND REACTIVITY OF FUNCTIONALIZED ELECTROPHILIC PHOSPHINIDENE COMPLEXES

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By
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Rakesh A. Rajagopalan, candidate for the degree of Doctor of Philosophy in Chemistry, has presented a thesis titled, *Synthesis and Reactivity of Functionalized Electrophilic Phosphinidene Complexes*, in an oral examination held on March 25, 2014. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Electrophilic phosphinidene complexes play an important role in organophosphorus synthesis. The chemistry of neutral phosphinidene complexes has been well studied, but cationic phosphinidene complexes are not as well understood. Therefore, new cationic phosphinidene complexes have been synthesized and their reactivity towards bond activation, cycloaddition and nucleophilic addition has been examined.

The terminal chloroisopropyl phosphido complex $[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)\text{-i-Pr}}\}]$ was synthesized, and abstraction of chloride from it generates the transient cationic alkylphosphinidene complex $[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(i-Pr)}\}]^+$, which can be trapped with diphenylacetylene to form a phosphirene complex. Trapping with $\text{P(C}_6\text{H}_5)_3$ leads to a phosphine coordinated phosphinidene complex. Trapping with diphenylsilane leads to SiH activation and a secondary silyl phosphine complex, while trapping with ferrocene leads to CH activation and a ferroceny phosphine complex.

Chloride abstraction from dichlorophosphido complex $[\text{Cp}^*\text{Mo(CO)}_3\text{PCl}_2]$ did not lead to a chlorophosphinidene but instead to a bimetallic bridging $\text{P}_2\text{Cl}_3$ complex. Chloride abstraction in the presence of $\text{P(C}_6\text{H}_5)_3$ results in $[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PPh}_3\})][\text{AlCl}_4]$. Reaction of $[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PPh}_3\})]^+$ with a second equivalent of $\text{P(C}_6\text{H}_5)_3$ and AlCl$_3$ leads to a metal-free triphosphenium salt. Reaction with bis-diphenylphosphinoethane leads to a cyclic triphosphenium salt, while, reaction with bis-diphenylphosphinomethane leads to a dangling phosphine coordinated chlorophosphinidene complex. Photolysis then leads to a chelated phosphine-coordinated chlorophosphinidene complex. Reaction of the dichlorophosphido complex with a stable N-heterocyclic carbene leads to a carbene coordinated chlorophosphinidene complex.
Reaction with a second equivalent of carbene and AlCl$_3$ leads to a bis-carbene coordinated phosphonium salt.

Reaction of [Cp*Mo(CO)$_3$PCl$_2$] with diisopropylzinc leads to [Cp*Mo(CO)$_3${P(Cl)(i-Pr)}], the precursor to [Cp*Mo(CO)$_3${P(i-Pr)}]$^+$. Reaction with phenoxide anions leads to a range of chloroaryloxyphosphido complexes. Chloride abstraction leads to aryloxyphosphinidenes, which can be trapped with diphenylacetylene to form aryloxy phosphirene complexes, or with triphenylphosphine to form phosphine coordinated aryloxyphosphinidene complexes. Reactions of [Cp*Mo(CO)$_3$PCl$_2$] with (-)-menthoxide and (-)-borneoxide result in chloromenthoxy and chloroborneoxyphosphido complexes. Chloride abstraction then generates transient chiral alkoxyphosphinidene complexes. Trapping with phenylacetylene leads to chiral P centers and forms diastereomeric mixtures of alkoxyphosphirene complexes (diastereomeric excess = 20%).

With P(C$_6$H$_5$)$_3$, the menthoxypyrophosphinidene forms a diastereomeric mixture of the phosphine coordinated menthoxypyrophosphinidene complex (diastereomeric excess = 52%).

Reaction of [Cp*Mo(CO)$_3$PCl$_2$] with a thiophenolate anion results in [Cp*Mo(CO)$_3${P(Cl)(SPh)}], and chloride abstraction generates a transient cationic thiophenoxypyrophosphinidene complex, which can be trapped with diphenylacetylene to form a thiophenoxypyrophosphirene complex, or with triphenylphosphine to form a phosphine coordinated thiophenoxypyrophosphinidene complex. Reactivity of these functionalized phosphinidene complexes have been compared with that of the analogous aminophosphinidene complex experimentally and computationally. Their increasing order of electrophilicity at the phosphinidene phosphorus has been determined as follows amino $< <$ alkyl $< <$ chloro $\sim$ phenoxy $\sim$ thiophenoxo.
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<table>
<thead>
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<th>Abbreviation</th>
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<tr>
<td>Anal</td>
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<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>BINAP</td>
<td>2,2’-Bis(diphenylphosphino-1,1'-binaphthyl)</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>BuLi</td>
<td>butyl lithium</td>
</tr>
<tr>
<td>C.N</td>
<td>Coordination number</td>
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<tr>
<td>Calcd</td>
<td>calculated</td>
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<tr>
<td>Cp</td>
<td>η⁵-cyclopentadienyl (η⁵- C₅H₅)</td>
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<td>Cp*</td>
<td>η⁵-pentamethylycyclopentadienyl (η⁵- C₅(CH₃)₅)</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<td>DMAD</td>
<td>dimethylacetylenedicarboxylate</td>
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<td>EPR</td>
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<td>Et</td>
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<tr>
<td>FMO</td>
<td>Fragment Molecular Orbital</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>i-Pr</td>
<td>isopropyl ((CH₃)₂CH-)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
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<td>Mes*</td>
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</tr>
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</tr>
<tr>
<td>N-′-Pr₂</td>
<td>diisopropylamino (-N(CH(CH₃)₂)₂)</td>
</tr>
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</tr>
<tr>
<td>OS</td>
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</tr>
<tr>
<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Plot</td>
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<tr>
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<tr>
<td>1′Bu</td>
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</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>HOFO</td>
<td>Highest Occupied Fragment Orbital</td>
</tr>
<tr>
<td>LUFO</td>
<td>Lowest unoccupied Fragment Orbital</td>
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CHAPTER 1

INTRODUCTION

The increasing applications of organophosphorus compounds have stimulated the growth of synthetic phosphorus chemistry. Along with the conventional applications of organophosphorus compounds such as agricultural chemicals and medicinal agents, the other recent developments in applications of these compounds, especially in organic synthesis and asymmetric catalysis have fuelled an even wider interest in organophosphorus synthesis. Synthetic organophosphorus chemistry, which deals with phosphorus-carbon bond formation, therefore has many potential applications in chemical synthesis. Because of the growing number of applications of organophosphorus compounds, more powerful and convenient synthetic approaches to these compounds are always of interest. In this research, I will look at P-C and P-element bond formations via a transition metal mediated synthetic approach, which would eventually enable us to develop new alternative synthetic routes to organophosphorus compounds.

1.1 Phosphorus

Phosphorus (P) has an atomic number 15 and a ground state electronic configuration [Ne] \(3s^2\ 3p^3\). It belongs to group 15 of the periodic table and resides just below nitrogen. Unlike nitrogen, the relatively large atomic size allows phosphorus to form a wide range of compounds with various coordination numbers. The coordination number of phosphorus varies from 1 to 6. The oxidation state of phosphorus can range from +5 to -3.
Figure 1.1 Phosphorus compounds with different coordination and oxidation numbers.

1.2 Organophosphorus compounds

Organophosphorus compounds can be generally defined as compounds having phosphorus bonded to one or more organic fragment. However, another specific definition is more preferred, ie., organophosphorus compounds are compounds having at least one direct P-C linkage. On the basis of the valency of phosphorus atom, organophosphorus compounds can be classified into two categories: high-valent (P (V)) and low-valent (P (III) and lower).

Most of the biologically and naturally occurring phosphorus compounds are high-valent phosphorus compounds. Many of these compounds are used as pesticides and herbicides in agriculture. The medicinal and pharmacological values of these compounds are also well known. They are also useful in organic synthesis. For example, Wittig reagents like methylenetriphenylphosphorane (Ph₃P=CH₂) are widely used in synthesizing alkenes.
Tri-valent phosphorus compounds (P(III) compounds) serve as ligands in organometallic chemistry.\textsuperscript{4} The coordinating properties exhibited by these compounds make them useful as ligands in low valent and electron rich transition metal complexes, which are relevant in homogenous catalysis.\textsuperscript{5,6} A large number of asymmetric catalysts bearing chiral organophosphorus ligands were reported during the last 20 years and are being widely used for various organic transformations.\textsuperscript{7,8} A few organophosphorus ligands in catalysis are given in Figure 1.\textsuperscript{2,5,6}

![Figure 1.2 Organophosphorus ligands](image)

BINAP has proved as an efficient ligand in synthetic organometallic chemistry. The Ru and Rh complexes of BINAP are powerful catalysts for enantioselective hydrogenation across asymmetric alkenes.\textsuperscript{9,10} Rh complexes of benzophospholide serve as catalysts for regioselective hydroformylation reactions across alkenes.\textsuperscript{11} The chelated Pd complexes of phosphaferrocene are excellent catalysts for Suzuki and Miyaura coupling reactions.\textsuperscript{12}
Lo-valent phosphorus compounds (P(I), P(0) compounds) are uncommon, however there are few di-valent phosphorus compounds (P(II) compounds), which serve as ligands in organometallic chemistry.\textsuperscript{12}

1.3 Metal mediated organophosphorus synthesis

Phosphorus-carbon and phosphorus-element bond forming reactions play a vital role in the synthesis of organophosphorus compounds. Phosphorus-carbon and phosphorus-element bond formation can be performed through traditional main group chemistry. Even though a large number of organophosphorus compounds have been synthesized using these methods, traditional main group chemistry has some practical limitations. The methods are usually not general and often not functional group tolerant. The reactions are often not selective and in most cases there are difficulties in handling volatile and toxic reagents. For example, the synthesis of a simple reagent $i$-PrP\textsubscript{2}Cl can be attempted via a stoichiometric reaction between PCl\textsubscript{3} and $i$-PrMgCl, but the reaction ends up with a mixture of mono, di and tri isopropyl substituted phosphines, which makes its further separation difficult.\textsuperscript{13}

An alternative synthetic approach to phosphorus-element bond formation is metal mediated organophosphorus synthesis. These methods may have the potential to overcome some of the difficulties of the traditional main group methods. In metal mediated organophosphorus synthesis, phosphorus-carbon and phosphorus-element bond formations take place within the coordination sphere of the metal, where the reactive site of the molecule can experience a considerable amount of steric protection, resulting in control over reactivity. Since most of the metal complexes are crystalline and non volatile in nature, the chemistry can be usually performed with less potential exposure to toxic
chemicals. Metal coordination can stabilize reactive fragments, and also serves as a protecting group for the phosphorus lone pair. Transition metal mediated chemistry is a powerful synthetic tool for carbon-carbon bond formation in organic synthesis. For example, organotransition-metal compounds in general, Fischer carbene complexes in particular serve as powerful reagents to synthesize carbocyclic and heterocyclic molecules, which are not readily accessible through conventional routes. Metal mediated reactions could also have the same impact in organophosphorus synthesis via phosphorus-carbon and phosphorus-element bond formations.

1.4 Phosphorus Carbon Analogy

Since phosphorus is in group 15 and carbon is in group 14 of the periodic table, one might expect an entirely different chemistry for their respective compounds. This is true for many of their compounds. However, because of their similarity in electronegativity, phosphorus behaves more like its diagonal counterpart carbon than nitrogen. This diagonal carbon-phosphorus analogy is most obvious in low valent organophosphorus compounds in which the phosphorus atom usually exhibits a coordination number of one or two. The P-C analogy can be best explained by the replacement of a CR₂ moiety with PR. For example, the replacement of a CR₂ group of an alkene with a P unit will give a di-coordinate phosphorus species called a phosphaalkene (CR₂=PR) (Figure 1.3). The replacement of a CR group of an alkyne with a P unit will give a mono-coordinate phosphorus species called phosphalkyne (Figure 1.3). Phosphaalkenes and phosphalkynes show strong resemblance in their chemistry with alkenes and alkynes but have little resemblance to imines and nitriles. Similarly, the
replacement of a CR group present in a carbene with a P unit may give a carbene analogue of mono-valent phosphorus species called phosphinidene (P-R).

![Figure 1.3 Phosphorus carbon analogy](image)

In addition to their application as ligands in catalysis, the low coordinate phosphorus compounds serve as synthetic tools for P-C and P-element bond formation, which are crucial steps in the synthesis of organophosphorus compounds. Among the low coordinated phosphorus compounds, phosphinidenes and metal phosphinidene complexes, which are the phosphorus analogues of carbenes and metal carbene complexes, deserve a special attention. The well established carbene chemistry may serve as a guideline to understand the chemistry of phosphinidenes. The highly reactive electron deficient phosphorus atom of a phosphinidene may have the potential to serve as a synthetic precursor to a variety of organophosphorus compounds. An introduction, explaining the generation, stabilization and the reactivity of phosphinidene and phosphinidene complexes is given in following sections.
1.5 Phosphinidenes

Phosphinidenes are low-valent phosphorus compounds with one singly bonded substituent on phosphorus. They are generally represented as P-R. In a phosphinidene, phosphorus has only one bond, rather than the more typical three or five. The phosphorus atom shares an electron to form a covalent bond with an atom or a group, leaving behind four nonbonding electrons (Figure 1.5). Phosphinidenes have therefore only six valance electrons and are thus very unstable and reactive. Phosphinidenes are the phosphorus analogous of well studied carbenes (CR$_2$). Therefore, in order to have a better understanding of phosphinidene, it is useful to examine carbenes first.

Carbenes are highly reactive, neutral, electron deficient species having a divalent carbon atom with only six valence electrons, two in each bond and two nonbonding electrons. Based on the distribution of the two nonbonding electrons, carbenes can be classified in two types: singlet carbenes and triplet carbenes. In singlet state, the electrons are paired up in a single orbital, leaving behind a lone pair and an empty p orbital on the carbene carbon, but in the triplet state, there is one electron in each of the p orbital (Figure 1.4). Because of the electron deficiency at carbon, most free carbenes are highly reactive and unstable. However, their reactivity can be substantially reduced with substituents that can alleviate the electron deficiency at the carbene center. Metal complexes incorporating carbene ligands, which are known as metal carbenes, are stable. The metal carbene complexes are not normally synthesized via the coordination of a free carbene with a metal fragment, unless in the case, where the carbene is already stabilized by $\pi$ donor substituents. Transition metal carbene complexes can be classified in two
types based on reactivity: nucleophilic metal carbenes (Schrock type) and electrophilic metal carbene (Fischer type).

In Schrock carbene complexes, the carbene ligand can be considered to be formally derived from a free triplet carbene, which contains two unpaired electrons in each \( \text{sp}^2 \) orbital. The triplet carbene fragment forms two covalent bonds with a metal fragment having two unpaired electrons (Figure 1.4). The \( \text{M} = \text{C} \) double bond formed is polarized towards carbon, because C is more electronegative than M, leading to a nucleophilic carbene carbon. Schrock carbenes are usually favoured by higher oxidation state, early transition metals, having non-\( \pi \) acceptor ligands and non-\( \pi \) donor R groups. As Schrock carbenes posses a polarized \( \text{M}^\delta+ = \text{C}^\delta- \) double bond, most of their chemistry takes place across the \( \text{M} = \text{C} \) bond.

In Fischer carbene complexes, the carbene ligand can be considered to be formally derived from a free singlet carbene, which contains a lone pair in \( \text{sp}^2 \) orbital and an empty \( \text{p}_z \) orbital. The singlet carbene fragment forms a \( \sigma \) donor interaction with the metal center via coordination of its lone pair into the empty metal \( \text{d} \) orbital, which leaves on carbon an empty \( \text{p}_z \) orbital perpendicular to the carbon trigonal plane. The empty \( \text{p}_z \) orbital on carbon is also a weak acceptor for \( \pi \) back donation from the \( \text{M(d\pi)} \) orbitals (Figure 1.4). Since the \( \sigma \) donation from the carbene carbon is only partially compensated by the \( \pi \) back donation, the carbene carbon carries a \( \delta^+ \) partial positive charge and is electrophilic.\(^{24}\)

Low oxidation state late transition metals with \( \pi \) acceptor ligands, and \( \pi \) donor substituents favour Fisher carbene character.
Like carbenes, phosphinidenes can have either a triplet electronic state with one lone pair and two singly occupied P orbitals on the phosphorus atom or a singlet electronic state with two lone pairs and an empty $p_z$ orbital on the phosphorus atom (Figure 1.5). (Note: For convenience, it is shown that the phosphinidene phosphorus is $sp^2$ hybridized). Ab initio studies conducted on different phosphinidenes showed a triplet to singlet energy separation of 22 kcal/mol.\textsuperscript{25} The triplet to singlet energy separation for methylene carbene ($:CH_2$) is found to be 12 kcal/mol.\textsuperscript{25} Theoretical studies conducted on [Me-P] shows a triplet ground state with a triplet to singlet energy separation of 22.6 kcal/mole.\textsuperscript{26} Similar studies on [Ph-P] shows a triplet to singlet gap of 21-22 kcal/mole.\textsuperscript{27}
When the phosphinidene is stabilized by a substituent bearing a lone pair such as amino or phosphino, the energy of the singlet state approaches that of the triplet state. This is because of the stabilization results of the π donation from the lone pair orbital of the substituents to the empty $p_z$ orbital of the phosphinidene (Figure 1.5). Like carbenes, phosphinidenes can be stabilized by metal coordination. The transition-metal phosphinidene complexes can be considered analogues of carbene complexes. The later section of this chapter discusses terminal phosphinidene complexes in detail.

**Figure 1.5** Singlet and triplet electronic states of free carbene and phosphinidene

**Figure 1.6** Heteroatom stabilization of singlet phosphinidene
1.5.2 Generation of free phosphinidenes

As with carbenes, the electron deficient phosphorus atom of a free phosphinidene makes it highly reactive and unstable. Therefore, the detection of this reactive species had remained a great challenge until 1994, when Gasper and coworkers first identified a mesitylphosphinidene using EPR spectroscopy during the photolysis of a mesitylphosphirane at low temperature (Scheme 1.1).²⁹

Scheme 1.1 Generation of mesitylphosphinidene

Several other precursors have also been used to generate free phosphinidenes, including thermal depolymerisation of cyclopolyphosphines (RP)_n and reduction of dihalophosphines with a variety of electropositive metals (Li, Mg, Zn, Sn(II), Ge(II)) (Scheme 1.2).³⁰ Cycloreversion of phosphiranes, triazaphospholenes and oxazaphospholenes have also been used to generate phosphinidenes (Scheme 1.3).³¹,³² Later Gasper and Cowely reported the generation of phosphinidene by the photolysis of phospholenes and phosphorous bis(azides) (Scheme 1.4).³³,³⁴
Scheme 1.2 Formation methods of phosphinidene

Scheme 1.3 Formation methods of phosphinidene

Scheme 1.4 Photolysis of phospholenes and phosphorous bis(azide)
1.5.3 Reaction of phosphinidenes

The reactivity of free phosphinidene has been studied using trapping reactions. Reaction of phosphinidenes with sigma bonds and various unsaturated systems (e.g. alkenes, alkynes, and conjugated dienes) has been well studied. The sigma bond insertion in to O-H, S-S bonds and the [4+1] cycloaddition with conjugated dienes are shown in Scheme 1.5.\(^{35}\)

Scheme 1.5 Reactions of phosphinidene towards O-H, S-S bonds and conjugated diene

Phosphinidene [R-P] shows [2+1] cycloaddition towards unsaturated bonds, resulting in the formation of three membered ring compounds (Scheme 1.6).\(^{33}\)
In all these methods, the phosphinidenes generated were highly reactive and transient in nature and the intermediacy of these reactive species was confirmed from the formation of the trapped products. However, the generation of free phosphinidene has lots of practical limitations due to its high reactivity. In most cases, phosphinidenes are not generated under useful synthetic conditions. The difficulty in generating the free species limits their suitability for synthetic applications.

### 1.6 Terminal phosphinidene complexes

Like carbenes, phosphinidenes can be stabilized and their reactivity can be moderated by coordination to a metal complex. The phosphinidene complexes are still very reactive, but are easier to synthesise and more selective in their reactivity, and are thus more useful in synthetic chemistry. Like carbene complexes, depending on the nature of the coordinating transition metal and the ancillary ligands, the reactivity of the terminal phosphinidene complexes ranges from nucleophilic to electrophilic extremes. The
nucleophilic versions correspond to Schrock carbenes and the electrophilic versions correspond to Fischer carbenes.\textsuperscript{36}

1.6.1 Nucleophilic phosphinidene complexes

1.6.1.1 Bonding in nucleophilic phosphinidene complexes

The bonding in nucleophilic phosphinidene complexes is viewed as being analogous to that of Schrock carbene complexes. The phosphinidene ligand can be considered to be formally derived from a free triplet phosphinidene, which contains one lone pair in a sp\textsuperscript{2} orbital and an unpaired electron in p\textsubscript{z} orbital and the other sp\textsuperscript{2} orbital. The unpaired electron in the sp\textsuperscript{2} orbital forms a typical covalent bond with the metal center, which leaves on phosphorus a lone pair and a p\textsubscript{z} orbital with an unpaired electron perpendicular to the plane formed by M, P and R and leading to a bent geometry at the phosphinidene center. The p\textsubscript{z} orbital overlaps with an appropriate metal d orbital to form a π bond (Figure 1.7). The M-P bond can be considered as a normal M=P double bond with a M\textsuperscript{5+}-P\textsuperscript{5−} polarization due to the higher electronegativity of phosphorus.\textsuperscript{37-39} The localization of the partial negative charge on the phosphinidene phosphorus makes them nucleophilic in nature and they are synthetically equivalent to [RP]\textsuperscript{2−} dianions.\textsuperscript{40} High oxidation state metal centers, σ donor ancillary ligands and early transition metals usually favour nucleophilic phosphinidenes.
1.6.1.2 Generation of nucleophilic phosphinidene complexes

Several stable nucleophilic phosphinidene complexes have been reported and their chemistry has been well explored. There are several well established synthetic routes to nucleophilic phosphinidene complexes, including salt metathesis, insertion and elimination, σ-hydrogen migration, oxidation and deprotonation, phosphinidene group transfer, dehydrohalogenation and ligation. As my thesis is focused on the chemistry of electrophilic terminal phosphinidene complexes, the synthesis of nucleophilic phosphinidenedes are only briefly discussed here.

In 1987, Lappert synthesized the first stable nucleophilic phosphinidene complexes by reacting \([\{M(\eta^5-C_5H_5)_2HLi\}_4]\) tetramers with bulky dichlorophosphines \(RPCl_2\) (R= Mes* or \((\text{Me}_3\text{Si})_2\text{CH}\), M = Mo, W). The geometry at phosphorus is bent with a stereoactive lone pair and the metal-phosphorus bond distance is consistent with a double bond (Scheme 1.7).
Later, Niecke et al. reported the aminophosphinidene complexes of molybdenum and tungsten by the reaction of metal hydrides with chloroiminophosphines via a \([1, 3]\) hydrogen shift (Scheme 1.8).\(^{43}\)

![Scheme 1.7 Generation of nucleophilic phosphinidene via salt metathesis](image)

**Scheme 1.7** Generation of nucleophilic phosphinidene via salt metathesis

In 1994, Stephan et al. reported the synthesis of the first stable terminal phosphinidene complexes of zirconium. They synthesized the zirconium complex by the reaction of \(\text{Cp}_2\text{ZrClMe}\) with \(\text{LiPHMes}^*\) (Scheme 1.9). The transient phosphinidene formed was sterically protected by the zirconium coordinated \(\text{PMe}_3\). The phosphinidene phosphorus was found to have a bent geometry and the \(\text{Zr-P}\) bond length was consistent with a double bond character.\(^{44}\)
1.6.2. Electrophilic phosphinidene complexes

1.6.2.1 Bonding in electrophilic phosphinidene complexes

The bonding in electrophilic phosphinidene complexes is viewed as being analogous to that of Fischer carbene complexes. The phosphinidene ligand can be considered to be formally derived from a free singlet phosphinidene, which contains two lone pairs in two sp\(^2\) orbitals and an empty p\(_z\) orbital. The lone pair in one of the sp\(^2\) orbitals forms a typical coordinate bond with the empty metal d orbital, which leaves on phosphorus a lone pair and an empty p\(_z\) orbital perpendicular to the plane formed by M, P and R and leading to a bent geometry at the phosphinidene center (Figure 1.8). The M-P bond can be considered as a dative σ bond with a +1 oxidation state on the phosphorus atom. The presence of the empty p\(_z\) orbital on phosphorus makes it electrophilic in nature. The empty p\(_z\) orbital is also a weak acceptor for π back donation from the M(dπ) orbitals.\(^{36,38,40}\) Analogous to Fischer carbene complexes, the bonding of singlet phosphinidenes to the metal fragment is also favoured by low oxidation state metallic centers with π acceptor ancillary ligands, strong π donor substituent at the phosphinidene phosphorus and late transition metals.
**1.6.2.2 Generation of electrophilic phosphinidene complexes**

Several transient electrophilic phosphinidene complexes have been reported and their chemistry has been well studied. For a long period of time, electrophilic terminal phosphinidene complexes were only known as transient species, generated and trapped *in situ*. Most of the electrophilic phosphinidene complexes reported were neutral with the transition metal bearing carbonyl ligands only. Several approaches to the synthesis of these transient species have been made. It was in 1982 that Marinetti and Mathey reported the generation of transient electrophilic phosphinidenes by the thermal decompositions of 7-phosphanorbornadiene precursors. The requisite phosphanorbornadienes were obtained by the [4+2] cycloadditions between the appropriate metal coordinated phosphole complexes and dimethylacetylenedicarboxylate (DMAD) (Scheme 1.10).
Scheme 1.10 Thermal decomposition of 7-phosphanorbornadiene

The transient electrophilic phosphinidenes were trapped with various trapping reagents like alcohols, olefins and alkynes as shown in the Scheme 1.11. The kinetic studies revealed that the reaction was first order in the concentration of the phosphanorbornadiene and did not depend on the nature or the concentration of the trapping reagent, indicating the intermediary of a phosphinidene complex.\textsuperscript{46}

Scheme 1.11 Trapping reactions of transient electrophilic phosphinidene

In 1989, Mathey reported a new route to the synthesis of amino substituted terminal phosphinidene complexes via the thermal decomposition of aminophosphiranes.\textsuperscript{47} The elimination of ethylene is considered to be the driving force for
this reaction and the intermediacy of the transient aminophosphinidene formed was confirmed via various trapping reactions (Scheme 1.12).

![Scheme 1.12](image)

**Scheme 1.12** Generation of aminophosphinidene from aminophosphiranes

Streubel’s group developed an alternative route to the generation of electrophilic terminal phosphinidene complexes. This method relies on the thermal decomposition of an azophosphirane ring that results in the formation of the terminal phosphinidene complex via the decomposition of a transient nitrilium phosphine ylide (Scheme 1.13).

![Scheme 1.13](image)

**Scheme 1.13** Streubel’s method of formation of transient electrophilic phosphinidene

Based on the work of King et al. in the late 1980s, Lammertsma’s group developed a different route to the formation of amino substituted terminal phosphinidenes. The method is based on the condensation reaction of an amino
chlorophosphine with Na₂[Fe(CO)₄] (Collman’s reagent). The transient amino phosphinidene thus formed can be trapped with allene and diallene (Scheme 1.14).⁵⁰

Scheme 1.14 Generation and trapping of aminophosphinidene

Recently, Lammertsma has used benzophosphepine complexes as precursor for terminal electrophilic phosphinidene complexes. The decomposition takes place at 80 °C, and the naphthalene side product can be easily removed by sublimation. This method offers access to a wider range of transition metal complexes than the 7-phosphanorbornadiene complexes, but the phosphorus substituent range is more limited, although bulky groups such as tert-butyl are accessible. (Scheme 1.15).⁵¹

Scheme 1.15 Lammertsma’s method of preparation of electrophilic phosphinidene
1.6.2.3 Generation of stable electrophilic phosphinidene complexes

Until 2001, terminal electrophilic phosphinidene complexes were known only as transient species. Carty and Sterenberg reported the first stable cationic terminal electrophilic aminophosphinidene complexes in 2001.\textsuperscript{52} A series of stable cationic aminophosphinidene complexes of Mo, W, Re, Fe, Ru, Os and Co that display some of the characteristic reactions of transient electrophilic phosphinidenes were reported thereafter.\textsuperscript{52-55} The chlorodiisopropylaminophosphido complexes were used as precursors and the chloride abstraction with a Lewis acid (e.g. AlCl\textsubscript{3}) was used to generate the stable cationic terminal phosphinidenes. The \(\pi\) donation from the nitrogen lone pair to the empty phosphorus \(p_z\) orbital accounts for high stability of these species. The synthetic method is shown in Scheme 1.16.

\textbf{Scheme 1.16} Generation of stable electrophilic phosphinidene complexes

All these complexes were characterized by X-Ray crystallography. The M-P-N bond angle shows a bent geometry at the phosphinidene phosphorus with a stereo active
lone pair. The $^{31}$P resonance for all these cationic phosphinidene complexes appears at very low field (e.g. $\delta^{31}$P 1007 for the molybdenum complex). The electrophilic nature of these cationic phosphinidene complexes was confirmed from their reactivity towards alkynes (diphenylacetylene) and nucleophilic phosphines (PEt$_3$ and dmpm), resulting in phosphirene complexes and phosphine-coordinated phosphinidenes respectively (Scheme 1.17).$^{54}$

![Scheme 1.17 Formation of a cobalt phosphirene complex](image)

After the report of stable aminophosphinidenes, other stable terminal phosphinidene complexes have been reported. Hillouse et al. reported a stable neutral terminal phosphinidene complex of Ni formed via the oxidation of a primary phosphido complex using tropylium hexafluorophosphate (Scheme 1.18). The electronic behaviour of the Hillouse complex remains ambiguous.$^{56}$ The Ni-P bond distance of 2.0772(9) Å suggests a typical double bond character. Unlike the other reported electrophilic phosphinidene complexes, reaction with an alkene (1,2-di-deuteroethylene) does not generate a stable phosphirane complex but leads to a [2+2] cycloadditions reaction, followed by a reductive elimination and formation of a free phosphirane (Scheme 1.19).$^{57}$
Scheme 1.18 Hillhouse method of generation of nickel phosphinidene

Scheme 1.19 Reaction of Hillouse complex with 1, 2-trans- dideuteroethylene

1.6.3 Reactions of nucleophilic and electrophilic phosphinidene complexes

1.6.3.1 Reactions of nucleophilic phosphinidenes

Because of the presence of a genuine M=P double bond with a polarity M⁺⁺P⁻⁻, most of the nucleophilic phosphinidene chemistry involve both metal and phosphorus centers. Like Schrock carbene complexes, nucleophilic phosphinidenes undergo 1,2 addition reactions with polar reagents. Reaction with alkenes and alkynes results in [2+2] cycloadditions across the M=P double bond. With carbonyl compounds, the [2+2] cycloadduct formed can further undergo decomposition to generate phosphaalkenes.⁵⁸,⁵⁹ These reactions are summarised in Scheme 1.20.
1.6.3.2 Chemistry of electrophilic phosphinidenes

Electrophilic phosphinidenes exhibit an entirely different chemistry from their nucleophilic counterparts. Because of the presence of an empty $p_z$ orbital at the phosphinidene phosphorus, most of their chemistry takes place at the phosphorus center. The reaction of electrophilic phosphinidenes can be classified into three categories, $\sigma$ bond insertion reactions or bond activation reactions, cycloadditions reactions and reactions with nucleophiles.

1.6.3.2.1 $\sigma$ bond insertion reactions

In $\sigma$ bond insertion reactions, the phosphinidene phosphorus undergoes an electrophilic insertion into various $\sigma$ bonds, resulting in phosphine complexes. The insertion reaction of electrophilic terminal phosphinidenes into the O-H, N-H, C-N, S-H, C-O, C-X, C-M (X= Cl, Br and I, M= transition metal), Si-H and C-H bonds have been reported.\(^{52,60-63}\)
Scheme 1.21 Sigma bond insertion reaction

Insertion reactions of electrophilic phosphinidenes into the C-N and C-O bonds are observed in strained three membered heterocycles (aziridines and oxiranes). The initial ring insertion leads to a four membered cyclic product. For oxophosphirane, the four membered cyclic product further undergoes a Wittig-like [2+2] cycloreversion, forming the phenylphosphinidene oxide complex (Scheme 1.22).

Scheme 1.22 Insertion of phosphinidene in to a C-N and C-O bonds

Insertion reactions into the C-M (M= transition metal) bonds are observed in tetrahedral Ni₂C₂ clusters (Scheme 1.23).
Scheme 1.23 Insertion of phosphinidene in to C-M bond

Streubel et al. reported the insertion of phosphinidene into C-X bonds (X= Br, I). The electrophilic phosphinidene complex inserts into the C-X bond of benzyl bromide and methyl iodide to give corresponding phosphine complexes (Scheme 1.24). The reaction occurs through an initial coordination of X to the phosphinidene phosphorus, followed by C-X cleavage.66,67

Scheme 1.24 C-X bond activation reaction of electrophilic terminal phosphinidene

1.6.3.2.2 Cycloaddition reactions

Cycloadditions are the most versatile and well studied reaction of electrophilic phosphinidene complexes. Electrophilic phosphinidenes undergo cycloaddition with a wide range of unsaturated substrates. For example, with alkenes and alkynes, they undergo a (1+2) cycloaddition across the multiple bonds to form phosphirane and phosphirene rings respectively.51,68-70 These reactions are usually considered to be the
characteristic reactions of electrophilic phosphinidenes. Scheme 1.25 shows the [1+2] cycloaddition reaction of the phosphinidene phosphorus across an alkene double bond.

\[
\begin{align*}
\text{[R-P-M(CO)\textsubscript{6}]} + \text{H} = \text{H} &\rightarrow \text{H} \quad \text{H} \\
\text{R} &\quad \text{R} \\
\text{(OC)}\textsubscript{6}M &\quad \text{(OC)}\textsubscript{6}M
\end{align*}
\]

**Scheme 1.25** [1+2] cycloaddition reaction of electrophilic phosphinidene

These reactions take place with a complete retention of stereochemistry at the C=C double bond, which suggest a concerted mechanism.\(^{71}\) This is a common reaction for electrophilic phosphinidenes and can be used to check the effective formation of an electrophilic phosphinidene complex. A few of the characteristic cycloaddition reactions of the electrophilic terminal phosphinidene complexes are given in Scheme 1.26. Intramolecular cycloaddition reactions of electrophilic phosphinidene complexes have also been reported. An intramolecular cycloaddition for a phosphinidene complex bearing an olefinic substituent is shown in Scheme 1.27.\(^{72}\)
Though the phosphirane complexes are stable, in some cases unexpected ring openings or isomerisations have also been reported. For example, with vinyl bromide a migration of bromine from carbon to phosphorus occurs upon heating (Scheme 1.28).\textsuperscript{73}
Scheme 1.28 Ring opening reaction of phosphirane complex

The cycloaddictions can also be extended to hetero double bonds too. Scheme 1.29 shows the cycloaddition of a phosphinidene phosphorus into the carbonyl bond of an aldehyde.\textsuperscript{74}

Scheme 1.29 Cycloaddition of the phosphinidene phosphorous into the carbonyl bond

The reaction of terminal phosphinidenes with nucleophilic or weakly electrophilic carbene complexes results in a [1+2] cycloaddition across the transition metal carbon double bond. The transient metallophosphirane formed decomposes to give P=C double bonds (phosphaalkenes), resulting from a formal phosphinidene carbene coupling (Scheme 1.30).\textsuperscript{75}

Scheme 1.30 Reaction of phosphinidene with metal carbene
1.6.3.2.3 Reaction with nucleophiles

Electrophilic terminal phosphinidene complexes react with nucleophiles at the phosphinidene phosphorus. Nucleophilic attack of an electron rich phosphine on the phosphinidene phosphorus results the formation of a phosphine-coordinated phosphinidene. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectra of phosphine-coordinated phosphinidenes show a large P-P coupling constants ranging from 300 to 500 Hz.$^{76}$

The reaction of transient terminal phosphinidenes with trialkyl phosphines produces phosphine coordinated phosphinidene complexes with a polarized P-P bond, which can react with aldehydes, leading to phosphaalkene complexes (phospha-Wittig reaction, Scheme 1.31).$^{76}$

![Scheme 1.31 Reaction with nucleophilic phosphines](image)

Cationic phosphinidene complexes also react with alkyl phosphines. The aminophosphinidene complexes of Mo and W react with triethylphosphine. The initial attack takes place on the phosphinidene phosphorus, leading to an unstable phosphine coordinated phosphinidene complex, which upon warming to room temperature...
undergoes a carbonyl loss followed by migration of the phosphine to the metal. (Scheme 1.32). 77

Scheme 1.32 Reaction of cationic phosphinidene complexes with triethylphosphine

With bis-phosphines like bis-(dimethylphosphino)methane (dmpm), the reaction proceeds by a nucleophilic attack at the phosphinidene phosphorus by one end of the diphosphine, followed by carbonyl loss and coordination of the other end of the ligand to the metal. 77 This compound was isolated and characterized. X-ray crystallography shows the P-P bond distance 2.2664(8) Å, suggesting a single bond character and the $^{31}$P NMR shows a large P-P coupling constant of 506 Hz.

