Abstract

Addition polymerization of phosphaalkenes has been successfully used in the preparation of poly(methyleneosphine)s, but the candidate monomers are limited to phosphaalkenes bearing relatively bulky substituents like mesityl group. This thesis presents the investigations on the preparation and anionic polymerization of new phosphaalkene monomers bearing smaller substituents.

In Chapter 1, the advantages of synthesizing inorganic polymers by addition polymerization is first introduced. Achievements in the synthesis of poly(methyleneosphine)s by addition polymerization of phosphaalkenes is briefly reviewed, followed by the illustration of the intriguing and challenging aspects of the preparation of phosphaalkenes bearing small substituents.

In Chapter 2, studies on the anionic polymerization of XylP=CPh$_2$ are described. It was shown by the NMR characterization of the polymer obtained and the molecular model built for the polymerization that there was intramolecular H-transfer during the anionic polymerization. This isomerization should account for the slow propagation rate of the anionic polymerization of XylP=CPh$_2$.

In Chapter 3, investigations on the preparation of PhP=CPh$_2$, $o$-TolP=CPh$_2$ and MesP=C(H)Ph by the phospha-Peterson reaction are presented. It was found that PhP=CPh$_2$ and $o$-TolP=CPh$_2$ had the tendency to dimerize and afford 1,2-diphosphetane upon formation. The coordination chemistry of PhP=CPh$_2$ and $o$-TolP=CPh$_2$ is also described with the...
characterization of \( \text{W(CO)}_4(\text{PhP=CPH}_2)_2 \) by single-crystal X-ray crystallography.

The anionic polymerization of “masked phosphaalkenes” is an alternative route to polymers containing phosphorus atoms in the main chain without the use of isolated phosphaalkenes. The development of a facile synthetic pathway to “masked phosphaalkenes” is illustrated in Chapter 4.

To conclude, results presented in this thesis pave the road to new poly(methyleneaphosphine)s by anionic polymerization.
Preface

Parts of the work presented in this thesis were accomplished in collaboration with other researchers. All the synthetic research in Chapter 2 was conducted by myself except that the triphenylmethyl chloride was purified by Andrew M. Priegert. The NMR characterization done on the Bruker Avance 600 MHz spectrometer was conducted with Benjamin W. Rawe’s help. The GPC analysis of all the polymers was done with Dr. Eamonn D. Conrad and Benjamin W. Rawe’s help. The crystallographic data of 2.9 was collected by Brian O. Patrick. The solution and refinement of the molecular structure of 2.9 were also performed by Brian O. Patrick.

All the synthetic work in Chapter 3 was done by myself with the exception that W(CO)$_5$(MeCN) was provided by Justin Chang. The crystallographic data of 3.2 and 3.6 was collected, solved and refined by Spencer C. Serin.

For Chapter 4, the synthetic pathway to dichloro(chloromethyl)phosphine (4.9) was designed by Patrick Werz, but all the synthetic work described in Chapter 4 was conducted by myself.

The results presented in Chapter 2 and 4 will be submitted for publication in due course. A version of Chapter 3 will be submitted for publication shortly.
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</tr>
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom (1 x 10(^{-10}) meters)</td>
</tr>
<tr>
<td>Bu</td>
<td>Butyl</td>
</tr>
<tr>
<td>°C</td>
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<td>Heavy main group elements</td>
</tr>
<tr>
<td>E</td>
<td>Entgegen (configurational)</td>
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<td>Electron impact</td>
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<tr>
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<tr>
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<td>${^1H}$</td>
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<td>h</td>
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Min  
Minute(s)

$M_n$  
Number-average molecular weight

mol  
Mole(s)

$M_p$  
Peak molecular weight

$M_w$  
Weight-average molecular weight

$n$  
Normal ($"$Butyl)

Total number of units

NMR  
Nuclear magnetic resonance

$o$  
Ortho

ORTEP  
Oak ridge thermal ellipsoid plot

$α$-Tol  
2-methylphenyl

$π$  
Type of orbital

%  
Percent (parts per hundred)

$p$  
Type of orbital

PDI  
Polydispersity index ($M_w / M_n$)

PDMS  
Polydimethylsiloxanes

Ph  
Phenyl

PMPs  
Poly(methyleneephosphine)s

rt  
Room temperature

SBS  
Styrene-butadiene-styrene
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<thead>
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<td>Angle</td>
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<td>$t$</td>
<td>Tertiary ('Butyl)</td>
</tr>
<tr>
<td>$T$</td>
<td>Time</td>
</tr>
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</tr>
<tr>
<td>$trans$</td>
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<td>Triple detection GPC</td>
<td>Gel permeation chromatography with light scattering instrument, viscometer and differential refractometer</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>Halide</td>
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<td>Xyl</td>
<td>2,6-dimethylphenyl</td>
</tr>
<tr>
<td>Z</td>
<td>Zusammen (configurational)</td>
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</tbody>
</table>
Acknowledgements

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Chapter 1  Introduction: New Challenges in Inorganic Polymer Chemistry

1.1 Macromolecules

Polymers, usually defined as covalently bonded macromolecules containing many repeating units with elements of C, N and O in the backbone,\(^1\) play significant roles in human’s daily life. Natural polymers like protein serves as the building blocks of the human body, whereas starch, cotton and natural rubber are used for applications ranging from food to clothing to tools (Figure 1.1). No matter how important natural polymers are, what really fueled the development of modern society are synthetic polymeric materials that were discovered in early 20\(^{th}\) century.\(^2\) Their low density, good electrical and thermal insulation capability, low price, and corrosion resistance made them stand out from traditionally used metals and ceramics. Society relies so much on synthetic polymers that “it is estimated that about half of all industrial research chemists are involved in some aspect of polymer chemistry”.\(^3\) The three main synthetic materials: plastics, rubbers and fibers are all synthetic polymers (Figure 1.2).

![cotton fiber (cellulose)](cotton_fiber.png)  ![natural rubber (poly-cis-isoprene)](natural_rubber.png)

**Figure 1.1** Examples of natural polymers.
However with society’s demands for high-performance materials growing more and more critical, the shortcomings of polymeric materials have begun to emerge. For example, space exploration requires materials that can withstand temperatures of up to thousands of degrees, deep-sea exploration requires materials that remain strong at low temperatures, and medical science demands drug delivery materials that are biocompatible. All these requirements are the disadvantages of most synthetic polymers people use today.\textsuperscript{4,5} Common synthetic polymers are flammable, brittle at low temperature and non-biodegradable. In order to satisfy the requirements of the fast developing high-technology in the 21\textsuperscript{st} century, new synthetic polymers with unique properties are urgently sought. Interestingly, some disadvantages of polymers are the advantages of inorganic materials used in the past. For example, ceramics have very high melting temperatures, good ability to withstand thermal shock, and good chemical resistance. However, these inorganic materials are fragile and not easily processable into shapes like films or fibers.
The combination of advantages of organic and inorganic materials together may provide an avenue to improve the properties of polymeric materials to meet society’s requirements. Therefore, inorganic polymers are a hot topic in material science. In the next section, the attractive properties and useful applications of some important inorganic polymers are described to illustrate the popularity of inorganic polymers in both academic and industrial research.

1.1.1 Introduction to inorganic polymers

It is of interest to clarify the definition of inorganic polymers first since there is still some inconsistency in the definitions found in the literature. Some researchers define inorganic polymers as macromolecules without carbon atoms in the backbone.\(^6\)\(^,\)\(^7\) Some researchers proposed to broaden the definition to “linear polymers having at least two different elements in the repeat unit”,\(^8\) but this definition classifies some organic polymers like polyamides as inorganic polymers. Some other researchers define polymers with both organic and inorganic elements in the main chain as inorganic/organic hybrid polymers, especially when there are metal ions in the main chain.\(^9\) In this thesis, the term inorganic polymer is referred to macromolecules that contain at least one element other than C, O and N in the main chain.