Scheme 1.33 Reaction of cationic terminal phosphinidene complexes with dppm
1.7 Rational and objectives

In synthetic organophosphorus chemistry, nucleophilic phosphinidene complexes may have more limited applications because most of their chemistry takes place across the reactive polarized M\(^{6+}\)-P\(^{δ-}\) double bond. On the other hand, the electron deficient \(p_z\) orbital of electrophilic phosphinidenes permits most of their chemistry to take place exclusively at the phosphinidene phosphorus, which enables the phosphinidene phosphorus to directly undergo bond forming reaction with a wide range of atoms or groups. As phosphorus-element bond formations are the major objective of this research, I chose to focus on the chemistry of electrophilic phosphinidenes.

The P-C, P-P, P-Si, P-Cl, P-Br, P-N and P-O bond forming reactions of neutral phosphinidene complexes are well described in the literature.\(^{66,68,76,78-80}\) However, the reactivity of cationic electrophilic phosphinidene complexes and their subsequent applications in chemical synthesis have not been well explored. Because of the positive charge, the phosphinidene center of cationic phosphinidene complexes is expected to be more electrophilic and therefore more reactive than their neutral counterparts. Cationic phosphinidene complexes can be readily generated under ambient reaction conditions, which allow us to perform the phosphinidene chemistry at room temperature or even lower.

Chloride abstraction is an efficient synthetic route to electrophilic phosphinidene complexes, but phosphinidene complexes formed via this route are thus far limited to aminophosphinidenes, which are stable and react only with electron rich substrates.\(^{52,80}\) Therefore, in order to expand the synthetic utility of electrophilic phosphinidene complexes, new cationic phosphinidene complexes with increased reactivity at the
phosphinidene center have to be developed. In order to meet this goal, it was decided to undertake the synthesis and reactivity of cationic phosphinidene complexes with new substituents, such as alkyl, Cl, OR and SR at the phosphinidene phosphorus. As these proposed cationic alkylphosphinidene complexes are not stabilized by a heteroatom, they are expected to be more reactive at the phosphinidene center and thereby more synthetically useful than the aminophosphinidene analogues.

The major objective of this research is to investigate the chemistry of cationic electrophilic terminal phosphinidene complexes and their application towards chemical synthesis. Consistent with this objective, my research will focus on two major themes. (I) Develop easily accessible and convenient synthetic methodologies to novel cationic terminal phosphinidene complexes. (II) Investigate the synthetic potential of these newly formed reactive phosphinidene species towards P-C, P-P, P-Si and P-X bond formations. The fundamental understanding of this chemistry may help us to develop new metal mediated synthetic routes to organophosphorus compounds.

1.8 Scope of this research

The chloride abstraction methodology will be extended to new cationic phosphinidene complexes by introducing other substituents at the phosphorus center. Chloroalkylphosphido complexes will be synthesized by substituting chloride of a dichlorophosphine (RPCl₂) with an electron rich anionic metal center, which will be then used as precursors to new cationic alkyl phosphinidene complexes. Cationic alkylphosphinidene complexes will be synthesized with the expectation that the replacement of the π donor amino substituent with an alkyl will increase the electrophilicity of the
resulting phosphinidene complex. The synthetic potential of these cationic alkyl-
phosphinidenes will then be examined towards P-C, P-P, P-Si and P-X bond formations
via the characteristic reactions of electrophilic phosphinidenes complexes such as
cycloadditions, nucleophilic substitutions and bond activation reactions. The reactivity of
the alkyl-phosphinidene will be compared with that of the aminophosphinidene analogue.

Terminal dichlorophosphido complexes (MPCl$_2$) will be examined as precursors
to cationic-chlorophosphinidene complexes, which can further provide products, such as
P-heterocycles and C-H activation products, containing a P-Cl bond ready for further
substitution. Terminal dichlorophosphido complexes may also have the potential to serve
as precursors to a range of functionalized chlorophosphido complexes via nucleophilic
substitution at the P-Cl bond. The reactivity of the dichlorophosphido complex will be
therefore investigated towards a range of nucleophiles. For example, the reactivity of the
dichlorophosphido will be investigated towards alkyl, alkoxy, aryloxy, alkynyl and
thiophenolate anions. These reactions are expected to generate new terminal alkyl, alkoxy
alkynyl and thiophenoxy chlorophosphido complexes. Chloride abstraction of the
resulting functionalized chlorophosphido complexes will then be performed to generate
corresponding cationic phosphinidene complexes. The reactivity of these newly generated
functionalized phosphinidene complexes will be examined and experimental and
computational studies will be carried out to determine the effects of different substituents
on phosphinidene reactivity.
CHAPTER 2

FORMATION AND REACTIVITY OF A TRANSIENT CATIONIC ALKYL PHOSPHINIDENE COMPLEX

2.1 INTRODUCTION

Over the last three decades, the chemistry of terminal phosphinidene complexes has been extensively studied by various research groups.\textsuperscript{38,40} The carbene like behavior of terminal phosphinidene complexes has been well established through their reactions towards a wide range of substrates, which in turn suggest their synthetic potential as building blocks for variety of organophosphorus compounds that are not otherwise easily accessible.\textsuperscript{38,40}

Neutral phosphinidene complexes have been extensively studied and their chemistry is well established. Most of their reactions, including cycloadditions, nucleophilic additions and bond activations are described in chapter I. Cationic phosphinidene complexes have been reported more recently, and their reactivity is not yet as well studied as that of the neutral phosphinidenes. Stable cationic aminophosphinidene complexes of Mo, W and Ru were first reported in 2001.\textsuperscript{52-55} They were formed via chloride abstraction from chloroaminophosphido complexes and are stabilized by N to P π donation. Although the electrophilicity on the phosphinidene phosphorus is reduced by the π donation from N, they still react as electrophiles. Later, analogous complexes of Fe, Os, Co and Re were also reported.\textsuperscript{52-55}

The reactivity of the stable aminophosphinidene complex [CpFe(CO)\textsubscript{2}{P(Ni-Pr\textsubscript{2})}][AlCl\textsubscript{4}] (II), generated from the chloroaminophosphido complex [CpFe(CO)\textsubscript{2}{P(Cl)Ni-Pr\textsubscript{2}}] (I) via chloride abstraction has been investigated towards a
range of substrates. The aminophosphinidene complex II reacts with alkenes and alkynes via (1+2) cycloaddition to form phosphirene and phosphirane complexes respectively (III and IV in Scheme 2.1).

Scheme 2.1 Reactivity of aminophosphinidene complex

The electrophilic insertion of the aminophosphinidene into the Si-H bonds of various silanes has also been reported by Sterenberg et al. The formation of corresponding silane phosphine complexes by reacting with primary, secondary and tertiary silanes are shown in Scheme 2.2. A computational study showed that the insertion occurs via a concerted mechanism with a triangular transition state.
In contrast to the transient neutral phosphinidenes W(CO)_5PR, which are generated by thermal decomposition of phosphanorbornadiene precursor complexes, the thermally stable and isolable aminophosphinidene complexes allow reactions to be carried out at room temperature or lower. However, the stability of these phosphinidenes that result from heteroatom π donation to phosphorus has the disadvantage of lowering the reactivity. Though, aminophosphinidene complexes provide a synthetic route to P-Si bonds via the Si-H activation, they are not reactive enough to activate C-H bonds.

Since C-H bond is strong and almost non-polar, it generally requires highly reactive reagents to activate. Transition metal complexes can activate C-H bonds via an oxidative addition. Carbon-hydrogen bond activation reactions are potentially important in C-C bond formation and several catalytic systems having different transition metals have been reported that use C-H activation to form C-C bonds.
Electrophilic phosphinidene complexes can activate C-H bonds via both intramolecular and intermolecular mechanism. Most of the reported C-H bond activations by electrophilic phosphinidene complexes are intramolecular.

An intramolecular insertion of the terminal phosphinidene into the C-H bonds was first reported by Cowley et al. The reaction is shown in Scheme 2.3.

Later, Mathey et al. reported the reactivity of electrophilic phosphinidenes with azobenzene. The reaction proceeds via a Lewis acid/base adduct formation followed by insertion into the ortho-C-H bonds, leading to the phosphine complex VIII (Scheme 2.4).

Carty et al. reported the similar reaction with the electrophilic phosphinidene complex \([\text{Re(CO)}_5\{\text{P(Ni-Pr}_2\}]}[\text{AlCl}_4]\) and obtained the benzodiazophosphole complex.
[Re(CO)_5{P(PhNNHC_6H_4)(Ni-Pr_2)}][AlCl_4] (IX) via ortho C-H activation (Scheme 2.5).^85

Scheme 2.5 Intramolecular C-H activation

However, intermolecular C-H bond activation of terminal electrophilic phosphinidene complexes is not well developed. There are only few phosphinidene complexes reported so far that activate C-H bonds directly. Mathey et al. reported an intermolecular insertion of the electrophilic terminal phosphinidene [Ph-P-W(CO)_5] into the C-H bond of the electron rich aromatic ring of ferrocene (Scheme 2.6).^72 All the attempts to generalize insertion of terminal phosphinidene complexes into the C-H bonds of other electron rich aromatic rings have been failed so far.
Inspired by the reactivity of the previously reported aminophosphinidene complexes, I decided to synthesize a cationic alkylphosphinidene complex and explore its reactivity towards bond activation reactions.

Nucleophilic phosphinidene complexes and neutral electrophilic phosphinidene complexes with alkyl and aryl substituents have already been reported.\textsuperscript{42,72} Roper et al. has reported the intermediacy of a cationic phenylphosphinidene complex of osmium.\textsuperscript{86} However, cationic alkylphosphinidene complexes have not been described, and their chemistry has not been explored so far.

2.1.1 Rational and objectives

As aminophosphinidene complexes are not electrophilic enough to activate stronger bonds like C-H and H-H, their electrophilicity at the phosphinidene center has to be further increased. This can be attained by introducing new substituents at the phosphinidene center. I was therefore interested in extending the synthetic methodology of aminophosphinidenes to the formation of a new cationic terminal phosphinidene complex with an alkyl substituent, with an expectation that replacement of the π-donor amino substituent with an alkyl substituent would eliminate the heteroatom stabilization and increase the electrophilicity of the resulting phosphinidene complex. Alkyl
phosphinidenes are expected to be highly electrophilic and should be capable of Si-H, C-H, and H-H bond activations, which may provide a new route to Si-P, C-P and H-P bonds. The major objective of this research is therefore to synthesize a new cationic alkylphosphinidene complex and investigate its reactivity towards bond activation and other conventional phosphinidene reactions.

The major topics discussed in this chapter are:

- Synthesis of a new alkyl phosphido complex.
- Generation of a transient cationic alkylphosphinidene complex by chloride abstraction from a chloro alkylphosphido complex.
- Demonstration of electrophilicity by (1+2) cycloaddition, coordination by nucleophiles and bond insertion reactions.

2.1.2 Scope of this research

A terminal chloroalkylphosphido complex will be synthesized by substituting chloride of a dichloroisoprolyl phosphine (i-PrPCl₂) with [Cp*Mo(CO)₃]. Chloride abstraction of the chloroisopropyl phosphido will be carried to generate the corresponding cationic isopropylphosphinidene complex. The generation of the alkylphosphinidene will then be confirmed by a trapping reaction with alkynes (e.g., diphenylacetylene). The electrophilicity at the phosphinidene center will be further examined by its reaction with nucleophilic phosphines. Phosphinidene insertion into acidic X-H bonds is well established. However, insertion into hydridic and non-polar X-H bonds has not been well studied. Since the alkylphosphinidene is expected to be more electrophilic than aminophosphinidenes, it may be reactive enough to activate C-H bonds. The bond
activation reaction of the alkylphosphinidene will be investigated with a range of substrates. Si-H bond activation will be studied by reacting alkylphosphinidene with secondary silanes. C-H bond activation by alkylphosphinidenes will be first studied with electron rich aromatic rings (e.g., ferrocene). The reactivity will then be further extended to other aromatic rings. The reactivity of the alkylphosphinidene will be compared with that of the aminophosphinidene analogue to show if the alkylphosphinidene is more electrophilic, as expected.

2.2 RESULTS AND COMPOUND CHARACTERIZATION

2.2.1 Formation of the isopropylphosphido complex

The precursor used for the generation of the transient isopropyl phosphinidene complex is the terminal chloroisopropylphosphido complex of molybdenum [Cp*Mo(CO)₃P(Cl)i-Pr] (1). The phosphido complex is formed by reacting the [Cp*Mo(CO)₃]⁻ anion with i-PrPCl₂ as shown in Scheme 2.7.

![Scheme 2.7 Synthesis of the chloroisopropylphosphido complex](image)

The addition of the anion to the dichlorophosphine solution was conducted at -80 °C, and for all subsequent steps, temperature was kept at 0 °C. The compound 1 was crystallized in hexane as orange crystals at -30 °C. The infrared spectrum of 1 shows three
sharp carbonyl stretching bands at 2006, 1945 and 1916 cm\(^{-1}\), clearly indicating that molybdenum retains three carbonyl ligands. The resulting electron count indicates that the phosphido ligand must be an anionic two-electron donor. The \(^{31}\)P \{\(^1\)H\}-NMR spectrum of 1 shows a singlet at \(\delta\) 268. The absence of an electronegative heteroatom like nitrogen makes the phosphido phosphorus more shielded than that of the previously reported di-isopropylaminophosphido (\(\delta\) 313).\(^{87}\)

### 2.2.2 Chloride abstraction

The chloride on the chloro isopropylphosphido ligand of complex 1 can be readily abstracted using AlCl\(_3\), but the abstraction of the chloride ion does not generate a stable phosphinidene. The \(^{31}\)P\{\(^1\)H\} NMR spectrum of the reaction solution shows a complex mixture. Attempts to observe a phosphinidene complex at low temperature were not successful. At temperatures below 0 °C, the chloride abstraction reaction from 1 was effectively suppressed. Above this temperature, decomposition of the phosphinidene is rapid, and only the decomposition products were observed. The instability of the phosphinidene 2 is not surprising, because of the absence of hetero atom substituents. The vacant orbital on phosphorus generated by chloride abstraction is not stabilized by \(\pi\) donation, making 2 a highly electrophilic species. I have therefore generated it \textit{in situ} in the presence of various trapping reagents.

### 2.2.3 Reaction of [Cp*Mo(CO)\(_3\)P(i-Pr)] (2) with diphenylacetylene

Reaction with alkyne to form phosphirene is a characteristic reaction of terminal phosphinidene complexes.\(^{88}\) In order to prove the intermediacy of [Cp*Mo(CO)\(_3\)P(i-
Pr)[AlCl₄] (2), the terminal chloro isopropyl phosphido 1 was allowed to react with AlCl₃ in presence of diphenylacetylene. As shown in Scheme 2.8, the reaction occurs readily at room temperature and results in a cycloaddition of transient phosphinidene with the triple bond of the diphenylacetylene to form the phosphirene complex [Cp*Mo(CO)₃{P(i-Pr)C(Ph)C(Ph)}][AlCl₄] (3). This reaction strongly supports the proposed formation of the transient electrophilic isopropyl phosphinidene.

\[
\text{Scheme 2.8 Reaction of } [\text{Cp}^*\text{Mo(CO)}_3\{\text{P(i-Pr)C(Ph)C(Ph)}\}][\text{AlCl}_4] \text{ with diphenylacetylene}
\]

The $^{31}$P {$^1$H} NMR spectrum of compound 3 shows a highly shielded phosphorus resonance at $\delta$ -106, which is characteristic for phosphirene complexes. The $^1$H NMR spectrum shows a doublet of doublets (dd) for the isopropyl methyl groups and a broad septet for the methine hydrogen of the isopropyl group. The IR spectrum of compound 3 shows three carbonyl stretching bands at 2035, 1970 and 1944 cm$^{-1}$. These peaks show a shift to the high frequency compared to those of the phosphido complex 1.

Single crystals were obtained by the slow diffusion of diethyl ether into dichloromethane solution and the structure was confirmed by single crystal X-ray crystallography (Figure 2.1). Compound 3 shows a four-legged piano stool geometry. Three legs are occupied by carbonyl ligands and the fourth by the phosphirene ligand.
phosphorus atom. The Mo-P bond length is 2.509(5) Å, which is typical for a Mo-P single bond.42 The P-C bond lengths in the phosphirene ring are 1.784(2) Å and 1.779(2) Å, and the C-C bond length is 1.329(3) Å, typical for a C-C double bond. The angles within the phosphirene ring are 43.78(9)°, 67.9(1)° and 68.3(1)°. The isopropyl group is oriented away from the Cp* ring and the methyl groups of the i-Pr ligand are oriented away from the metal.

![Figure 2.1 ORTEP diagram of [Cp*Mo(CO)₃{P(i-Pr)C(Ph)C(Ph)}][AlCl₄] (3). Hydrogen atoms and the counter ion have been omitted. Selected distances (Å) and angles (deg): Mo-P 2.5090(5), P-C4 1.779(2), P-C5 1.784(2), C4-C5 1.329(3), P-C5-C4 67.9(1), P-C4-C5 68.3(1), C4-P-C5 43.78(9).](image)

2.2.4 Reaction of [Cp*Mo(CO)₃P(i-Pr)] (2) with PPh₃

The electrophilicity of the isopropylphosphinidene 2 towards the moderately nucleophilic phosphine PPh₃ was examined. The phosphido complex [Cp*Mo(CO)₃P(i-
Pr)Cl] (1) was allowed to react with AlCl₃ in presence of PPh₃. The reaction occurs readily at room temperature as shown in the Scheme 2.9, resulting in a nucleophilic attack by the triphenyl phosphate at the phosphinidene phosphorus to form the phosphine coordinated phosphinidene complex \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P(PPh}_3\text{i-Pr})\}]\text{[AlCl}_4\text{]}\) (4). This reactivity contrasts with that of the analogous aminophosphinidene complex, which does not react with triphenylphosphine, although it reacts with more basic phosphines.⁷⁷

![Scheme 2.9 Reaction of \([\text{Cp}^*\text{Mo}(\text{CO})_3\text{P(i-Pr})]\) with triphenylphosphine](image)

The triphenylphosphine trapped complex 4 was spectroscopically characterized. The ³¹P{¹H} NMR of the compound 4 shows two doublets at δ 36.3 and -19.8 with a common ¹J_pp of 459 Hz. This large coupling constant indicates a direct P-P bond, and is comparable with the coupling constants 340-455 Hz observed in phosphine coordinated phosphonium ions⁵² and the 361-444 Hz coupling constants observed in phosphine coordinated phosphinidene complexes formed via the trapping of transient phosphinidene complexes with phosphines.⁶⁸,⁷⁷ The solution IR spectrum of the compound 4 shows three carbonyl-stretching bands at 2036, 1970(sh) and 1946 cm⁻¹ respectively. The band at 1970 cm⁻¹ is broad. As observed in the case of compound 3, the carbonyl stretching bands of 4 also show a shift to the high frequency compare to those of phosphido complex 1.

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The compound 4 was isolated as red crystals by the slow diffusion of hexane into dichloromethane solution and the structure was confirmed by single crystal X-ray crystallography (Figure 2.2). The geometry at the metal centre is again a four-legged piano stool with carbonyl ligands on the three legs and the phosphine coordinated-phosphinidene ligand on the other leg. The geometry at P1 is pyramidal with bond angles of 115.04(6)°, 103.47(6)°, and 116.35(2)°, indicating the presence of a stereoactive lone pair. The lone pair is directed towards the Cp* ring, allowing the isopropyl group and the PPh3 to point away from the Cp* ring. The geometry at P2 is tetrahedral and the P1-P2 bond distance is 2.163Å. This distance is closer to a P-P single bond (typically 2.21Å) than a P=P double bond (1.985-2.050 Å in diphosphenes). However, it is significantly shorter than the P-P bond lengths observed in the analogous phosphine coordinated amino phosphinidenes (2.215 – 2.266 Å). The shortening of the P-P bond in compound 4 may be due to the stronger Lewis acidity of the alkylphosphinidene 2, which forms a stronger and shorter bond with the phosphine Lewis base.
Figure 2.2 ORTEP diagram of [Cp*Mo(CO)₃{P(PPh₃)(i-Pr)}][AlCl₄] (4).
Hydrogen atoms and the counter ion have been omitted. Selected distances (Å) and angles (deg): Mo1-P1 2.5826(5), P1-P2 2.1630(6), P1-C4 1.890(2), Mo1-P1-P2 116.35(2), Mo1-P1-C4 115.04(6), C4-P1-P2 103.47(6).

2.2.5 Reaction of [Cp*Mo(CO)₃P(i-Pr)] (2) with PEt₃

After the observation of the desired reactivity 2 with moderately nucleophilic PPh₃, the reactivity of 2 was further investigated with a more basic triethylphosphine. Though PEt₃ is more basic than PPh₃, it does not react with 2 in the absence of a chloride abstractor. However, abstraction of the chloride from 2 in the presence of one equivalent of triethylphosphine leads to the triethylphosphine coordinated phosphinidene complex [Cp*Mo(CO)₃{P(PEt₃)(i-Pr)}][AlCl₄] (5) (Scheme 2.10). The $^{31}$P NMR spectrum of 5 shows two doublets at $\delta$ 42.2 and $\delta$ 23.7 with a common coupling constant of 432 Hz, which indicates the formation of a direct P-P bond.
2.2.6 Reaction of \([\text{Cp}^*\text{Mo}(\text{CO})_3\text{P}(i-\text{Pr})]\) (2) with dmpm

After the observation of the desired reactivity of 2 with \(\text{PPh}_3\) and \(\text{PEt}_3\), the reactivity of 2 was investigated with a bis-phosphine. The phosphido complex 1 was thus reacted with \(\text{AlCl}_3\) in presence of bis(dimethylphosphino)methane (dmpm). The previous studies on the reactivity of dmpm towards \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{PCl}(\text{N}(i-\text{Pr})_2)\}]\) had shown the formation of a phosphine coordinated phosphinidene complex.\(^{77}\) The phosphido complex \([\text{Cp}^*\text{Mo}(\text{CO})_3\text{P}(i-\text{Pr})\text{Cl}]\) (1) was allowed to react with \(\text{AlCl}_3\) in presence of dmpm. At room temperature, besides the formation of the expected phosphine coordinated phosphinidene complex, a metal coordinated phosphine complex was also observed. In order to avoid the phosphine substitution at the metal, the dmpm was added to the phosphido solution at -80 °C. The phosphido/phosphine solution was kept at -80 °C and then added to a flask containing \(\text{AlCl}_3\), which was at RT. The reaction occurs as shown in the Scheme 2.11, resulting in the formation \([\text{Cp}^*\text{Mo}(\text{CO})_2\{\text{P}(i-\text{Pr})\text{P}(\text{Me})_2\text{CH}_2\text{P}(\text{Me})_2\}^k_2,\text{P}^1\text{P}^4\}]\{\text{AlCl}_4\}\) (6) as the exclusive product (Scheme 2.11).
Scheme 2.11 Reaction of \([\text{Cp}^*\text{Mo(CO)}_3\text{P(i-Pr)}]\) with dmmp

The \(^{31}\)P NMR spectrum of 6 shows three resonances at \(\delta\) 34.1 (P\(^C\)), 27.2 (P\(^B\)) and -6.71 (P\(^A\)) (Scheme 2.2.4). A large one bond coupling of 366 Hz is observed between P\(^A\) and P\(^B\), while P\(^B\) and P\(^C\) show a two-bond P-P coupling of 56.2 Hz across the dmmp methylene group. Finally a two bond coupling of 6.0 Hz is observed between the two metal bound phosphorus atoms. The proton NMR spectrum of 6 shows a multiplet for the isopropyl methine at \(\delta\) 2.33 and the two diastereotopic methyl groups of the isopropyl unit appears as two doublets of doublets at \(\delta\) 1.04 and 0.98. The four-methyl groups of the dmmp ring show a broad multiplet at \(\delta\) 1.29. The solution IR spectrum of the compound 6 shows two carbonyl stretching bands at 1940 and 1869 cm\(^{-1}\), which clearly indicates the presence of two carbonyl ligands on the metal center.

Single crystals of 6 were obtained by the slow diffusion of hexane into the dichloromethane solution. X-ray crystallography was conducted and the ORTEP diagram of the compound is shown in Figure 2.3. The geometry at the metal centre is again a four-legged piano stool with a phosphine and a phosphine coordinated phosphinidene ligand on the two legs with a cisoid arrangement to each other. The two other legs are occupied by two carbonyl ligands. The molybdenum, the three phosphorus atoms and the methylene carbon form a deformed pentagonal ring. The Mo1-P1 distance of 2.5821(5)\(\text{Å}\)
is slightly longer than the Mo-P distance of 2.5430(7) Å in the previously reported di-isopropylamino analogues \([\text{Cp}^*\text{Mo(CO)}_2\{\text{P(N(i-Pr)}_2\text{P(Me)}_2\text{CH}_2\text{P(Me)}_2-\kappa^2, P^4}\}]^+.\) This distance is slightly longer than the Mo-P3 distance in the same complex 6 which is 2.4673(5) Å. The pyramidal geometry at the phosphinidene phosphorous P1 with bond angles Mo-P1-C3 = 116.06(7)°, Mo-P1-P2 = 107.84(2)°, C3-P1-P2 = 99.75(7)° clearly indicates the presence of a stereo active lone pair on the phosphinidene phosphorus. The P1-P2 distance of 2.1525(7) Å is closer to a P-P single bond distance\(^{89,90}\) but is considerably shorter than the P-P distance of 2.2664(8) Å in the diisopropylamino analogue.\(^77\) This shorter P-P bond in compound 6 is due to the high Lewis acidity of the phosphinidene phosphorous (P1). On the other hand, in the case of compound \([\text{Cp}^*\text{Mo(CO)}_2\{\text{P(N(i-Pr)}_2\text{P(Me)}_2\text{CH}_2\text{P(Me)}_2-\kappa^2, P^4}\}]^+,\) the electrophilicity of the phosphinidene phosphorus has been reduced to a great extend by \(\pi\) donation from the N atom. The P1-P2 distance of 2.1525(7) Å is slightly shorter than the P-P distance (2.1630(6) Å) observed in the triphenylphosphine trapped product 4. This shorter P-P bond length may be due to the greater Lewis basicity of dmpm.
Figure 2.3 ORTEP diagram of the cation of \([\text{Cp}^*\text{Mo(CO)}_2\{\text{P}(\text{i-Pr})\text{P}((\text{Me})_2\text{CH}_2\text{P(\text{Me})}_2\kappa^2,P^1P^4)\}][\text{AlCl}_4]\) (6). Hydrogen atoms and the counterion have been omitted. Selected distances (Å) and angles (deg): Mo1-P1 2.5821(5), Mo1-P3 2.4673(5), P1-P2 2.1525(7), Mo-P1-C3 116.06(7), Mo-P1-P2 107.84(2), C3-P1-P2 99.75(7).

2.2.7 Bond activation reactions

The reactivity of the cationic terminal isopropyl phosphinidene complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P}(\text{i-Pr})\}][\text{AlCl}_3]\) (2) with alkynes and phosphines clearly demonstrates the high electrophilicity at the phosphinidene phosphorus. Inspired by this result, I have investigated the possibilities for using compound 2 for bond activation reactions.

2.2.7.1 Si-H bond activation reactions

The reactivity of the isopropyl phosphinidene 2 towards a Si-H bond has been investigated by reacting the terminal chloroisopropyl phosphido 1 with AlCl₃ in the
presence of silanes. The phosphinidene complex 2 readily reacts with diphenylsilane and triethylsilane at room temperature, resulting in insertion of the phosphinidene phosphorus into the Si-H bonds, forming the silyl isopropyl secondary phosphine complexes \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P}(\text{SiEt}_3)(\text{i-Pr})\}][\text{AlCl}_4]\) (7) and \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P}(\text{SiHPh}_2)(\text{i-Pr})\}][\text{AlCl}_4]\) (8) respectively (Scheme 2.12).

Scheme 2.12 Reaction of \([\text{Cp}^*\text{Mo}(\text{CO})_3\text{P}(\text{i-Pr})]\) with silanes

The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 7 shows a singlet at \(\delta\) -72.7. The \(^1\text{H}\) NMR spectrum of 7 shows a doublet of doublet (dd) at \(\delta\) 4.67 which corresponds to the P-H. The large \(J_{P-H}\) coupling of 366 Hz indicates the direct P-H bond and the smaller coupling of 6 Hz is due to the three-bond coupling to the isopropyl C-H. The solution IR spectrum of 7 shows carbonyl stretching bands at 2039, 1980 and 1958 cm\(^{-1}\), indicating that the
three carbonyls on the starting phosphido are retained in the product. In addition, the Si-H stretch is observed as a broad band at 2100 cm$^{-1}$.

The $^{31}$P{$^1$H} NMR spectrum of compound 8 shows a singlet at $\delta$ -64.5 with $^{29}$Si satellites and a $^1J_{P,Si}$ of 26 Hz. The presence of the strongly electron donating isopropyl group and the relatively electropositive silyl and hydrogen groups shifts the P resonance to high field. The $^1$H NMR spectrum of compound 8 shows a doublet of doublet of doublet (ddd) at $\delta$ 4.35 which corresponds to the P-H. The large $^1J_{P,H}$ coupling of 327 Hz indicates the direct P-H bond. The smaller couplings of 4 Hz and 2 Hz are due to three-bond coupling to the silicon bound hydrogen and the isopropyl C-H respectively. The Si-H resonance appears at $\delta$ 5.54 as a doublet of doublets with a couplings of 29 Hz to phosphorus and 4 Hz to the P-H. The proton NMR shows additional peaks for the phenyl groups, the cyclopentadienyl ligand and the isopropyl group. The solution infrared spectrum of 8 shows three carbonyl stretching bands at 2051, 1988 and 1966 cm$^{-1}$, indicating that the three carbonyls on the starting phosphido are retained in the product. In addition, the Si-H stretch is observed as a broad band at 2171 cm$^{-1}$.

Single crystals of 8 were obtained by the slow diffusion of hexane into a dichloromethane solution. X-ray crystallography was conducted and the ORTEP diagram of the compound is shown in Figure 2.4. The geometry at the metal centre is again a four legged piano stool with three carbonyl ligands and one isopropyl-silyl secondary phosphine. The Mo-P1 bond length is 2.533(1)Å, which is close to the Mo-P distance observed in the acetylene and phosphine trapped complexes 3 and 4. The P1-Si1 bond length is 2.296(2)Å, which is typical for a P-Si single bond. Both P and Si are tetrahedral and the substituents staggered, with the two hydrogen substituents in relative
gauche position (dihedral angle 79.6°). The groups on P are oriented such that the large SiHPh₂ group is directed away from Cp*. The two-phenyl groups on the silane fragments are mutually perpendicular and oriented away from the isopropyl group.

![ORTEP diagram](image)

**Figure 2.4** ORTEP diagram of [Cp*Mo(CO)₃{P(H)(SiHPh₂)(i-Pr)}][AlCl₄] (8). Hydrogen atoms other than Si-H and P-H, and the counter ion have been omitted. Selected distances (Å) and angles (deg): Mo1-P1 2.533(1), P1-Si1 2.296(2), Mo1-P1-C4 118.7(2), Mo1-P1-Si1 117.70(7), Si1-P1-C4 105.9(2).

### 2.2.7.2 C-H bond activation

*In situ* generation of the terminal isopropylphosphinidene 2 in the presence of one equivalent of ferrocene resulted in electrophilic insertion of the phosphinidene phosphorus into the C-H bond of the ferrocene to form the ferrocenylisopropylphosphine
complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(H)}(i-\text{Pr})(\text{C}_{10}\text{H}_9\text{Fe})\}][\text{AlCl}_4]\) (9) (Scheme 2.13). The insertion reaction is fast at room temperature.

\[ \text{Scheme 2.13 Reaction of } [\text{Cp}^*\text{Mo(CO)}_3\text{P}(i-\text{Pr})] \text{ with ferrocene} \]

The \(^{31}\text{P}\) NMR spectrum shows a singlet at \(\delta 17.2\). The \(^1\text{H}\) NMR spectrum shows a doublet at \(\delta 5.73\) that corresponds to the P-H. The large coupling of 378 Hz indicates the direct P-H bond. The five hydrogen atoms of the free cyclopentadienyl moiety of ferrocene form a singlet at \(\delta 4.31\). The phosphine bound cyclopentadienyl moiety of ferrocene has four hydrogen environments, showing singlets at \(\delta 4.58\) (1H), 4.55 (2H) and 4.27 (1H). The \(^1\text{H}\) NMR also shows additional peaks for Cp* (singlet at \(\delta 1.87\)), two overlapped doublet of doublets at \(\delta 1.37\) and 1.30 for the two diastereotopic methyl groups of the isopropyl unit and a broad septet at \(\delta 3.17\) for the methine proton. Although compound 9 could not be structurally characterized, strong support for the proposed structure comes from the electrospray mass spectrum, which shows an isotope pattern with a base peak at \(m/z = 575\) (\(\text{C}_{26}\text{H}_{32}\text{O}_{35}^{56}\text{FeP}^{98}\text{Mo}\)) that corresponds to the predicted masses for the cation of the product (Figure 2.5). The solution infrared spectrum shows three carbonyl-stretching bands at 2056, 2043 and 1972 cm\(^{-1}\), clearly indicating that the three-carbonyl ligands of starting phosphido 1 are retained in the product. The reactivity
of the alkylphosphinidene 2 was then investigated with other aromatic compounds such as toluene and anisole. However, the transient alkylphosphinidene 2 does not activate the C-H bond of these compounds as expected.

![Image of calculated and experimental isotope pattern for the molecular ion peak of [Cp*Mo(CO)\_3{P(H)(i-Pr)(C\textsubscript{10}H\textsubscript{9}Fe)}\}_]{(9)}.