As mentioned above, the area of inorganic polymers has grown rapidly in the last several decades, probably because inorganic moieties may impart many potential new properties to polymeric materials. Polydimethylsiloxanes (PDMS) or silicones (1.1 in Figure 1.3) are one of the most well-studied and commercially important inorganic polymers. The alternating silicon
and oxygen atoms in the backbone provide PDMS with exceptional thermostability and
unmatched flexibility at low temperatures ($T_g \approx -125 \, ^\circ C$).\textsuperscript{10,11} The higher bond dissociation
energy of Si-O bonds (346 kJ mol\(^{-1}\)) compared with C-C bonds (313 kJ mol\(^{-1}\)), the longer Si-O
bond length (1.63 Å) compared with the C-C bond length (1.53 Å), and the wider bond angle of
Si-O-Si (143 °) compared with the bond angle of C-C-C (109 °) all contribute to the stability of
PDMS at high temperatures and the elasticity of PDMS at low temperatures.\textsuperscript{12,13,14} Other
properties like a small viscosity temperature coefficient, water impermeability, high gas
permeability and high hydrophobicity make PDMS not only be widely used as a surfactant, but
also play important roles in the fields of medicine and cosmetics.\textsuperscript{15,16,17,18}

![Figure 1.3](image)

**Figure 1.3** Examples of important inorganic polymers.

Another important class of silicon-containing inorganic polymers are the
polysilanes (1.2 in Figure 1.3). In contrast to PDMS and many other inorganic polymers,
polysilanes contain only one element in the main chain. With respect to structure, polysilanes are
similar to most organic polymers (e.g., polyalkenes) with only carbon in their main chain.
However, compared to organic polymers, polysilanes show special optical and electronic
properties, such as strong UV absorption, photodegradability, and semiconducting ability.\textsuperscript{19,20,21} These interesting properties have motivated continuous research on polysilanes since the 1980s. Today polysilanes are good candidates for use in photolithography, electronic devices and light emitting diodes.\textsuperscript{22,23,24,25,26}

Although PDMS and polysilanes are very important materials and have been well-studied, the largest family of inorganic polymers are neither of them, but the polyphosphazenes (1.3 in Figure 1.3), which contain alternating phosphorus and nitrogen atoms in the main chain.\textsuperscript{18} One of the advantages of polyphosphazenes is that their properties can be easily tuned by the wide variety of possible organic substituents on the phosphorus in the backbone.\textsuperscript{27,28,29} Furthermore, polyphosphazenes have great potential to be used as biomaterials due to both the capability of hydrolytic degradation of the inorganic backbone and the ability to interface with biological systems through noncovalent bonding and supramolecular assemblies.\textsuperscript{30} Therefore, possible commercial applications of polyphosphazenes now include diverse areas such as electrolytes in solar cells and drug delivery vehicle in medicine.\textsuperscript{31,32,33}

PDMS, polysilanes and polyphosphazenes are only three examples of the large family of known inorganic polymers, but they have already illustrated various unique properties and potential applications in daily life. Inorganic polymers are good candidates of the “new materials” that the society is requesting. Therefore, a lot of studies are now being conducted on the synthesis and modification of inorganic polymers, although this area remains an extremely challenging frontier of research.
1.1.2 Addition polymerization

One of the main challenges in both academic and industrial areas is to synthesize polymers efficiently. Addition polymerization of unsaturated monomers is an important synthetic route to organic polymers in industry. It has a long history and is used on large scale. It is estimated that over 60% of synthetic polymers, such as polyethylene, polyvinyl chloride and polystyrene (Figure 1.4), are produced by addition polymerization. Its popularity is highly dependent on the ready accessibility of various suitable monomers.

![Polymer structures](image)

**Figure 1.4** Examples of polymers synthesized by addition polymerization.

Addition polymerization makes use of multiple bond containing molecules like olefins. It consists of three main steps: initiation, propagation and termination (Scheme 1.1). An active site is created first by the reaction of the initiator (R*) and the multiple bond (Initiation). Subsequently, the active end keeps consuming monomers and the chain length keeps growing (Propagation). Finally, the active end is destroyed in the termination step and the addition polymerization is completed (Termination).
Addition polymerization can be classified as either radical polymerization, cationic polymerization, anionic polymerization or coordination polymerization (e.g., polymerization initiated by Ziegler-Natta catalysts) based on different types of initiators used. Among these types of polymerization, the discovery of anionic polymerization was a big breakthrough in polymer science since it opened the door to controlled polymers with low molecular weight dispersity. When Szwarc and co-workers studied the mechanism of anionic polymerization of styrene initiated by sodium naphthalenide, they found that the carbanion chain-end were free from chain transfer or chain termination. As a result, the polymerization is “living”, meaning
after the initial batch of monomers is used up, the chain propagation can continue with a new batch of monomers. Thus, the number-average molecular weight $M_n$ of the polymer obtained can be calculated and controlled by the amount of initiators and monomers used. Since all the polymer chains are initiated at the same time and the propagation rate is the same for all the initiated polymer chains, the polydispersity should be very narrow.$^{37}$ Furthermore, if a different type of monomers is added to the polymerization system after the first batch of monomers has been consumed, a block copolymer with unique physical and chemical properties imparted by the different segments can be synthesized. Living polymerization is now widely used in the synthesis of block copolymers. One well-known example is the styrene-butadiene-styrene (SBS) block copolymer with various applications including footwear, road marking and adhesives.$^{39}$

Addition polymerization has contributed so much to the synthesis and the development of organic polymers that it should also help broaden the chemistry of inorganic polymers remarkably, if it is used in the synthesis of inorganic polymers.

1.1.3 Research objectives

Although addition polymerization is still not reported in the synthesis of well-known inorganic polymers like PDMS or polyphosphazenes, it has been shown by former members in our group that addition polymerization of phosphaalkenes can act as an efficient route to poly(methyleneophosphine)s (PMPs) (Scheme 1.2)$^{40,41}$ To date, successful polymerization of phosphaalkenes is limited to the polymerization of monomers with relatively bulky
substituents (e.g., $R_1 = \text{Mes}$, $R_2 = \text{Ph}$, $R_3 = \text{Ph}$, 1-Naphthyl or 9-Phenanthyrl).\textsuperscript{40,42} Therefore, it is of interest to expand the generality of addition polymerization to phosphaalkenes bearing smaller substituents. Ground work towards this ultimate goal is described in this thesis involving both the synthesis of new phosphaalkenes bearing smaller substituents and the polymerization of suitable monomers. In the next several sections, necessary background information is provided to help readers understand why addition polymerization is rarely reported in making inorganic polymers, why phosphaalkenes are chosen as monomers in the Gates Group, and the challenging and intriguing aspects of the synthesis of phosphaalkenes bearing small substituents. The outline of these background materials is:

- Section 1.2 Challenges in the isolation and polymerization of unsaturated inorganic molecules;
- Section 1.3 Addition polymerization of phosphaalkenes;
- Section 1.4 Chemistry of phosphaalkenes bearing small substituents.

![Scheme 1.2](image)

Scheme 1.2 Addition polymerization of phosphaalkenes.
1.2 Challenges in the isolation and polymerization of unsaturated inorganic molecules

One of the main reasons for the limited research done on addition polymerization in inorganic polymer science is the difficult isolation of unsaturated inorganic molecules. In the area of organic polymers, it is usually easy to obtain suitable unsaturated monomers such as ethylene. Global ethylene production reached 141 million tons in 2011, which is produced mainly by steam cracking of petroleum.\(^{43}\) The ready accessibility of ethylene lies in the relatively high energy of the \(\pi\) bond formed by the two \(p\)-orbitals of carbons,\(^{34}\) which makes it stable at room temperature. The heats of hydrogenation of different alkenes show that ethylene has the least thermodynamic stability compared to substituted alkenes. Substituents on the double bond tend to provide more stabilization to alkenes, therefore it is not very difficult to isolate various alkene monomers. Thus, the addition polymerization is well-developed and widely used in organic polymerization.

In contrast, the formation of multiple bonds between heavier main group elements is more difficult, because as the atom grows larger, the bond length between the two atoms also becomes larger and the overlap of the two \(p\)-orbitals is much poorer. Thus, the \(\pi\) bond formed is very weak and reactive (Figure 1.5). Some \(\pi\) bond energies are listed in Table 1.1.\(^{12,34,44,45,46}\)
Figure 1.5  Two $p$-orbitals approach to form $\pi$ bonds between carbons or between heavy main group elements.

Table 1.1  $\pi$ bond energies of selected multiple bonds between main group elements.$^{12,34,44,45,46}$

<table>
<thead>
<tr>
<th>Multiple bond</th>
<th>C=C</th>
<th>P=C</th>
<th>P=N</th>
<th>Si=C</th>
<th>P=P</th>
<th>Si=Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2p-2p)</td>
<td>(3p-2p)</td>
<td>(3p-2p)</td>
<td>(3p-2p)</td>
<td>(3p-3p)</td>
<td>(3p-3p)</td>
</tr>
<tr>
<td>$\pi$ bond energy (kJ mol$^{-1}$)</td>
<td>264</td>
<td>219</td>
<td>185</td>
<td>160</td>
<td>143</td>
<td>105</td>
</tr>
</tbody>
</table>

Compared with the energy of the carbon-carbon $\pi$ bond (264 kJ mol$^{-1}$), the energy of phosphorus-phosphorus $\pi$ bond (143 kJ mol$^{-1}$) is around half of it and the energy of silicon-silicon $\pi$ bond (105 kJ mol$^{-1}$) is almost one third of it.$^{12,34,44,45,46}$ Therefore, it is not surprising that oligomers (PhP)$_5$ and (PhP)$_6$ are obtained when the synthesis of PhP=PPh is attempted.$^{47}$ It is also reasonable that H$_2$Si=SiH$_2$ is highly reactive and pyrophoric in the air.$^{48}$ Because of the weakness of these $\pi$ bonds, there was a “classical double-bond rule” in textbooks in the mid-20$^{th}$ century stating “elements having a principal quantum number greater than two should not be able to form ($p$-$p$) $\pi$ bonds with themselves or with other elements”.$^{49,50}$ This rule
was widely accepted until many unsaturated inorganic molecules were isolated by introducing bulky substituents to the multiple bonds (Figure 1.6). Bulky substituents can provide steric protection to the multiple bonds, thus kinetically stabilizing reactive π bonds between the heavy main group elements.

**Figure 1.6** Examples of isolable unsaturated inorganic molecules with kinetic stabilization provided by bulky substituents.

However, isolable unsaturated inorganic molecules are not necessarily addition-polymerizable monomers. The presence of bulky substituents increases the activation energy ($E_a$) of the multiple bond towards polymerization. If the activation energy ($E_a$) is too high, the reaction of the initiator and the multiple bond is inhibited. Therefore, both sufficient kinetic stabilization and enough reactivity of the multiple bond are required for the successful addition polymerization of unsaturated inorganic molecules. The substituents on many isolable
unsaturated inorganic molecules are so large that it is too difficult for the initiators to react with the multiple bond or for the active end to approach the monomers for chain propagation, limiting the development of addition polymerization in inorganic polymer science.

1.3 Addition polymerization of phosphaalkenes

As illustrated above, the addition polymerization of unsaturated inorganic molecules can serve as a good way to introduce inorganic elements into a polymer backbone, potentially imparting unique physical and chemical properties to the polymer materials obtained. Most importantly, the synthesis of inorganic polymers by addition polymerization is challenged by the lack of suitable monomers. Our research group is interested in applying addition polymerization to the synthesis of polymers with phosphorus atoms in the main chain, and we have chosen phosphaalkenes as monomers. Two reasons led to our investigation in this area. First, a large number of phosphaalkenes have been isolated, offering many monomer candidates to choose from. Secondly, there is well-known resemblance between the molecular chemistry of C=C and P=C bonds, suggesting the feasibility of polymerizing P=C bonds. Important properties of phosphaalkenes and some significant achievements we have made in the addition polymerization of phosphaalkenes are illustrated in this section.
1.3.1 Introduction to phosphaalkenes

Phosphaalkenes are compounds containing double bonds between carbon and trivalent phosphorus. To isolate phosphaalkenes, thermodynamic or (and) kinetic stabilization is required to protect the weak P=C double bond. The earliest discoveries of compounds containing such P=C bonds can be dated back to the phosphamethincyanine cation (1.4 in Figure 1.7) reported by Dimroth and Hoffmann in 1964. Two years later, this was followed by the successful isolation of 2,4,6-triphenylphosphabenzene (1.5 in Figure 1.7). In both cases, thermodynamic stabilization is offered by conjugation effects in the delocalization of the P=C bond.

![Figure 1.7](image)

Figure 1.7 Early discoveries of P=C bonds containing compounds.

The first stable acyclic compound with a P=C bond was not reported until 1.6 was prepared by Becker in 1976 through silatropic migration (Scheme 1.3). This phosphaalkene is stabilized by the electronic effects of the heteroatom substituent. It was shown that “the p-orbital overlap was sufficient within the π system” when the polarity between P=C bond is reduced by heteroatom substituents that can donate electron density. In addition to phosphaalkenes isolated with the help of thermodynamic stabilization, the family of isolable phosphaalkenes keeps
growing with the introduction of kinetic stabilization to the P=C bond. Some examples of isolable phosphaalkenes with steric protection provided by bulky substituents are shown in Figure 1.8.\textsuperscript{42,60,61}

\begin{center}
\begin{tabular}{c}
\includegraphics[width=\textwidth]{Scheme1.3.png}
\end{tabular}
\end{center}

\textbf{Scheme 1.3} Synthesis of the first acyclic compound with P=C bond by silatropic migration.\textsuperscript{59}

\begin{center}
\begin{tabular}{c}
\includegraphics[width=\textwidth]{Figure1.8.png}
\end{tabular}
\end{center}

\textbf{Figure 1.8} Examples of isolable phosphaalkenes with kinetic stabilization provided by bulky substituents.\textsuperscript{42,60,61}

The similar electronegativities of phosphorus (2.2) and carbon (2.5) contribute much to the resemblance between P=C and C=C bonds. For example the π bond of HP=CH\textsubscript{2} is very slightly polar and the π bond of CH\textsubscript{2}=CH\textsubscript{2} is nonpolar.\textsuperscript{62} Theoretical calculations have shown that the HOMO of HP=CH\textsubscript{2} is the π\textsubscript{P–C} bond and its energy (-10.30 eV) is close to the energy of the π\textsubscript{C–C} bond in CH\textsubscript{2}=CH\textsubscript{2} (-10.50 eV).\textsuperscript{63} The similar polarities of double bonds and close HOMO energies lead to many analogous molecular reactions between phosphaalkenes and
olefins (Scheme 1.4).\textsuperscript{64,65,66,67} These similarities inspire our group to further explore their potential resemblance not only in molecular chemistry, but also in polymer chemistry.

\begin{center}
\includegraphics[width=0.8\textwidth]{olefins.png}
\end{center}

**Scheme 1.4** Similarities between C=C and P=C bonds.\textsuperscript{64,65,66,67}

### 1.3.2 Addition polymerization of phosphaalkenes

As discussed at the beginning of this section, phosphaalkenes with sufficient kinetic stabilization for isolation and enough reactivity for initiation and propagation are required for successful addition polymerization. It was finally discovered in 2003 that MesP=CPh\textsubscript{2} (1.7) met these requirements and that they could afford PMPs by addition polymerization (Scheme 1.5).\textsuperscript{40} Phosphaalkene 1.7 can be initiated by both radical and anionic initiators at elevated temperatures. It takes a couple hours for the polymerization to reach completion. When a mixture of styrene and 1.7 is initiated by radical initiators (VAZO 88), a hybrid inorganic-organic copolymer with moderate molecular weights of 3600-9000 g mol\textsuperscript{-1} and PDI of 1.4-1.7 is obtained.\textsuperscript{68} Importantly,
this copolymer can be used as a polymer support of catalysts for Suzuki cross-coupling reactions.\textsuperscript{68}