**Figure 2.5** Calculated and experimental isotope pattern for the molecular ion peak of [Cp*Mo(CO)\_3{P(H)(i-Pr)(C\textsubscript{10}H\textsubscript{9}Fe)}\] (9).

### 2.3 DISCUSSION

The bonding in electrophilic phosphinidene complexes is best conceptualized by considering them to be derived from the singlet state of free phosphinidene, which contains two lone pairs and an empty p\_z orbital. One lone pair forms a σ-donor interaction to the transition metal while the second lone pair remains stereoactive, leading to the bent geometry at phosphorus. The electrophilicity at P results from the empty p\_z orbital. In aminophosphinidene complexes, this empty p\_z orbital is stabilized by π-donation from the heteroatom substituent and from filled metal d orbitals (Figure 2.6). The heteroatom stabilization of terminal electrophilic phosphinidene complexes is analogous to the heteroatom stabilization of Fischer carbenes, and accounts for the fact that the only
known stable terminal electrophilic phosphinidene complexes are aminophosphinidenes. In contrast, the empty \( p_z \) orbital in an electrophilic alkyl phosphinidene complexes is only stabilized by metal-to-phosphorus back donation. Since the \( \text{Cp}^*\text{Mo(CO)}_3 \) fragment is cationic and relatively electron poor, the alkyl phosphinidene complex described here is expected to be strongly electrophilic because there is little electronic stabilization of the empty \( p_z \) orbital.

![Diagram of bonding in aminophosphinidene and alkylphosphinidene](image)

**Figure 2.6** Bonding in aminophosphinidene and alkylphosphinidene

The trapping reaction of the phosphinidene with diphenylacetylene results the formation of an expected phosphirene complex. This is a characteristic reaction for a terminal electrophilic phosphinidene. In the phosphine trapping reactions, the isopropyl phosphinidene is more reactive than its aminophosphinidene analog. In contrast with aminophosphinidenes, the isopropyl phosphinidene shows a clean and fast reaction with \( \text{PPh}_3 \) resulting in the formation of a phosphine-coordinated phosphinidene complex. The
higher reactivity of the isopropyl phosphinidene 2 suggests the higher electrophilicity at the phosphinidene phosphorus that results from the lack of a π donor substituent. The X-ray data of these phosphine-coordinated phosphinidenes support the high Lewis acidity at the phosphinidene phosphorus. The P-P bond observed in the PPh₃ and dmpm adducts are significantly shorter and stronger than any of the structurally characterized phosphine coordinated aminophosphinidene analogs.⁵⁵,⁷⁷

X-H bond activation reactions are characteristic reactions of terminal electrophilic phosphinidene complexes. These reaction occur either by initial coordination to P followed by proton transfer, or by a concerted mechanism. Here, I have shown that Si-H bond can be activated by the transient alkyl phosphinidene complex, resulting in insertion of the phosphinidene P atom into the Si-H bond. This reaction most likely proceeds through a concerted mechanism, because the same reactivity has previously been demonstrated with aminophosphinidenes, and is expected for the alkyl phosphinidene too.

In contrast to aminophosphinidenes, the alkyl phosphinidene is also capable of activating the CH bond of ferrocene. The greater reactivity towards C-H bonds reflects the alkyl phosphinidene’s greater electrophilicity. However, this cationic phosphinidene is still not sufficiently electrophilic to activate C-H bonds other than those of ferrocene. I have investigated the reactivity of this isopropyl phosphinidene toward the C-H bonds present in other compounds such as toluene and anisole, but the electrophilicity was not sufficient to activate the C-H bonds of these compounds. The reactivity of the cationic alkyl phosphinidene complex 2 toward ferrocene suggests that its electrophilicity is similar to that of the well-studied transient phosphinidene complexes [W(CO)₅(PPh)], which behave similarly toward ferrocene and also fail to activate other C-H bonds.⁷²
However, while most of the reported C-H bond activations by terminal phosphinidene complexes require prolonged reaction conditions, the cationic alkylphosphinidene complex 2 reacts rapidly at room temperature. Thus, the donor ability of the Cp* ligand in 2, which is expected to decrease electrophilicity at P, is offset by the positive charge on the complex, which increases electrophilicity.

Direct C-H activation by electrophilic phosphinidene complexes has potential as a synthetic tool for P-C bond formation. Intramolecular C-H activation has been described. However, examples of direct intermolecular C-H activation are limited to activation of the C-H bonds in ferrocene. In order to develop C-H activation by terminal electrophilic phosphinidene complexes into a useful synthetic tool, the electrophilicity of the phosphinidene must be furthered increased to extend the range of potential substrates.

2.4 CONCLUSIONS

I have shown that a transient cationic alkyl phosphinidene complex can be generated by chloride abstraction from a chloro alkyl phosphido complex. This is the first cationic alkyl phosphinidene complex to be described. The intermediacy of this alkyl phosphinidene has been confirmed from the trapping reaction with diphenylacetylene. As expected, it reacts as an electrophilic phosphinidene, and we have demonstrated examples of three characteristic reactions of electrophilic phosphinidenes: (1+2) cycloaddition, coordination by nucleophiles, and bond insertion reactions. The ability of the alkyl phosphinidene to activate the C-H bond in ferrocene clearly demonstrates that alkyl phosphinidene are more electrophilic than the corresponding aminophosphinidenes.
2.5 EXPERIMENTAL

2.5.1 General Comments

All procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in an inert atmosphere glove box. THF was distilled from Na/benzophenone. Dichloromethane and hexane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper oxide catalyst (hexane). Deuterated chloroform was distilled from P₂O₅. The NMR spectra were recorded in CDCl₃ using a Varian Mercury 300 NMR spectrometer operating at 300.179 MHz (¹H), 121.515 MHz (³¹P{¹H}), 75.47 MHz (¹³C{¹H}). Infrared spectra were recorded in THF, CH₂Cl₂ or hexane using a Digilab FTIR spectrophotometer. Mass spectra of metal complexes were carried out using a Finnigan-Matt TSQ-700 mass spectrometer equipped with electro spray ionization and a Harvard syringe pump. Dichloroisopropyl phosphine (Aldrich), Mo(CO)₆ (Aldrich or Alfa Aesar), butyllithium (Aldrich), cyclopentadiene (Strem), phenylacetylene (Aldrich), triphenylphosphine (Aldrich), triethylphosphine (Aldrich), dmpm (Strem), triethylsilane (Aldrich), diphenylsilane (Aldrich), ferrocene (Aldrich), sodium tetraphenyl borate (Aldrich) were directly purchased and used without purification. AlCl₃ (Aldrich) was purified by sublimation before use.

2.5.2 Synthesis of [Cp*Mo(CO)₃{P(Cl)i-Pr}] (1)

This compound was prepared using a modification of the method developed by Senturk et al. To pentamethylcyclopentadiene (0.52 g, 3.8 mmol, 0.60 mL) in 50 mL of THF was added n-butyl lithium (1.5 mL of 2.5 M solution in hexane, 3.8 mmol). Molybdenum
hexacarbonyl (1.00 g, 3.78 mmol) was then added and the resulting suspension was heated under reflux for 12 h, resulting in an orange solution of Li[Cp*Mo(CO)₃]. This solution was added in small portions to a solution of dichloroisopropylphosphine (0.93 mL, 7.5 mmol) in 50 mL THF at -80 °C. The reaction mixture was stirred for 30 min at -80 °C and then warmed to 0 °C. The solvent was removed under vacuum at 0 °C. The dark red residue obtained was extracted into pentane (25 mL). The pentane was removed under vacuum at 0 °C and the oily red residue obtained was dissolved in a minimum amount hexane. The dark red hexane solution was then cooled to -30 °C for 24 h, resulting in the formation of large orange crystals. Yield: 890 mg, 56%, IR (hexane solution, cm⁻¹, ν(CO)): 2007, 1945, 1916. 

P{¹H} NMR: δ 268.7, ¹H NMR (25 °C): δ 2.31 (d sept, 1H, ²J_HP = 27.9 Hz, ³J_HH = 7 Hz, CH(CH₃)₂), 1.96 (s, 15H, C₅(CH₃)₅), 1.37 (dd, 3H, ³J_HP = 23.4 Hz, ³J_HH = 7.2 Hz, CH(CH₃)₂). ¹³C NMR: δ 236.8 (d, ²J_CP = 9 Hz, MoCO), 229.1 (s, MoCO), 225.0 (s, MoCO), 106.6 (s, C₅(CH₃)₅), 36.4 (d, ¹J_CP = 47 Hz, PCH(CH₃)₂), 22.7 (d, ²J_CP = 18 Hz, PCH(CH₃)₂), 21.3 (d, ²J_CP = 3 Hz, PCH(CH₃)₂), 10.6 (d, J_CP = 6 Hz, C₅(CH₃)₅). Anal. Calcd for C₁₆H₂₂O₃PClMo: C, 45.25; H, 5.22. Found: C, 45.06; H, 5.34.

### 2.5.3 Synthesis of [Cp*Mo(CO)₃{P(i-Pr)C(Ph)C(Ph)}][AlCl₄] (3)

[Cp*Mo(CO)₃{P(i-Pr)Cl}] (1) (20 mg, 0.047 mmol) and diphenylacetylene (17 mg, 0.017 mmol) were dissolved in CH₂Cl₂ (0.5 mL). The resulting solution was added to AlCl₃ (12.6 mg, 0.094 mmol) at room temperature, resulting in a color change from pale yellow to dark red. The product was isolated as orange crystals by the slow diffusion of diethyl ether into the CH₂Cl₂ solution. Yield: 21 mg, 63%. IR (cast, cm⁻¹, ν(CO)): 2035, 1970,
1944. $^{31}$P($^1$H) NMR: $\delta$ -106.9. $^1$H NMR: $\delta$ 7.9-7.3 (multiplets, Ph), 2.28 (septet, 1H, $^2$J$_{HH}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.66 (s, 15H, Cp*), 0.93 (dd, 6H, $^2$J$_{HP}$ = 21.0 Hz, $^3$J$_{HH}$ = 7.2 Hz, CH(CH$_3$)$_2$). $^{13}$C NMR: $\delta$ 229.3 (d, $^2$J$_{CP}$ = 3 Hz, MoCO), 229.2 (d, $^2$J$_{CP}$ = 36 Hz, MoCO), 132.5 (s, Ph), 131.7 (s, Ph), 130.7 (d, $^3$J$_{CP}$ = 6 Hz, ipso-Ph), 125.7 (d, $^1$J$_{CP}$ = 14 Hz, phosphirene ring C), 109.4 (s, C$_5$(CH$_3$)$_5$), 39.8 (d, $^1$J$_{CP}$ = 8 Hz, PCH(CH$_3$)$_2$), 20.3 (d, $^2$J$_{CP}$ = 2 Hz, PCH(C$_5$H$_3$)$_2$), 10.9 (s, C$_5$(CH$_3$)$_5$. MS (electrospray, CH$_2$Cl$_2$ solution): $m/z$ = 563-572 (M$^+$ isotope pattern, base peak at $m/z$ = 569). Anal. Calcd for C$_{30}$H$_{32}$O$_3$PAlCl$_4$Mo: C, 48.94; H, 4.38. Found: C, 48.59; H, 4.42.

2.5.4 Synthesis of [Cp*Mo(CO)$_3$P(PPh$_3$i-Pr)][AlCl$_4$] (4)

Cp*Mo(CO)$_3$P(i-Pr)Cl (1) (20 mg, 0.047 mmol) and PPh$_3$ (19 mg, 0.071 mmol) were dissolved in CH$_2$Cl$_2$ (0.5 ml). The resulting solution was added to AlCl$_3$ (9 mg, 0.071 mmol) resulting in an immediate color change from yellow to dark red. The solvent was removed in vacuum and the residue was extracted into CH$_2$Cl$_2$ (0.5 mL) and crystallized as dark red crystals by slow diffusion of hexane into the CH$_2$Cl$_2$ solution. Yield: 30 mg, 77%. IR (CH$_2$Cl$_2$ solution., cm$^{-1}$, ν(CO)): 2056, 1975. $^{31}$P($^1$H) NMR: $\delta$ 36.38 (d, $^1$J$_{PP}$ = 459.3 Hz, MoPP), -19.88 (d, $^1$J$_{PP}$ = 459.2 Hz, MoPP). $^1$H NMR: $\delta$ 7.85-7.60 (multiplets, Ph), 2.17 (m, CH(CH$_3$)$_2$), 1.93 (s, 15H, Cp*), 1.09 (ddd, 6H, $^3$J$_{HP}$ = 15.6 Hz, $^3$J$_{HH}$ = 6.9 Hz, $^4$J$_{HP}$ = 0.9 Hz, CH(CH$_3$)$_2$). $^{13}$C NMR: $\delta$ 228.3 (d, $^2$J$_{CP}$ = 26 Hz, MoCO), 226.6 (s, MoCO), 225.4 (s, MoCO), 134.1 (dd, J$_{CP}$ = 9 Hz, J$_{CP}$ = 3 Hz, Ph), 133.9 (s, Ph), 130.0 (d, J$_{CP}$ = 12 Hz, Ph), 123.7 (dd, $^1$J$_{CP}$ = 67 Hz, $^2$J$_{PC}$ = 8 Hz, ipso-Ph), 109.4(s, C$_5$(CH$_3$)$_5$), 28.6 (dd, $^1$J$_{CP}$ = 28 Hz, $^2$J$_{CP}$ = 2 Hz, PCH(CH$_3$)$_2$), 25.1 (d, $^2$J$_{CP}$ = 8 Hz, PCH(CH$_3$)$_2$), 25.0 (d,
$J_{CP} = 8$ Hz, $PCH(CH_3)_2$. 10.8 (d, $J_{CP} = 6$ Hz, $C_5(CH_3)_5$). Anal. Calcd. for $C_{34}H_{32}O_3P_2AlCl_4Mo$: C, 49.78; H, 4.55. Found: C, 49.51; H, 4.75.

2.5.5 Synthesis of $[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(PEt}_3\text{i-Pr)}\}]\text{[AlCl}_4\text{]}$ (5)

$[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(i-Pr)}\text{Cl}\}]$ (1) (20 mg, 0.047 mmol) was dissolved in CH$_2$Cl$_2$ (5.0 mL) and PEt$_3$ (3.50 mg, 4.70 µL, 0.047 mmol) was added to this phosphido solution at -80 °C. The phosphido/phosphine solution at -80 °C was then transferred via cannula to a flask containing AlCl$_3$ (9.40 mg, 0.070 mmol), which was at room temperature, and stirred for 30 min, resulting in a color change from yellow to red. The reaction solution was then concentrated to 0.5 mL and 10 mL of pentane was added to the concentrated solution with rapid stirring, resulting in the precipitation of a dark red oily residue. The residue was washed several times with pentane and dried under vacuum overnight. Yield = 14.7 mg, 55%. $^{31}$P NMR: δ 42.2 (d, $^1J_{PP} = 432.4$ Hz, MoPPET$_3$), -23.8 (d, $^1J_{PP} = 432.4$ Hz, MoPPEt$_3$). $^1$H NMR: 2.38, broad multiplets, 9H, $PCH(\text{CH}_3)_2$), 2.16, multiplets, 6H, PCH$_2$CH$_3$), 1.98 (s, 15H, $C_5(\text{CH}_3)_5$), 1.36 (multiplets, CH(CH$_3)_2$).

2.5.6 Synthesis of $[\text{Cp}^*\text{Mo(CO)}_2\{\text{P(i-Pr)}\text{P(Me)}_2\text{CH}_2\text{P(Me)}_2-\kappa^2p_1,p^4\}]\text{[AlCl}_4\text{]}$ (6)

$[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(i-Pr)}\text{Cl}\}]$ (1) (20 mg, 0.047 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and dmpm (13 mg, 15 µL, 0.094 mmol) was added to this phosphido solution at -80 °C. The resultant solution was transferred via cannula to a flask containing AlCl$_3$ (12.6 mg, 0.094 mmol) at room temperature, and stirred for 2 h, resulting in a color change from yellow to red. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and the residue obtained was dissolved in
dichloromethane. The product was isolated as yellow crystals by slow diffusion of hexane into the CH$_2$Cl$_2$ solution. Yield: 21 mg, 68%. IR (CH$_2$Cl$_2$ soln., cm$^{-1}$, ν(CO)): 1940, 1869. $^{31}$P{$^1$H}NMR: δ 34.1 (dd, $^2$J$_{PP}$ = 56.2 Hz, $^2$J$_{PP}$ = 6.0 Hz, PMoPP), 27.2 (dd, $^1$J$_{PP}$ = 366 Hz, $^2$J$_{PP}$ = 56.2 Hz, MoPCH$_2$P), -6.71 (dd, $^1$J$_{PP}$ = 368 Hz, $^2$J$_{PP}$ = 5.92 Hz, PMoPP), $^1$H NMR: δ 2.33 (multiplets, 1H, C$_3$H$_2$(CH$_3$)$_2$). 1.79 (S, 15H, Cp*), 1.29 (multiplets, 12H, P(CH$_3$)$_2$), 1.04 (dd, 3H, $^3$J$_{HP}$ = 9.0 Hz, $^3$J$_{HH}$ = 3.0 Hz, CH$_3$), 0.98 (dd, 3H, $^3$J$_{HP}$ = 9.0 Hz, $^3$J$_{HH}$ = 3.0 Hz, CH$_3$), MS (electrospray, CH$_2$Cl$_2$ solution) m/z = 492-502 (M$^+$ isotope pattern, base peak at m/z = 496). Anal. Calc for C$_{20}$H$_{36}$O$_2$P$_3$Mo$_1$AlCl$_4$: C, 36.0; H, 5.45. Found: C, 35.4; H, 5.70.

2.5.7 Synthesis of [Cp*Mo(CO)$_3${P(H)(SiPEt$_3$)(i-Pr)}][AlCl$_4$] (7)

[Cp*Mo(CO)$_3${P(i-Pr)Cl}] (1) (20 mg, 0.047 mmol) was dissolved in CH$_2$Cl$_2$ (5.0 ml) and SiH(Et$_3$) (11.2 μL, 0.072 mmol) was added. The resulting solution was mixed well and added to AlCl$_3$ (9.4 mg, 0.070 mmol), resulting a color change from yellow to dark red. The solvent volume was reduced to ~2 mL, and pentane (10 mL) was added to the concentrated reaction solution with rapid stirring, resulting in the formation of a dark red oil. The supernatant was decanted and the oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 17 mg, 54 %. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, ν(CO)) = 2039, 1980, 1958, ν(SiH) = 2100. $^{31}$P{$^1$H} NMR: δ -72.7. $^1$H NMR: δ 4.63 (dd, 1H, $^1$J$_{PP}$ = 366 Hz, $^3$J$_{HP}$ = 9.0 Hz, P-H), 2.42 (multiplets, 1H, CH(CH$_3$)$_2$), 2.03 (s, 15H, Cp*), 1.40 (dd, 3H, $^3$J$_{HP}$ = 15 Hz, $^3$J$_{HH}$ = 6.0 Hz, CH(CH$_3$)), 1.25 (dd, 3H, $^3$J$_{HP}$ = 21.0 Hz, $^3$J$_{HH}$ = 9.0 Hz, CH(CH$_3$)), 0.91 (t, 9H, $^3$J$_{HH}$ = 9.0 Hz, SiCH$_2$CH$_3$), 0.52 (dq, 6H, $^3$J$_{HP}$ = 9 Hz, $^3$J$_{HH}$ = 3.0 Hz, SiCH$_2$CH$_3$)).
2.5.8 Synthesis of $[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(H)(SiHPh}_2\}(\text{i-Pr})]\) (8)

$[\text{Cp}^*\text{Mo(CO)}_3\{\text{P(\text{i-Pr})Cl}\} \text{(1)} \text{ (20 mg, 0.047 mmol) was dissolved in CH}_2\text{Cl}_2 \text{ (5.0 ml) and SiH}_2\text{(Ph)}_2 \text{ (17 }\mu\text{L, 0.094 mmol) was added. The resulting solution was mixed well and added to AlCl}_3 \text{ (9.0 mg, 0.071 mmol), resulting in a colour change from yellow to dark red. The solvent was removed in vacuum and the residue was extracted into CH}_2\text{Cl}_2 \text{ (0.5 mL) and crystallized as pale yellow crystals by slow diffusion of hexane into the CH}_2\text{Cl}_2 \text{ solution. Yield: 29 mg, 82%. IR (CH}_2\text{Cl}_2 \text{ solution, cm}^{-1}, \nu(\text{CO}): = 2051, 1988, 1966, \nu(\text{SiH}) = 2171. ^{31}\text{P}\{^1\text{H}\} \text{ NMR: } \delta -64.5. ^1\text{H NMR: } 7.80-7.44 \text{ (m, Ph), } \delta 5.54 \text{ (ddd, 1H, }^2\text{J}_{\text{HP}} = 29 \text{ Hz, }^3\text{J}_{\text{HH}} = 4 \text{ Hz, }^3\text{J}_{\text{HH}} = 2 \text{ Hz, Si-H)}, 4.35 \text{ (dd, }^1\text{J}_{\text{HP}} = 327 \text{ Hz, }^3\text{J}_{\text{HH}} = 4 \text{ Hz, P-H}), 2.48 \text{ (m, CH(CH}_3)_2 \text{ ), } 2.04 \text{ (s, 15H, Cp}^\text{a}), 1.29 \text{ (dd, 3H, }^3\text{J}_{\text{HP}} = 9.9 \text{ Hz, }^3\text{J}_{\text{HH}} = 7.4 \text{ Hz, CH(CH}_3)_2 \text{), } 1.22 \text{ (dd, }^3\text{J}_{\text{HP}} = 13.0 \text{ Hz, }^3\text{J}_{\text{HH}} = 7.2 \text{ Hz, CH(CH}_3)_2 \text{).} ^{13}\text{C}\{^1\text{H}\} \text{ NMR: } \delta 231.5 \text{ (s, MoCO), } 228.4 \text{ (d, }^2\text{J}_{\text{CP}} = 26 \text{ Hz, MoCO), } 227.3 \text{ (d, }^2\text{J}_{\text{CP}} = 24 \text{ Hz, MoCO), } 136.3 \text{ (d, }^1\text{J}_{\text{CP}} = 2 \text{ Hz, Ph), } 136.1 \text{ (d, }^1\text{J}_{\text{CP}} = 2 \text{ Hz, Ph), } 135.8 \text{ (s, Ph), } 134.7 \text{ (s, Ph), } 132.43 \text{ (s, Ph), } 132.39 \text{ (s, Ph), } 131.4 \text{ (s, Ph), } 130.1 \text{ (s, Ph), } 129.5 \text{ (s, Ph), } 129.4 \text{ (s, Ph), } 128.5 \text{ (s, Ph), } 128.3 \text{ (s, Ph), } 108.6 \text{ (s, C}_5\text{(CH}_3)_5 \text{), } 26.4 \text{ (d, }^1\text{J}_{\text{CP}} = 18 \text{ Hz, PCH(CH}_3)_2 \text{), } 25.5 \text{ (d, }^2\text{J}_{\text{CP}} = 6 \text{ Hz, PCH(CH}_3)_2 \text{), } 20.3 \text{ (d, }^2\text{J}_{\text{CP}} = 2 \text{ Hz, PCH(CH}_3)_2 \text{), } 11.0 \text{ (s, C}_5\text{(CH}_3)_5 \text{). Note: the silyl phosphine complex is extremely sensitive to Si-P bond cleavage. As a result, satisfactory elemental analysis for 8 could not be obtained, as bulk samples always contain decomposition products (see reference 80) for a discussion of the Si-P cleavage mechanism in related silyl phosphines).}
2.5.9 Synthesis of \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(H)(i-Pr)}(\text{C}_{10}\text{H}_9\text{Fe})\}]\)[\text{AlCl}_4]\) (9)

\([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(i-Pr)}\text{Cl}\}]\) (1) (20 mg, 0.047 mmol) and ferrocene (8.8 mg, 0.047 mmol) were dissolved in CH\(_2\)Cl\(_2\) (5.0 mL). The resulting solution was added to AlCl\(_3\) (9.5 mg, 0.071 mmol), resulting in an immediate color change from yellow to dark red. The solvent was removed in vacuum and the residue was extracted into CH\(_2\)Cl\(_2\) (0.5 mL) and crystallized as orange crystals by slow diffusion of diethyl ether into the CH\(_2\)Cl\(_2\) solution. Yield: 30 mg, 85%. IR (CH\(_2\)Cl\(_2\) solution, cm\(^{-1}\), \(\nu(\text{CO})\)): 2055, 2043, 1972.

\(^{31}\text{P}\{^1\text{H}\}\text{NMR:}\) 17.2 (s).

\(^1\text{H}\) NMR: \(\delta\) 5.73 (d, 1H, \(^1J_{\text{PH}} = 378\) Hz, \(\text{P-}\text{H}\)), 4.58 (s, 1H, \(\text{Cp}\)), 4.55 (s, 2H, \(\text{Cp}\)), 4.31 (s, 5H, \(\text{Cp}\)), 4.27 (s, 1H, \(\text{Cp}\)), 3.17 (septet, 1H, \(\text{CH(CH}_3)_2\)), 1.87 (s, 15H, \(\text{Cp}^*\)), 1.37 (dd, 3H, \(^3J_{\text{PH}} = 12\) Hz, \(^3J_{\text{HH}} = 9\) Hz, \(\text{C}_5\text{H}_3\)), 1.30 (dd, \(^3J_{\text{PH}} = 12\) Hz, \(^3J_{\text{HH}} = 9\) Hz, \(\text{C}_5\text{H}_3\)).

\(^{13}\text{C}\{^1\text{H}\}\text{NMR:}\) \(\delta\) 231.1 (s, \(\text{MoC=O}\)), 229.1 (d, \(^2J_{\text{CP}} = 27\) Hz, \(\text{MoC=O}\)), 228.3 (s, \(\text{MoC=O}\)), 108.6 (s, \(\text{C}_5\text{(CH}_3)_3\)), 74.1 (d, \(J_{\text{CP}} = 9\) Hz, \(\text{C}_5\text{H}_4\text{P}\)), 73.1 (d, \(^1J_{\text{CP}} = 46\) Hz, \(\text{C}_5\text{H}_4\text{P}\)), 73.0 (d, \(J_{\text{CP}} = 8.3\) Hz, \(\text{C}_5\text{H}_4\text{P}\)), 71.7 (d, \(J_{\text{CP}} = 14.8\) Hz, \(\text{C}_5\text{H}_4\text{P}\)), 71.3 (d, \(J_{\text{CP}} = 8.3\) Hz, \(\text{C}_5\text{H}_4\text{P}\)), 70.6 (s, \(\text{FeC}_5\text{H}_5\)), 33.3 (d, \(^1J_{\text{CP}} = 31\) Hz, \(\text{PCH(CH}_3)_2\)), 20.8 (d, \(^2J_{\text{CP}} = 26\) Hz, \(\text{PCH(CH}_3)_2\)), 16.1 (d, \(^2J_{\text{PC}} = 14\) Hz, \(\text{PCH(CH}_3)_2\)), 10.9 (s, \(\text{C}_5\text{(CH}_3)_5\)). MS (electrospray, CH\(_2\)Cl\(_2\) solution): \(m/\text{z} = 569-582\) (M\(^+\) isotope pattern, base peak at \(m/\text{z} = 575\), See Figure 2.5). Anal. Calcd. for C\(_{28}\)H\(_{32}\)O\(_3\)Al\(_4\)FePMo: C, 41.97; H, 4.33. Found: C, 41.48; H, 4.36.

2.5.10 X-ray crystallography

Suitable crystals of 3, 4, 6 and 8 were mounted on a glass fiber. Programs for diffractometer operation, data collection, cell indexing, data reduction and absorption correction were those supplied by Bruker AXS Inc., Madison, WI. Diffraction measurements were made on a PLATFORM diffractometer/SMART 1000 CCD using
graphite-monochromated Mo-K-α radiation at -80 °C. The unit cell was determined from randomly selected reflections obtained using the SMART CCD automatic search, center, index and least-squares routines. Integration was carried out using the program SAINT and an absorption correction was performed using SADABS. Crystal data collection was done by staff crystallographers at the University of Alberta. Structure solution was carried out using the SHELX97 suite of programs and the WinGX graphical interface. Initial solutions were obtained by direct methods and refined by successive least-squares cycles. All non-hydrogen atoms were refined anisotropically.
CHAPTER 3

REACTIVITY OF A DICHLOROPHOSPHIDO COMPLEX.

NUCLEOPHILIC SUBSTITUTION REACTIONS AT METAL COORDINATED PHOSPHORUS

3.1 INTRODUCTION

Terminal dichlorophosphido complexes (MPCl₂) are relatively rare, however the reactivity of the known complexes has been well explored and typical reactions include oxidation of the lone pair, coordination to Lewis acids, and reductive coupling. Though the chemistry of the dichlorophosphido complexes has been well studied, direct chloride abstraction from the dichlorophosphido has not been attempted so far. I was therefore, interested in looking at chloride abstraction reactions, because it may have the potential to serve as a direct synthetic route to cationic chlorophosphinidenes. Chlorophosphinidenes can directly provide products, such as P-heterocycles, adducts of nucleophilic or C-H activation products, containing a P-Cl bond ready for further substitution. In this chapter, I will also discuss the P-P bond forming reactions of the dichlorophosphido complex via a selective nucleophilic substitution reactions using phosphines. These reactions would expect to provide a convenient and direct synthetic route to terminal phosphine coordinated chlorophosphinidene complexes, which can be further functionalized at the phosphinidene center to generate new organophosphorus products.

Low coordinate phosphorus compounds with P-P bonds are receiving widespread attention because of their potential use as reagents in organophosphorus synthesis.
Among them, one widely studied class of compound is phosphoranylidene phosphines, which can be formulated as phosphine adducts of singlet phosphinidenes.\textsuperscript{103,104}

![Resonance structures for phosphoranylidene phosphines](image)

**Figure 3.1** Resonance structures for phosphoranylidene phosphines\textsuperscript{104}

Phosphoranylidene phosphines are generally represented as $\text{RP} = \text{PR}_3$. Numerous synthetic approaches to these reactive species have been reported in the literature.\textsuperscript{104} In most cases, the P-P bond is formed via a nucleophilic attack by a phosphine on an electrophilic phosphorus atom. Such reactions have been done with main group compounds and in transition metal complexes. Since we focus mainly on metal mediated synthetic approaches to P-P bond formation, a very brief introduction to P-P bond formation reaction using main group methods will be given first, followed by a detailed description of the work done on the P-P bond formation using metal mediated approaches.

The parallels between phosphines and stable carbenes, particularly N-Heterocyclic carbenes (NHC) led me to consider the formation of P-carbene bonds. As N-Heterocyclic carbenes are good $\sigma$ donors, their interaction with electrophilic phosphorus may provide a convenient and direct synthetic route to P-C bonds. In this chapter, I will discuss the P-C bond forming reactions of the dichlorophosphido complex via a selective nucleophilic substitution reaction using a stable N-Heterocyclic carbene. These reactions are expected to generate carbene coordinated chlorophosphinidene complexes. The nature and
reactivity of the resulting P-C bond will be studied and compared with that of the phosphine analogues.

3.1.1 Main group P-P bond forming reactions

Phosphoranylidenephosphines were first generated by Burg and Mahler by the action of excess PMe$_3$ on the cyclophosphines (CF$_3$P)$_4$ or (CF$_3$P)$_5$ (Scheme 3.1.1). This phosphoranylidenephosphine $X$ was found to be thermally unstable and highly reactive towards air and water (Scheme 3.1).

![Scheme 3.1 Generation of phosphoranylidenephosphine](image)

Later, Zurmuhlen and Regitz reported a synthetic route to phosphoranylidenephosphines $\text{XI}$ and $\text{XII}$, which are stabilized by bulky mesityl groups, from silylated phosphides and acid chlorides (Scheme 3.2). The P-P double bond was introduced by 1, 3-silyl migration.\textsuperscript{106,107}
Scheme 3.2 Generation of stable phosphoranylidenephosphine

Cyclic phosphoranylidenephosphine XIII was reported by Regitz and Bertrand in 1995, and was formed by photolysis of a mixture of $i$-Pr$_2$PC(N$_2$)SiMe$_3$ with tert-butylphosphaalkyne (Scheme 3.3).\textsuperscript{108,109}

Scheme 3.3 Generation of a cyclic phosphoranylidenephosphine

Triphosphenium salts XIV and XV were isolated and characterized by Schmidpeter et.al.\textsuperscript{110,111} These compounds were formed from the direct reaction of PCl$_3$ with phosphines in presence of excess Lewis acids (Scheme 3.4).
Baker et al. have reported the formation of a phosphine-diaminophosphenium salt \textbf{XVII} via the P-P bond formation reaction between a free phosphine and a stable cationic diaminophosphenium ion \textbf{XVI} (Scheme 3.5).\textsuperscript{112}

\begin{equation}
\begin{array}{c}
\text{Ar} \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{P} \\
\text{N} \\
\text{Ar}
\end{array}
\end{array}
\xrightarrow{\text{PMMe}_3}
\begin{array}{c}
\text{Ar} \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{P} \\
\text{N} \\
\text{Ar}
\end{array}
\end{array}
\end{equation}

\textbf{XVI} \quad \text{Ar} = 4-\text{MeO-C}_6\text{H}_4 \\
A = \text{OSO}_2\text{CF}_3

\begin{equation}
\begin{array}{c}
\text{Ar} \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{P} \\
\text{Ar}
\end{array}
\end{array}
\xrightarrow{\text{PMe}_3}
\begin{array}{c}
\text{Ar} \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{P} \\
\text{Ar}
\end{array}
\end{array}
\end{equation}

\textbf{XVII}

\textbf{Scheme 3.5} Generation of phosphine-diaminophosphenium salt

Burford et al. have reported an alternative approach to P-P bond formation via the coordination of a phosphine to the phosphorus atom of a phosphenium cation.\textsuperscript{113} The triphenylphosphine coordinated diphenylphosphenium cation \textbf{XVIII} can be used as a precursor to other P-P bonds. A series of new phosphine coordinated phosphonium
cations (XIX and XX) have been synthesized simply by the phosphine exchange reaction at the phosphonium center (Scheme 3.6).

Scheme 3.6 P-P bond formation via phosphine coordination to phosphonium ion

3.1.2 P-P bond formations in metal complexes

An alternative synthetic method to P-P bond formation is a metal mediated approach, in which the P-P bond formation takes place within the coordination sphere of a transition metal. Nucleophilic addition to terminal electrophilic phosphinidene complexes with phosphines result in phosphine coordinated phosphinidene (phosphoranylidenephosphine) complexes.76,77 This method serves as a convenient route to P-P bonds and offers stable phosphoranylidenephosphine complexes.

In 1990 Mathey et al. first isolated a stable phosphoranylidenephosphine complex [Bu3P=P(Ph)-W(CO)5] (XXI) by reacting the transient tungsten pentacarbonylphosphinidene complex [PhPW(CO)5] with tributylphosphine (Scheme 3.7).76
Scheme 3.7 Generation of phosphoranylidenephosphine

The phosphoranylidenephosphine complex **XXI** shows zwitterionic character at the P-P bond and reacts with a range of aldehydes to give phosphaalkenes **XXII** via a phospha-Wittig reaction (Scheme 3.8).