\begin{center}
\includegraphics[width=0.5\textwidth]{scheme1}
\end{center}

**Scheme 1.5** Addition polymerization of 1.7.\textsuperscript{40}

Later in 2006, it was discovered that high temperatures were not necessary for this addition polymerization to proceed, and that it was possible to conduct living anionic polymerization of 1.7 at ambient temperatures.\textsuperscript{41} When the polymerization of 1.7 is initiated by \textsuperscript{n}BuLi at room temperature, the conversion rate of the monomers can reach as high as 100%. Copolymerization of 1.7 and styrene has also been achieved by treating living polystyrene with 1.7. The living nature of this anionic polymerization makes it easier to control the molecular weights and obtain a narrow PDI. Furthermore, polymer 1.8 can be functionalized in many different ways (Scheme 1.6).\textsuperscript{40,69,70} which broadens potential utilities of PMPs.
When 1.8 was first obtained, the polymerization of 1.7 was taken as a simple analogy of the polymerization of olefins. Therefore the microstructure of 1.8 was proposed to be the structure shown in Scheme 1.5. But recent results from our group show that the microstructure of 1.8 may be more complicated (1.8') than previously believed when the polymerization is initiated by radical initiators (Scheme 1.7). The C-H bond on the o-CH$_3$ group of Mes is activated during the polymerization. As a result the dominant structure does not contain alternating phosphorus and carbons in the main chain.$^{71}$

\[ \text{Scheme 1.6} \quad \text{Functionalization of 1.8.}^{40,69,70} \]

\[ \text{Scheme 1.7} \quad \text{Addition polymerization of 1.7 by radical initiation.}^{71} \]
Although this addition-isomerization mechanism is unprecedented in polymer science, it is not the first C-H activation or H-transfer observed in P=C system. When AlCl$_3$ is attempted to be used as a cationic initiator to activate Mes$^\circ P=\text{CH}_2$, an intramolecular C-H bond activation is also observed (Scheme 1.8).$^{72}$

\[ \text{Mes}^\circ P=\text{CH}_2 \rightarrow \text{Mes}^\circ P=\text{CPh}_2 \]

**Scheme 1.8** C-H activation observed in attempts to activate Mes$^\circ P=\text{CH}_2$ by AlCl$_3$.$^{72}$

Therefore, there are still many important questions left unanswered, such as:

1) Is the C-H bond on $o$-CH$_3$ also activated if the polymerization is initiated by anionic initiators?

2) Is the C-H bond on $o$-CH$_3$ activated only when MesP=CPh$_2$ is polymerized or is it activated when any phosphaalkenes that contain $o$-CH$_3$ group is polymerized?

3) Is it possible to synthesize PMPs with pure alternating “P-C-P-C-” bonds in the main chain if phosphaalkenes with smaller substituents that contain no $o$-CH$_3$ group are used as monomers?

4) Is it possible to isolate phosphaalkenes with smaller substituents?

There is much more to be explored in the addition polymerization of phosphaalkenes.
1.4 Chemistry of phosphaalkenes bearing small substituents

It is fascinating to synthesize PMPs by the new addition-isomerization polymerization mechanism of phosphaalkenes and to discover the alternative microstructure of 1.8'. Until now, monomers used for polymerization research in our group are limited to phosphaalkenes bearing relatively bulky substituents (e.g., Mes group on the phosphorus side) due to their easy isolation. However, research on the chemistry of phosphaalkenes without large substituents is of the same importance. The C-H activation of the o-CH$_3$ group may be avoided if phosphaalkenes bearing smaller substituents (e.g., Ph group on the phosphorus side) are polymerized, potentially generating PMPs with alternating phosphorus and carbon atoms in the main chain. Furthermore, unique chemistry may be discovered in the preparation of these phosphaalkenes due to the higher reactivity of the P=C bond. Therefore, it is of interest to investigate the synthesis and polymerization of phosphaalkenes bearing smaller substituents. In this section, investigations on the chemistry of phosphaalkenes bearing smaller substituents are presented to illustrate the intriguing and challenging aspects of the preparation of these less protected unsaturated molecules.

Due to the lack of kinetic protection, it is difficult to directly study the chemistry or even detect the existence of phosphaalkenes bearing very small substituents. So these phosphaalkenes are usually studied in indirect ways. Chemical trapping is usually used to help prove the existence of phosphaalkenes bearing substituents as small as H or Me groups. In the absence of trapping reagents, usually only “phosphines formed by intermolecular reactions” of
phosphaalkenes or “polymeric materials” can be detected.\textsuperscript{73,74} Self-oligomerization other than polymerization can take place, if the substituents of the phosphaalkenes are larger than H and Me groups, but not bulky enough to provide sufficient steric protection to the P=\text{C} bond. In such cases, dimers are the most common species obtained by either “head-to-tail” or “head-to-head” self-cycloaddition.\textsuperscript{75,76} Metal coordination can help stabilize and isolate monomeric phosphaalkenes to some extent, but dimerized phosphaalkene complexes formed by the [2 + 2] cycloaddition of the P=\text{C} bonds have also been reported in the literature.\textsuperscript{77,78}

1.4.1 Chemical trapping of phosphaalkenes

When insufficient thermodynamic stabilization or steric protection is employed, \pi bonds in phosphaalkenes are very reactive and tend to break. Thus, these phosphaalkenes are usually short-lived species, and it is difficult to detect their existence. Trapping reagents are used to help prove the formation of these highly reactive species.

The thermolysis of 2-phosphabicyclo[2.2.2]octa-5,7-dienes leads to the generation of MeP=\text{CH}_2 and PhP=\text{CH}_2 (Scheme 1.9).\textsuperscript{73} These phosphaalkenes only contain substituents on phosphorus and “allow a study of their reactivity without the encumbrance of the stabilizing groups”. However they are too reactive to isolate. If no trapping reagent is used, a mixture of products with broad $^{31}$P NMR signals is detected. According to Quin and co-workers, these products were supposed to be phosphines formed by “head to head” or “head to tail” intermolecular reactions. When there is an excess of 1,3-diene \textit{in situ}, these phosphaalkenes can
be trapped through [4 + 2] cycloadditions.

Scheme 1.9  Chemical trapping of MeP=CH₂ and PhP=CH₂.⁷³

Phosphaalkene 1.⁹ can be synthesized by isomerization of vinylphosphines in the presence of base catalysts and further isolated by distillation (Scheme 1.10).⁷⁹ But in a similar reaction, when the substituent on the phosphorus is changed to small groups like H or Me, no phosphaalkene can be isolated. It is supposed that these phosphaalkenes are very short-lived transient species. Their formation can only be proved by the addition of trapping reagents (2,3-dimethylbutadiene) into the reaction mixture (Scheme 1.11). If no trapping reagents are present, “a slow polymerization is observed”.⁷⁴
Scheme 1.10  Synthetic route to phosphaalkenes by isomerization of vinylphosphines.\textsuperscript{79}

\[ \begin{align*}
    \text{Scheme 1.11} \quad & \text{Chemical trapping of HP}=\text{CH}_2 \text{ and MeP}=\text{CH}_2. \textsuperscript{74}
\end{align*} \]

1.4.2 Oligomerization of phosphaalkenes

Due to the high reactivity of the P=C bond when sufficient steric protection is absent, oligomerization, especially dimerization can take place upon formation of phosphaalkenes. In 1981, when Wessely and co-workers tried to synthesize phosphaalkenes from silylphosphines by the phospha-Peterson reaction, they found that 1.10 could be detected by $^{31}$P NMR spectroscopy \textit{in situ} and that it tended to dimerize upon formation (Scheme 1.12). When the substituent on the phosphorus is the Me group, the dimerization caused by the low thermal stability of π bond can take place very fast. The "head to tail" four-membered ring structure of 1.11 (1,3-diphosphetane) was confirmed by single-crystal X-ray analysis.\textsuperscript{75}
Scheme 1.12  Synthetic route to 1.10 and the formation of 1.11 by the dimerization of 1.10.\textsuperscript{75}

Such dimerization is also reported in the synthesis of many other phosphaalkenes and the structure of the dimer formed is not limited to 1,3-diphosphetane. Although the 'Bu group is usually considered as a bulky substituent, phosphaalkene 1.12 is unstable and generates dimer 1.13 (1,2-diphosphetane) by “head to head” cycloaddition (Scheme 1.13), the structure of which was confirmed by single-crystal X-ray analysis.\textsuperscript{76}

Scheme 1.13  Formation of 1.13 by the dimerization of 1.12.\textsuperscript{76}

Another example of the oligomerization of phosphaalkenes is the mixture of various dimers (1.14) and trimer (1.15) formed by CF$_3$P=CF$_2$ (Scheme 1.14).\textsuperscript{80} Phosphaalkene CF$_3$P=CF$_2$ is extruded from Me$_3$SnP(CF$_3$)$_2$ by thermolysis under vacuum. It can be detected at
very low temperature, but it is very reactive and only cycloaddition products are detected at room temperature. Different dimers (*trans* head-to-tail dimer \textbf{1.14a}, *cis* head-to-tail \textbf{1.14b}, and *trans* head-to-head dimer \textbf{1.14c}) are formed through self-cycloaddition with \textbf{1.14a} being the main product. The ratio of the amount of \textbf{1.14a} : \textbf{1.14b} : \textbf{1.14c} : \textbf{1.15} in the oligomer mixture was reported to be 85 : 9 : 2 : 4 based on the results of $^{19}$F NMR spectroscopy.