![Scheme 3.7](image)

**Scheme 3.8** Reactivity of the phosphine coordinated phosphinidene complex

Phosphine additions to stable cationic aminophosphinidene complexes of Mo and W were investigated by Sterenberg et al.\(^6\) Reaction of the aminophosphinidene complexes of Mo **XXIII** with triethylphosphine led to the phosphine coordinated phosphinidene complex **XXIV**, detected using \(^{31}\text{P}\) NMR at low temperature (-30 °C) (Scheme 3.9). Upon warming, carbonyl loss and phosphine migration led to metal coordinated phosphinidene complex **XXV**.\(^6\)
Reaction of **XXIII** with bis(dimethylphosphino)methane (dmpm) and bis(dimethylphosphino)ethane (dmpe) led initially to a dangling phosphine coordinated phosphinidene complex **XXVI** and a chelated phosphine coordinated phosphinidene complex **XXVII** respectively. The complex **XXVI** was observed at low temperature using NMR spectroscopy. Upon warming to room temperature, carbonyl loss was followed by coordination of the dangling phosphine to the metal (Scheme 3.10).\(^{68}\)
A similar reversible phosphine addition reaction was observed for the tungsten version. Unlike in the molybdenum version, reaction of the tungsten phosphinidene complex XXVIII with bis(dimethylphosphino)ethane (dmpe) led to a mixture of the expected chelated phosphine coordinated phosphinidene XXIX and a binuclear complex XXX (Scheme 3.11).

Scheme 3.11 Reaction of the tungsten phosphinidene towards dppe

In 2005, Carty et al. reported a stable aminophosphinidene complex of rhenium and described its reactivity towards phosphines (Scheme 3.12). Unlike the other reported aminophosphinidene complexes, the rhenium aminophosphinidene reacts with moderately nucleophilic triphenylphosphine (PPh₃) and forms a stable adduct XXXI without chelation. Crystallographic studies on phosphine coordinated aminophosphinidene complexes revealed that their P-P bond length was substantially longer than a P=P bond and more consistent with a P-P single bond.
Recently, Sterenberg et al. reported the generation of a tungsten complexed $\eta^1$-phosphirenyl cation by chloride abstraction from a corresponding chlorophosphirene complex, which reacts with triphenylphosphine to form the P-P bonded adduct XXXII (Scheme 3.13).\textsuperscript{114}

3.1.3 P-C bond formation via phosphinidene carbene interaction

Stable carbenes, in particular N-heterocyclic carbenes are isolobal to phosphine ligands. Therefore, they can act as phosphine alternatives to stabilize the reactive phosphinidene fragments via donations of the carbene lone pair to the phosphinidene
phosphorus. The carbene phosphinidene adduct formation can be therefore used as an alternative synthetic methodology to P-C bond formations.

Interaction of stable carbenes with phosphinidenes and the formation of stable carbene-phosphinidene adducts were first reported in 1997 by Arduengo and Cowley. They found that like phosphines, stable N-Heterocyclic carbenes were also nucleophilic enough to depolymerise cyclopolyphosphines (Scheme 3.14).

Robinson et al. have isolated carbene-stabilized bis-phosphinidene and carbene-stabilized parent phosphinidene complexes. The potassium graphite reduction of the hypervalent phosphorus carbene adducts afforded the carbene stabilized bisphosphinidene XXXIII (Scheme 3.15). Reduction of XXXIII with metallic lithium resulted in a lithiated-NHC parent phosphinidene adduct XXXIV (Scheme 3.16).
The P-C bond distances of these adduct are between P=C double bond and P-C single bond distances. The relatively longer P-C bond lengths favour a bis-phosphinidene formulation for XXXIII, and a phosphinidene formulation for XXXIV.

Carty et al. reported the reactivity of electrophilic bridging phosphinidene complexes with N-heterocyclic carbenes.\textsuperscript{119} The reactions of Mn\textsubscript{2}- and Co\textsubscript{2}- containing $\mu$-PNI-Pr\textsubscript{2} complexes with N-heterocyclic carbenes were reported to proceed via an unexpected 2,4 ylidene migration and resulted in abnormal carbene adducts (Scheme
3.1.7. The X-ray crystallography studies of these carbene adducts revealed that the P-C bond is a weak single bond.119

![Scheme 3.17 NHC-phosphinidene adducts](image)

**Scheme 3.17** NHC-phosphinidene adducts

### 3.1.4 Rational and objectives

The cationic electrophilic phosphinidene complexes formed via chloride abstraction show similar reactivity to transient neutral electrophilic phosphinidene.77,78,80 However, they have the advantage of shorter synthetic routes and can be generated at lower temperature. I was interested in expanding the range of possible P substituents. Of particular interest to me is a simple route to P-Cl phosphinidenes. This led me to explore the chemistry of dichlorophosphido complexes, which are potential precursors to cationic chlorophosphinidene complexes. As far as I know, direct halide abstraction as a route to chlorophosphinidene complexes has not been attempted, although a neutral chlorophosphinidene complex has been prepared by a different route.79 Of known PCl₂ complexes, we were drawn to [Cp*Mo(CO)₃PCl₂], reported by Malisch,95 because the synthesis is straight forward, and also it is analogous to the well studied phosphinidene precursor [Cp*Mo(CO)₃{P(Cl)(N-i-Pr₂)}],52,68,77 and also to the chloroisopropyl phosphido complex discussed in Chapter 2.
The reactivity of electrophilic phosphinidene complexes towards nucleophiles is exemplified by their reaction with phosphines. However, the subsequent chemistry of these P-P bonded adducts and their application towards chemical synthesis has not been well explored. Recently, Sterenberg et al. elaborated the chemistry of phosphine coordinated aminophosphinidenes by introducing a P-Cl functionality at the phosphinidene center via a P-N cleavage reaction using HCl. Terminal dichlorophosphido complex can offer a more direct synthetic route to phosphine coordinated chlorophosphinidene complexes via nucleophilic substitution reactions at the metal coordinated phosphorus.

Stable N-heterocyclic carbenes have been shown to be excellent phosphine substitutes. The carbene phosphinidene interaction chemistry has been well described in the literature but the interaction of a carbene with a terminal phosphinidene complex has not been reported so far. These reactions may give direct access to either a carbene stabilized terminal phosphinidene complex or a terminal phosphaalkene complexes via a P-C bond formation.

In this study, I will investigate the reaction chemistry of the [Cp*Mo(CO)₃PCl₂] with respect to chloride abstraction and substitution, and its utility as a precursor to phosphine coordinated chlorophosphinidene complexes.

The initial objective of this research was to form a chlorophosphinidene via chloride abstraction and to investigate its reactivity towards C-H sigma bonds (bond activation reactions) and cycloaddition. When this was not successful, the objectives were revised as follows:
• Generate phosphine coordinated chlorophosphinidene complexes via phosphine addition to the terminal dichlorophosphido complex.
• Elaborate the chemistry of the phosphine coordinated chlorophosphinidenes by reacting the P-Cl bond with a second equivalent of phosphine and generate new dicationic di-phosphine coordinated phosphido complexes.
• Investigate the reactivity of the dichlorophosphido ligand towards a stable NHC carbene.

3.1.5 Scope of the Study

Chloride abstraction of the dichlorophosphido ligand will be carried out using Lewis acids and the formation of the chlorophosphinidene will be confirmed by trapping reactions using alkynes. Phosphine addition reactions to the dichlorophosphido complex will be investigated with a range of phosphines and bis phosphines. These reactions are expected to generate new phosphine coordinated chlorophosphinidene complexes. Phosphine coordinated chlorophosphinidenes are interesting because they provide an additional reaction site at the phosphinidene phosphorus, which will be useful for further elaboration of the chemistry of the phosphine coordinated phosphinidene complexes. The reactivity at the P-Cl bond of the phosphine coordinated chlorophosphinidene complexes will then be further examined with a second equivalent of phosphine. These reactions are expected to generate new dicationic diphosphine coordinated phosphido complexes or di(phosphonio)-phosphido complexes with a unique P-P-P linkage on it.

Nucleophilic addition reactions of the dichlorophosphido will be further extended towards stable N-heterocyclic carbene. Deprotonation of the corresponding imidazolium
salt will be used to generate the free carbene. Being a good σ donor, the NHC carbon is expected to undergo a nucleophilic substitution at the phosphido center, which may result in the formation of a NHC coordinated chlorophosphinidene complex. The nature of bonding between the phosphinidene phosphorus and the carbene carbon will be examined with the help of NMR and X-ray crystallography. In order to get further insight into the nature of the P-C bond, the structure will be optimized and the nature of the phosphinidene-carbene bond will be examined using computational chemistry. The reactivity of this carbene coordinated phosphinidene complexes toward other reagents will then be further explored. These reactivity studies would help us to synthesis a range of novel phosphorus containing complexes.

3.2 RESULTS AND COMPOUND CHARACTERIZATION

3.2.1 Synthesis of the dichlorophosphido complex

The dichlorophosphido complex [Cp*Mo(CO)₃PCl₂] (10) was synthesized from Cp*Mo(CO)₃⁻ and PCl₃ using a modification of the published procedure. The phosphido complex 10 can be isolated as orange crystals from pentane with a yield of 73%. The IR spectrum of the phosphido shows three sharp carbonyl stretching bands at 2018, 1951 and 1931 cm⁻¹, clearly indicating that the molybdenum center retains three carbonyl groups. The ³¹P NMR shows a singlet at 408, matching the reported value.
Scheme 3.18 Synthesis of \([\text{Cp}^*\text{Mo}(\text{CO})_3\text{PCl}_2]\)

### 3.2.2 Reaction of dichlorophosphido complex towards chloride abstraction

The chloride groups on the dichlorophosphido complex can be abstracted using \(\text{AlCl}_3\), \(\text{AgBF}_4\) and \(\text{NaBPh}_4\). All three reagents led to the same product \([(\text{Cp}^*)_2\text{Mo}_2(\text{CO})_6\text{P}_2\text{Cl}_3][\text{AlCl}_4] (11)\) as the sole phosphorus containing product (Scheme 3.2.2). The \(^{31}\text{P}\) NMR spectrum of the 11 shows doublets at \(\delta 318\) and 258 with a coupling constant of 527 Hz. This large coupling constant indicates a direct P-P bond, and falls in the middle of the range of P-P coupling observed in other reported compounds with P-P bond.\(^{68,78}\) The IR spectrum of 11 shows three carbonyl stretching bands at 2020, 1932 and 1953 cm\(^{-1}\). The \(^1\text{H}\) NMR spectrum shows two chemically different Cp* groups at \(\delta 1.95\) and 1.89. The electrospray mass spectrum shows an isotope pattern \((m/z = 780-809)\) that corresponds to the predicted mass for \([(\text{Cp}^*)_2\text{Mo}_2(\text{CO})_6\text{P}_2\text{Cl}_3]^+\). Based on these data, compound 11 is assigned as a bimetallic complex containing a bridging P\(_2\)Cl\(_3\) ligand and an overall +1 charge, which results from the displacement of chloride from one molecule of the dichlorophosphido ligand of 10 by a second equivalent of 10 (Scheme 3.19).
The observed product could potentially be formed through a chlorophosphinidene intermediate. In order to demonstrate the intermediacy of a chlorophosphinidene, the chloride abstraction reaction was carried out in the presence of the trapping reagent diphenylacetylene. Reaction with alkynes to form phosphirenes is considered a characteristic reaction of terminal electrophilic phosphinidene complexes.\(^8\) Formation of a chlorophosphirene would indicate that a chlorophosphinidene intermediate was being formed. However in this attempted trapping reaction, compound 11 was the only observed product, and no phosphirene complex was detected, even with a large excess of alkyne and high dilution. This suggests that 11 does not form via a chlorophosphinidene intermediate but by another mechanism. We suggest that 11 forms via a Lewis acid assisted nucleophilic substitution mechanism (Scheme 3.20).
3.2.3 Reaction of dichlorophosphido towards external nucleophiles

In order to provide support for this mechanism, the reaction was carried out in the presence of an external nucleophile. The reactivity of 10 was first examined with triphenylphosphine. Compound 10 does not react directly with triphenylphosphine, but in the presence of AlCl₃ or NaBPh₄, one of the chloride group on 10 undergoes nucleophilic substitution by one equivalent of triphenylphosphine, resulting in the formation of a triphenylphosphine coordinated chlorophosphinidene complex [Cp*Mo(CO)₃{P(Cl)(PPh₃)}][X] (12a, X=BPh₄⁻, 12b, X = AlCl₄⁻) (Scheme 3.21).

Scheme 3.21 Reaction of dichlorophosphido with PPh₃
The $^{31}$P NMR spectrum of 12 shows doublets at δ 179 and δ 38.0 with a coupling constant of 454 Hz. The large coupling constant indicates a direct P-P bond and falls in the range of P-P coupling observed in other reported complexes. The IR spectrum of 12 shows three carbonyl stretching bands at 2019, 1972 and 1934 cm$^{-1}$, which indicates that the molybdenum center retains three carbonyl groups. The structure of 12 was further supported by the electrospray mass spectrum, which shows an isotope pattern with a base peak at m/z 644 that corresponds to the predicted masses for the cation of the product. The structure of compound 12 has been confirmed by X-ray crystallography and an ORTEP diagram of the cation is shown in Figure 3.2. The geometry at the metal center is a four legged piano stool with carbonyl ligands on the three legs and the P(Cl)(PPh$_3$) unit on the other leg. The metal bound phosphorus P1 is pyramidal with bond angles of 111.98, 109.34 and 93.21, indicating the presence of a stereoactive lone pair. The PPh$_3$ is coordinated to the metal bound phosphorus, and is directed away from the Cp* ring, while the chloro group is directed such that the P-Cl bond is nearly parallel to the Cp* ring. In this position, the Cl atom lies directly between the bulky Cp* and PPh$_3$ groups. The reactivity of 10 towards nucleophiles, but not towards alkynes, supports the proposed Lewis acid assisted nucleophilic substitution mechanism.
Figure 3.2 ORTEP diagram of \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PPh}_3\})]\) (12). Hydrogen atoms and the counter ion have been omitted. Selected distance (Å) and angles (deg): Mo1-P1 = 2.5337(11), P1Cl1 = 2.1057(14), P1-P2 = 2.2018(14); Mo1-P1-P2 = 111.98(5), Mo1-P1-Cl1 = 109.34(5), Cl1-P1-P2 = 93.21(6).

Reactivity of 10 towards alkylphosphines has also been investigated. In contrast to PPh$_3$, the more strongly nucleophilic phosphines, PEt$_3$ and PBu$_3$ react directly with 10 without a chloride abstracting reagent, resulting in the formation of analogous phosphine coordinated chlorophosphinidene complexes \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PEt}_3\})]\)[Cl] (13) and \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PBu}_3\})]\)[Cl] (14) respectively (Scheme 3.22). The $^{31}\text{P}$ NMR spectrum of 13 shows two doublets at $\delta$167 and $\delta$ 49.5 with a coupling constant of 438 Hz. The electrospray mass spectrum of 13 shows an isotope pattern with a base peak at m/z 501 that corresponds to the predicted masses for the cation of 13. The $^{31}\text{P}$ NMR spectrum of the complex 14 shows two doublets at $\delta$ 170 and $\delta$ 42.6 with a coupling
constant of 438 Hz. The electrospray mass spectrum shows an isotope pattern with a base peak at m/z 585 that corresponds to the predicted masses for the cation of 14.

![Scheme 3.22 Reactions of dichlorophosphido with alkyl phosphines](image)

### 3.2.4 Reactivity of the phosphine coordinated chlorophosphinidenes towards carbonyl compounds

Compounds like 12, 13 and 14 with dative P-P bonds are of interest because they may have the potential to undergo phospha-Wittig reactions with aldehydes and ketones to form a phosphaalkene.\(^{76,121,122}\) Though the single crystal X-ray diffraction studies on 12 suggests a more single bond character to the P-P bond, I was interested to investigate the reactivity of these P-P bonds towards carbonyl compounds. The compound 12 was therefore reacted with benzaldehyde and benzophenone. However, the P-P bond of 12 is inactive towards carbonyl compounds, which suggests its not polar enough. The polarity of the P-P bond could be substantially increased by coordinating the phosphido center with more basic phosphines. As triethyl and tributyl phosphines are more basic than PPh\(_3\), compounds 13 and 14 were expected to be more polar at their P-P bond.

At room temperature, however, 13 and 14 do not react with benzaldehyde, but at elevated temperature, the \(^{31}\)P NMR spectrum of the reaction solution shows the formation of phosphine oxides, along with other unidentified products. The formation of phosphine
oxides suggests that phosphaalkene may be formed in the reaction, however, attempts to trap them were not successful (Scheme 3.23).

Scheme 3.23 Reaction of 13 and 14 towards carbonyl compounds

3.2.5 Reactivity of [Cp*Mo(CO)₃{P(Cl)(PPh₃)}][AlCl₄] with organic nucleophiles

A compound like 12 has the potential to act as a phosphine protected chlorophosphinidene. As the phosphinidene center is stabilized by a triphenylphosphine moiety, the P-Cl bond of the chlorophosphinidene can be easily functionalized with external nucleophiles, which may give direct access to a range of new functionalized PPh₃ coordinated phosphinidene complexes. The subsequent displacement of the labile PPh₃ unit is then expected to generate corresponding phosphinidenes complexes.

In order to examine the feasibility of this proposed methodology, the reaction of 12 was investigated with an isopropyl magnesium chloride (i-PrMgCl). However, the
isopropyl anion substitutes the PPh₃ unit rather than the chloro, resulted the formation of the known chloroisopropyl phosphido complex [Cp*Mo(CO)₃{P(Cl)Pr}] (1) (Scheme 3.24). Reaction of 12 with phenyllithium and lithium phenylacetylide also led to phosphine substitution.

![Scheme 3.24 Reaction of 12 with organic nucleophiles](image)

**3.2.6 Reactivity of [Cp*Mo(CO)₃{P(Cl)(PPh₃)}][AlCl₄] (12) with PPh₃**

The triphenylphosphine coordinated chlorophosphinidene complexes provide an additional reaction site (P-Cl bond) at the phosphorus center. I decided to investigate the reactivity of 12 towards a second equivalent of triphenylphosphine, with the idea that this reaction would give access to a new dicationic di(phosphonio)-phosphido complex. This proposed di(phosphonio)-phosphido complex would be the first of its kind, with a novel di(phosphonio) phosphonium ligand (PPh₃-P-PPh₃⁺) coordinated to a Cp*Mo(CO)₃ unit.

Compound 12 does not directly react with triphenylphosphine, but reaction of 12 with excess NaBPh₄ or AlCl₃ and excess phosphine leads to the second chloride substitution. The substitution is confirmed by the ³¹P NMR spectrum, which shows a doublet at δ 30.8 and a triplet at δ -172.1 with a common coupling constant of 510 Hz, indicating that the product contains a P-P-P unit. However, this reaction did not generate the expected di(phosphonio)-phosphido complex, but leads to the di(phosphonio)-
phosphonium salt $[(\text{PPh}_3)_2\text{P}][\text{AlCl}_4]$ (16), via the dissociation of the P3 unit from the metal (Scheme 3.25). The fate of the metal fragment in this reaction is not known. However, if the same reaction is carried out with an additional equivalent of PPh$_3$, the Cp*Mo(CO)$_3^+$ fragment can be trapped, forming the known complex $[\text{Cp}^*\text{Mo(CO)}_3(\text{PPh}_3)]^+$ (17). \textsuperscript{110} The di(phosphonio)-phosphonium salt 16 formed is a known compound, which was isolated and characterized by Schmidpeter et al.\textsuperscript{111} The $^{31}\text{P}$ NMR data for 16 matches that reported by Schmidpeter.

\begin{center}
\begin{center}
\includegraphics[width=\textwidth]{scheme325.png}
\end{center}
\end{center}

\textbf{Scheme 3.25} Nucleophilic addition at the P-Cl bond

The chloride substitution reaction at 12 most likely proceeds through the dicationic di(phosphonio)-phosphido complex 15. However, 15 was not observed even as an intermediate, indicating that the dicationic di (phosphonio)-phosphido complex, if formed, has a short life time. Attempts to observe 15 at low temperature were not successful. At temperatures below 0 °C, the chloride abstraction from 12 was effectively suppressed. Similar results were observed with sterically less demanding trimethyl and triethylphosphines, clearly suggesting that the instability associated with the dicationic di(phosphonio)-phosphido complexes is independent of the phosphine size and not a result of steric congestion. Metal complexes of ligands having P-P-P units may be accessible if the decomplexation is avoided using bidentate phosphines that can also
coordinate to the metal center as proposed in Scheme 3.26. The reactivity of 10 towards bidentate phosphines bis-(diphenylphosphino)ethane (dppe, \(n = 2\)) and bis-(diphenylphosphino)methane (dppm, \(n = 1\)) was therefore investigated.

Scheme 3.26 Proposed strategy for P-P-P bond formation

3.2.7 Reactivity of [Cp*Mo(CO)_3PCl_2] with Bis-(diphenylphosphino)ethane (dppe)

In the presence of AlCl_3 or NaBPh_4, bis-(diphenylphosphino)ethane (dppe) displaces both the chloride groups at the phosphido center, leading to a cyclic P-P-P structure 20. This double substitution is confirmed by the \(^{31}\)P NMR spectrum, which shows a doublet at \(\delta 63.7\) and a triplet at \(\delta -237.2\) with a common coupling constant of 454 Hz, indicating that the product contains a P-P-P unit. As in the triphenylphosphine chemistry, the P-P-P unit dissociates from the metal, leading to the di(phosphonio)-phosphenium salt \([P(Ph_2CH_2CH_2Ph_2-\kappa^2P^1,P^4)][AlCl_4]\) (21) (Scheme 3.27). The di(phosphonio)-phosphenium salt 21 formed is again a known compound. The \(^{31}\)P NMR spectrum for 2 matches that reported by Schmidpeter. et al.\(^{111}\)

Reactivity of the dichlorophosphido complex with bis-(diphenylphosphino)ethane (dppe) has two possible pathways as shown in Scheme 3.27. The initial nucleophilic addition at the dichlorophosphido center may result in a dangling phosphine coordinated phosphinidene complex 18 as shown in Scheme 3.27. This dangling dppe coordinated
phosphinidene complex 18 can undergo either decarbonylation (which is observed in other reported phosphinidene complexes\textsuperscript{77}) or nucleophilic substitution at P (Scheme 3.27).

![Scheme 3.27 Reaction of [Cp*Mo(CO)\textsubscript{3}PCl\textsubscript{2}] with dppe](image)

3.2.8 Reactivity of [Cp*Mo(CO)\textsubscript{3}PCl\textsubscript{2}] with Bis-(diphenylphosphino)methane (dppm)

In contrast to the dppe reaction, reaction of 10 with bis-(diphenylphosphino)methane leads to substitution of one chloride at the phosphido center, resulting in the dangling phosphine coordinated chlorophosphinidene complex [Cp*Mo(CO)\textsubscript{3}{P(Cl)P(Ph\textsubscript{2})CH\textsubscript{2}P(Ph\textsubscript{2})]}[AlCl\textsubscript{4}] (22) (Scheme 3.28). The \textsuperscript{31}P NMR spectrum of 22 shows three resonances at \(\delta\) 190.9 (P\textsubscript{A}), 35.7 (P\textsubscript{B}), -29.7 (P\textsubscript{C}). The phosphinidene phosphorus P\textsubscript{A} appears at \(\delta\) 190.9 as a doublet of doublets, showing a one
bond P-P coupling of 443 Hz with \( P^B \) and a three bond coupling of 58 Hz to \( P^C \). The end of the diphosphine that coordinates to the phosphinidene phosphorus \( P^B \) appears as a doublet of doublets, showing a one-bond P-P coupling of 445 Hz with \( P^A \) and a two bond coupling of 65.2 Hz to \( P^C \) across the dpmm methylene group. The phosphorus resonance at the dangling end of the dpmm ligand \( P^C \) appears at -29.7 as a doublet of doublets, close to the chemical shift of the free dpmm, and shows a two bond coupling of 65 Hz with \( P^B \) and a three bond coupling of 58 Hz with \( P^A \). The IR spectrum of 22 shows three carbonyl stretching bands at 2033, 2020 and 1935, showing that the molybdenum centre retains three carbonyl groups. The electrospray mass spectrum shows an isotope pattern with a base peak at m/z 766 that corresponds to the predicted masses for the cation of the product.

Scheme 3.28 Reaction of \([\text{Cp}^*\text{Mo(NO)}_3\text{PCl}_2]\) with dpmm

Unlike the other reported dangling phosphine coordinated phosphinidene complexes,\(^{52}\) the dpmm coordinated chlorophosphinidene complex is stable at room temperature and does not spontaneously lose CO. The relatively less basic dpmm ligand, which is coordinated to the phosphinidene phosphorus \( P^A \) may lead to less stabilization of the 16-electron intermediate formed upon the carbonyl loss from 22.
Photolysis of \(22\) leads to \([\text{Cp}^*\text{Mo(CO)}_2{\{\text{P(Cl)P(Ph)CH}_2\text{P(Ph)}_2\}^-}^2\text{P}^*\text{P}^*]^-[\text{AlCl}_4]\) (23), in which the dangling phosphine of the dppm is now coordinated to the metal (Scheme 3.29). The chelated chlorophosphinidene complex 23 formed was identified using the \(^{31}\text{P}\) NMR spectrum, which shows three resonances at \(\delta\ 225\) \((\text{P}^A)\), 52.3 \((\text{P}^C)\), 31.1\((\text{P}^B)\). The phosphinidene phosphorus P\(^A\) appears at \(\delta\ 225\) as a doublet of doublets, showing a P-P bond coupling of 422 Hz with P\(^B\) and a two bond coupling of 10 Hz across the molybdenum with P\(^C\). The end of the diphosphine P\(^B\) that coordinates to the phosphinidene phosphorus appears at \(\delta\ 31.1\) as a doublet of doublets, showing a P-P coupling of 442 Hz with P\(^A\) and a two bond coupling of 62 Hz across the dppm methylene group with P\(^C\). The metal coordinated phosphine phosphorus P\(^C\) appears at \(\delta\ 52.3\) as a doublet of doublets, showing a two bond coupling of 64 Hz across the dppm methylene group with P\(^B\) and a two bond coupling constant of 10 Hz across the molybdenum center with P\(^A\). The IR spectrum now shows two carbonyl stretching bands at 2041 and 1968 cm\(^{-1}\), indicating that the molybdenum center retains only two carbonyl groups. The electrospray mass spectrum shows an isotope pattern with a base peak at m/z 736 that corresponds to the predicted masses for the cation of the product, confirming the loss of carbonyl.

\[\text{Scheme 3.29} \text{ Photolysis of } [\text{Cp}^*\text{Mo(CO)}_2{\{\text{P(Cl)P(Ph)CH}_2\text{P(Ph)}_2\}^-}^2\text{P}^*\text{P}^*]^-[\text{AlCl}_4]\]
In order to generate the proposed P-P-P linkage, the reactivity of the chelated chlorophosphinidene complex 23 was investigated towards phosphines. In the presence of AlCl$_3$, the triethylphosphine substitutes the chloride group at the phosphinidene centre, leading to the dicationic complex $\text{[Cp}^*\text{Mo(CO)}_2\{\text{P(PEt}_3\text{)}\text{P(Ph}_2\text{)CH}_2\text{P(Ph}_2\text{)-}k^2\text{,P}_1\text{P}_4\}\text{][AlCl}_4]_2$ (24) with the expected P-P-P linkage (Scheme 3.30). The structure of 24 was identified using the $^{31}$P NMR spectrum, which shows four resonances at $\delta$ 31.3 (P$^A$), -53.4 (P$^B$), 36.1 (P$^C$), 71.2 (P$^D$). The triethylphosphine phosphorus P$^A$ that coordinates to the phosphinidene phosphorus appears at $\delta$ 31.3 as a doublet of doublets, showing a P-P coupling of 361 Hz with P$^B$ and a two bond coupling of 103 Hz with P$^C$. The phosphinidene phosphorus P$^B$ appears at -53.4 as a doublet of doublet of doublets, showing P-P coupling of 394 Hz with P$^A$ and 374 Hz with P$^C$ and a two bond coupling of 22.2 Hz across the molybdenum center with P$^D$. The end of the diphosphine P$^C$ that coordinates to the phosphinidene phosphorus appears at $\delta$ 36.1 as a doublet of doublet of doublets, showing a P-P coupling of 374 Hz with P$^B$ and a two bond coupling of 82.8 Hz across the dppm methylene group with P$^D$ and a two bond coupling constant of 8.8 Hz with P$^A$. The metal coordinated phosphine phosphorus P$^D$ appears at $\delta$ 71.2 as a doublet of doublet of doublets, showing a two bond coupling of 82.8 Hz across the dppm methylene group with P$^C$ and a two bond coupling constant of 20.7 Hz across the molybdenum center with P$^B$ and a three bond coupling constant of 5.9 Hz with P$^A$. However, the reactivity was not clean and 24 could not be isolated from the reaction mixture.
3.2.9 Carbene addition to dichlorophosphido complex

After Arduengo reported stable N-heterocyclic carbenes (NHC) in 1991, the parallel chemistry between phosphines and NHC has been well studied.\textsuperscript{123,124} It has been reported that stable N-heterocyclic carbenes behave similarly to electron rich phosphines.\textsuperscript{120} It was this fact and reports of stable NHC adducts with free phosphinidenes that prompted me to extend the NHC chemistry towards the dichlorophosphido system.

Although a number of 1,3-substituted N-heterocyclic carbenes have been reported, because of the steric size of the metal complex, the relatively less sterically demanding 1,3-diisopropylimidazol-2-ylidene (\textit{t}Pr\textsubscript{2}) (26) was chosen for this study. The precursor 1,3-diisopropylimidazolium chloride (\textit{t}Pr\textsubscript{2}-HCl) (25) was synthesized according to the literature procedure,\textsuperscript{125} and the carbene \textit{t}Pr\textsubscript{2} was made by deprotonation using butyllithium (Scheme 3.31).
Scheme 3.31 Generation of NHC

The carbene (\textit{i}-Pr\textsubscript{2}) does not react directly with [Cp\textsuperscript{*}Mo(CO)\textsubscript{3}PCl\textsubscript{2}] (10), however, in the presence of AlCl\textsubscript{3} one chloride is displaced, resulting in the carbene substituted chlorophosphinidene complex [Cp\textsuperscript{*}Mo(CO)\textsubscript{3}P{Cl(iPr\textsubscript{2})}][AlCl\textsubscript{4}] (27) (Scheme 3.32). The \textsuperscript{31}P NMR spectrum of 27 shows a singlet at δ 148, which is considerably shielded compared to that of the phosphine analogues. The \textsuperscript{1}H NMR spectrum of 27 shows two broad singlets at δ 7.46 and 7.36 for the two backbone C-H groups. The C-H hydrogen atoms of the two isopropyl units form two broad peaks at δ 5.05 and 4.64, and the isopropyl methyl groups give broad singlets at δ 1.76, 1.57, 1.53 and 1.38. Steric interaction between the N-bonded isopropyl unit of the NHC and the metal complex restricts rotation about the P-C\textsubscript{NHC} bond, leading to four different methyl environments, evident in the \textsuperscript{1}H NMR spectrum. The IR spectrum of 27 shows carbonyl stretching bands at 2020, 1955 and 1933 cm\textsuperscript{-1}. The electrospray mass spectrum shows an isotope pattern with a base peak at m/z = 535, which corresponds to the predicted masses for the cation of the product. Compound 27 is the first NHC coordinated cationic terminal phosphinidene complex.
Both phosphinidene and carbene can exist in either triplet or singlet electronic states. If the adduct formation takes place via the interaction of two triplet states, then a phosphaalkene with a genuine P-C double bond (RP=CR₂) would result (Figure 3.3). On the other hand, if both the carbene and phosphinidene are in the singlet state, then the interaction between these two species would most likely take place via the donation of the carbene lone pair in to the empty phosphinidene orbital. Then, we might consider the adduct formed as a carbene stabilized phosphinidene or a carbene coordinated phosphinidene. Another aspect that must be taken into account here is the possible π back donation from the phosphinidene phosphorus to the empty orbital of the singlet carbene carbon. Based on the extent of this π bonding interaction, two extreme canonical forms (A and B) can be assigned for this adducts (Figure 3.3). An intermediate π bonding interaction may result a structure somewhere in between these two extremes. Figure 3.3 depicts these two bonding patterns.
Like the free carbene phosphinidene adducts, two extreme resonance forms, namely, carbene-coordinated-phosphinidene B and phosphaalkene A may be suggested for 27. In the carbene-coordinated-phosphinidene form, the P-C bond is a dative single bond and the resulting complex can therefore be best regarded as a carbene stabilized chlorophosphinidene complex. On the other hand, if the π back donation from the phosphinidene phosphorus to the empty p_z orbital of the carbene carbon predominates, then the P-C bond is a double bond and the resulting complex can be regarded as a terminal phosphaalkene complex. However, the relatively shielded $^{31}$P chemical shift of 27 indicates a strong σ donation from the carbene ligand, which in turn suggests that the π bonding interaction between P and C_NHC is not strong in 27. Therefore, out of the two possible resonance forms (A and B), 27 has most likely have a carbene coordinated chlorophosphinidene form B. The P-C bond length of the reported free phosphinidene

![Diagram of carbene-phosphinidene interactions](image-url)
carbene adducts also suggest that the π back donation from the phosphinidene phosphorus to the empty orbital of the carbene carbon is not prominent.126

3.2.10 Computation

My attempts to isolate single crystals of compound 27 were not successful. In this context, in order to get further insight into the nature of the P-C bond, a DFT calculation was performed on 27 at the B3LYP level of theory. The optimized structure of 27 is shown in Figure 3.4.

![Figure 3.4 Optimized structure of the carbene-phosphinidene adduct 27](image)

It is clear from the optimized structure that the coordinated NHC unit lies perpendicular to the plane formed by the Mo-P-C bond, suggesting that the carbene empty $p_z$ orbital and the phosphinidene lone pair are perpendicular to each other. This particular orientation of the NHC unit eliminates the possibility of effective carbene-phosphinidene π overlap in compound 27. Fragment molecular orbital (FMO) analysis has been used to further decompose the P-C interaction into σ donation and π back
donation components. The computed carbene to phosphinidene σ donation is 38.25 %, meanwhile the π back donation from the phosphinidene phosphorus to the empty p\textsubscript{z} orbital of the carbene carbon is only 2.80 %. This negligibly small P-to-C π back donation suggests that in compound 27, the NHC unit acts as a strong σ donor rather than a π acceptor, which in turn supports the proposed carbene coordinated chlorophosphinidene form for 27.

The computed Mayer bond orders and bond lengths are also in good agreement with the above conclusions (Table 3.1). The calculated bond order of 0.934 clearly suggests a single bond character to the P-C bond. The P-C bond length 1.866 Å is also typical for a P-C single bond.

**Table 3.1** Computed Mayer bond orders and bond lengths for [Cp*Mo(CO)\textsubscript{3}P{Cl(\textit{i}Pr\textsubscript{2})}][AlCl\textsubscript{4}] (27)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond order</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-P</td>
<td>0.765</td>
<td>2.631</td>
</tr>
<tr>
<td>P-C</td>
<td>0.934</td>
<td>1.866</td>
</tr>
<tr>
<td>C-N</td>
<td>1.215</td>
<td>1.359</td>
</tr>
</tbody>
</table>

3.2.11 Reactivity of the carbene coordinated chlorophosphinidene

The NHC stabilized chlorophosphinidene complex 27 has an additional reactive chloride. In presence of AlCl\textsubscript{3}, it reacts with a second equivalent of NHC, leading to a second chloride substitution. The \textsuperscript{31}P NMR of the product shows a singlet at δ -134. This
shift to higher field (δ 148 to -133) indicates the presence of two strongly σ donating NHC groups at the phosphorus. However, this reaction did not generate bis-NHC-coordinated phosphido complex 28 but leads to the bis-NHC-coordinated phosphenium salt [(I′Pr₂)₂P][AlCl₄] (29), via the dissociation of the (I′Pr₂)₂P unit from the metal (Scheme 3.33). The dissociation was confirmed by electrospray MS, which shows a base peak at \( m/z = 335 \) that corresponds to the predicted masses for the cation of the decomplexed salt 29.