![Scheme 1.14](image)

\textbf{Scheme 1.14} Formation of dimer \textbf{1.14} and trimer \textbf{1.15} by the cycloaddition of CF$_3$P=CF$_2$.\textsuperscript{80}

Interestingly, in some cases the monomeric phosphaalkenes and dimerized phosphaalkenes are interchangeable. The 1,3-diphosphetane \textbf{1.17} is formed through “head to tail” \([2 + 2]\) cycloaddition when phosphaalkene \textbf{1.16} is synthesized by dehydrochlorination of the dichlorophosphine (Scheme 1.15a). The four-membered ring structure is not favored when bulky substituents are introduced to \textbf{1.17} by nucleophilic substitution. The four-membered ring is broken and monomeric phosphaalkenes \textbf{1.18} are formed (Scheme 1.15b).\textsuperscript{76}
Scheme 1.15  a) Formation of 1.17 by the dimerization of 1.16; b) formation of monomeric phosphaalkene 1.18 from 1.17.\(^\text{76}\)

The 1,3-diphosphetanes can change back to the original monomeric phosphaalkenes. When phenylphosphine is treated with 1-(dimethoxymethy)piperidine (Scheme 1.16a), the formation of phosphaalkene monomer 1.19 and dimer 1.20 in a 1:1 ratio can be detected by \(^{31}\)P NMR spectroscopy. When the reaction mixture is distilled, the dimer 1.20 dissociates to generate phosphaalkene monomers 1.19 (Scheme 1.16b).\(^\text{81}\)

Scheme 1.16  a) Formation of 1.20 by the dimerization of 1.19; b) reformation of monomeric phosphaalkene 1.19 from 1.20.\(^\text{81}\)
1.4.3 Coordination of phosphaalkenes to metal complexes

Coordination can serve as a method to help stabilize and isolate reactive phosphaalkenes. The lone pair on phosphorus makes it possible for phosphaalkenes to coordinate to metal complexes. As reported by F. Mathey and his coworkers, most of the phosphaalkenes they obtained by phospha-Wittig method were not isolable if they were not coordinated to metal complexes. Only with the coordination of phosphaalkenes to transition metals like tungsten or molybdenum could they isolate the phosphaalkene complexes by a rapid chromatographic workup (Figure 1.9).\(^7^7\) Another similar example is shown in Scheme 1.17. Isolable phosphaalkene complexes 1.22 and 1.23 can be synthesized from the phosphorylphosphine complex 1.21.

![Figure 1.9](image)

**Figure 1.9** Examples of isolable phosphaalkene complexes.\(^7^7\)
Scheme 1.17  Synthetic route to isolable phosphaalkenes with coordination to metal complexes from the phosphorylphosphine complex.\(^{77}\)

This method has its limitations. When the substituent on phosphorus is changed to the small Me group (1.24), the clean formation of phosphaalkene complex 1.25 can be detected by \(^{31}\)P NMR spectroscopy, but this phosphaalkene complex is not isolable. Only its methanolysis product 1.26 can be isolated (Scheme 1.18).\(^{82}\)

Scheme 1.18  Synthetic route to the phosphaalkene complex 1.25 and its methanolysis product 1.26.\(^{82}\)
Similar to some monomeric phosphaalkenes, phosphaalkene complexes can dimerize. When the 7-phosphanorbornadiene complex (1.27) is treated with the carbene complex (1.28), no monomeric phosphaalkene complex is detected. Instead, a 1,2-diphosphetane product (1.30) is obtained. It was proposed that the expected phosphaalkene complex 1.29 was formed as a transient product, and that a [2 + 2] cycloaddition took place immediately, only leaving the four-membered-ring dimer 1.30 in the reaction mixture (Scheme 1.19).

![Scheme 1.19](image)

**Scheme 1.19** Synthetic route to the dimer 1.30 from the 7-phosphanorbornadiene complex 1.27. 

1.5 Outline of thesis

As discussed above, more and more research is being conducted in inorganic polymers due to the special properties that inorganic elements may offer. The important but rarely reported addition polymerization of unsaturated inorganic monomers has been successfully used in the
polymerization of phosphaalkenes and it has been found that the C-H bond on the o-CH₃ group is activated when MesP=CPh₂ (1.7) is polymerized. It has also been shown that phosphaalkenes with insufficient steric protection have the tendency to oligomerize or polymerize upon formation. Therefore, it is hypothesized that appropriately chosen phosphaalkenes bearing smaller substituents have the potential to form useful polymers if proper conditions can be discovered to favor intermolecular chain growth initiation and propagation. Research described in this thesis centers on the ground work towards the synthesis of new PMPs bearing smaller substituents by addition polymerization. Studies presented include investigations on the anionic polymerization of XylP=CPh₂, the preparation and chemistry of PhP=CPh₂, o-TolP=CPh₂ and MesP=C(H)Ph, and the preliminary research on the facile synthesis of “masked phosphaalkenes” for polymerization studies.

When I joined the Gates Group, the microstructure of PMPs 1.8′ was just discovered. Research conducted to further study the microstructure of PMPs with similar but smaller substituents on the phosphorus is presented in Chapter 2. The successful preparation of XylP=CPh₂ and its anionic polymerization will be first described. It is followed by the characterization of the microstructure of the polymer obtained and kinetic studies on this anionic polymerization to further clarify the mechanism of the chain growth initiation and propagation.

Smaller substituents decrease the steric protection on phosphaalkenes, leading to the higher reactivity of the P=C bond. In Chapter 3, the size of substituents on phosphaalkenes is further reduced and the intriguing chemistry of the phosphaalkenes caused by the decreased
kinetic stabilization is presented. Work on the synthesis and coordination chemistry of PhP=CPh$_2$ and o-TolP=CPh$_2$ will be discussed. Furthermore, the structure of the dimer (1,2-diphosphetane) formed from PhP=CPh$_2$ and the thermodynamics of the equilibrium between PhP=CPh$_2$ and its dimer will be described. The synthesis of MesP=C(H)Ph, which bears smaller substituents on the carbon side will also be mentioned.

Concluded from research on the chemistry of XylP=CPh$_2$, o-TolP=CPh$_2$, PhP=CPh$_2$, and MesP=C(H)Ph, the smaller the substituents are, the harder it is to isolate the phosphaalkenes in large scale with enough purity for polymerization. Therefore a new method, i.e., anionic polymerization of “masked phosphaalkenes”, will be a good alternative route to PMPs because it can avoid the isolation of phosphaalkenes. Preliminary research on the facile preparation of “masked phosphaalkenes” will be included in Chapter 4. At last, a short summary of the work I have done and proposed future directions related to this work will be presented in Chapter 5.