![Scheme 3.33 Bis-carbene reaction](image)

This reactivity clearly demonstrates that the stable N-heterocyclic carbene (I′Pr₂) mimics the phosphine chemistry. As reported with PPh₃, the expected bis-NHC coordinated phosphido complex 28 was not observed spectroscopically, however the formation of the decomplexed salt 29 strongly suggests its intermediacy.

### 3.3 CONCLUSIONS

A terminal dichlorophosphido complex of molybdenum has been synthesized and its reactivity has been investigated. The dichlorophosphido complex does not serve as a
precursor to chlorophosphinidene, but undergoes Lewis acid assisted nucleophilic substitutions with weak nucleophiles, including itself and PPh\(_3\). The reason for the inability to obtain even a transient chlorophosphinidene is most likely due to alternative lower energetic pathways that lead to substitution reactions rather than abstraction. This alternative reaction, likely results from the lack of steric protection provided by the chloro substituents. In order to get more insights into the instability of the chlorophosphinidene, a detailed computational study was conducted. Detail descriptions about these computational results are discussed in chapter 4.

Chloride abstraction in the presence of triphenylphosphine results a phosphine coordinated chlorophosphinidene complex [Cp*Mo(CO)\(_3\)P{(Cl)PPh\(_3\)}][AlCl\(_4\)] (12). The reactivity of 12 with organic nucleophiles reveals that the PPh\(_3\) unit is more labile and easily displaceable than the chloro. With carbonyl compounds, the P-P bond of 12 does not undergo a phospha-Wittig reaction, which suggests it less polarity. However, the PEt\(_3\) and PBu\(_3\) analogous are more polar at their P-P bond and thereby more reactive towards carbonyl compounds. Attempts to isolate a di-(phosphonio)-phosphido complex by substituting the P-Cl bond of 12 with a second equivalent of PPh\(_3\) were not successful, but resulted in the formation of a known di(phosphonio)-phosphenium salt via the dissociation of the P\(_3\) unit from the metal. Reaction of the dichlorophosphido complex with bis-(diphenylphosphino)ethane (dppe) resulted in a known 1,1,3,3-tetraphenyl-1,2,3-triphospholenyl salt via an intramolecular nucleophilic substitution reaction. In these reactions, the dichlorophosphido complex effectively acts as a source of P\(^+\). Reaction of the dichlorophosphido complex with bis-(diphenylphosphino)methane (dpdm) led to a dangling dpdm coordinated chlorophosphinidene complex.
[Cp*Mo(CO)_3{P(Cl)P(Ph_2)CH_2(Ph)_2}][AlCl_4] (22), which upon photolysis transformed into a chelated chlorophosphinidene complex [Cp*Mo(CO)_2{P(Cl)P(Ph_2)CH_2P(Ph_2)-k^2,P^1,P^4}][AlCl_4] (23) via a carbonyl loss followed by the coordination of the dangling phosphine phosphorus to the metal. The formation of the dicationic complex [Cp*Mo(CO)_2{P(P(Et_3))P(Ph_2)CH_2P(Ph_2)-k^2,P^1,P^4}][AlCl_4]_2 (24) demonstrates that our proposed methodology can be successfully applied to make metal complexes with unique P-P-P linkages. The reactivity of the dichlorophosphido towards a stable NHC carbene resulted in a carbene coordinated chlorophosphinidene 27. The strong σ donating nature of NHC was revealed by the ^31P NMR chemical shift of 27 which suggests a carbene coordinated chlorophosphinidene form for 27. Compound 27 is the first NHC stabilized terminal phosphinidene complex reported. Attempts to isolate a bis-NHC-coordinated phosphido complex by substituting the P-Cl bond of 27 with a second equivalent of NHC were not successful, but resulted in the formation of a bis-NHC coordinated phosphenium salt 29 via the dissociation of the bis-NHC-coordinated phosphorus unit from the metal.

3.4 EXPERIMENTAL

3.4.1 General Comments

All procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in an inert atmosphere glovebox. THF and diethyl ether were distilled from Na/benzophenone. Dichloromethane and hexane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper catalyst (hexane). Deuterated chloroform was distilled from P_2O_5. The NMR spectra were recorded in CDCl_3 using a Varian Mercury 300 spectrometer operating at
300.179 MHz (\(^1\)H), 121.515 MHz (\(^{31}\)P\(^1\)H)) and 75.479 MHz (\(^{13}\)C\(^1\)H)). Infrared spectra were recorded in solution in THF or CH\(_2\)Cl\(_2\) using a Digilab FTIR spectrophotometer. Photolysis was carried out in pyrex flasks using Rayonet photochemical reactor equipped with nine lamps with a maximum output of 260 nm. Mass spectra were recorded using a Finnigan-Matt TSQ-700 mass spectrometer equipped with electrospray ionization and a Harvard syringe pump. Paraformaldehyde (Alfa Aesar), isopropylamine (Alfa Aesar), 4 M HCl in dioxane (Alfa Aesar), 40% aqueous glyoxal (Alfa Aesar), Na\(_2\)CO\(_3\) (Aldrich), dppe (Aldrich) and dppm (Aldrich) were used as supplied without purification. Phosphorus trichloride (Aldrich) was purified by vacuum distillation before use.

### 3.4.2 Synthesis of [Cp*Mo(CO)\(_3\)PCl\(_2\)] (10)

To pentamethylcyclopentadiene (0.52 g, 3.8 mmol, 0.60 mL) in 50 mL THF was added n-butyllithium (2.40 mL of 1.6 M solution in hexane, 3.80 mmol). Molybdenum hexacarbonyl (1.00 g, 3.78 mmol) was then added, and the resulting solution was heated under reflux for 16 h, resulting in an orange solution of Li[Cp*Mo(CO)\(_3\)]. This solution was added in small portions to a solution of trichlorophosphine (1.03 g, 7.5 mmol, 0.66 mL) in 75 mL of THF at 0 °C. The reaction mixture was stirred for 30 min and the solvent was removed under vacuum at 0 °C. The orange residue obtained was extracted into pentane (40 mL) and the resulting solution was filtered using inverse filtration. The extraction step was repeated two times with the same volume of pentane. The pentane filtrate was concentrated under vacuum and the concentrated solution was then cooled to -30 °C for 1 h, resulting in the formation of large orange crystals. The crystals obtained were collected and stored at -35 °C. Yield = 1.15 g, 73%. IR (THF solution, cm\(^{-1}\), v(CO):
2018, 1952, 1932. $^{31}$P{¹H} NMR: δ 408.5. ¹H NMR: δ 1.96 (d, 15H, $J_{HP} = 9.0$ Hz, C₅(CH₃)₅). Spectral data match the reported values.⁹⁵

3.4.3 Synthesis of [{Cp*Mo(CO)₃}(µ-P₂Cl₃)][X] (11a, X = BPh₄ ; 11b, X = AlCl₄)

11a. [Cp*Mo(CO)₃PCl₂] (10, 20 mg, 0.047 mmol) was dissolved in CH₂Cl₂ (0.5 mL). The resulting solution was added to NaBPh₄ (16.4 mg, 0.047 mmol) and stirred for 30 min. A slow colour change from orange to dark red was observed. The solution was filtered through Celite and the solvent was removed under vacuum. The residue obtained was extracted in CH₂Cl₂ (0.5 mL) and crystallized as orange crystals by slow diffusion of diethyl ether into the CH₂Cl₂ solution. 11b. In a second trial, NaBPh₄ was replaced by AlCl₃ (6.3 mg, 0.0479) and the same procedure was followed. Yield (11a) = 14.7 mg, 55.0 %. (11b): Yield: 19.4 mg, 52.2% . IR (CH₂Cl₂ solution, cm⁻¹, ν(CO)): 2020, 1953, 1933. $^{31}$P{¹H} NMR: δ 318 (d, $¹J_{PP} = 527$ Hz, MoPP), 258 (d, $¹J_{PP} = 527$ Hz, MoPP).¹H NMR: δ 5.29 (s, CH₂Cl₂), δ 2.16 (d, $J_{HP} = 1.50$ Hz, 15H, C₅(CH₃)₅), 2.05 (s, 15 H, C₅(CH₃)₅). $^{13}$C{¹H} NMRS:

R: δ 233.2 (d, $J_{CP} = 8$ Hz, MoCO), 227.7 (s, MoCO), 227.3 (d, $J_{CP} = 4$ Hz, MoCO), 224.8 (s, MoCO), 224.4 (s, MoCO), 221.6 (s, MoCO), 110.9 (s, C₅(CH₃)₅), 108.4 (s, C₅(CH₃)₅), 11.1 (s, C₅(CH₃)₅), 10.7 (d, $J_{CP} = 4$ Hz, C₅(CH₃)₅). MS (electrospray, CH₂Cl₂ solution): $m/z = 789-809$ (M⁺, base peak at $m/z = 799$). Anal. Calcd for C₂₆H₃₀AlCl₇Mo₂P₂O₆·CH₂Cl₂: C, 30.81; H, 3.06. Found: C, 30.82; H, 3.16. Co-crystallized CH₂Cl₂ was observed in the ¹H NMR spectrum of the crystals.
Figure 3.5 Electrospray MS of [{Cp*Mo(CO)}₃(µ-P₂Cl₃)]⁺ (11) showing molecular ion cluster. (L). Calculated for C₂₆H₃₀O₆Cl₃P₂Mo₂. (R).

Experimental.

3.4.4 Synthesis of [Cp*Mo(CO)₃{P(Cl)(PPh₃)}][AlCl₄] (12)

[Cp*Mo(CO)₃PCl₂] (10, 20 mg, 0.047 mmol) and PPh₃ (12.5 mg, 0.047 mmol) were dissolved in CH₂Cl₂ (0.5 mL). The resulting solution was added to AlCl₃ (6.39 mg, 0.047 mmol) and stirred for 30 min. An immediate colour change from yellow to dark red was observed. The solvent was then removed under vacuum. The residue was extracted into CH₂Cl₂ (0.5 mL) and crystallized as yellow crystals by slow diffusion of diethyl ether into the CH₂Cl₂ solution. Yield: 24.6 mg, 63%. IR (THF solution, cm⁻¹, ν(CO)): 2017, 1967, 1932. ³¹P{¹H} NMR: δ 177 (d, JPP = 453 Hz, MoPP), 35.7 (d, JPP = 451 Hz, MoPP). ¹H NMR: δ 7.71–6.78 (multiplets, Ph), 1.88 (s, 15H, C₅(CH₃)₅). ¹³C NMR: δ 233.6 (dd, JCP = 10 Hz, JCP = 3 Hz, MoCO), 228.1 (s, MoCO), 221.5 (s, MoCO), 134.7 (d, JCP = 4 Hz, Ph), 133.9 (s, Ph), 133.8 (s, Ph), 133.5 (dd, JCP = 15 Hz, JCP = 4 Hz, Ph), 130.5 (d, JCP = 12 Hz, Ph), 120.6 (dd, JCP = 58 Hz, JCP = 6 Hz, ipso-Ph), 108.5 (s, C₅(CH₃)₅), 10.7 (d, JCP = 6 Hz, C₅(CH₃)₅). MS (electrospray, CH₂Cl₂ solution): m/z = 639-652 (M⁺, base peak.
at \( m/z = 644 \). Anal. Calcd. for \( C_{31}H_{30}MoO_{3}Cl_5AlP_2 \): C, 45.80; H, 3.72. Found: C, 45.70; H, 3.69.

**Figure 3.6** Electrospray MS of \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PPh}_3\}\}]^+ \) (12) showing molecular ion cluster. (L) Calculated for \( C_{31}H_{30}O_2P_2ClMo \). (R) Experimental.

### 3.4.5 Synthesis of \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(PEt}_3\}\}][\text{BPh}_4] \) (13)

\([\text{Cp}^*\text{Mo(CO)}_3\text{PCl}_2] \) (10, 30 mg, 0.072 mmol) was dissolved in 5.0 mL of \( \text{CH}_2\text{Cl}_2 \) and \( \text{PEt}_3 \) (8.49 mg, 0.0719 mmol, 10.5 \( \mu \text{L} \)) was added to the phosphido solution at \(-80 \) °C. The resulting solution was added to \( \text{NaBPh}_4 \) (24.6 mg, 0.0719 mmol) and stirred for 30 min. An immediate colour change from orange to dark red was observed. The reaction solution was concentrated to 0.5 mL and 10 mL of pentane was added to the concentrated solution with rapid stirring. The resulting orange precipitate was washed several times with pentane and dried overnight under vacuum. Yield: 32.4 mg, 60%. IR (THF solution, \( \text{cm}^{-1} \), \( \nu \) (CO)): 2028, 1950, 1939. \(^{31}\text{P} \{^1\text{H}\} \) NMR: \( \delta \) 167 (d, \( J_{\text{PP}} = 438 \) Hz, MoPP), 49.5 (d, \( J_{\text{PP}} = 438 \) Hz, MoPP). \(^1\text{H} \) NMR: \( \delta \) 7.50-6.85 (multiplets, Ph), 1.97 (s, 15H, \( \text{C}_5(\text{CH}_3)_3 \)), 1.76 (dq, 6H, \(^2J_{\text{HP}} = 11.4 \) Hz, \(^3J_{\text{HH}} = 7.50 \) Hz, -PCH\(_2\text{CH}_3\)), 0.99 (dt, 9H, \(^3J_{\text{HP}} = 18.0 \) Hz,
$^3J_{HH} = 7.80 \text{ Hz}, \text{-PCH}_2\text{CH}_3$). MS (electrospray, CH$_2$Cl$_2$ solution): $m/z$ 494-504 (M$^+$, base peak at $m/z = 501$).

![Electrospray MS](image)

**Figure 3.7** Electrospray MS of [Cp*Mo(CO)$_3$(P(Cl)(PEt$_3$))]$^+$ (13) showing molecular ion cluster. (L) Calculated for C$_{19}$H$_{30}$O$_3$P$_2$ClMo. (R) Experimental.

### 3.4.6 Synthesis of [Cp*Mo(CO)$_3$(P(Cl)(PBu$_3$))][BPh$_4$] (14)

[Cp*Mo(CO)$_3$PCl$_2$] (10; 50 mg, 0.119 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and PBu$_3$ (24.2 mg, 0.119 mmol, 28.9 µL) was added to this phosphido solution at -80 °C. The resulting solution was added to NaBPh$_4$ (41.0 mg, 0.119 mol) and stirred for one hour. The solution was then concentrated to 0.5 mL and 10 mL of pentane was added with rapid stirring. The yellow precipitate obtained was washed several times with pentane and dried overnight under vacuum. Yield 60.4 mg, 65.0%. IR (cast, cm$^{-1}$, ν(CO)): 2029, 1951 (broad). $^{31}$P{${^1}$H} NMR: δ 170 (d, $J_{PP} = 438$ Hz, MoPP), 42.6 (d, $J_{PP} = 438$ Hz, MoPP). $^1$H NMR: δ 7.80-6.80 (multiplets, Ph), 1.96 (s, 15H, C$_5$(CH$_3$)$_5$), 1.40 (broad, butyl protons), 0.94 (broad multiplets, butyl protons). MS (electrospray, CH$_2$Cl$_2$ solution): $m/z$ 579-589 (M$^+$, base peak at $m/z = 585$).
3.4.7 Reaction of [Cp*Mo(CO)₃{P(Cl)(PPh₃)}][AlCl₄] (12) with PPh₃ and AlCl₃

[Cp*Mo(CO)₃{P(Cl)(PPh₃)}][AlCl₄] (12, 50 mg, 0.061 mmol) and PPh₃ (16.1 mg, 0.0615 mmol) were dissolved in CH₂Cl₂ (5.0 mL). The resulting solution was transferred to a Schlenk tube charged with AlCl₃ (19.1 mg, 0.143 mmol), and stirred for 24 h at 38 ºC. A slow colour change from yellow to dark red was observed. The reaction solution was then concentrated to 0.5 mL and 10.0 mL of pentane was added with rapid stirring. The resulting orange precipitate formed was dried and extracted in CH₂Cl₂ (0.5 mL). The white crystals formed by the slow diffusion of diethyl ether in to the CH₂Cl₂ solution was identified as the di(phosphonio)-phosphenium salt [(PPh₃)₂P][AlCl₄]⁺ (16) using ³¹P NMR. Yield: 30.0 mg, 60.0%. ³¹P{¹H}NMR: δ 30.8 (d, JPP = 510 Hz, P-P-P), -172.1 (t, JPP = 500 Hz, P-P-P). ¹H NMR: δ 7.8-6.8 (multiplets, Ph). Spectral data match the reported values.¹¹₀

Figure 3.8 Electrospray MS of [Cp*Mo(CO)₃{P(Cl)(PBu₃)}]⁺ (14) showing molecular ion cluster. (L) Calculated for C₁₉H₃₀O₃P₂ClMo. (R) Experimental.
3.4.8 Reaction of [Cp*Mo(CO)₃PCl₂] with dppe and AlCl₃

[Cp*Mo(CO)₃PCl₂] (10, 50 mg, 0.119 mmol) and dppe (47.76 mg, 0.1198 mmol) were dissolved in CH₂Cl₂ (5.0 mL). The resulting solution was transferred to a vial charged with AlCl₃ (31.8 mg, 0.2384 mmol) and stirred for 30 min. An immediate colour change from yellow to dark red was observed. The solvent was removed in vacuum and the residue obtained was extracted in CH₂Cl₂. The white crystals formed by the slow diffusion of diethyl ether in to the CH₂Cl₂ solution was identified as the di(phosphonio)-phosphenium salt [P(Ph₂CH₂CH₂CH₃-k²P₁,P₄)₂][AlCl₄] (21) using ³¹P NMR. Yield: 45.0 mg, 62.0%. ³¹P{¹H} NMR: δ 63.70 (d, Jₚₚ = 456 Hz, P-P-P), -237.2 (t, Jₚₚ = 455 Hz, P-P-P). Spectral data match the reported values.¹¹¹

3.4.9 Synthesis of [Cp*Mo(CO)₃{P(Cl)P(Ph₂)CH₂CH₂P(Ph₂)}][AlCl₄] (22)

[Cp*Mo(CO)₃PCl₂] (10, 50 mg, 0.119 mmol) and dppm (46.08 mg, 0.1198 mmol) were dissolved in CH₂Cl₂ (2.00 mL). The resulting solution was transferred into a vial charged with AlCl₃ (15.9 mg, 0.1198 mmol) and stirred for 30 min. A slow colour change from yellow to dark red was observed. The reaction solution was then concentrated to 0.5 mL and 10 mL of pentane was added to the concentrated solution with rapid stirring, resulting in the precipitation of a dark red oily residue. The residue was washed with pentane and dried under vacuum overnight. Yield: 100 mg, 89.2%. IR (CH₂Cl₂ solution, cm⁻¹, ν (CO)): 2033, 2020, 1935. ³¹P{¹H} NMR: δ 190.3 (dd, Jₚₚ = 443 Hz, Jₚₚ = 57.8 Hz MoPPCH₂P), 35.7 (dd, Jₚₚ = 445 Hz, Jₚₚ = 65.2 Hz, MoPPCH₂P), -29.6 (dd, Jₚₚ = 65.2 Hz, Jₚₚ = 57.8 Hz, MoPPCH₂P). ¹H NMR: δ 7.0-8.0 (multiplets, Ph), 3.40 (d, 2H, Jₕₘ =
MoPPCH$_2$PP), 2.10 (s, 15H, C$_5$(CH$_3$)$_5$). MS (electrospray, CH$_2$Cl$_2$ solution): m/z 760-770 (M$^+$, base peak at m/z = 765).

**Figure 3.9** Electrospray MS of Cp*Mo(CO)$_3$[P(Cl)P(Ph$_2$)CH$_2$CH$_2$P(Ph$_2$)]$^+$ (22) showing molecular ion cluster. (L) Calculated for C$_{38}$H$_{35}$O$_3$P$_3$ClMo. (R) Experimental.

3.4.10 Synthesis of [Cp*Mo(CO)$_2$[P(Cl)P(Ph$_2$)CH$_2$CH$_2$P(Ph$_2$)]$^-$]Cl$_4$ (23)

[Cp*Mo(CO)$_3$[P(Cl)P(Ph$_2$)CH$_2$CH$_2$P(Ph$_2$)]][AlCl$_4$] (22, 112.0 mg, 0.1198 mmol) was prepared in CH$_2$Cl$_2$ according to the procedure described above (See 3.4.9). The CH$_2$Cl$_2$ solution of 22 was transferred to a Schlenk tube, which was then mounted inside a photo reactor and cooled to 0 °C. The reaction solution was then subjected to photolysis using UV radiation for 1.5 h. A gradual colour change from dark red to orange was observed. The reaction solution was then concentrated to 0.5 mL and pentane (10 mL) was added with rapid stirring. The resulting dark red coloured precipitate was washed several times with pentane and dried under vacuum. Yield: 48.6 mg, 50.0%, IR: (CH$_2$Cl$_2$ solution, cm$^{-1}$,
ν (CO): 2041, 1968. $^{31}$P$^1{^1}$H NMR: δ 225 (dd, $^1$J$_{PP}$ = 422 Hz, $^2$J$_{PP}$ = 10.4 Hz, MoPPCH$_2$P), 52.3 (dd, $^2$J$_{PP}$ = 63.7 Hz, $^1$J$_{PP}$ = 10.4 Hz, MoPPCH$_2$P), 31.1 (dd, $^1$J$_{PP}$ = 422 Hz, $^2$J$_{PP}$ = 62.2 Hz, MoPPCH$_2$P).$^1$H NMR: δ 7.57-7.25 (multiplets, Ph), 3.52 (multiplets, -CH$_2$), 1.86 (s, 15H, C$_5$(CH$_3$)$_5$. MS (electrospray, CH$_2$Cl$_2$ solution): m/z 731-743 (M$^+$, base peak at m/z = 737).

![Figure 3.10](image)

**Figure 3.10** Electrospray MS of [Cp*Mo(CO)$_2${P(PEt$_3$)P(Ph$_2$)CH$_2$CH$_2$P(Ph$_2$)-$^2$P$^1$P$^3$}]$^+$ (23) showing molecular ion cluster. (L) Calculated for C$_{37}$H$_{35}$O$_2$P$_3$ClMo. (R) Experimental.

### 3.4.11 Synthesis of [Cp*Mo(CO)$_2${P(PEt$_3$)P(Ph$_2$)CH$_2$CH$_2$P(Ph$_2$)-$^2$P$^1$P$^3$}]$^+[AlCl$_4$]_2$ (24)

[Cp*Mo(CO)$_2${P(Ph$_2$)CH$_2$CH$_2$P(Ph$_2$)-$^2$P$^1$P$^3$}]$^+[AlCl$_4$]_2$ (23, 50.0 mg, 0.0551 mmol) was dissolved in CH$_2$Cl$_2$ (5.0 mL) and PEt$_3$ (5.20 µL, 4.19 mg, 0.0051 mmol) was added. The resulting solution was transferred to a vial charged with AlCl$_3$ (7.35 mg, 0.0551 mmol) and stirred for 30 min. An immediate color change from red to dark red was observed. The reaction solution was then concentrated to 0.5 mL and 10 mL of pentane was added to the concentrated solution with rapid stirring, resulting in the precipitation of
a dark red oily residue. $^{31}$P{¹H} NMR: δ 31.3 (dd, $^1J_{PP} = 361$ Hz, $^2J_{PP} = 103$ Hz, P$^A$), -53.4 (ddd, $^1J_{PP} = 394$ Hz, $^1J_{PP} = 374$ Hz, $J_{PP} = 22.2$ Hz, P$^B$), 36.1 (ddd, $^1J_{PP} = 374$ Hz, $^2J_{PP} = 82.8$ Hz, $J_{PP} = 8.8$ Hz, P$^C$), 71.2 (ddd, $^2J_{PP} = 82.9$ Hz, $J_{PP} = 20.7$ Hz, $J_{PP} = 5.9$ Hz, P$^D$).

3.4.12 Synthesis of 1,3-Diisopropylimidazolium chloride (25)

The imidazolium chloride 25 was prepared according to a slightly modified reported procedure. Paraformaldehyde (0.375 g, 12.5 mmol) was added with vigorous stirring to a toluene solution (15 mL) of isopropylamine (1.06 mL, 12.5 mmol). The solution was stirred for 30 min. It was then cooled to 0 °C and a second equivalent of isopropylamine (1.06 mL, 12.5 mmol) was added. The resulting solution was then stirred for 10 min at 0 °C and then 4 M HCl in dioxane (3.13 mL, 12.5 mmol) was added dropwise. After warming to room temperature, 40% aqueous glyoxal (1.81 mL, 12.5 mmol) was added and the resulting cloudy solution was stirred at 37 °C for 68 h. After cooling to room temperature, the reaction solution was transferred to a separatory funnel and diethyl ether (15 mL) and saturated aqueous Na$_2$CO$_3$ (10 mL) were added. After shaking, the mixture separated in to three layers. The top and middle layers (dark brown) were collected. The bottom aqueous layer was washed three times with diethyl ether. The ether washes were combined with the organic layers. The solvent was removed under vacuum and the residue was extracted into CH$_2$Cl$_2$ (10 mL), dried over Na$_2$SO$_4$ and filtered. The solid residue obtained after the removal of the CH$_2$Cl$_2$ was washed with diethyl ether (2 x 10 mL) to yield a yellowish powder. Yield: 1.58 g, 67.0 %. ¹H NMR: 10.7 (s, 1H, Im-CH), 7.50 (s, 2H, HC=CH), 4.90 (septet, 1H, $J_{HH} = 6.70$ Hz, CH(CH$_3$)$_2$), 1.60 (d, 12H, $J_{HH} = 6.70$ Hz, CH(CH$_3$)$_2$).
3.4.13 Synthesis of 1,3-Diisopropylimidazol-2-ylidene (I\textsuperscript{I}Pr\textsubscript{2}) (26)

A solution of n-butyllithium (0.20 mL of 1.6 M solution in THF, 0.316 mmol) was added dropwise with constant stirring to a suspension of 1, 3-diisopropylimidazolium chloride (25, 50.0 mg, 0.264 mmol) in THF (5 mL). A slow precipitation of LiCl was observed and the solution turned grey. The reaction solution was then stirred for another 2 h at room temperature and the solvent was removed under vacuum. The pale yellowish oily residue obtained was extracted in CH\textsubscript{2}Cl\textsubscript{2} and filtered. The filtrate was directly used for subsequent reactions without further purification. The formation of carbene was confirmed by the \textsuperscript{1}H NMR spectrum, which does not show the imidazolium C-H resonance at δ 10.7. \textsuperscript{1}H NMR: 7.50 (s, 2H, H\textsubscript{C}=C\textsubscript{H}), 5.00 (septet, 1H, J\textsubscript{HH} = 6.70 Hz, CH(CH\textsubscript{3})\textsubscript{2}), 1.63 (d, 12H, J\textsubscript{HH} = 6.70 Hz, CH(CH\textsubscript{3})\textsubscript{2}).

3.4.14 Synthesis of [Cp*Mo(CO)\textsubscript{3} P{(Cl)(I\textsuperscript{I}Pr\textsubscript{2})}][AlCl\textsubscript{4}] (27)

[Cp*Mo(CO)\textsubscript{3}PCl\textsubscript{2}] (10, 100 mg, 0.239 mmol) was dissolved in 20 mL of CH\textsubscript{2}Cl\textsubscript{2} and added to the freshly prepared carbene solution. The resulting mixture was then transferred to a Schlenk tube charged with AlCl\textsubscript{3} (31.9 mg, 0.239 mmol), and stirred for 1 h. A slow colour change from orange to dark red was observed. The reaction solution was then concentrated to 1 mL and pentane (10 mL) was added with rapid stirring. The resulting yellow precipitate was then dried under vacuum. Yield: 85.0 mg, 50.4 %. IR: (THF solution, cm\textsuperscript{-1}, ν (CO)): 2020, 1955, 1933. \textsuperscript{31}P{\textsuperscript{1}H}NMR: δ148.7. \textsuperscript{1}H NMR: δ 7.46 (br s, 1H, HC=CH), 7.36 (br s, 1H, H\textsubscript{C}=CH), 5.05 (br multiplets, 1H, CH(CH\textsubscript{3})\textsubscript{2}), 4.64 (br multiplets, 1H, CH(CH\textsubscript{3})\textsubscript{2}), 1.94 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 1.76-1.38 (br multiplets, 12H,
CH(CH₃)₂. MS (electrospray, CH₂Cl₂ solution): m/z 529-540 (M⁺, base peak at m/z = 535).

**Figure 3.11** Electrospray MS of [Cp*Mo(CO)₃ P{(Cl)(iPr₂)}] (27) showing molecular ion cluster. (L) Calculated for C₂₂H₃₁O₃PN₂ClMo. (R) Experimental.

### 3.4.15 Formation of [(iPr₂)₂P][AlCl₄] (29)

[Cp*Mo(CO)₃PCl₂] (10, 50.0 mg, 0.119 mmol) was dissolved in 20 mL of CH₂Cl₂ and added to the freshly prepared carbene solution (see 3.4.13). The resulting mixture was then transferred to a Schlenk tube charged with AlCl₃ (30.9 mg, 0.239 mmol), and stirred for 1 h. A slow colour change from orange to dark red was observed. The reaction solution was then concentrated to 0.5 mL and pentane (10.0 mL) was added with rapid stirring. The resulting dark red coloured oily residue was then dried under vacuum. Yield: 30.2 mg, 50.0%. ³¹P{¹H}NMR: δ =134. ¹H NMR: 7.20 (br s, HC=CH), 4.65 (br septet, CH(CH₃)₂), 1.20 (d, CH(CH₃)₂). MS (electrospray, CH₂Cl₂ solution): m/z = 335 (M⁺). Spectral data match the reported values.¹¹¹
CHAPTER 4
SYNTHESIS AND REACTIVITY OF FUNCTIONALIZED PHOSPHINIDENE COMPLEXES

4.1 INTRODUCTION

The carbene like chemistry of terminal electrophilic phosphinidene complexes has been well established through their reaction towards a wide range of organic substrates like alcohols, amines, olefins, alkynes, conjugated dienes, \( \alpha,\beta \)-unsaturated ketones, enamines and ferrocene.\(^46,60,71,72\) In phosphinidene chemistry, the substituent on phosphorus plays a key role in phosphinidene reactivity. In order to expand the synthetic usefulness of terminal phosphinidene complexes in organophosphorus chemistry, phosphinidenes bearing new functionalized and hetero atomic groups have been therefore developed. Most known examples of heteroatom substituted phosphinidenes have been made using Mathey’s method of thermal decomposition of functionalized 7-phosphanorbornadiene complexes.\(^45\) The required 7-phosphanorbornadiene precursor complexes were obtained via the [4+2] cycloaddition between functionalized phosphole complexes and dimethylacetylenedicarboxylate (DMAD).\(^45,61\) A wide range of functionalized neutral phosphinidene complexes were reported through this method and a few characteristic examples are given below.

4.1.1 Ethoxycarbonylphosphinidene

An ethoxycarbonyl substituted 7-phosphanorbornadiene complex XXXV was used as a precursor for the transient ethoxycarbonylphosphinidene XXXVI. The required 7-phosphanorbornadiene precursor complex was obtained from the [4+2] cycloaddition
between a 1-(ethoxycarbonyl) phosphole complex and dimethyl acetylenedicarboxylate. The reactivity of this transient phosphinidene complex has been studied with various trapping reagents MeOH, Et₂NH and PhCCPh. (Scheme 4.1).¹²⁷

Scheme 4.1 Ethoxycarbonylphosphinidene

**4.1.2 Functionalized Alkylphosphinidenes**

A wide range of alkyl substituted terminal phosphinidene complexes have been reported using the same methodology. The generation of a (chloromethylphosphinidene) pentacarbonyltungsten complex XXXVII is shown in Scheme 4.2. When generated in the presence of CuCl, the chloromethylphosphinidene was reported to undergo a rearrangement to a π complex through migration of chlorine from carbon to phosphorus.¹²⁸
Scheme 4.2 Generation of chloromethylphosphinidene

Terminal phosphinidene complexes incorporating C=C bond have also been reported. The required 7-phosphanorbornadiene complex was generated as shown in Scheme 4.3. The 4-pentenylphosphinidene complex, generated from the corresponding phosphanorbornadiene precursor was reported to undergo a self condensation to give a bicyclic complex XXXVIII. The cyclization observed was so fast that the phosphinidene complex could not be trapped using external trapping reagents.\textsuperscript{129}

Scheme 4.3 Generation of 4-pentenylphosphinidene complex
4.1.3 Alkoxyphosphinidenes

The generation of neutral alkoxyphosphinidene complexes from a cyanophosphole complex has been reported by Marinetti et al.\textsuperscript{130} The required cyanophosphole complex was obtained via the reaction of cyanogen bromide (BrCN) with a phospholyllithium complex. The reaction of the cyanophosphole complex with alkoxy anions and subsequent [4+2] cycloaddition with DMAD and thermolysis resulted neutral alkoxyphosphinidene complexes XL. The transient alkoxyphosphinidenes formed were trapped with diphenylacetylene and the resulting phosphirene complexes were characterized (Scheme 4.4).\textsuperscript{35,131}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme4.4}
\caption{Scheme 4.4 Generation of alkoxyphosphinidenes}
\end{figure}

4.1.4 Alkynylphosphinidenes

Later, Mathey et.al extended the same synthetic methodology to the formation of alkynylphosphinidene complexes. They synthesized a 1-alkynyl phosphole complex XLI as shown in Scheme 4.5. The [4+2] cycloaddition of XLI with DMAD and subsequent thermolysis resulted the transient alkynylphosphinidene complex XLII, which was then
trapped by diphenylacetylene, resulting in the alkynylphosphirene complex XLIII (Scheme 4.5). \(^{132}\)

**Scheme 4.5 Synthesis of alkynylphosphinidene complex**

### 4.1.5 Fluoro and Chlorophosphinidenes

The generation of a neutral transient fluorophosphinidene complex, from a 7-fluoro-7-phosphanorbornadiene precursor was reported in 2006. \(^{133}\) The required phosphanorbornadiene precursor XLIV was synthesized via the [4+2] cycloaddition of a fluorophosphole molybdenum complex and DMAD. The transient fluorophosphinidene generated from the 7-fluro-7-phosphanorbornadiene at 120 °C in xylene was trapped with diphenylacetylene and 2,3-dimethylbutadiene as shown in Scheme 4.6.
Recently, Mathey et al. have shown that the [4+2] cycloaddition between a 1-chloro-3,4-dimethylphosphole complex and DMAD leads to a precursor for a transient chlorophosphinidene complex XLVI. The required chlorophosphole complex was synthesized directly from a lithiated phosphole complex as shown in Scheme 4.7. The transient chlorophosphinidene generated was trapped with diphenylacetylene and 2,3-dimethylbutadiene and the resulting compounds were characterized (Scheme 4.7).\textsuperscript{134}
4.1.6 Rational and objectives

The approach via phospholes and 7-phosphanobornadines, developed by Mathey et al., is a versatile synthetic methodology to a wide range of neutral phosphinidene complexes. Though the chemistry of these neutral functionalized phosphinidene complexes is well established, known cationic phosphinidene complexes have a more limited range of substituents. So far, cationic electrophilic phosphinidene complexes with amino and alkyl substituents at the phosphinidene center have been reported.\textsuperscript{55,78} As I have shown in Chapter 2, cationic electrophilic phosphinidene complexes can be readily generated under ambient reaction conditions via chloride abstraction reactions. This methodology will enable us to perform the phosphinidene chemistry at room temperature or even lower and would therefore, potentially avoid problems associated with decompositions at high temperature.
The chloride abstraction and the subsequent phosphine addition reactions at the dichlorophosphido complex are described in chapter 3. Though the dichlorophosphido complex does not serve as a precursor to the chlorophosphinidene, its facile nucleophilic substitution reactions, prompted me to consider its use as a precursor to other phosphido complexes. For example, reactions of the dichlorophosphido with anionic nucleophiles like alkyl, alkynyl and alkoxy anions may provide a direct synthetic route to chloro alkyl, alkynyl and alkoxyphosphido complexes, which could in turn serve as precursors to cationic alkyl, alkynyl and alkoxyphosphinidene complexes.