1.6 Contributions by other researchers to this work

Some of the work presented in this thesis was accomplished in collaboration with other researchers. For Chapter 2, all the synthetic research was conducted by myself except that the triphenylmethyl chloride was purified by Andrew M. Priegert. The NMR characterization performed on the Bruker Avance 600 MHz spectrometer was conducted with Benjamin W. Rawe’s help. The GPC analysis of all the polymers was done with Dr. Eamonn D. Conrad and Benjamin W. Rawe’s help. For Chapter 3, W(CO)$_5$(MeCN) was provided by Justin Chang and all
the other synthetic research was done by myself. For Chapter 4, the synthetic pathway to dichloro(chloromethyl)phosphine (4.9) was designed by Patrick Werz, but all the synthetic work described in Chapter 4 was conducted by myself. All the crystallographic data were collected by Spencer C. Serin and Brian O. Patrick. The solution and refinement of the molecular structure of 2.9 were performed by Brian O. Patrick and the solution and refinement of the molecular structures of 3.2 and 3.6 were performed by Spencer C. Serin.
Chapter 2  Polymerization Studies of XylP=CH$_2$

2.1 Introduction

As discussed in Part 1.3.2, when MesP=CPh$_2$ (1.7) was polymerized, microstructure 1.8 seemed most plausible due to the analogy between C=C and P=C bonds (Scheme 1.5). Molecular models have been built to study the initiation and termination steps of the anionic polymerization of 1.7 (Scheme 2.1). Structures of 2.1, 2.2 and 2.3 were all confirmed by single-crystal X-ray crystallography. It seemed that the microstructure of 1.8 was supported by these models.

Scheme 1.5  Addition polymerization of 1.7.$^{40}$

Scheme 2.1  Synthetic routes to the molecular models of initiation and termination steps of the anionic polymerization of 1.7.$^{83}$
However, our recent research results have shown that the microstructure of the polymer obtained is more complicated than the structure shown as \textbf{1.8}, \textit{i.e.}, when the polymerization is initiated by radical initiators, the C-H bond on the \(\alpha\)-CH\(_3\) group of the mesityl group is activated (Scheme 1.7). This activation is supported by the molecular structure of the molecular model compound \textbf{2.4}, which is obtained by treating \textbf{1.7}·AuCl with TEMPO (Scheme 2.2).\(^{\text{71}}\) Results of \(^1\)H and \(^{13}\)C\(\{^1\)H\} NMR analysis of the polymer obtained also support that there is C-H bond activation on the \(\alpha\)-CH\(_3\) group during the polymerization of \textbf{1.7}, hence the microstructure of the polymer obtained should mainly be \textbf{1.8}', which does not contain alternating “P-C-P-C” bonds in the main chain.\(^{\text{71}}\)

Scheme 1.7 Addition polymerization of \textbf{1.7} by radical initiation.\(^{\text{71}}\)

Scheme 2.2 The synthetic route to \textbf{2.4}.\(^{\text{71}}\)
In order to further study the mechanism of the formation of PMPs, it is of interest to study the synthesis and polymerization of phosphaalkenes bearing similar P- or C- substituents. Such studies will also help clarify whether it is possible to obtain polymers with alternating phosphorus and carbon atoms in the main chain via addition polymerization of phosphaalkenes. To achieve these goals, it is practical to start with the polymerization of XylP=CHPh₂ (2,6-Me₂C₆H₃P=CHPh₂), which has a similar structure with 1.7 and is isolable as a solid. Herein, the synthesis and anionic polymerization of XylP=CHPh₂ in solution are first reported, followed by studies on the microstructure of the polymer obtained and the molecular model built for the polymerization. Kinetic studies of the anionic polymerization are also discussed.

2.2 Results and discussion

2.2.1 Synthesis of XylP=CHPh₂ (2.5)

Phosphaalkene 2.5 was first synthesized by Bickelhaupt and co-workers through the elimination of HCl from XylP(Cl)C(H)Ph₂. In this thesis, phosphaalkene 2.5 is synthesized by the phosha-Peterson reaction (Scheme 2.3). In a typical experiment, XylP(SiMe₃)₂ is dissolved in THF, followed by addition of MeLi (1.0 equiv) in diethyl ether. After the reaction mixture is heated to 55 °C for 1-2 h, the solution is cooled to -78 °C and a solution of benzophenone (1.0 equiv) in THF is added. An immediate color change of the solution from yellow to dark red is observed. After addition of excess TMSCI, the color of the solution turns
back to yellow. Subsequently, all the volatiles are removed in vacuo. Compound 2.5 is extracted into hexanes and purified by distillation and recrystallization from hexanes. The $^1$H and $^{31}$P NMR spectra of 2.5 are shown in Figure 2.1 and 2.2, respectively. The chemical shift of the signal observed in the $^{31}$P NMR spectrum ($\delta_{31p} = 231.2$) is similar to the chemical shifts of similar phosphaalkenes reported in the literature (MesP=CPh$_2$: $\delta_{31p} = 233.0$, MesP=C(4-FC$_6$H$_4$)$_2$: $\delta_{31p} = 234.3$, E-2,6-(CF$_3$)$_2$C$_6$H$_3$P=CMePh: $\delta_{31p} = 209.3$).$^{79,85}$ Thus, this signal is consistent with the desired formulation of the product as 2.5. Proton assignments for 2.5 are made by comparison to the similar NMR data of 1.7 reported in the literature.$^{55}$

![Scheme 2.3](image)

**Scheme 2.3** Synthetic route to 2.5 by the phospha-Peterson reaction.

![Figure 2.1](image)

**Figure 2.1** $^1$H NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of 2.5.
2.2.2 Anionic polymerization of phosphaalkene 2.5 in solution

With the successful synthesis and purification of 2.5, its anionic polymerization can now be investigated. In a typical anionic polymerization experiment (Scheme 2.4), phosphaalkene 2.5 is first dissolved in THF, forming a light yellow solution. Subsequently, $^n$BuLi (4 mol %) is added to the solution at room temperature, and an immediate color change of the solution from yellow to dark red is observed. The solution is stirred for 22 h and the dark red color remains. The $^{31}$P{\textsuperscript{1}H} NMR spectrum of an aliquot removed from the reaction mixture shows that the signal assigned to monomer 2.5 ($\delta_{31P} = 231.3$) is consumed and replaced by a broad signal (centered at $\delta_{31P} = -10.9$) assigned to polymer 2.6 (Figure 2.3). The polymerization is

![chemical structure](image)

**Scheme 2.4** Anionic polymerization of 2.5.
quenched by degassed methanol. An immediate color change from dark red to light yellow is observed when methanol is added. A pale yellow powder is isolated after precipitation with dry hexanes (50 mL) and filtration. After repeated precipitations from concentrated THF solution of “crude polymer” with dry hexanes (2 × 50 mL), the pale yellow polymer is isolated by filtration and dried in vacuo. GPC analysis results of polymer 2.6 are listed in Table 2.1 and the refractive index traces of 2.6 are shown in Figure 2.4.

![Figure 2.3](image)

**Table 2.1** GPC analysis results of polymer 2.6.

<table>
<thead>
<tr>
<th>Trial</th>
<th>$M_n$ calcd. (g mol$^{-1}$)</th>
<th>$M_n$ obsd. (g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7600</td>
<td>6100</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>7600</td>
<td>5700</td>
<td>1.16</td>
</tr>
</tbody>
</table>
Refractive index traces of 2.6 prepared with 4 mol % \(^{n}\)BuLi as initiator (Table 2.1).

The microstructure of 2.6 is characterized by NMR spectroscopy (Figure 2.5 and 2.6). Selected NMR data of 1.8' and 2.6 are listed in Table 2.2 for comparison. Similar \(^1\)H NMR and \(^{13}\)C{\(^1\)H} NMR chemical shifts of protons and carbons in 1.8' and 2.6 are observed, with the exception that \(p\)-CH\(_3\) is not observed in 2.6, indicating the similar microstructures of 1.8' and 2.6. Hence, the microstructure of the polymer obtained should mainly be 2.6', although the presence of small amounts of –P(Xyl)-CPh\(_2\) cannot be ruled out. In the \(^1\)H-\(^{13}\)C HSQC NMR spectrum of 1.8', two important correlations are observed (\(\delta_{1H} = 4.8, \delta_{13C} = 52.4\) assigned to the \(-\text{CHPh}_2\) moiety, and \(\delta_{1H} = 3.6, \delta_{13C} = 33.0\) assigned to the \(-\text{CH}_2\)- moiety). In the \(^1\)H-\(^{13}\)C HSQC NMR spectrum of 2.6 (Figure 2.7), two similar correlations (\(\delta_{1H} = 5.0, \delta_{13C} = 51.6\) and \(\delta_{1H} = 3.5, \delta_{13C} = 31.4\)) are also observed. Thus, these signals are assigned to the \(-\text{CHPh}_2\) moiety and the \(-\text{CH}_2\)- moiety, respectively. The NMR spectroscopic analysis suggests that the C-H bond of the \(\alpha\)-CH\(_3\) group in phosphaalkene 2.5 is also activated during the anionic polymerization.
Figure 2.5 $^1$H NMR spectrum (CDCl$_3$, 600 MHz, 298 K) of 2.6.

Figure 2.6 $^{13}$C($^1$H) NMR spectrum (CDCl$_3$, 150 MHz, 298 K) of 2.6.

Figure 2.7 $^1$H-$^{13}$C HSQC NMR spectrum (CDCl$_3$, 600 MHz for $^1$H, 298 K) of 2.6.
Table 2.2  NMR data of 1.8' and 2.6 (NMR data of 1.8' is retrieved from Ref. 71).

<table>
<thead>
<tr>
<th></th>
<th>δ_{1H}</th>
<th>δ_{13C}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>7.1 (br)</td>
<td>146.9 (br), 142.2 (br), 146.7 (br), 142.3 (br), 126.3 (br)</td>
</tr>
<tr>
<td>b</td>
<td>4.8 (br)</td>
<td>137.9 (br), 128.2 (br), 129.3 (br), 128.2 (br), 126.2 (br)</td>
</tr>
<tr>
<td>c</td>
<td>3.6 (br)</td>
<td>52.4 (br), 51.6 (br)</td>
</tr>
<tr>
<td>d</td>
<td>2.1 (br)</td>
<td>33.0 (br), 31.5 (br)</td>
</tr>
<tr>
<td>e</td>
<td>2.1 (br)</td>
<td>23.5 (br), 24.6 (br), 23.1 (br)</td>
</tr>
</tbody>
</table>

2.2.3 Molecular model built for the anionic polymerization of 2.5

Molecular studies of the initiation and termination steps are conducted to further confirm the microstructure of 2.6. As discussed in Part 2.1, in 2007 the initiation step and termination step of anionic polymerization of 1.7 were modeled. At that time, MeLi was chosen as the initiator, and MeOH, ClP(NEt₂)₂, and Me₃SiCl were chosen as terminators (Scheme 2.1). The molecular structures of 2.1, 2.2 and 2.3 seemed to suggest that the electrophiles were always on the P-Ph₂C' carbonanion end in the anionic polymerization of 1.7.
Scheme 2.1 Synthetic routes to the molecular models of initiation and termination steps of the anionic polymerization of 1.7.

However, the steric bulk of the phosphaalkene monomers was not taken into consideration when these molecular studies were conducted. The size of the phosphaalkene monomer is much larger than MeOH, CIP(NEt)\_2 or Me_3SiCl molecules, making it much harder to approach the carbanion end (P-Ph\_2C). Therefore, the C-H bond of the o-CH\_3 group may be forced to get activated to make it easier to approach the phosphaalkene monomers. When molecular studies of the initiation and termination steps of the anionic polymerization of 2.5 are investigated, the more hindered electrophile triphenylmethyl chloride (trityl chloride) is chosen as the terminator. MeLi (1.0 equiv) is added to a solution of phosphaalkene 2.5 in toluene (Scheme 2.5). An immediate color change of the solution from yellow to dark red is observed, which is similar to the color change in the anionic polymerization of 2.5. An aliquot was removed from the reaction mixture for the \textsuperscript{31}P{\{\textsuperscript{1}H\}} NMR spectroscopy (Figure 2.8a). It is shown that the signal assigned to phosphaalkene 2.5 is almost quantitatively consumed and
replaced by two new signals ($\delta_{31p} = -24.6, -46.0$), which are tentatively assigned to 2.7 and 2.8. The solution turns from dark red to milky orange after trityl chloride (1.0 equiv) in toluene is added dropwise to the reaction mixture. A doublet ($\delta_{31p} = -36.4$) is observed in the $^{31}P\{^1H\}$ NMR spectrum (Figure 2.8b). Upon standing for 1 d, the doublet is replaced by a new signal ($\delta_{31p} = -23.6$) assigned to 2.9 (Figure 2.8c). The solution is filtered, and compound 2.9 is isolated by crystallization from toluene. Its $^1H$ NMR spectrum is shown in Figure 2.9. Single-crystal X-ray crystallography was performed to further confirm its structure. The molecular structure is shown in Figure 2.10. Important metrical parameters are included in the figure caption.

Scheme 2.5  Synthetic route to the molecular model built for the anionic polymerization of 2.5.
Figure 2.8 $^{31}$P($^1$H) NMR spectra (toluene, 122 MHz, 298 K) of an aliquot removed from a) the reaction mixture of Scheme 2.5 after MeLi is added; b) the reaction mixture of Scheme 2.5 after trityl chloride is added; c) the reaction mixture of Scheme 2.5 after the solution is stirred for 15 h.

Figure 2.9 $^1$H NMR spectrum (C$_6$D$_6$, 400 MHz, 298 K) of 2.9.
Figure 2.10 Molecular structure of 2.9 by ORTEP $^{3.86}$ Ellipsoids are drawn at the 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-C(7) 1.8749(16), P(1)-C(28) 1.8555(16), P(1)-C(29) 1.8990(16), C(1)-C(2) 1.530(2), C(6)-C(8) 1.5289(18), C(8)-C(9) 1.5868(18), C(9)-C(10) 1.5689(18), C(9)-C(16) 1.5651(18), C(9)-C(22) 1.5531(18); C(7)-P(1)-C(29) 99.72(7), C(28)-P(1)-C(7) 105.84(7), C(28)-P(1)-C(29) 104.71(6), P(1)-C(29)-C(36) 113.03(9), C(7)-C(2)-C(1) 124.95(12), C(2)-C(7)-P(1) 124.81(10), C(2)-C(7)-C(6) 118.61(12), C(6)-C(7)-P(1) 116.56(9), C(6)-C(8)-C(9) 118.22(10), C(10)-C(9)-C(8) 111.01(11), C(16)-C(9)-C(8) 108.30(10), C(16)-C(9)-C(10) 104.83(10), C(22)-C(9)-C(8) 108.91(10), C(22)-C(9)-C(10) 112.40(10), C(22)-C(9)-C(16) 111.27(11), C(36)-C(29)-C(30) 113.33(10).
The molecular structure of 2.9 confirms that the C-H bond of the $\alpha$-CH$_3$ group of 2.5 is activated and -CPh$_3$ group is attached to the carbon of the $\alpha$-CH$_3$ group. The length of P-CHPh$_2$ [P(1)-C(29) (1.8990 Å)] is a little longer than the typical length of P-C single bond (1.85 Å). The bond length of P-CHPh$_2$ in 2.9 is also longer than the P-CHPh$_2$ bond (1.857 Å) in compound 2.4 whose C-H bond of the $\alpha$-CH$_3$ group is activated and connected to TEMPO.$^{13,71}$ The elongation should be caused by the sterics of phenyl groups on the former phosphaalkene carbon [C(29)] and the trityl carbon [C(9)]. Expectedly, the former phosphaalkene carbon [C(29)] changes from $sp^2$ hybridization to $sp^3$ hybridization, although the bond angles of C$_{Ph}$-C$_{Ph}$ [C(36)-C(29)-C(30): (113.33°)] and P-C$_{Ph}$ [P(1)-C(29)-C(36): (113.03°)] are slightly larger than 109.6°. Similar enlarged bond angles are observed in compound 2.4 (116.3° and 114.1°). The bond angle of C-CH$_2$-C$_{trityl}$ [C(6)-C(8)-C(9)] is 118.22°, but in compound 2.4, this bond angle is only 109.0°. The enlarged bond angle of C-CH$_2$-C$_{trityl}$ [C(6)-C(8)-C(9)] should also be influenced by the sterics of the three phenyl groups on the trityl carbon [C(9)], which may push the trityl carbon [C(9)] away from the -CH$_2$-carbon [C(8)]. The elongated CH$_2$-C$_{trityl}$ [C(8)-C(9)] bond (1.5868 Å) compared to typical C-C single bond length (1.53 Å) is consistent with this trend. The confirmation of the structure of 2.9 lends more support to our hypothesis that the C-H bond of the $\alpha$-CH$_3$ group in 2.5 is activated during the anionic polymerization.
2.2.4 Kinetic studies of the anionic polymerization of phosphaalkene 2.5

To further investigate the mechanism of anionic polymerization of phosphaalkene 2.5, kinetic studies are performed on the system. As reported by Noonan, the polymerization of 1.7 is much slower than the polymerization of olefins, therefore the anionic polymerization of 1.7 was monitored by $^{31}$P NMR spectroscopy. Similarly, the anionic polymerization of phosphaalkene 2.5 is monitored by $^{31}$P NMR spectroscopy for kinetic studies.