In this chapter, I will discuss the reactivity of the terminal dichlorophosphido complex and will investigate the development of new synthetic methodologies to functionalized cationic phosphinidene complexes.

The major objectives and topic discussed in the chapter are:

- Generate alkyl, alkynyl, alkoxy and thionylchlorophosphido complexes from the dichlorophosphido precursor via nucleophilic substitution reactions.
- Use the phosphido complexes as precursors to form and trap cationic alkyl, alkynyl, alkoxy and thionylphosphinidene complexes.
- Investigate the effect of different substituents on the electrophilicity and reactivity of cationic phosphinidene complexes.

4.1.7 Scope of the study

Nucleophilic substitution reactions at the dichlorophosphido will be investigated with a range of anionic nucleophiles. A chloroalkylphosphido complex will be synthesized by the reaction of the dichlorophosphido with an alkyl anion. Chloride
abstraction from the chloroalkylphosphido, using Lewis acid AlCl$_3$ will be used to generate corresponding alkylphosphinidene complexes. Nucleophilic substitution reactions at the dichlorophosphido with phenoxide and alkoxide anions will be used to generate chloroalkoxy and chlorophenoxyphosphido complexes. Chloride abstraction, using AlCl$_3$ will then be carried out to generate corresponding cationic alkoxy and phenoxyphosphinidene complexes. Formation of these cationic phosphinidene complexes will be confirmed by trapping reactions with alkynes and the reactivity of these phosphinidene complexes will be further studied with other reagents (e.g. phosphines and bisphosphines). A chlorothionylphosphido complex will be synthesized via the nucleophilic substitution reaction of the dichlorophosphido with a thiolate anion, which will be then used as precursors to thionylphosphinidenes. The reactivity of this newly formed thionylphosphinidene will be investigated towards alkynes and phosphines.

The reactivity of these various functionalized phosphinidene complexes ranging from alkyl to thionyl will be compared with the aminophosphinidene analogue and the effect of substituents on the phosphinidene reactivity will be eventually studied. In order to get further insight into their reactivity trends, a computational study on these various phosphinidene complexes will be performed and the results obtained will be compared with the experimental observations.

4.2 RESULTS AND COMPOUND CHARACTERIZATION

4.2.1 Generation of terminal chloroalkylphosphido complexes

The reaction of 10 with an alkyl nucleophile can be used as an alternative synthetic route to chloroalkylphosphido complexes. The subsequent chloride abstraction
using Lewis acids can generate corresponding alkylphosphinidenes. I have applied this methodology to the known chlorophosphido complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)}(\text{i-Pr})\}]\) (1), which was previously synthesized from \(\text{i-PrPCl}_2\) and \([\text{Cp}^*\text{Mo(CO)}_3]^-\) (See chapter 2). Isopropyl magnesium chloride (\(\text{i-PrMgCl}\)) was initially used as the nucleophile, but the reaction led to a mixture of unreacted starting material, mono- and di-substitution (Scheme 4.9). These products were identified using \(^{31}\text{P}\) NMR, which shows signals at \(\delta\) 410, 268 and 132 respectively. Diisopropylzinc reagent (Scheme 4.8), however, is more selective and leads to \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(i-Pr)}\}]\) (1) as the major product (Scheme 4.9). Compound 1 can be isolated through pentane extraction and crystallization. The spectroscopy of 1 matches that of the chloroalkylphosphido complex prepared earlier by the other route discussed in Chapter 2. The new method reported here, which does not require the usage of expensive dichloroisopropylphosphine serves as a good alternative synthetic route to terminal chloroalkylphosphido complexes. Abstraction of chloride from 1 leads to the transient alkylphosphinidene complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(i-Pr)}\}]\)[\(\text{AlCl}_4\)] (2), the chemistry of which was described in chapter 2.

\[
2 \text{i-PrMgCl} + \text{ZnCl}_2 \xrightarrow{0.5 \text{ hr}} \text{(i-Pr)}_2\text{Zn} + 2 \text{MgCl}_2 
\]

**Scheme 4.8** Formation of diisopropylzinc reagent
4.2.2 Reactivity of [Cp*Mo(CO)_3PCl_2] towards alkynyl, aryl and amide anions

Given the success of the isopropyl addition, I thought that a selective P-Cl bond substitution from the dichlorophosphido, using alkynyl anions could be used to form chloroalkynylphosphido complexes, precursors for alkynylphosphinidene complexes. The reaction of 10 was therefore investigated towards alkynyl anions. Lithium phenylacetylide, generated by the deprotonation of phenylacetylene using butyl lithium was used as the alkynyl source (Scheme 4.10). However, the reaction led only to the dialkynyl phosphido complex, regardless of stoichiometry. The poor selectivity could be due to the small steric size of the linear phenylacetylide moiety. Efforts to improve the selectivity of this reaction have been partially successful at low temperature. At -80 °C, the reaction was more selective towards the targeted mono-substituted product. However, during isolation and purification, this product apparently disproportionated into the di-substituted product and the starting PCl_2 complex (Scheme 4.11). Formation of the mono
and di substituted alkynylphosphido complexes 30 and 31 were identified from the $^{31}$P NMR spectrum, which shows signals at $\delta$ 157 and -105 respectively.

Scheme 4.10 Formation of lithium phenylacetylide

Scheme 4.11 Reaction of the dichlorophosphido towards phenylacetylide

Reaction of 10 with phenylmagnesium bromide (PhMgBr) does not give the expected chlorophenylphosphido complex but a rapid decomposition was observed. The use of a more sterically demanding mesitylmagnesium bromide gave the desired chloromesitylphosphido complex ($\delta$ 309 in $^{31}$P NMR), but the removal of the solvent and subsequent extraction in pentane resulted in decomposition. The reason for the instability of these phosphido complexes is not known (Scheme 4.12).

Reaction of 10 with one equivalent of lithium diisopropylamide (LDA) does not generate the expected di-isopropylaminophosphido, but again a rapid decomposition was observed (Scheme 4.12).
4.2.3 Generation of terminal chloroaryloxyphosphido complexes

The dichlorophosphido complex 10 is an effective precursor to aryloxyphosphido complexes. Reaction of 10 with one equivalent of aryloxide anions results in the formation of the corresponding chloroaryloxyphosphido complexes in good yield. The required aryloxide anions can be readily generated by deprotonating the corresponding phenol with butyl lithium. A range of chloroaryloxyphosphido complexes can be readily generated through this method as shown in Scheme 4.13. This method is simple, fast and offers access to a wide range of new chloroaryloxyphosphido complexes. These resulting chloroaryloxyphosphido complexes can serve as precursors to cationic aryloxyphosphinidenes, which have not been previously reported so far.
Scheme 4.13 Generation of chloroaryloxyphosphido complexes

The chlorophenoxy and chloronaphthoxyphosphido complexes \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)}(\text{OC}_6\text{H}_5)\}] (32)\) and \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)}(\text{OC}_{10}\text{H}_7)\}] (33)\) were isolated as oils. The chloro-t-butylphenoxyphosphido complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)}(\text{OC}_6\text{H}_4\text{C(CH}_3)_3)\}] (34)\) was isolated in 88 % yield as dark red crystals from hexane. The \(^{31}\text{P}\) NMR spectra of 32, 33 and 34 all show singlets at \(\delta\) 404. Their IR spectra show three sharp carbonyl stretching bands at 2013, 1945,1925 cm\(^{-1}\); 2012, 1942, 1928 cm\(^{-1}\) and 2017, 1953, 1931 cm\(^{-1}\) respectively.

4.2.4 Generation of terminal cationic aryloxyphosphinidenes

The chloride group on the phosphido complexes 32-34 can be readily abstracted using \(\text{AlCl}_3\), however, attempts to observe stable aryloxyphosphinidene complexes were not successful. At low temperatures, the abstraction reaction is suppressed, but at higher temperatures, decomposition is rapid. In the absence of trapping reagents, decomposition
of the aryloxyphosphinidenes led to \([\text{Cp}^\ast\text{Mo} (\text{CO})_3\{\text{PH(OR)}_2\}]^+\) (35) (Scheme 4.14). The
\(^{31}\text{P}\) NMR spectrum 35 shows a singlet at \(\delta 183\). The proton coupled \(^{31}\text{P}\) NMR shows the
peak at \(\delta 183\) as a doublet with a coupling constant of 455 Hz, indicating the presence of
a P-H bond. The P-H bond was further confirmed from the \(^1\text{H}\) NMR spectrum, which
shows a doublet at \(\delta 9.06\) with \(^{1}J_{\text{PH}} = 454\) Hz and also the integration of tert-butyl groups
vs Cp* show that two tert-butyl groups are present. The electrospray mass spectrum of 35
shows an isotope pattern with a base peak at \(m/z\) 647 that corresponds to the predicted
mass for the cation of the compound 35.

\[
\text{Scheme 4.14 Chloride abstraction from arylchlorophosphido complexes}
\]

The formation of 35 presumably occurs via a nucleophilic attack on the
phosphinidene complex by the oxygen atom of the second equivalent of the
phosphinidene, followed by hydrolysis by adventitious water. The fate of the second
metal complex is however unknown. The proposed mechanism is shown in Scheme 4.15.
4.2.5 Reaction of aryloxyphosphinidenes with diphenylacetylene

Although, stable aryloxyphosphinidenes could not be identified, transient phosphinidenes are readily identified through trapping reactions. Abstraction of chloride from compounds 32-34 with AlCl$_3$ in the presence of diphenylacetylene leads to the expected phosphairene complexes \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P}(\text{OC}_6\text{H}_5)\text{C(Ph)C(Ph)})\}][\text{AlCl}_4]\) (36), \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P}(\text{OC}_{10}\text{H}_7)\text{C(Ph)C(Ph)})\}][\text{AlCl}_4]\) (37) and \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P}(\text{OC}_6\text{H}_4\text{C(CH}_3)_3\text{C(Ph)C(Ph)})\}][\text{AlCl}_4]\) (38) (Scheme 4.16).
Scheme 4.16 Generation and trapping of phenoxyphosphinidenes

The $^{31}$P NMR spectrum of 36, 37 and 38 shows singlets at $\delta -21.1$, -21.0 and -21.4 respectively, in the high field region expected for phosphirene complexes. These resonance are deshielded compared to other comparable phosphirene complexes,\(^{54,81}\) as a result of the electronegative oxygen of the aryloxy substituent. Further support for these observed phenoxyphosphirene complexes 36-38 comes from the electrospray mass spectrum, which shows an isotope pattern with a base peak at $m/z$ 618, 668, 675 respectively, that corresponds to the predicted masses for the cations of their products. Since reaction with alkynes to form phosphirenes is considered a characteristic reaction of terminal electrophilic phosphinidene complexes\(^ {71}\), the observed products are strong supporting evidence for transient cationic phenoxyphosphinidenes.
4.2.6 Reaction of aryloxyphosphinidenes with PPh$_3$

In addition to the phosphirene complexes, I was able to successfully trap and isolate the aryloxyphosphinidenes using PPh$_3$, resulting in phosphine-coordinated aryloxyphosphinidene complexes \([\text{Cp}^\ast\text{Mo(CO)}_3\{\text{P(OC}_6\text{H}_5)\text{PPh}_3\}\}[\text{AlCl}_4]\) (39), \([\text{Cp}^\ast\text{Mo(CO)}_3\{\text{P(OC}_{10}\text{H}_7)\text{PPh}_3\}\}[\text{AlCl}_4]\) (40) and \([\text{Cp}^\ast\text{Mo(CO)}_3\{\text{P(OC}_6\text{H}_4\text{C(CH}_3)_3)\text{PPh}_3\}\}[\text{AlCl}_4]\) (41) (Scheme 4.17).

![Scheme 4.17 Reaction of aryloxyphosphinidenes with PPh$_3$](image)

The triphenylphosphine trapped aryloxyphosphinidene complexes were spectroscopically characterized. The $^{31}\text{P}\{^1\text{H}\}$ NMR of compounds 39-41 show two doublets at $\delta$ 242.0 and 27.0 with a common $^1J_{PP}$ of 490 Hz. This large coupling constant indicates a direct P-P bond, and is comparable with the coupling constants 340-455 Hz observed in phosphine coordinated phosphonium ions$^{52}$ and the 361-444 Hz coupling constants observed in phosphine coordinated phosphinidene complexes formed via the
trapping of transient phosphinidene complexes with phosphines.\textsuperscript{68,77} The IR spectra of \textbf{39} and \textbf{41} show three carbonyl-stretching bands at 2062, 1985, 1927 cm\textsuperscript{-1} and 2013, 1945, 1925 cm\textsuperscript{-1} respectively.

**4.2.7 Reaction of aryloxyphosphinidenes with bisphosphines**

After the observation of the desired reactivity of aryloxyphosphinidenes with moderately nucleophilic PPh\textsubscript{3}, its reactivity was further investigated with bisphosphines. The phosphido complex \textbf{34} was thus reacted with AlCl\textsubscript{3} in presence of bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)ethane (dppe). In both cases, reaction occurs readily at room temperature as shown in Scheme 4.18, resulting in the formation of the stable dangling phosphine coordinated phosphinidene complexes \[\text{[Cp*Mo(CO)\textsubscript{3}\{P(OC\textsubscript{6}H\textsubscript{4}C(CH\textsubscript{3})\textsubscript{3})P(Ph\textsubscript{2})CH\textsubscript{2}P(Ph\textsubscript{2})\}]AlCl\textsubscript{4}} \] (\textbf{42}) and \[\text{[Cp*Mo(CO)\textsubscript{3}\{P(OC\textsubscript{6}H\textsubscript{4}C(CH\textsubscript{3})\textsubscript{3})P(Ph\textsubscript{2})CH\textsubscript{2}CH\textsubscript{2}P(Ph\textsubscript{2})\}]AlCl\textsubscript{4}} \] (\textbf{43}) respectively.
The $^{31}$P NMR spectrum of 42 shows three resonances at $\delta$ 233 ($P^A$), 35.0 ($P^B$), -27.1 ($P^C$). The phosphinidene phosphorus $P^A$ appears at $\delta$ 233 as a doublet of doublets, showing a one bond $P$-$P$ coupling of 463 Hz with $P^B$ and a three bond coupling of 7.41 Hz to $P^C$. The end of the diphosphine that coordinates to the phosphinidene phosphorus $P^B$ appears at $\delta$ 35.0 as a doublet of doublet, showing a $P$-$P$ bond coupling of 463 Hz with $P^A$ and a two bond coupling of 53.3 Hz to $P^C$ across the dppm methylene group. The phosphorus resonance at the dangling end of the dppm ligand $P^C$ appears at -27.1 as a doublet of doublets, close to the chemical shift of the free dppm, and showing a two bond coupling of 53.3 Hz with $P^B$ and a three bond coupling of 7.41 Hz with $P^A$.

Similarly, the $^{31}$P NMR spectrum of 43 shows three resonances at $\delta$ 227 ($P^A$), 35.0 ($P^B$), -13.0 ($P^C$). The phosphinidene phosphorus $P^A$ appears at $\delta$ 227 as a doublet, showing a one bond $P$-$P$ coupling of 469 Hz with $P^B$. The end of the diphosphine that coordinates...
to the phosphinidene phosphorus \( P^B \) appears at \( \delta \ 35.0 \) as a doublet of doublet, showing a P-P bond coupling of 469 Hz with \( P^A \) and a three bond coupling of 37.0 Hz to \( P^C \) across the dppe ethylene group. The phosphorus resonance at the dangling end of the dppe ligand \( P^C \) appears at \(-13.0 \) as a doublet, close to the chemical shift of free dppe, and showing a three bond coupling of 37.0 Hz with \( P^B \). The solution IR spectra of 42 and 43 show three carbonyl-stretching bands at 2030, 1969, 1944 (sh) cm\(^{-1}\) and 2013, 1983, 1925 cm\(^{-1}\) respectively, clearly indicating that molybdenum retains three carbonyl ligands.

As observed in the case of the dangling phosphine coordinated chlorophosphinidene complexes (Chapter 3), the dangling phosphine coordinated aryloxyphosphinidene complexes 42 and 43 are also stable and do not undergo a spontaneous carbonyl loss at room temperature. However, the photolysis of a solution of 42 induces the carbonyl loss and leads to

\[
[Cp^*\text{Mo(CO)}_2\{P(\text{OC}_6\text{H}_4\text{C(CH}_3)_3)\text{P(Ph}_2)\text{CH}_2\text{P(Ph}_2)\}_k^2, \text{P}^1\text{P}^4]\text{[AlCl}_4\text{]} \quad (44),
\]

in which the dangling phosphine of the dppm is now coordinated to the metal (Scheme 4.19).

![Scheme 4.19 Photolysis of \([Cp^*\text{Mo(CO)}_2\{P(\text{OC}_6\text{H}_4\text{C(CH}_3)_3)\text{P(Ph}_2)\text{CH}_2\text{P(Ph}_2)\}_k^2, \text{P}^1\text{P}^4]\text{[AlCl}_4\text{]} \quad (44)](image)

The chelated aryloxyphosphinidene complex 44 formed was identified using the \(^{31}\text{P} \) NMR spectrum, which shows three resonances at \( \delta \ 263 \ (P^A), \ 58.2 \ (P^C), \ 25.4(P^B) \). The
phosphinidene phosphorus $P^A$ appears at $\delta$ 263 as a doublet, showing a $P$-$P$ bond coupling of 460 Hz with $P^B$. The end of the diphosphine $P^B$ that coordinates to the phosphinidene phosphorus appears at $\delta$ 25.4 as a doublet of doublets, showing a $P$-$P$ coupling of 460 Hz with $P^A$ and a two bond coupling of 81.5 Hz across the dppm methylene group with $P^C$. The metal coordinated phosphine phosphorus $P^C$ appears at $\delta$ 58.2 as a doublet, showing a two bond coupling of 81.5 Hz across the dppm methylene group with $P^B$.

4.2.8 Generation of chiral chloroalkoxyphosphido complexes

Reaction of 10 with enantiomerically pure alkoxide anions results in the formation of a diastereomeric mixture of alkoxyphosphido complexes, which can be used as precursors for chiral alkoxyphosphinidene complexes. Here, I report the synthesis of two specific chiral chloroalkoxyphosphido complexes, which were generated from the reaction of 10 with enantiomerically pure lithium menthoxide and lithium borneoxide nucleophiles.

4.2.8.1 Generation of chloromenthoxyphosphido complex

The reaction of 10 with an enantiomerically pure (-)-menthoxide anion results in the formation of a diastereomeric mixture of the phosphido complex [Cp*Mo(CO)$_3$\{P(Cl)(OC$_{10}$H$_{19}$)\}] (45). The complex 45 can be isolated from hexane in 62.5 % yield as red crystals. Two diastereomers were identified in the $^{31}$P NMR spectrum at $\delta$ 421 and $\delta$ 406, with a diastereomeric ratio of 27:73 (de = 46%) (Scheme 4.20). The IR spectrum of 45 shows three carbonyl stretching bands at 2009, 1939 and 1919 cm$^{-1}$. 

143
4.2.8.2 Generation of menthoxyporphosphinidene

Chloride abstraction from 45 using AlCl₃ results in the formation of the transient chiral menthoxyporphosphinidene complex \([\text{Cp}^{\ast}\text{Mo(CO)}_3\{\text{P}({\text{OC}}_{10}{\text{H}}_{19})\}]\) (46). The intermediacy of 46 has been demonstrated via trapping with diphenylacetylene and the stable phosphirene complex \([\text{Cp}^{\ast}\text{Mo(CO)}_3\{\text{P}({\text{OC}}_{10}{\text{H}}_{19})\text{C(Ph)C(Ph)})][\text{AlCl}_4]\) (47) was isolated and characterized (Scheme 4.21). Complex 47 was identified based on its $^{31}$P NMR spectrum, which shows a singlet at $\delta$ -32.6 and its electrospray mass spectrum, which shows an isotope pattern with a base peak at m/z 680 that corresponds to the predicted mass for the cation of the product.
After the generation of the chiral phosphinidene complex 46, I was curious to look into the asymmetric induction at the prochiral phosphinidene center. Therefore, the reactivity of 46 was investigated with the asymmetric alkyne phenylacetylene, leading to the phosphirene complex [Cp*Mo(CO)₃{P(OC₁₀H₁₉)C(H)C(Ph)}][AlCl₄] (48) as a mixture of two diastereomers as shown in scheme 4.22.

![Scheme 4.22 Reaction of menthoxyphosphinidene with phenylacetylene](image)

The $^{31}$P NMR of 48 shows singlets at -29.9 and -30.0, with a diastereomeric ratio of 60:40 (de = 20%). The low diastereomeric excess might be a result of the conformational flexibility of the P-O-C linkage, which may average the bias at the two diastereotopic phases and thereby reduces the asymmetric induction at the prochiral phosphinidene center. The $^1$H NMR spectrum shows two doublets at δ 9.53 and 9.38 with relative integrations of 60:40 for the phosphirene ring C-H of the two diastereomers. The structure of 48 was further supported by the electrospray mass spectrum, which shows an isotope pattern with a base peak at m/z 605 that corresponds to the predicted mass for the cation of the product 48.
The asymmetric induction at the phosphinidene center of 46 was then studied with triphenylphosphine, which leads to the formation of the phosphine coordinated phosphinidene complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(OC}_{10}\text{H}_{19})\text{PPh}_3\}\}]\text{[AlCl}_4\text{]}\) (49) as two diastereomers as indicated by \(^{31}\text{P}\) NMR spectrum (Scheme 4.23). The \(^{31}\text{P}\) NMR shows two sets of doublets at \(\delta\) 256, 27.9 and \(\delta\) 235, 26.3 in a ratio of 24:76 (de = 52 %). The diastereoselectivity observed here is considerably better than the phenylacetylene reaction.

![Scheme 4.23 Reaction of menthoxyphosphinidene with PPh₃](image)

### 4.2.8.3 Generation of chloroborneoxyphosphido complex

The reaction of 10 with an enantiomerically pure (-)-borneoxide anion results in the formation of a diastereomeric mixture of the phosphido complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(OC}_{10}\text{H}_{17})\}\}]\) (50). Two diastereomers were identified in the \(^{31}\text{P}\) NMR spectrum at \(\delta\) 418 and \(\delta\) 409, with a diastereomeric ratio of 51:49 (Scheme 4.24). The IR spectrum of 50 shows three carbonyl stretching bands at 2009, 1945 and 1922 cm\(^{-1}\).
4.2.8.4 Generation of borneoxyphosphinidene

Chloride abstraction from 50 using AlCl₃ results in the formation of the transient chiral borneoxyphosphinidene complex 51, which was trapped with diphenylacetylene to form \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(OC}_{10}\text{H}_{17})\text{C(Ph)C(Ph)}\}]\)[AlCl₄] (52) (Scheme 4.25).

The $^{31}$P NMR spectrum of 52 shows two isomers at δ -27.0 and -29.7 with relative integrations of 83:17. The formation of diastereomers is not expected here because the alkyne is symmetrical, and the phosphorus is not stereogenic in the product. The isomers observed could be therefore rotamers, which may arise due to the restricted rotation of the
sterically crowded borneoxy moiety across the C-O bond. The structure of 52 was further supported by the electrospray mass spectrum, which shows an isotope pattern with a base peak at m/z 679 that corresponds to the predicted mass for the cation of the product 52.

Reaction of 51 with phenylacetylene led to a diastereomeric mixture of the phosphirene complex \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(OC}_{10}\text{H}_{17})\text{C(H)}\text{C(Ph)}\}][\text{AlCl}_4]\) (53) as shown in scheme 4.26. The $^{31}$P NMR spectrum shows two diastereomers at $\delta$ -25.3 and -27.5 with a diastereomeric ratio of 52:48. In the $^1$H NMR spectrum, the phosphirene ring C-H resonances of the two diastereomers appear as doublets at $\delta$ 9.39 and 9.37 with a common $^2J_{PH}$ value of 16.8 Hz and a relative integration of 52:48. Formation of 53 was further confirmed from the electrospray mass spectrum, which shows an isotope pattern with a base peak at m/z 603 that corresponds to the predicted mass for the cation of the product 53.

![Scheme 4.26 Reaction of borneoxyphosphinidene with phenylacetylene](image)

The reactivity of the aryloxy and alkoxyphosphinidene complexes was further examined towards the C-H bonds of ferrocene. However, the attempts to trap these phosphinidene complexes with ferrocene were not successful, and the product was the same as those obtained in absence of trapping reagent. This contrasts with the
alkylphosphinidene [Cp*Mo(CO)₃{P-ᵢ-Pr}]⁺, which inserts in to the C-H bond of ferrocene.

### 4.2.9 Generation of chlorothiophenoxyphosphido complex

The dichlorophosphido complex 10 can be used as an effective precursor to thiophosphido complexes. Here, I have shown the formation of a terminal chlorothiophenoxyphosphido complex 54 via a nucleophilic substitution at 10 using a thiophenolate nucleophile (Scheme 4.27). The thiophenolate anion can be readily generated by deprotonating the thiophenol with butyl lithium. The resulting chlorothiophenoxy phosphido complex can serve as a precursor to cationic thiophenoxyphosphinidene.

**Scheme 4.27** Generation of thiophenoxyphosphido complex

The chlorothiophenoxyphosphido complex [Cp*Mo(CO)₃{P(Cl)(SC₆H₅)}] (54) was isolated in 65.5 % from hexane as orange crystals. The ³¹P NMR spectrum of 54 shows a singlet at δ 290. The IR spectrum of 54 shows three carbonyl stretching bands at 2017, 1946 and 1934 cm⁻¹, clearly indicating that the metal center retains three carbonyl ligands.
4.2.10 Generation of thiophenoxyphosphinidene

The chloride ligand on the phosphido complex 54 can be abstracted using AlCl₃. The chloride abstraction however, does not generate a stable thiophenoxyphosphinidene complex but forms an unidentified product, which resonates at δ 191 in the $^{31}$P NMR spectrum. Though I was unable to observe a stable thiophenoxyphosphinidene, its intermediacy has been confirmed by trapping reactions. When generated in presence of diphenylacetylene, the transient thiophenoxyphosphinidene readily undergoes a 1+2 cycloaddition and results in the formation of the expected phosphirene complex [Cp*Mo(CO)$_3${P(SPh)C(Ph)C(Ph)}][AlCl$_4$] (55) (Scheme 4.28).

![Scheme 4.28 Generation of thiophenoxy phosphirene complex](image)

The compound 55 was identified using the $^{31}$P NMR, which shows a signal at δ -78.9. Since reaction with alkynes to form phosphirenes is considered a characteristic reaction of terminal electrophilic phosphinidene complexes, the observed phosphirene complex is a strong supporting evidence for the transient cationic thionylphosphinidene. This is the first known terminal thionylphosphinidene complex reported.
4.2.11 Reaction of thiophenoxyphosphinidene with \( \text{PPh}_3 \)

In order to get an insight into the electrophilicity at the phosphinidene phosphorus, its reactivity was investigated with triphenylphosphine. The reaction readily takes place at room temperature, resulting in the formation of a phosphine coordinated thiophenoxyphosphinidene complex \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{P(SPh)}\text{PPh}_3]\}]\text{[AlCl}_4]\) (56) (Scheme 4.29). The phosphine coordinated phosphinidene complex 56 was identified using the \(^{31}\text{P}\) NMR, which shows two doublets at \( \delta\) 32.7 and 22.4 with a common \(^1J_{PP}\) of 488 Hz. This reactivity suggests that thiophenoxyphosphinidenes are similar in their reactivity to aryloxyphosphinidenes.

![Scheme 4.29 Reaction of thiophenoxyphosphinidene with \( \text{PPh}_3 \)]

4.3 COMPUTATIONAL STUDIES

In order to get further insight into the structure, bonding and reactivity of these various cationic phosphinidene complexes, detailed DFT computations were carried out at the B3LYP level of theory as implemented in Gaussian 09 Software program.\(^{135,141}\) Mayer bond\(^{136}\) orders and NBO charges\(^{137}\) were calculated, and fragment molecular orbital (FMO) analysis\(^{138,139}\) was carried out for each of the complexes. The optimized structures of these complexes \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\text{PX}\}]^+\), where \(X = \text{i-Pr}\) (57), N-\text{i-Pr}_2\) (58), OPh (59), and Cl (60), are shown in Figure 4.1. The optimized structure of the
aminophosphinidene complex (58) provided a good agreement with the experimentally determined structure.\(^5^2\)

![Figure 4.1 Optimized structures of phosphinidene complexes 57-60. Selected bond distances (Å) and angles: 57, Mo-P = 2.397, P-C = 1.873, Mo-P-C = 115.76. 58, Mo-P = 2.476, P-N = 1.671, Mo-P-N = 119.65. 59, Mo-P = 2.423, P-O = 1.658, Mo-P-O = 108.98. 60, Mo-P = 2.384, P-Cl = 2.065, Mo-P-Cl = 114.02.](image)

Qualitatively, it is expected for complexes 58, 59, 60 and 61 that the presence of non-bonding electrons of π-donor substituents X would compete with the metal based electrons to populate the empty p orbital of phosphorus. This competing π donation from the π donor substituents would result less effective M-to-P π-overlap and lower M-P bond orders (Figure 4.2). This expected trend is apparent from the computed Mayer bond
orders (Table 4.1). The P-\textit{i}-Pr complex 57, in which the M-to-P \(\pi\)-overlap is the only possibility to populate the empty p orbital of P shows the highest M-P bond order. In PN(\textit{i}-Pr\textsubscript{2}) complex, the more effective P-N \(\pi\)-overlap leads to less effective M-to-P \(\pi\)-overlap and therefore, it has the lowest M-P bond order. In the P-OPh complex, as the electronegativity of the \(\pi\)-donor substituent increased, the P-O \(\pi\)-overlap is significantly diminished and leads to increased M-P \(\pi\)-overlap and bond order. In the P-Cl complex, the P-Cl \(\pi\)-overlap is relatively more pronounced than the P-O \(\pi\)-overlap of 59, however, the associated higher electronegativity of the chloro substituent substantially leads to a very effective M-to-P \(\pi\)-overlap and a relatively higher M-P bond order. Interestingly, in the P-SPh complex, the P-S \(\pi\)-overlap is significantly increased and leads to decreased M-P \(\pi\)-overlap and bond order. This observed trend in the M-P bond orders of these phosphinidene complexes clearly tells that the P-\textit{i}-Pr and P-Cl phosphinidenes are the strongest \(\pi\)-acceptors, while, PN-\textit{i}-Pr\textsubscript{2}, PSPh and POPh are weaker \(\pi\)-acceptors. As the P-\textit{i}-Pr complex does not have a \(\pi\) donor substituent at the P atom, it shows the lowest P-X bond order. The PN-\textit{i}-Pr\textsubscript{2} complex has the highest P-X bond order, indicating a strong N-P \(\pi\) donation. The PSPh complex has a P-X bond order, which is very close to that of the PN-\textit{i}-Pr\textsubscript{2} complex, indicating a relatively strong X-P overlap. The PCl and POPh complexes show a P-X bond order intermediate between these extremes, showing evidence for weak X-P overlap.

Figure 4.2 M-P-X \(\pi\) bonding interaction
Table 4.1 Computed Mayer bond orders for phosphinidene complexes 57-61

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituent</th>
<th>Mo-P</th>
<th>P-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>i-Pr</td>
<td>1.326</td>
<td>0.908</td>
</tr>
<tr>
<td>58</td>
<td>N-i-Pr2</td>
<td>1.016</td>
<td>1.381</td>
</tr>
<tr>
<td>59</td>
<td>OPh</td>
<td>1.163</td>
<td>1.084</td>
</tr>
<tr>
<td>60</td>
<td>Cl</td>
<td>1.302</td>
<td>1.070</td>
</tr>
<tr>
<td>61</td>
<td>SPh</td>
<td>1.075</td>
<td>1.307</td>
</tr>
</tbody>
</table>

Computed NBO charges for complexes 57-61 are given in Table 4.2, which also provide the same scenario, with the positive charge, mainly accumulated on P. The charges listed are the summed charges of the [Cp*Mo(CO)3]^+ fragment, charge on P, and the summed charges of the phosphorus substituent. The summed charges of the [Cp*Mo(CO)3]^+ fragment gives an indication of the relative donor/acceptor abilities of the various phosphinidene ligands. As evident from the Table 4.2, the positive charge on the metal fragment is lowest for the PN-i-Pr2 complex, indicating that the PN-i-Pr2 is the weakest π acceptor/strongest donor among this series. This, in turn suggests that N to P π donation precludes significant metal to P π back donation, resulting in a ligand that is primarily a σ-donor, consistent with the bond order results. The P-Cl and P-i-Pr complexes have relatively higher positive charges on the [Cp*Mo(CO)3]^+ fragment, indicating that they act as π acceptors. As the P-i-Pr complex does not have a nonbonding electron pair at the i-Pr substituent, there is no π overlap with the substituent, and the
phosphorus p orbital is readily available to accept π back donation from the metal. Based on the positive charge on the metal fragment, the P-Cl ligand is a stronger π acceptor than the P-i-Pr. The P-OPh ligand, which shows a slight positive charge on the metal fragment, is a weak π acceptor. The relatively high positive charge on the metal fragment of the PSPh complex is ambiguous and in contrast to the bond order results.

Table 4.2 Computed NBO charges of phosphinidene complexes 57-61

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituent</th>
<th>Charge</th>
<th>[Cp*Mo(CO)]</th>
<th>P</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>i-Pr</td>
<td>0.260</td>
<td>0.933</td>
<td>-0.192</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>N-i-Pr₂</td>
<td>0.113</td>
<td>0.968</td>
<td>-0.082</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>OPh</td>
<td>0.197</td>
<td>1.124</td>
<td>-0.321</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Cl</td>
<td>0.339</td>
<td>0.823</td>
<td>-0.161</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>SPh</td>
<td>0.245</td>
<td>0.546</td>
<td>0.209</td>
<td></td>
</tr>
</tbody>
</table>

The summed charges on the phosphorus substituent also give an indication about the electron donating and electron accepting behaviour of the substituent. The lowest negative charge on the N-i-Pr₂ substituent indicates that the N-i-Pr₂ is the strongest π donor to P, while all other substituents have significantly lower π overlap. The summed negative charges on the i-Pr substituent is higher than that on the chloro, which is
contrary to expectation, suggesting that there is some Cl-to-P π donation. It is also noteworthy that the OPh substituent is the weakest π donor to P among this series. As a result of this weak π overlap, both from the OPh substituent and the metal center, and also due to the high electronegativity of oxygen, the P-OPh complex has the highest positive charge on P, suggesting that the P-OPh complex is the most electrophilic among this series. The SPh substituent is the only one among this series, which shows a positive charge, suggesting that there is a significant amount of S-to-P π donation. The results are summarized in Figure 4.4.

From the fragment molecular orbital (FMO) analysis of complexes 57-61, two primary interactions such as σ-donation and π back-donation interaction in molybdenum-phosphinidene bonding are established. In all these complexes, the σ-interaction mainly occurs from the highest occupied fragment orbital (HOFO) of the phosphinidene fragment to the lowest unoccupied fragment orbital (LUFO) of the \([\text{Cp}^*\text{Mo(CO)}_3]^+\) fragment (Figure 4.3[i]), and the π-interaction essentially occurs from the HOFO-1 of \([\text{Cp}^*\text{Mo(CO)}_3]^+\) to LUFO (empty p orbital of P) of the phosphinidene fragment (Figure 4.3 [ii]). The σ-donation interaction in the Mo-P bonds, interaction [i] in Figure 4.3, is stronger and similar in all complexes as witnessed by the population analysis of the \([\text{Cp}^*\text{Mo(CO)}_3]^+\) fragment LUFO (57[44.7%]; 58[44.9%]; 59[44.7%]; 60[42.7%]; 61 [40.1%]). The M-to-P π back-donation interaction, interaction [ii] in Figure 4.3.3, is comparatively weaker and increases in the order of 58<61<59<57~60 as is evident from the population analysis of the phosphinidene fragment LUFO (57[22.4%]; 58[09.1%]; 59[16.3%]; 60[23.3%]; 61 [14.4%]). This observed variation in the M-to-P π back donation is in agreement with the conclusions gained from bond orders and NBO charges.
that the M-to-P \( \pi \) back donation is strongest in the chloro and alkyl phosphinidenes, and weakest in the aminophosphinidene. The thiophenoxy and phenoxy are intermediate.

Figure 4.3 Fragment molecular orbitals of phosphinidene complexes

Isosurface plots (isovalue: 0.02) of selected fragment molecular orbitals (FOs) of \([\text{Cp}^*\text{Mo(CO)}_3]^+\) and \(\text{P(N-i-Pr}_2\) involved in \(\sigma\)-donation [i] and \(\pi\) back-donation [ii]. Isosurface plots of FOs of other complexes (\(X = i\)-Pr, OPh, Cl, SPh) are similar to those of the N-\(i\)-Pr\(_2\) complex shown. The values in brackets correspond to the percent changes in FO occupancies upon formation of complexes 57-61 from their corresponding \([\text{Cp}^*\text{Mo(CO)}_3]^+\) and PR fragments.
Finally, the reaction energies (kcal mol\(^{-1}\)) to abstract chloride using AlCl\(_3\) from their precursor complexes to generate phosphinidene complexes 57-61 have been computed. The results show that all reactions are exothermic and the generation of the aminophosphinidene 58 is found to be the most exothermic (-33.1 kcal/mol), suggesting that formation of 58 is relatively easier than others. The reaction energies of other complexes are in the order POPh (-15.4 kcal/mol), P-\(i\)-Pr (-12.3 kcal/mol) and PCl (-7.1 kcal/mol).

**Figure 4.4** Summary of the DFT calculations
4.4 DISCUSSION

I have examined cationic phosphinidene complexes with five different functional groups on P, formed via chloride abstraction. Among all, aminophosphinidene is stable\textsuperscript{52}, alkyl, alkoxy and thiophenoxyphosphinidenes are transient and chlorophosphinidene could not be formed by this route. Our inability to observe stable alkoxy or aryloxy phosphinidenes suggests that the alkoxy and aryloxy groups do not provide sufficient $\pi$-overlap to stabilize the electron deficient phosphorus, making them comparable to the alkyl phosphinidene. However, in contrast to the analogous alkyl phosphinidene, the alkoxy phosphinidenes do not activate the C-H bonds of ferrocene,\textsuperscript{78} suggesting that they may be less electrophilic than the alkyl phosphinidene. The replacement of oxygen with its heavier analogue sulfur leads to thionyl phosphinidenes. Since sulfur is more electropositive than oxygen, a relatively good extent of $\pi$ donation from the thionyl group to the phosphinidene orbital was expected. This is further supported from the computational calculations. Computed Mayer bond orders and the FMO analysis of the thiophosphinidene complex clearly suggest a significant amount of S-to- P $\pi$ donation. However, the inability to observe the stable thionylphosphinidene suggests that the $\pi$ donation from the thionyl group is not sufficiently enough to stabilize the phosphinidene as expected.

The computational study clearly shows why the aminophosphinidene is the only stable and isolable complex. Its formation is far more exothermic than the formation of any of the other phosphinidenes. The key difference is the extent of N to P $\pi$-donation, which is far greater than the $\pi$ donation in any of the other complexes, and I attribute its stability to this $\pi$-stabilization. Previous computational studies have shown that in $\pi$-donor
substituted free phosphinidenes, the ground spin state depends on the extent of π-overlap of the non-bonding electrons of π-donor substituent with an empty p orbital of phosphorus. In amino phosphinidenes, effective π-overlap favours the singlet state, but in alkoxy and halo phosphinidenes, less effective π-overlap favours the triplet ground state. The cationic metal complexes described here show the same trend: strong π donation for the aminophosphinidene, and weak π-donation in phenoxy and chloro phosphinidenes. The same trend is observed experimentally in related phosphonium ions, which are generally stable only when at least one substituent is an amino group. Clearly, the amino group is uniquely effective at stabilizing electron deficient phosphorus centers.

The extent of metal to phosphorus π-back donation also varies considerably between the different complexes. In the case of the aminophosphinidene, strong N-P π donation appears to precludes strong metal to P π back donation. In contrast, the chloro and alkyl phosphinidenes, which have weak or no X-P π overlap, are stronger π acceptors from the metal. Although π-back donation effectively alleviates positive charge on P in the alkyl and chloro phosphinidenes (Table 4.2), it does not appear to have the same stabilizing effect as N-P overlap.

Interestingly, the phenoxy phosphinidene has neither strong O-P overlap nor metal back donation. This suggests that repulsion by the oxygen lone pairs make π-back donation less favorable even if O-P π overlap is weak. The lack of π donation results in the highest positive charge at P, suggesting that the phenoxy phosphinidene should be the most electrophilic. Its failure to activate the C–H bonds of ferrocene is therefore most likely not a result of insufficient electrophilicity, but rather a result of an alternative, more
facile reaction, namely nucleophilic attack by the oxygen of a second equivalent of the phosphinidene complex (Scheme 4.15).

Although the chlorophosphinidene is clearly the least stable complex in the series, its formation is still exothermic, and the calculations reveal no inherent reason for instability. In fact, its P atom carries less positive charge than the alkyl or phenoxy phosphinidenes. This suggests that it should have similar stability and reactivity to the alkyl or alkoxy phosphinidenes, and should thus be trappable. Our inability to generate it as a transient species and trap it is therefore likely not a result of inherent instability, but rather a result of alternate lower energy pathways that lead to substitution reactions, rather than abstraction. This alternate reaction, unique to the chlorophosphinidene, likely results from the lack of steric protection provided by the chloro substituent.

4.5 CONCLUSIONS

Nucleophilic substitution reactions at the dichlorophosphido complex 10 using anionic nucleophiles serve as an efficient synthetic methodology to a range of new functionalized chlorophosphido complexes. I have successfully used this route to generate alkyl, phenoxy, alkoxy and thiophenoxy phosphinidenes. Unlike aminophosphinidenes, alkoxy or aryloxy and thiophenoxyphosphinidenes are not stable, but can be readily trapped with alkynes. In the phosphine trapping experiments, alkoxy, phenoxy and thiophenoxyphosphinidenes show higher reactivity than its aminophosphinidene analogue but do not C-H activate ferrocene. This may be due to the fact that there is an alternative, faster reaction, and not due to them not being electrophilic.
4.6 EXPERIMENTAL

4.6.1 General Comments

All procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in an inert atmosphere glove box. THF was distilled from Na/benzophenone. Dichloromethane and hexane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper oxide catalyst (hexane). Deuterated chloroform was distilled from P₂O₅. The NMR spectra were recorded in CDCl₃ using a Varian Mercury 300 spectrometer operating at 300.179 MHz (¹H), 121.515 MHz (³¹P{¹H}) and 75.479 MHz (¹³C{¹H}). Infrared spectra were recorded in THF, CH₂Cl₂ or hexane using a Digilab FTIR spectrophotometer. Mass spectrometry of metal complexes was carried out using a Finnigan-Matt TSQ-700 mass spectrometer equipped with electro spray ionization and a Harvard syringe pump. Isopropylmagnesium chloride (Aldrich), Zinc chloride (Aldrich), phenol (Aldrich), 2-napthol (Alfa Aesar), 4-tert-butylphenol (Alfa Aesar), (-)-menthol (Aldrich), (-)-borneol (Aldrich) and Thiophenol (Aldrich) were used as supplied without purification. Phenylacetylene (Aldrich) was purified by vacuum distillation before use.

4.6.2 Alternative synthesis of [Cp*Mo(CO)₃{P(Cl)(i-Pr)}] (1)

To ZnCl₂ (100 mg, 0.734 mmol) in 5 mL of THF was added i-PrMgCl (0.734 mL of 2M solution in THF, 1.460 mmol) dropwise with constant stirring. An immediate precipitation of MgCl₂ was observed, which upon stirring gradually dissolved and resulted a pale yellow solution. After the addition was completed, the reaction mixture was stirred for 30 min and the THF solution of the resulting Zn(i-Pr)₂ reagent was used in
situ for subsequent reactions without isolation. [Cp*Mo(CO)_3PCl_2] (10; 100 mg, 0.239 mmol) was dissolved in 25 mL of THF. The freshly prepared Zn(i-Pr)_2 reagent (0.922 mL of 0.13 M solution in THF, 0.119 mmol) was added dropwise via syringe to the phosphido solution with constant stirring. Upon the addition of the Zn(i-Pr)_2 reagent, an immediate colour change from orange to dark red was observed. After the addition was completed, the resulting solution was stirred for 30 min and the solvent was removed under vacuum. The dark red residue obtained was extracted in pentane (20 mL) and filtered. The pentane was removed under vacuum and the orange oil obtained was dissolved in minimum amount of hexane. The hexane solution was then cooled to -35 ºC for two days, resulting in the formation of orange crystals. Yield: 50.9 mg, 50%. Complete spectroscopic data is provided in chapter 2.

4.6.3 Synthesis of [Cp*Mo(CO)_3{P(Cl)(OC_6H_5)}] (32)

To phenol (11.3 mg, 0.119 mmol) in 5 mL of THF was added n-butyllithium (74.9 µL of 1.6 M solution in THF, 0.119 mmol) dropwise with constant stirring. After the addition was completed, the reaction mixture was stirred for 30 min. [Cp*Mo(CO)_3PCl_2] (10; 50 mg, 0.119 mmol) was dissolved in 10 mL of THF and the freshly prepared phenoxide ion solution was added dropwise via syringe. The solution was stirred for 30 min and the solvent was removed under vacuum. The orange residue was extracted into pentane (10 mL) and filtered. The pentane was evaporated, resulting in an orange oil. Yield: 33 mg, 56 %. IR (THF solution, cm^{-1}, ν(CO)): 2013, 1945, 1925. \(^{31}P\{^1H\} NMR: \delta 404.1. \(^1H\) NMR: 7.39-7.01 (multiplets, Ph), 1.96 (d, 15H, \(J_{HP} = 12.0 \text{ Hz, } C_5(CH_3)_3\)). \(^{13}C\) NMR: \(\delta 245.0 \text{ (s, MoCO), 233.3 (d, }^2J_{CP} = 6 \text{ Hz, MoCO), 226.2 (s, MoCO), 150.7 (d, }^2J_{CP} = 12\).
Hz, ipso-Ph), 128.3 (s, Ph), 122.5 (d, $^5J_{CP}$ 2 Hz, Ph), 118.2 (d, $^3J_{CP}$, 9 Hz, o-Ph), 107.6 (s, $C_5$(CH$_3$)$_5$), 105.04 (s, $C_5$(CH$_3$)$_5$), 9.61 (d, $J_{CP}$ = 3.62 Hz, $C_5$(CH$_3$)$_5$), 9.28 (d, $J_{CP}$ = 6 Hz, $C_5$(CH$_3$)$_5$).

4.6.4 Synthesis of [Cp*Mo(CO)$_3$P(Cl)(OC$_{10}$H$_7$)] (33)

To 2-naphthol (17.2 mg, 0.119 mmol) in 5 mL of THF was added n-butyllithium (74.9 µL of 1.6 M solution in THF, 0.119 mmol) dropwise with constant stirring. After the addition was completed, the reaction mixture was stirred for 30 min. [Cp*Mo(CO)$_3$PCl$_2$] (10; 50 mg, 0.119 mmol) was dissolved in 10 mL of THF and the freshly prepared naphthoxide ion solution was added dropwise via syringe. The reaction solution was stirred for 30 min and a slow colour change from orange to dark red was observed. The solvent was removed under vacuum and the dark red colored residue obtained was extracted into pentane (10 mL) and filtered. The pentane was removed under vacuum and the orange amorphous powder obtained was dissolved in minimum amount of hexane and cooled to -30 ºC for one day. Orange opaque crystals were formed at -30 ºC, but the crystals immediately turned into oil at room temperature. Yield: 42.9 mg, 68.3%. IR (THF solution, cm$^{-1}$, ν(CO)): 2012, 1942 sh, 1928. $^{31}$P{$^1$H} NMR: δ 404.1. $^1$H NMR: δ 8.0-7.2 (multiplets, Ph), 1.99 (d,15H, $J_{HP}$ = 3.60 Hz, $C_5$(CH$_3$)$_5$). $^{13}$C NMR: δ 246. 3 (s, MoCO), 234.5 (d, $^2J_{CP}$ = 6 Hz, MoCO), 227.0 (s, MoCO), 149.7 (d, $^2J_{CP}$ = 10.64 Hz, ipso-Naph), 134.4 (s, Naph), 129.56 (s, Naph), 127.8 (d, $J_{CP}$ = 3.62 Hz, Naph), 127.7 (d, $J_{CP}$ = 2 Hz, Naph), 124.0 (s, Naph), 122.9 (d, $J_{CP}$ = 4 Hz, Naph), 120.5 (d, $J_{CP}$ = 4 Hz, Naph), 118.7 (d, $J_{CP}$ = 4 Hz, ortho- Naph), 115.0 (d, $J_{CP}$ = 12 Hz, ortho-Naph), 108.8 (s, $C_5$(CH$_3$)$_5$), 106.3 (s, $C_5$(CH$_3$)$_5$), 10.88 (s, $C_5$(CH$_3$)$_5$).
4.6.5 Synthesis of [Cp*Mo(CO)$_3$(P(Cl)(OC$_6$H$_5$C(CH$_3$)$_3$))] (34)

Butyllithium (0.749 mL of 1.6 M solution in THF, 1.198 mmol) was added dropwise to a solution of 4-tert-butylphenol (180 mg, 1.198 mmol) in THF (5 mL). The solution was stirred for 30 min. Compound 10 (500 mg, 1.198 mmol) was dissolved in THF (25 mL). The 4-tert-butylphenoxide ion solution was then added dropwise, resulting in gradual colour change from orange to dark red. The solvent was removed under vacuum and the dark residue obtained was extracted in pentane (10 mL) and filtered. The pentane was removed under vacuum and the residue was dissolved in minimum amount of hexane. The hexane solution was then cooled to -35 ºC for 24 h, resulting in the formation of large dark red crystals. Yield: 558 mg, 87.7 %. IR (hexane solution, cm$^{-1}$, ν(CO)): 2017, 1953, 1931. $^3$P{$^1$H} NMR: δ 403.3. $^1$H NMR: δ 7.32 (d, 2H, $^3$J$_{HH}$ = 9 Hz, Ph), 7.10 (d, 2H, $^3$J$_{HH}$ = 9 Hz, Ph), 1.98 (d, 15H, $^1$J$_{HP}$ = 0.60 Hz, C$_5$(CH$_3$)$_5$), 1.29 (s, 9H, C(CH$_3$)$_3$). $^{13}$C NMR: δ 245.0 (s, MoC=O), 233.4 (d, $^2$J$_{CP}$ = 7 Hz, MoCO), 266.1 (s, MoC=O), 155.6 (d, $^2$J$_{CP}$ = 3 Hz, ipso-Ph), 145.2 (d, $^1$J$_{CP}$ = 1 Hz, Ph), 125.2 (s, Ph), 117.5 (d, $^3$J$_{CP}$ = 9 Hz, ortho-Ph), 107.5 (s, C$_5$(CH$_3$)$_5$), 104.9 (s, C$_5$(CH$_3$)$_5$), 33.3 (s, C(CH$_3$)$_3$), 30.4 (s, C(CH$_3$)$_3$), 9.64 (s, C$_5$(CH$_3$)$_5$), 9.28 (d, $^1$J$_{CP}$ = 7 Hz, C$_5$(CH$_3$)$_5$). Anal. Calcd for C$_{23}$H$_{28}$O$_4$ClMoP: C, 52.04; H, 5.32. Found: C, 51.92; H, 5.80.

4.6.6 Synthesis of [Cp*Mo(CO)$_3$[P(OC$_6$H$_5$C(Ph)C(Ph))]][AlCl$_4$] (36)

[Cp*Mo(CO)$_3$(P(Cl)(OC$_6$H$_5$))] (32; 50.0 mg, 0.095 mmol) was prepared in THF according to the procedure described above (See 4.6.3). The solvent was removed under vacuum and the oily residue obtained was extracted into CH$_2$Cl$_2$ (5.0 mL) and filtered. The orange filtrate obtained was transferred into a vial charged with diphenylacetylene
(21.3 mg, 0.119 mmol). The resulting solution was added to AlCl₃ (15.9 mg, 0.119 mmol) and stirred for 30 min. An immediate colour change from orange to dark red was observed. The reaction solution was then concentrated in vacuum and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting red oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 56.5 mg, 60%. IR (THF solution, cm⁻¹, ν(CO)): 2013, 1956, 1927. ³¹P{¹H} NMR: δ -21.2. ¹H NMR: δ 7.66-6.72 (multiplets, Ph), 2.18 (d, 15H, J_HP = 1.50 Hz, C₅(CH₃)₅). ¹³C NMR: δ 228.2 (s, MoCO), 226.0 (s, MoCO), 225.5 (s, MoCO), 150.6 (d, ²J_CP = 16 Hz, ipso-Ph), 146.1 (d, ¹J_CP = 15.9 Hz, phosphirene ring C), 132.8 (s, Ph), 131.2 (s, Ph), 130.4 (d, ³J_CP = 2 Hz, O-Ph), 130.2 (s, Ph), 129.4 (d, ²J_CP = 5 Hz, O-Ph), 126.4 (d, ³J_CP = 3 Hz, ipso-Ph), 121.5 (d, ³J_CP = 4 Hz, O-Ph), 119.6 (s, Ph), 110.2 (s, C₅(CH₃)₅), 11.7 (s, C₅(CH₃)₅). MS (electrospray, CH₂Cl₂ solution): m/z 613-622 (M⁺, base peak at m/z = 619).

4.6.7 Synthesis of [Cp*Mo(CO)₃{P(Cl)(OC₁₀H₇)}C(Ph)C(Ph)][AlCl₄] (37)

[Cp*Mo(CO)₃{P(Cl)(OC₁₀H₇)}] (33; 50.0 mg, 0.095 mmol) was prepared in THF according to the procedure described above (See 4.6.4). The solvent removed under vacuum and the oily residue obtained was extracted into CH₂Cl₂ (5.0 mL) and filtered. The red filtrate obtained was transferred into a vial charged with diphenylacetylene (21.3 mg, 0.119 mmol). The resulting solution was added to AlCl₃ (15.9 mg, 0.119 mmol) and stirred for 30 min, an immediate colour change to dark red was observed. The reaction solution was then concentrated in vacuum and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting red coloured oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 53.8 mg, 85.5 %. IR(THF solution, cm⁻¹
$^1$, ν(CO)) 2010, 1963, 1927 sh. $^{31}$P{$^1$H} NMR = δ -20.6, $^1$H NMR: δ 7.98-6.89 (multiplets, Ph), 2.13 (d, 15H, $J_{HP} = 1.20$ Hz, C$_5$(CH$_3$)$_5$). MS (electrospray, CH$_2$Cl$_2$ solution): m/z 663-672 (M$^+$, base peak at m/z = 668).

4.6.8 Synthesis of [Cp*Mo(CO)$_3${P(OC$_6$H$_4$C(CH$_3$)$_3$)C(Ph)C(Ph)}][AlCl$_4$] (38)

[Cp*Mo(CO)$_3${P(Cl)(OC$_6$H$_4$C(CH$_3$)$_3$)}] (34; 50.0 mg, 0.0941 mmol) and diphenylacetylene (16.7 mg, 0.0941 mmol) were dissolved in CH$_2$Cl$_2$ (5.0 mL). The resulting solution was added to AlCl$_3$ (12.5 mg, 0.0941 mmol) and stirred for 30 min. The solvent volume was reduced to ~2 mL, and pentane (10 mL) was added to the concentrated reaction solution with rapid stirring, resulting in the formation of a dark oil. The supernatant was decanted and the oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 24.1 mg, 38.4%. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, ν(CO)): 2017, 1979, 1951. $^{31}$P{$^1$H} NMR: -21.4, $^1$H NMR: 7.56 (s, 10H, Ph), 7.12 (d, 2H, $^3J_{HH} = 9.0$ Hz, Ph), 6.66 (d, 2H, $^3J_{HH} = 9.0$ Hz, Ph), 2.12 (s, 15H, C$_5$(CH$_3$)$_5$), 1.08 (s, 9H, C(CH$_3$)$_3$). $^{13}$C NMR: δ 228.3 (s, MoCO), 225.9 (s, MoCO), 225.4 (s, MoCO), 149.6 (s, Ph), 148.4 (d, $^1J_{CP} = 17$ Hz, phosphirene ring C), 146.3 (d, $J_{CP} = 16$ Hz, Ph), 132.7 (s, Ph), 130.1 (s, Ph), 129.3 (d, $J_{CP} = 6$ Hz, O-Ph), 127.2 (d, $J_{CP} = 2$ Hz, Ph), 126.6 (d, 3 Hz, ipso-Ph), 120.8 (d, $J_{CP} = 5$ Hz, ipso-Ph), 110.1 (s, C$_5$(CH$_3$)$_5$), 34.6 (s, C(CH$_3$)$_3$), 31.3 (s, C(CH$_3$)$_3$), 11.7 (s, C$_5$(CH$_3$)$_5$). MS (electrospray, CH$_2$Cl$_2$ solution): m/z 669-678 (M$^+$, base peak at m/z = 675).
4.6.9 Synthesis of [Cp*Mo(CO)$_3$P(OC$_6$H$_5$)$_3$PPh$_3$][AlCl$_4$] (39)

[Cp*Mo(CO)$_3$P(Cl)(OC$_6$H$_5$)$_3$] (32; 50.0 mg, 0.1050 mmol) was prepared in THF according to the procedure described above (See 4.6.3). The solvent was removed under vacuum and the oily residue obtained was extracted into CH$_2$Cl$_2$ (5.0 mL) and filtered. The red filtrate obtained was transferred into a vial charged with triphenylphosphine (27.5 mg, 0.1050 mmol). The resulting solution was added to AlCl$_3$ (14.0 mg, 0.1050 mmol) and stirred for 30 min. The reaction solution was then concentrated in vacuum and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting red coloured oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 50.2 mg, 55.0 %. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, v(CO)): 2013, 1945, 1925. $^{31}$P{$_1$H}NMR: $\delta$ 242 (d, $^1J_{PP} = 480$ Hz, MoPP), 27.9 (d, $^1J_{PP} = 480$ Hz, MoPP). $^1$H NMR: $\delta$ 7.79-6.65 (multiplets, Ph), 1.93 (s, 15H, C$_5$(CH$_3$)$_5$). $^{13}$C NMR: $\delta$ 232.7 (s, MoCO), 227.8 (s, MoCO), 222.9 (d, $^2J_{CP} = 7$ Hz, MoCO), 156.9 (d, $^1J_{CP} = 10$ Hz, Ph), 133.1 (dd, $^2J_{CP} = 22$ Hz, $^3J_{CP} = 3$ Hz, Ph), 132.7 (s, Ph), 128.9 (d, $^1J_{CP} = 11$ Hz, Ph), 128.6 (s, Ph), 121.7 (s, Ph), 119.3 (dd, $^1J_{PC} = 64$ Hz, $^2J_{PC} = 6$ Hz, ipso-Ph), 118.3 (d, $^1J_{PC} = 6$ Hz, Ph), 116.3 (d, $^1J_{CP} = 10$ Hz, Ph), 107.1 (s, C$_5$(CH$_3$)$_5$), 9.94 (d, $^1J_{CP} = 3$ Hz, C$_5$(CH$_3$)$_5$), 9.80 (d, $^1J_{CP} = 6$ Hz, C$_5$(CH$_3$)$_5$).

4.6.10 Synthesis of [Cp*Mo(CO)$_3$P(OC$_{10}$H$_7$)$_3$PPh$_3$][AlCl$_4$] (40)

[Cp*Mo(CO)$_3$P(Cl)(OC$_{10}$H$_7$)$_3$] (33; 50.0 mg, 0.0950 mmol) was prepared in THF according to the procedure described above (See 4.6.4). The solvent was removed under vacuum and the oily residue obtained was extracted in CH$_2$Cl$_2$ (5.0 mL) and filtered. The
red filtrate obtained was transferred into a vial charged with triphenylphoshine (24.9 mg, 0.0950 mmol). The resulting solution was added to AlCl₃ (12.6 mg, 0.0950 mmol) and stirred for 30 min. The reaction solution was then concentrated in vacuum and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting red oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 43.8 mg, 50.0 %. IR (CH₂Cl₂ solution, cm⁻¹, ν(CO)): 2010, 1946, 1925. ³¹P{¹H} NMR: δ 242.0 (d, ¹Jₚₚ = 478 Hz, MoP₃), 25.8 (d, ¹Jₚₚ = 478 Hz, MoPP). ¹H NMR: δ 7.79-6.65 (multiplets, Ph), 1.93 (s, 15H, C₅(CH₃)₅).

4.6.11 Synthesis of [Cp*Mo(CO)₃{P(OC₆H₄C(CH₃)₃)PPh₃}][AlCl₄] (41)

[Cp*Mo(CO)₃{P(Cl)(OC₆H₄C(CH₃)₃)}] (34, 50.0 mg, 0.0941 mmol) and triphenylphosphine (24.7 mg, 0.0941 mmol) were dissolved in CH₂Cl₂ (5.0 mL). The resulting solution was added to AlCl₃ (12.5 gm, 0.0941 mmol) and stirred for 30 min. The solvent was reduced under vacuum and pentane (10 mL) was added to the concentrated reaction solution with rapid stirring. The supernatant was removed and the resulting dark oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 63.80 mg, 73.2%. IR (CH₂Cl₂ solution, cm⁻¹, ν(CO)): 2062, 1985 (b), 1927 (b). ³¹P{¹H} NMR: δ 242.9 (d, ¹Jₚₚ = 491.8 Hz, MoPP), 27.7 (d, ¹Jₚₚ = 490.4 Hz, MoPP). ¹H NMR: δ 7.69-7.47 (multiplets, Ph), 7.09 (d, ³Jₕₕ = 9.0 Hz, Ph), 6.76 (d, ³Jₕₕ = 9.0 Hz, Ph) 1.93 (s, 15H, C₅(CH₃)₅), 1.59(s, 9H, C(CH₃)₃). ¹³C NMR: δ 233.9 (d, ²Jₕₚ = 9 Hz, MoCO), 229.0 (s, MoCO), 224.1 (d, Jₕₖ = 6 Hz, MoCO), 156.0 (d, Jₕₖ = 8 Hz, ipso-Ph), 145.8 (s, Ph), 134.2 (dd, Jₕₖ = 16 Hz, Jₕₖ = 3 Hz, Ph), 134.0 (d, Jₕₖ = 3 Hz, Ph), 130.1 (d, Jₕₖ = 11.3 Hz, Ph),
126.5 (s, Ph), 120.7 (dd, \( J_{CP} = 64 \) Hz, \( J_{CP} = 5 \) Hz, ipso-Ph), 117.0 (d, \( J_{CP} = 10 \) Hz, Ph), 108.3 (s, C\(_5\)(CH\(_3\))\(_5\)), 34.3 (s, C(CH\(_3\)))\(_3\)), 31.5 (s, C(CH\(_3\)))\(_3\)), 11.07 (multiplets, C\(_5\)(CH\(_3\))\(_5\)).

4.6.12 Synthesis of \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(OC}_6\text{H}_4\text{C(CH}_3\text{))}_3\}\text{P(Ph}_2\text{)}\text{CH}_2\text{P(Ph}_2\text{)}]\)[AlCl\(_4\)] (42)

\([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(OC}_6\text{H}_4\text{C(CH}_3\text{))}\}_3\}]\) (34, 50.0 mg, 0.1050 mmol) and dppm (40.3 mg, 0.1050 mmol) were dissolved in CH\(_2\)Cl\(_2\) (5.0 mL). The resulting solution was added to AlCl\(_3\) (14.0 mg, 0.1050 mmol) and stirred for 30 min. The solvent was reduced in vacuum and hexane (10 mL) was added to the concentrated reaction solution with rapid stirring. The supernatant was removed and the resulting dark oil was washed with hexane (5.0 mL) and dried under vacuum. Yield: 76.9 mg, 69.9 %. IR (CH\(_2\)Cl\(_2\) solution, cm\(^{-1}\), \( \nu(\text{CO}) \)): 2030, 1969, 1944. \(^{31}\)P\{\(^1\)H\}NMR: \( \delta \) 233.0 (dd, \( J_{PP} = 463 \) Hz, \( J_{PP} = 7.41 \) Hz, MoPPCH\(_2\)P), 35.0 (dd, \( J_{PP} = 463 \) Hz, \( J_{PP} = 53.3 \) Hz, MoPPCH\(_2\)P), -27.1 (dd, \( J_{PP} = 53.3 \) Hz, \( J_{PP} = 7.41 \) Hz, MoPPCH\(_2\)P). \(^1\)H NMR: \( \delta \) 7.8-6.8 (multiplets, Ph), 3.12 (multiplets, 2H, PCH\(_2\)P), 1.90 (s, 15H, C\(_5\)(CH\(_3\))\(_5\)), 1.20 (s, 9H, C(CH\(_3\)))\(_3\)).

4.6.13 Synthesis of \([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(OC}_6\text{H}_4\text{C(CH}_3\text{))}_3\}\text{P(Ph}_2\text{)}\text{CH}_2\text{P(Ph}_2\text{)}]\)[AlCl\(_4\)] (43)

\([\text{Cp}^*\text{Mo(CO)}_3\{\text{P(Cl)(OC}_6\text{H}_4\text{C(CH}_3\text{))}\}_3\}]\) (34, 50.0 mg, 0.1050 mmol) and dppe (41.8 mg, 0.1050 mmol) were dissolved in CH\(_2\)Cl\(_2\) (5.0 mL). The resulting solution was added to AlCl\(_3\) (14.0 mg, 0.1050 mmol) and stirred for 30 min. The solvent was reduced in vacuum and hexane (10 mL) was added to the concentrated reaction solution with rapid stirring. The supernatant was removed and the resulting yellow oil was washed with hexane (5.0 mL) and dried under vacuum. Yield: 63.0 mg, 56.5 %. IR (CH\(_2\)Cl\(_2\) solution, cm\(^{-1}\), \( \nu(\text{CO}) \)): 2030, 1969, 1944.
2013, 1983, 1925. \textsuperscript{31}P{\textsuperscript{1}H}\text{NMR: }\delta 227.0 \text{ (d, } J_{PP} = 469 \text{ Hz, MoPPCH}_2\text{CH}_2\text{P), } 35.0 \text{ (dd, } J_{PP} = 469 \text{ Hz, MoPPCH}_2\text{CH}_2\text{P). } \text{H NMR: } \delta 7.8-6.8 \text{ (multiplets, Ph), 1.25 (multiplets, PCH}_2\text{CH}_2\text{P), 1.90 (s, 15H, C(CH}_3)_5\text{), 1.20 (s, 9H, C(CH}_3)_3\text{).}

4.6.14 Synthesis of [Cp*Mo(CO)\textsubscript{3}{P(Cl)(OC\textsubscript{10}H\textsubscript{19})}] (45)
Butyl lithium (74.9 µL of 1.6 M solution in THF, 0.119 mmol) was added dropwise to a solution of (-)-menthol (18.7 mg, 0.119 mmol) in THF (5 mL). The solution was stirred for 30 min. Compound 10 (50 mg, 0.119 mmol) was dissolved in THF (10 mL). The menthoxide solution then added dropwise, resulting in an immediate colour change from orange to dark red. The reaction solution was stirred for 30 min and the solvent was removed under vacuum. The dark red residue was extracted into pentane (10 mL) and filtered. The pentane was removed and the dark oily residue was redissolved in minimum amount of hexane. The hexane solution was then cooled to -35 °C, resulting the formation of dark red crystals. Yield: 40.2 mg, 62.5%. IR (CH\textsubscript{2}Cl\textsubscript{2} solution, cm\textsuperscript{-1}, ν(CO)): 2009, 1939 sh, 1919. \textsuperscript{31}P{\textsuperscript{1}H}\text{NMR: }\delta 421.4 \text{ (27%), 406.3 (73%). } \text{H NMR (major diastereomer): } 3.68 \text{ (ddd, } 1\text{H, } J_{HP} = 32.7 \text{ Hz, } J_{HH} = 11.1 \text{ Hz, } J_{HH} = 4.5 \text{ Hz, } H_A \text{ menthol), 2.37-2.07 (broad multiplets, menthol), 1.89 (s, } 15\text{H, } C(CH}_3)_5\text{), 1.77-1.24 (broad multiplets, menthol), 0.91 (d, } 3\text{H, } J_{HH} = 6.6 \text{ Hz, CH(CH}_3)_2\text{(menthol), 0.87 (d, } 3\text{H, } J_{HH} = 7.2 \text{ Hz, -CH}_3\text{(menthol) }, 0.77 \text{ (d, } J_{HH} = 6.9 \text{ Hz, CH(CH}_3)_2 \text{(menthol). } 13\text{C NMR (major diastereomer): } \delta 246.3 \text{ (s, MoCO), 235.2 (d, } J_{CP} = 7 \text{ Hz, MoCO), 227.3 (s, MoCO), 108.8 (s, menthol } C_1\text{), 106.0 (s, } C(CH}_3)_5\text{, 79.9 (d, } J_{CP} = 15 \text{ Hz, CH, menthol) 49.4 (s, CH, menthol), 42.5 (s, CH}_2\text{, menthol), 34.4 (s, CH}_2\text{, menthol), 31.9 (s, CH,}
menthol), 24.8 (s, (CH\(_3\))\(_2\)C, menthol), 23.1 (s, CH\(_2\), menthol), 22.3 (s, menthol CH\(_3\)), 21.3 (s, menthol CH(CH\(_3\))\(_2\)), 16.0 (s, menthol CH(CH\(_3\))\(_2\)), 10.5 (d, \(J_{CP} = 6\) Hz, C\(_5\)(CH\(_3\))\(_3\)).


4.6.15 Synthesis of [Cp*Mo(CO)\(_3\){P(OC\(_{10}\)H\(_{19}\))C(Ph)C(Ph)}][AlCl\(_4\)] (47)

[Cp*Mo(CO)\(_3\){P(Cl)(OC\(_{10}\)H\(_{19}\))} (45, 50.0 mg, 0.0931 mmol) and diphenylacetylene (16.6 mg, 0.0931 mmol) were dissolved in CH\(_2\)Cl\(_2\) (5 mL). The resulting solution was added to AlCl\(_3\) (0.0124, 0.0931 mmol) and stirred for 30 min. The solvent was reduced under vacuum (~2 mL) and pentane (10 mL) was added to the concentrated reaction solution with rapid stirring. The supernatant was removed and the resulting dark colored oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 62.6 mg, 62.5%. IR (THF solution, cm\(^{-1}\), \(v\)(CO)): 2007, 1959, 1920 sh. \(^{31}\)P\(_{\{^1\}H}\) NMR: \(\delta\) 32.6. \(^1\)H NMR: \(\delta\) 7.48-6.89 (multiplets, Ph), 3.18 ( multiplet, 1H, H\(_A\) menthol), 1.80-1.77 (multiplets, menthol), 1.76 (s, 15H, C\(_5\)(CH\(_3\))\(_5\)), 1.75-0.53 (broad multiplets, menthol), 0.50 (d, 3H, \(^3\)J\(_{HH}\) = 6.0 Hz, -CH(CH\(_3\))\(_2\) (menthol)), 0.39 (d, 3H, \(^3\)J\(_{HH}\) = 6.0 Hz, -CH\(_3\) (menthol)), 0.01 (d, 3H, \(^3\)J\(_{HH}\) = 9.0 Hz, -CH(CH\(_3\))\(_2\)). \(^{13}\)C NMR: \(\delta\) 229.2 (s, MoCO), 226.5 (d, \(J_{CP} = 8\) Hz, MoCO), 225.9 (s, MoCO), 148.0 (d, \(^1\)J\(_{CP}\) = 18 Hz, phosphirene ring C), 147.6 (d, \(^1\)J\(_{CP}\) = 15 Hz, phosphirene ring C), 133.0 (s, Ph), 132.8 (s, Ph), 130.4 (s, Ph), 130.2 (s, Ph), 129.7 (d, \(J_{CP} = 6\) Hz, \(o\)-Ph), 129.3 (d, \(J_{CP} = 6\) Hz, \(o\)-Ph), 129.1 (s, Ph), 128.7 (s, Ph), 127.2 (d, \(^2\)J\(_{CP}\) = 3 Hz, \(ipso\)-Ph), 126.8 (d, \(^2\)J\(_{CP}\) = 3Hz, \(ipso\)-Ph), 109.7 (s, C\(_5\)(CH\(_3\))\(_3\)), 79.9 (d, \(^2\)J\(_{CP}\) = 15 Hz, CH, menthol), 48.6 (d, \(J_{CP} = 5\) Hz, CH, menthol), 42.6 (s, CH\(_2\), menthol), 33.6 (s, CH\(_2\), menthol), 31.8 (s, CH, menthol), 25.7 (s, menthol CH(CH\(_3\))\(_2\)), 22.9 (s, CH\(_2\), menthol),
22.0 (s, menthol CH₃), 21.2 (s, menthol CH(CH₃)₂), 16.0 (s, menthol C(CH₃)₂), 11.5 (s, C₅(CH₃)₅). MS (electrospray, THF solution): m/z = 675-684 (M⁺, base peak at = 680).

4.6.16 Synthesis of [Cp*Mo(CO)₃{P(OC₁₀H₁₉)C(H)C(Ph)}][AlCl₄] (48)

Phenylacetylene (10.24 µL, 9.50 mg, 0.0931 mmol) was added to a solution of [Cp*Mo(CO)₃{P(Cl)(OC₁₀H₁₉)}] (45; 50.0 mg, 0.0931 mmol) in CH₂Cl₂ (5.0 mL). The resulting solution was added to AlCl₃ (0.0124 g, 0.0931 mmol) and stirred for 30 min. The solvent was reduced under vacuum (~2 mL) and pentane (10 mL) was added to the concentrated reaction solution with rapid stirring. The supernatant was removed and the resulting dark red oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 72.0 mg, 77.8%. IR (THF solution, cm⁻¹, ν(CO)): 2007, 1961, 1900. ³¹P{¹H} NMR: δ -29.9 (40%), -30.0 (60%). ¹H NMR: δ 9.53 (d, 1H, ²J₆₇ = 18.0 Hz, phosphirene C-H, 40%), 9.38 (d, 1H, ²J₆₇ = 18.0 Hz, phosphirene C-H, 60%), 7.85-7.21 (multiplets, Ph), 4.18 (multiplets, menthol), 3.33 (broad multiplets, 1H, C-H menthol), 2.14 (s, 15H, C₅(CH₃)₅), 1.95 (s, 15H, C₅(CH₃)₅), 1.03-0.58 (broad multiplets, menthol), 0.33 (d, 3H, ³J₃₃ = 7.41 Hz, CH(CH₃)₂ (menthol)). ¹³C NMR(major diastereomer): 229.8 (d, ²J₆₇ = 11 Hz, MoCO), 225.1 (d, ²J₆₇ = 4 Hz, MoCO), 224.6 (d, ²J₆₇ = 5 Hz, MoCO), 160.4 (d, ¹J₆₇ = 18 Hz, phosphirene carbon), 159.5 (d, ¹J₆₇ = 18 Hz, phosphirene carbon), 130.4 (d, J₆₇ = 6 Hz, Ph), 130.2 (d, J₆₇ = 5 Hz, Ph), 130.0 (s, Ph), 129.8 (s, Ph). 129.7 (s, Ph), 129.6 (s, Ph), 125.4 (d, J₆₇ = 4 Hz, ipso-Ph), 109.0 (s, C₅(CH₃)₅), 79.3 (d, J₆₇ = 14 Hz, CH, menthol), 48.3 (d, J₆₇ = 5 Hz, CH, menthol), 43.0 (s, CH₂, menthol), 33.8 (s, CH₂, menthol), 31.6 (s, CH, menthol), 25.6 (s, (CH₃)₂C, menthol), 22.8 (s, CH₂, menthol), 22.1 (s, CH₃, menthol), 21.2 (s, C(CH₃)₂, menthol), 16.1 (s, C(CH₃)₂, menthol), 11.3
(multiplets, C$_5$(CH$_3$)$_5$). MS (electrospray, CH$_2$Cl$_2$ solution): m/z 599-608 (M$^+$, base peak = 605).

4.6.17 Synthesis of [Cp*Mo(CO)$_3${P(OC$_{10}$H$_{19}$)PPh$_3$}][AlCl$_4$] (49)

[Cp*Mo(CO)$_3${P(Cl)(OC$_{10}$H$_{19}$)}] (45, 50.0 mg, 0.0931 mmol) and triphenylphosphine (24.4 mg, 0.0931 mmol) were dissolved in CH$_2$Cl$_2$ (5.0 mL). The resulting solution was added to AlCl$_3$ (12.4 mg, 0.0931 mmol) and stirred for 30 min. The solvent was reduced under vacuum (~2 mL) and pentane (10 mL) was added to the concentrated reaction solution with rapid stirring. The supernatant was removed and the resulting dark oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 62.4, 72.0 %. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, v(CO)): 2062, 1985 (b), 1927 (b), 31P{$^1$H} NMR: δ 256 (d, $^1$J$_{PP}$ = 518.0 Hz, MoP, 24.0 %), 27.9 (d, $^1$J$_{PP}$ = 518.0 Hz, MoPP, 24.0 %), δ 235 (d, $^1$J$_{PP}$ = 533.0 Hz, MoPP, 76 %), 26.3 (d, $^1$J$_{PP}$ = 533.0 Hz, MoPP, 76 %). $^1$H NMR (major diastereomer): δ 7.73-7.26 (multiplets, Ph), 3.02 (broad singlet, H$_A$ menthol), 2.66-2.50 (broad multiplets, menthol), 2.07 (multiplets, menthol), 1.87 (s, 15H, C$_5$(CH$_3$)$_5$), 0.99-0.58 (broad multiplets, menthol), 0.16 (d, 3H, $^3$J$_{HH}$ = 7.20 Hz, CH(CH$_3$)$_2$ (menthol)). $^{13}$C NMR (major diastereomer): δ 232.3 (s, MoCO), 228.6 (s, MoCO), 228.2 (s, MoCO), 134.2 (dd, $J_{CP}$ = 9 Hz, J$_{CP}$ = 3 Hz, Ph), 134.0 (d, $J_{CP}$ = 4 Hz, Ph), 138.8 (dd, $J_{CP}$ = 9 Hz, J$_{CP}$ = 3 Hz, Ph), 133.2 (s, Ph), 133.0 (d, $J_{CP}$ = 2 Hz, Ph), 132.8 (d, $J_{CP}$ = 3 Hz, Ph), 130.1 (d, $J_{CP}$ = 11 Hz, Ph), 129.9 (d, $J_{CP}$ = 11 Hz, Ph), 122.9 (dd, $^1$J$_{CP}$ = 60 Hz, $^2$J$_{CP}$ = 5 Hz, ipso-Ph), 109.4 (s, C$_5$(CH$_3$)$_5$), 82.1 (s, CH, menthol), 50.0 (d, CH J$_{CP}$ = 3 Hz, menthol), 41.6 (s, CH$_2$, menthol), 34.1 (s, CH$_2$, menthol), 31.8 (s, CH, menthol), 24.6 (s, (CH$_3$)$_2$C, menthol), 22.8
(d, $J_{CP} = 9$ Hz, CH$_2$, menthol), 22.4 (s, CH$_3$, menthol), 21.3 (s, C(CH$_3$)$_2$, menthol), 15.6 (s, C(CH$_3$)$_2$, menthol), 10.9 (multiplets, C$_5$(CH$_3$)$_5$).

4.6.18 Synthesis of [Cp*Mo(CO)$_3${P(Cl)(OC$_{10}$H$_{17}$)}] (50)

To (-)-borneol (36.9 mg, 0.239 mmol) in 5.0 mL of THF was added n-butyllithium (150.0 µL of 1.6 M solution in THF, 0.239 mmol) dropwise with constant stirring. After the addition was completed, the reaction mixture was stirred for 30 min. [Cp*Mo(CO)$_3$PCl$_2$] (10; 100 mg, 0.239 mmol) was dissolved in 10 mL of THF and the freshly prepared borneoxide ion solution was added dropwise via syringe. A slow colour change from orange to dark red was observed. The solution was stirred for 30 min and the solvent was removed under vacuum. The dark red residue obtained was extracted into pentane (20 mL) and filtered. The pentane was evaporated and the dark oily residue obtained was dissolved in minimum amount of hexane. The hexane solution was then cooled to -35 ºC for 24 h, resulting in the formation of dark red crystals. At room temperature, the crystals obtained were immediately turned into oil. Yield: 100 mg, 78.0%. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, $\nu$(CO)) 2009, 1945, 1921. $^{31}$P{$_1^H$} NMR: $\delta$ 418, 409 (diastereomeric ratio 51:49). $^1$H NMR: $\delta$ 4.16 (triplet, 1H, $^3J_{H-H} = 9.81$ Hz, C-H, borneoxy), 2.10-2.00 (broad multiplets, borneoxy), 1.93 (d, 15H, $J_{H-P} = 3.60$ Hz, C$_5$(CH$_3$)$_5$), 1.78-1.10 (broad multiplets, borneoxy), 0.94-0.76 (broad multiplets, borneoxy), 1.86 (broad singlet, 4H, borneoxy).

4.6.19 Synthesis of [Cp*Mo(CO)$_3${P(OC$_{10}$H$_{17}$)C(Ph)C(Ph)}][AlCl$_4$] (52)

[Cp*Mo(CO)$_3${P(Cl)(OC$_{10}$H$_{17}$)}] (50; 50.0 mg, 0.095 mmol) was prepared in THF according to the procedure described above (See 4.6.18). The solvent was removed under
vacuum and the oily residue obtained was extracted in CH$_2$Cl$_2$ (5.0 mL) and filtered. The red filtrate obtained was transferred into a vial charged with diphenylacetylene (21.3 mg, 0.119 mmol). The resulting solution was then added to AlCl$_3$ (15.9 mg, 0.119 mmol) and stirred for 30 min, an immediate colour change to dark red was observed. The reaction solution was then concentrated under vacuum (~2 mL) and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting dark red oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 90 mg, 88.7%. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, $\nu$(CO)): 2051, 1970 (b). $^{31}$P{$^1$H} NMR: $\delta$ -27.0, -30.0 (Isomeric ratio 83:17). $^1$H NMR: $\delta$ 7.76-7.18 (multiplets, Ph), 3.86 (triplet, 1H, $^3J_{H-H} = 12.0$ Hz, C-H, borneoxy), 2.26-2.10 (multiplets, borneoxy), 2.03 (s, 15H, C$_5$(CH$_3$)$_5$), 1.90-0.67 (multiplets, borneoxy). MS (electrospray, CH$_2$Cl$_2$ solution): $m/z$ 673-682 (M$^+$, base peak = 679).

**4.6.20 Synthesis of [Cp*Mo(CO)$_3${P(OC$_{10}$H$_{17}$)}C(H)C(Ph)}][AlCl$_4$] (53)**

Cp*Mo(CO)$_3${P(Cl)(OC$_{10}$H$_{17}$))} (50; 50.0 mg, 0.095 mmol) was prepared in THF according to the procedure described above (See 4.6.18). The solvent was removed under vacuum and the oily residue obtained was extracted in CH$_2$Cl$_2$ (5.0 mL) and filtered. In to the filtrate, phenylacetylene (13.1 µL, 12.2 mg, 0.119 mmol) was added and the resulting solution was then transferred to AlCl$_3$ (15.9 mg, 0.119 mmol) and stirred for 30 min. The reaction solution was then concentrated in vacuum (~2 mL) and pentane (10 mL) was added with rapid stirring. The supernatant was removed and the resulting dark red oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 45.8 mg, 63.8%. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, $\nu$(CO)): 2055, 2038, 1971. $^{31}$P{$^1$H} NMR: $\delta$ -25.3, -27.5
(diastereomeric ratio 52:48). $^1$H NMR: $\delta$ 9.39 (d, 1H, $^2J_{HP}$ = 16.80 Hz, C-H phosphirene, 52 %), 9.37 (d, 1H, $^2J_{HP}$ = 16.80 Hz, C-H phosphirene, 48 %), 7.20-7.80 (multiplets, Ph), 4.50 (triplet, 1H, $^3J_{HH}$ = 9.81 Hz, C-H, borneoxy), 2.60-2.20 (multiplets, borneoxy), 1.93 (s, 15H, $C_5(CH_3)_5$), 1.80-0.50 (multiplets, borneoxy). MS (electrospray, CH$_2$Cl$_2$ solution): m/z 597-606 (M$^+$, base peak = 603).

4.6.21 Synthesis of [Cp*Mo(CO)$_3$(P(Cl)(SC$_6$H$_5$))] (54)

To thiophenol (0.05 mL, 53.8 mg, 0.488 mmol) in 10 mL of THF was added butyl lithium (0.305 mL of 1.6 M solution in hexanes, 0.488 mmol) dropwise with constant stirring at room temperature. The reaction solution was stirred for 15 min and the THF solution of the resultant lithium thiophenolate reagent was used for subsequent reaction without isolation. [Cp*Mo(CO)$_3$P$i$Cl] (10; 50.0 mg, 0.1198 mmol) was dissolved in THF (10 mL) and cooled to -80 °C. The freshly prepared PhSLi reagent (1.28 mL of 0.047 M solution in THF, 0.0599 mmol) was added dropwise via syringe to the phosphido solution with constant stirring. The reaction solution was stirred for 30 min at -80 °C and then warmed to 0 °C. The solvent was removed under vacuum and the residue obtained was extracted in pentane (20 mL) and filtered. The pentane was removed under vacuum and the orange oil obtained was dissolved in minimum amount of hexane. The hexane solution was then cooled to -35 °C for two days, resulting in the formation of orange crystals. The crystals turned oily at room temperature. Yield: 38.5 mg, 65.5%. IR (CH$_2$Cl$_2$ solution, cm$^{-1}$, $\nu$(CO)): 2017, 1934, 1946. $^{31}$P{$^1$H}NMR: 290.5 , 290.4 (Isomers). $^1$H NMR: 7.63-7.09 (multiplets, Ph), 2.01 (s, 15H, $C_5(CH_3)_5$, 34.0 %), 1.94, 15H, $C_5(CH_3)_5$, 66.0 %). $^{13}$C NMR: $\delta$ 246.3 (s, MoCO), 227.3 (s, MoCO), 216.8 (s, MoCO), 131.0 (d, $J_{CP}$ = 7 Hz, ipso-
Ph), 129.0 (s, Ph), 128.5 (s, Ph), 127.4 (s, Ph), 108.8 (s, C\(_5\)(CH\(_3\))\(_3\)), 106.7 (s, C\(_5\)(CH\(_3\))\(_3\)), 10.8 (s, C\(_5\)(CH\(_3\))\(_3\)), 10.5 (d, \(J_{CP} = 6\) Hz, C\(_5\)(CH\(_3\))\(_3\)).

**4.6.22 Synthesis of [Cp*Mo(CO)\(_3\){P(SPh)C(Ph)C(Ph)}][AlCl\(_4\)] (55)**

[Cp*Mo(CO)\(_3\){P(Cl)(SC\(_6\)H\(_5\))}] (54; 50.0 mg, 0.1018 mmol) was prepared in THF according to the procedure described above (See 4.6.21). The solvent was removed under vacuum and the oily residue obtained was extracted in CH\(_2\)Cl\(_2\) (5.0 mL) and filtered. The orange filtrate was transferred to a vial charged with diphenylacetylene (18.1 mg, 0.1018 mmol). The resulting solution was added to AlCl\(_3\) (13.5 mg, 0.1018 mmol) and stirred for 30 min. An immediate colour change from orange to dark red was observed. The reaction solution was then concentrated under vacuum (~ 2 mL) and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting dark red oil was washed with pentane (5.0 mL) and dried under vacuum. Yield: 56.0 mg, 68.6 %. IR (CH\(_2\)Cl\(_2\) solution, cm\(^{-1}\),\(\nu\)(CO)): 2052, 1985, 1976. \(^{31}\)P\({\text{-}}^1\)H NMR: -78.9 %. \(^1\)H NMR: 7.62-7.25 (multiplets, Ph), 1.94 (s, 15H, C\(_5\)(CH\(_3\))\(_3\)).

**4.6.23 Synthesis of [Cp*Mo(CO)\(_3\){P(SPh)PPh\(_3\)}][AlCl\(_4\)] (56)**

Cp*Mo(CO)\(_3\){P(Cl)(SC\(_6\)H\(_5\))}] (54; 50.0 mg, 0.1018 mmol) was prepared in THF according to the procedure described above (See 4.6.21). The solvent was removed under vacuum and the oily residue obtained was extracted in CH\(_2\)Cl\(_2\) (5.0 mL) and filtered. The orange filtrate was transferred to a vial charged with triphenylphosphine (26.4 mg, 0.1018 mmol). The resulting solution was added to AlCl\(_3\) (13.5 mg, 0.1018 mmol) and stirred for 30 min. A gradual colour change from orange to dark red was observed. The reaction
solution was then concentrated under vacuum (~ 2 mL) and pentane (10 mL) was added to it with rapid stirring. The supernatant was removed and the resulting dark red oil was washed with pentane (5.0 mL) and dried under vacuum. $^{31}$P$^1$H NMR: δ 32.7 (d, $^1J_{PP} = 488$ Hz, MoPP), 22.4 (d, $^1J_{PP} = 488$ Hz, MoPP), $^1$H NMR: 7.90-7.20 (multiplets, Ph), 1.93 (d, $^1J_{HP} = 7$ Hz, C$_5$(CH$_3$)$_3$).
CHAPTER 5

CONCLUSIONS

Terminal electrophilic cationic phosphinidene complexes are interesting species because they have the potential to serve as precursors for a range of organophosphorus compounds. Though the chemistry of neutral phosphinidene complexes is well established, there are not many cationic phosphinidene complexes reported and their chemistry has not been well explored. Neutral phosphinidene complexes are reactive and they do undergo reactions with a wide range of electron rich species such as alkynes, alkenes and conjugated dienes.\(^{51,71}\) However, their reactivity is mostly confined to electron rich species. For example, the C-H bond activation reactions of the neutral \([\text{W(CO)}_5\text{PPh}]\) complex are limited to only an electron rich ferrocene ring.\(^{72}\) In this context, cationic phosphinidene complexes deserved attention. As there is a positive charge on the phosphinidene phosphorus, the cationic phosphinidene complexes are expected to be more electron deficient and thereby more reactive over their neutral analogues. This increased reactivity at the cationic phosphinidene center may enable us to extend the C-H bond activation toward other organic systems.

Reactivity studies of cationic terminal phosphinidene complexes with new substituents at the phosphinidene center have been carried out to gain a fundamental understanding of its chemistry and to investigate its utility towards organophosphorus synthesis. Chloride abstraction from a substituted chlorophosphido complex has been used to generate new phosphinidene complexes. I have investigated the reactivity of these phosphinidene complexes towards organic substrates and studied the effect of substituents
on phosphinidene reactivity. Reactivity of these phosphinidene complexes have also been compared with that of the well studied phosphinidene $[\text{MoCp}^*(\text{CO})_3\{\text{P(NiPr}_2\})^+]$.

Sable cationic aminophosphinidene complexes, reported by Sterenberg et al.\textsuperscript{52} are reactive enough to undergo all conventional reactions of electrophilic phosphinidene complexes.\textsuperscript{80,81} Though the phosphinidene phosphorus is electrophilic enough to activate relatively weak Si-H bonds, the attempts to activate C-H bonds were not successful. This is because of their stability, gained by the $\pi$ donation from nitrogen, which makes the phosphinidene orbital less electrophilic and thereby less reactive. The inability of the aminophosphinidenes to activate C-H bonds prompted me to think about a new cationic phosphinidene complex, with increased electrophilicity at the phosphinidene center. A terminal cationic alkylphosphinidene complex was my initial target. As alkylphosphinidenes are not stabilized by heteroatom, they were expected to have high electrophilicity and thereby more reactivity than the aminophosphinidenes. I have synthesized the alkylphosphinidene complex $[\text{Cp}^*\text{Mo(CO)}_3\text{P(i-Pr)}]^+$ from a chloroisopropylphosphido complex by chloride abstraction. This is the first cationic alkylphosphinidene complex reported. As I expected, the isopropylphosphinidene complex formed was as a highly reactive transient species and its generation has been confirmed by trapping reaction with alkynes. It reacts as an electrophilic phosphinidene and the electrophilicity at the phosphinidene center has been investigated with a range of phosphines. Its clean reactivity, observed with a moderately nucleophilic phosphine PPh$_3$ is a direct evidence for its higher electrophilicity than the aminophosphinidene analogue, which does not react with PPh$_3$. I have investigated the Si-H and C-H bond activation reactions using $[\text{Cp}^*\text{Mo(CO)}_3\text{P(i-Pr)}]^+$ and I have shown that it can activate Si-H bonds.
of silanes and C-H bonds of ferrocene. The ability of the alkylphosphinidene to activate the C-H bond of ferrocene clearly demonstrates that alkylphosphinidenes are more electrophilic than the corresponding aminophosphinidenes. However, the C-H bond activation of [Cp*Mo(CO)_3P(i-Pr)]⁺ is limited to ferrocene. This reactivity suggests that the electrophilicity of [Cp*Mo(CO)_3P(i-Pr)]⁺ is similar to that of the well studied transient phosphinidene complex [W(CO)_5(PR)], which behave similarly towards ferrocene and also fails to activate other C-H bonds. However, unlike [W(CO)_5(PR)], [Cp*Mo(CO)_3P(i-Pr)]⁺ can readily give access to a P-C bond at ambient reaction conditions.

Though [Cp*Mo(CO)_3P(i-Pr)]⁺ readily activates ferrocene C-H bonds, I was unable to extend this reactivity to other aromatic systems. In order to achieve this goal, the reactivity at the phosphinidene center has to be further increased. As the phosphinidene reactivity is determined by the nature of the substituent on P, I was interested in expanding the range of possible P substituents. A terminal dichlorophosphido complex of molybdenum [Cp*Mo(CO)_3PCl_2] reported by Malisch et.al. was chosen for this studies, because it has the potential to serve as precursors for chlorophosphinidenes and also for a range of other functionalized phosphinidene complexes. However, my attempts to generate a chlorophosphinidene complex by chloride abstraction from the dichlorophosphido were not successful. Instead of forming the chlorophosphinidene, the chloride abstraction always proceeds through an alternative lower energetic substitution pathway, leading to the bi metallic bridging P2Cl3 complex as the exclusive product. Computational studies reveal that the chlorophosphinidene is an energetically and electronically feasible species. The inability to generate and trap it even
as a transient species is therefore not because of its instability, but rather a result of alternative lower energetic pathways that led to substitution reaction.

Though the dichlorophosphido complex does not serve as a precursor to the chlorophosphinidene, the chloride groups at the phosphido center are susceptible to nucleophilic substitution. Selective substitutions at the phosphido center with nucleophilic phosphines can therefore lead to phosphine coordinated chlorophosphinidene complexes. I have synthesized both triphenyl and trialkyl phosphine coordinated chlorophosphinidene complexes using this methodology. The triphenylphosphine coordinated chlorophosphinidene complex \([\text{Cp}*\text{Mo(CO)}_3\text{P(Cl)PPh}_3]^+\) has been structurally characterized using X-ray crystallography. The phosphine coordinated chlorophosphinidene complexes \([\text{Cp}*\text{Mo(CO)}_3\text{P(Cl)PR}_3]^+\) (R = Ph, Et, Bu) are analogues to the known phospha-Wittig reagent \([\text{W(CO)}_5\text{P(Ph)PR}_3]\) reported by Mathey et.al.\(^{76}\) I have therefore investigated the reactivity of the P-P bonds of \([\text{Cp}*\text{Mo(CO)}_3\text{P(Cl)PR}_3]^+\) towards carbonyl compounds. None of these complexes showed reactivity towards ketones, but with aldehydes (benzaldehyde), the P-P bonds of the PEt\(_3\) and PBu\(_3\) coordinated chlorophosphinidene complexes showed some promising reactivity, which was identified by the formation of the phosphine oxide. However, under our reaction conditions, the phosphaalkene complexes presumably formed were not stable and underwent a rapid decomposition. My attempts to trap these phosphaalkene complexes using conjugated dienes were also not successful.

The phosphine coordinated chlorophosphinidene complexes were still interesting, because they provide an additional P-Cl bond at the phosphinidene center, which can be further functionalized using external organic nucleophiles. However, the results obtained
were contrary to my expectation that the organic nucleophiles, instead of displacing chloro, displace the PPh\textsubscript{3} unit from the phosphinidene P. This unexpected phosphine substitution suggests that complexes like \([\text{Cp}^\ast\text{Mo(CO)}_3\text{P(Cl)PPh}_3]^+\) do not act as phosphine protected chlorophosphinidene complex, but they do have the potential to serve as precursors for new functionalized chlorophosphido complexes.

Though the P-Cl bond of \([\text{Cp}^\ast\text{Mo(CO)}_3\text{P(Cl)PPh}_3]^+\) is inactive towards organic nucleophiles, it can be readily substituted with a second equivalent of PPh\textsubscript{3} unit. These reactions were expected to generate a dicationic diphosphine coordinated phosphido complex with a unique P-P-P linkage. However, the formation of the second P-P bond is always accompanied by dissociation from the metal complex, leading to the formation of the known triphosphenium salt \([\text{Ph}_3\text{PPPPh}_3][\text{AlCl}_4]\). In this reaction, the dichlorophosphido complex effectively acts as a source of P\textsuperscript{+}. I have shown that chelating phosphines can effectively prevent the decomplexation. I have synthesized a chelated bis-(diphenylphosphino)methane (dppm) coordinated chlorophosphinidene complex by the photolysis of the corresponding dangling phosphine coordinated phosphinidene precursor complex. While reacting with an external nucleophilic phosphine PEt\textsubscript{3}, the chelated chlorophosphinidene complex \([\text{Cp}^\ast\text{Mo(CO)}_2\{\text{P(PEt}_3)\text{P(Ph}_2\text{CH}_2\text{P(Ph}_2)-k^2,P^1,P^4}\}]^+\), thus generated does not undergo a decomplexation, but displaces the chloride at the phosphinidene center, leading to the expected dicationic complex \([\text{Cp}^\ast\text{Mo(CO)}_2\{\text{P(PEt}_3)\text{P(Ph}_2\text{CH}_2\text{P(Ph}_2)-k^2,P^1,P^4}\}]^+\)\textsuperscript{2} with a metal coordinated R\textsubscript{3}P-P-PR\textsubscript{3} group. However, the photo induced chelation step forms some unknown side products in the reaction solution, which makes the isolation of the final dicationic product difficult. This problem can be addressed by using a more basic phosphine such as bis-
(dimethylphosphino)methane (dmpm). As dmpm is strongly basic, it may undergo chelation with the metal even at room temperature and thereby we could potentially avoid the photolysis step.

Phosphine additions at the dichlorophosphido complex generate phosphine coordinated chlorophosphinidene complexes. As N-Heterocyclic carbenes are analogous to phosphine ligands, I was interested in studying the carbene additions at the dichlorophosphido center because this reaction was expected to give direct access for either a terminal phosphaalkene complex with a P=C double bond or a carbene coordinated chlorophosphinidene complex with a P-C single bond. In both ways, these reactions were interesting to me, because, the carbene-phosphinidene interaction studies are relatively new\textsuperscript{117,118} and a terminal phosphinidene-carbene interaction has not been described. I have synthesized a terminal phosphinidene-carbene adduct by this route. This is the first terminal phosphinidene-carbene adduct reported. The phosphorus NMR data of the product suggest that the NHC behaves as a strong sigma donor rather than a π acceptor. The phosphinidene-carbene adduct formed has therefore, more likely to have a P-C single bond character and the structure can be therefore best regarded as a carbene stabilized phosphinidene complex rather than a terminal phosphaalkene. Computational calculations are also in good agreement with this conclusion.

The facile nucleophilic substitution reactions at the dichlorophosphido with anionic nucleophiles serve as a simple and convenient synthetic methodology to new substituted chlorophosphido complexes. I have used this methodology to generate chloroalkyl, chloroaryloxy, chloroalkoxy and chlorothiophenoxy phosphido complexes. Chloride abstraction of these substituted phosphido complexes have been used to generate
corresponding phosphinidene complexes. All these newly formed cationic phosphinidene complexes are highly reactive transient species, and their formation has been confirmed by trapping reactions with alkynes. Although all of these phosphinidene complexes are transient, the electrophilicity at the phosphinidene center varies considerably with the substituent. This is evident from their bond activation and nucleophilic phosphine addition reactions. Among these cationic phosphinidene complexes, only the alkylphosphinidene can activate C-H bonds of ferrocene, suggesting that it is the most reactive among this series. However, according to computational chemistry, the alkoxyphosphinidene phosphorus is the most electron deficient among this series and would be expected to be the most electrophilic. However, they do not activate C-H bonds. This observed inactivity towards C-H bonds does not necessarily mean that alkoxyphosphinidenes are less reactive, but it is most likely due to an alternative facile reaction, namely nucleophilic attack by the oxygen of a second equivalent of the phosphinidene complex. When I replaced oxygen with its heavier analogue sulfur, a more pronounced π back donation to the phosphinidene orbital was expected. However, the resulting thiophenoxyphosphinidene complexes were also unstable and could only be trapped as transient species, suggesting that the π back donation from sulfur is not sufficient to stabilize the phosphinidene center. In terms of reactivity, the thiophenoxy phosphinidene complexes are similar to alkoxyphosphinidenes. However, a more detailed investigation of their electrophilicity and reactivity has to be carried out before reaching a final conclusion. In summary, among the cationic phosphinidene complexes, only the aminophosphinidene is stable and all others are transient species. Their increasing order of electrophilicity is as follows, $\text{MPN}^+\text{Pr}_2 << \text{MP}^+\text{Pr} ~ \text{MPCI} < \text{MPSPh} ~ \text{MPOPh}$. 
I have developed easily accessible synthetic methodologies to cationic phosphinidene complexes and demonstrated their reactivity through conventional phosphinidene reactions. Reactivity studies of these phosphinidene complexes give us a fundamental understanding of their electronics and the effect of substituents on phosphinidene reactivity, which will be useful for the future development of this chemistry. The P-P and P-C bond forming reactions of these cationic phosphinidene complexes via nucleophilic additions and [1+2] cycloaddition reactions prove their potential as building blocks for organophosphorus synthesis. However, their reactivity is now limited towards phosphines and alkynes only. Therefore, in order to use these phosphinidene complexes as effective reagents in organophosphorus synthesis, their reactivity has to be further expanded towards other organic substrates such as alkenes, conjugated dienes and α,β-unsaturated ketones. A suitable decomplexation technique has to be then developed to release the organophosphorus fragment from the metal center.

Though cationic phosphinidene complexes are highly reactive and readily accessible at room temperature, some of the disadvantages of this cationic approach have caused me many troubles during this project. Most of the compounds, I reported in this thesis are sensitive towards air and moisture and that make this chemistry difficult and challenging. Because of their cationic nature, column chromatography using silica and alumina cannot be used for purification. Crystallization, using an appropriate combination of polar and no-polar solvents under an inert condition is the only effective method to purify these compounds. Counter ions associated with these complexes, for example the [AlCl₄]⁻ can also interfere and divert the phosphinidene reactivity from the desired reaction pathway.
Intermolecular C-H activation mediated by cationic phosphinidene complexes was the major objective of this project. I have gained only an initial success in that goal. Among the phosphinidene complexes synthesized, only the alkylphosphinidene can activate C-H bonds, but its reactivity is limited to ferrocene. The chloro and alkoxyphosphinidene complexes were expected to be more reactive due to the high electronegativity of chlorine and oxygen atoms. But, unfortunately, under our reaction conditions, the proposed chlorophosphinidene could not be formed. Though the alkoxyphosphinidene formed was highly electrophilic at the phosphinidene center, some unexpected parallel reactions interfere its reactivity towards C-H bonds. Therefore, in order to develop C-H activation by terminal electrophilic phosphinidene complexes into a useful synthetic tool, the electrophilicity at the phosphinidene phosphorus must be further increased. By analyzing the reactivity trends of these various functionalized phosphinidene complexes ranging from amino to thio, it is clear that a heteroatom substituent with nonbonding electrons at the phosphinidene phosphorus interferes the phosphinidene reactivity by providing some alternative lower energy reaction pathways. This is most likely a result of the intermolecular interaction of the substituent lone pair with the electron deficient phosphinidene phosphorus. Therefore, rather than replacing the phosphinidene substituent with hetero atoms, replacing the electron rich Cp*Mo(CO)₃⁺ fragment with a more electron deficient metal fragment such as Re(CO)₅⁺ would be the best way to approach this problem. A terminal rheniumpentacarbonylisopropyl phosphinidene complex [Re(CO)₅P(i-Pr)]⁺ will be therefore the next target. As the phosphinidene phosphorus is bonded to an electron deficient metal center, the
[Re(CO)\textsubscript{5}P(i-Pr)]\textsuperscript{+} is expected to be more reactive than the [Cp\textsuperscript{*}Mo(CO)\textsubscript{3}P(i-Pr)]\textsuperscript{+}, and I believe that the research in this direction will give some fruitful results in the near future.
CHAPTER 6

REFERENCES


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