Kinetic experiments are conducted under identical conditions with different temperatures: 298.6 K, 301.0 K, 306.2 K, 311.3 K, 316.6 K and 321.9 K. In a typical experiment, phosphaalkene monomer 2.5 is first dissolved in glyme under N$_2$. $^n$BuLi with 1:50 initiator-to-monomer ratio is then added to the yellow phosphaalkene solution. An immediate color change to dark red is observed upon addition. A small portion of the solution is quickly transferred to an NMR tube and the progress of the polymerization reaction is subsequently monitored by $^{31}$P NMR spectroscopy every 15 min. The relaxation delay ($d_1$) is set to 3 s with a tip angle of 30° to permit reliable integration of the spectra. The polymer is quenched with 5 drops of degassed methanol after the conversion of monomer 2.5 to 2.6 is completed. An immediate color change from dark red to light yellow is observed when methanol is added. A pale yellow powder is isolated after precipitation with dry hexanes (50 mL) and filtration. After repeated precipitations from concentrated THF solution of “crude polymer” with dry hexanes (2 × 50 mL), the pale yellow polymer is isolated by filtration and dried in vacuo. The reproducibility of the NMR data collected is confirmed by repeating every experiment at least
twice at each temperature.

Selected $^{31}$P NMR spectra monitoring the progress of polymerization at 298.6 K are displayed in Figure 2.11. As shown in the figure, the signal assigned to monomer 2.5 is quantitatively replaced by the new broad signal assigned to 2.6 after 9 h. This propagation step is much slower than that of olefins like styrene, which usually reaches the completion of propagation in a time scale of seconds.\textsuperscript{88}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.11}
\caption{Selected $^{31}$P NMR spectra (glyme, 162 MHz, 298 K) of an aliquot removed from the anionic polymerization of 2.5 over time.}
\end{figure}

In the living anionic polymerization of olefins, the propagation step follows a pseudo-first-order behavior until the conversion rate of the monomers reaches around 90%. The rate constant of propagation ($k_p$) can be calculated from Equation 2.1, in which $[M]$ stands for the
concentration of monomers and \([I]\) stands for the concentration of the active ends.

\[-\frac{d[M]}{dt} = k_p[I][M]\]  \hspace{1cm} (Equation 2.1)

It is hypothesized that the anionic polymerization of phosphaalkene 2.5 follows the same rate law. Graphs showing \(\ln([M_0]/[M])\) vs \(t\) relationship of the \(^n\text{BuLi}\) initiated polymerization of 2.5 at different temperatures with conversion rate up to at least 50 % are generated (Figure 2.12). Linear \(\ln([M_0]/[M])\) vs \(t\) relationship is observed at all the different temperatures, which is similar to the anionic polymerization of olefins and 1.7. The apparent rate constant of propagation \((k_p)\) are determined based on these linear relationships and \(\ln([M_0]/[M]) = k_p[I]t\). The apparent activation energy \((E_a)\) of the polymerization of phosphaalkene 2.5 can also be obtained from Arrhenius plot \((k_p = A e^{-\frac{E_a}{RT}})\) generated by the apparent rate constant data \((k_p)\) (Figure 2.13). These \(k_p, E_a,\) and \(A\) values are listed in Table 2.3 and 2.4 with comparison to the value of the polymerization of 1.7.\(^{87}\)

![Figure 2.12](image.png)  
**Figure 2.12** Graphs showing \(\ln([M_0]/[M])\) vs \(t\) (h) relationship of the 2 mol % \(^n\text{BuLi}\) initiated polymerization of 2.5 at different temperatures with conversion rate up to at least 50 %.
Table 2.3  Apparent propagation constants ($k_p$) of the polymerization of 1.7 and 2.5 with 2 mol % 'BuLi as initiator.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k_p$ for 1.7 (L mol$^{-1}$ h$^{-1}$)</th>
<th>$T$ (K)</th>
<th>$k_p$ for 2.5 (L mol$^{-1}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.3</td>
<td>21.0 ± 2.5</td>
<td>298.6</td>
<td>32.3 ± 1.4</td>
</tr>
<tr>
<td>301.8</td>
<td>32.7 ± 3.9</td>
<td>301.0</td>
<td>41.5 ± 2.2</td>
</tr>
<tr>
<td>307.4</td>
<td>41.8 ± 4.9</td>
<td>306.2</td>
<td>71.5 ± 5.9</td>
</tr>
<tr>
<td>313.0</td>
<td>70.7 ± 8.9</td>
<td>311.3</td>
<td>106 ± 4</td>
</tr>
<tr>
<td>318.6</td>
<td>125 ± 15</td>
<td>316.6</td>
<td>134 ± 11</td>
</tr>
<tr>
<td>324.2</td>
<td>150 ± 17</td>
<td>321.9</td>
<td>166 ± 33</td>
</tr>
</tbody>
</table>

Table 2.4  Apparent activation energy ($E_a$) and the preexponential factor (A) of the polymerization of 1.7 and 2.5 with 2 mol % 'BuLi as initiator.$^{87}$

<table>
<thead>
<tr>
<th></th>
<th>$E_a$ (kcal mol$^{-1}$)</th>
<th>A (M$^{-1}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>14.0 ± 0.9</td>
<td>$4.4 \times 10^{11}$</td>
</tr>
<tr>
<td>2.5</td>
<td>13.6 ± 3.3</td>
<td>$3.1 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Compared with the $k_p$ values of the living polymerization of 1.7 (Table 2.3), all the $k_p$ values of the polymerization of 2.5 at similar temperatures are larger. This indicates that all the anionic polymerization of 2.5 proceeds a little faster than those of 1.7, but the anionic polymerization of 2.5 and 1.7 does not behave too different from each other. The $E_a$ value of the
polymerization of 2.5 in glyme (13.6 ± 3.3 kcal mol$^{-1}$) is smaller than the activation barrier of 1.7 polymerization in glyme ($E_a = 14.0 \pm 0.9$ kcal mol$^{-1}$). This phenomenon may be caused by the absence of $p$-methyl group in 2.5. The substituent on the phosphorus side is smaller, making the phosphaalkene monomer more accessible. Thus, the activation energy of the P=C bond is lower and the propagation proceeds faster. Compared to the polymerization of styrene in THF with Na$^+$ as counterion ($E_a = 5.9$ kcal mol$^{-1}$), the apparent activation energies of both 1.7 and 2.5 are much higher.

![Arrhenius plot for the 2 mol % "BuLi-initiated polymerization of 2.5. Error bars are reported with 95% confidence.](image)

**Figure 2.13** Arrhenius plot for the 2 mol % "BuLi-initiated polymerization of 2.5. Error bars are reported with 95% confidence.

Although the living anionic polymerization of phosphaalkene 1.7 and 2.5 behaves in a similar way to the living polymerization of C=C bond in the aspects like following pseudo-first-order kinetics at low conversion rates, some interesting and special phenomena
are observed in the polymerization of phosphaalkenes besides the much higher activation energy. In the anionic polymerization of styrene and α-methylstyrene, the pseudo-first-order kinetics can be kept until more than 90 % of the monomers are consumed.\textsuperscript{90,91} After 90 % conversion rate, deviation of linearity towards a lower $k_p$ is observed in the $\ln[M_0]/[M]$ vs $t$ graph, \textit{i.e.}, when the concentration of monomers gets closer to the concentration of the active ends, second order effects are observed.

In contrast, the polymerization of phosphaalkenes shows a more complicated kinetic behavior. As shown in Figure 2.14, at higher temperatures such as 316.6 K and 321.9 K, the deviation of linearity towards a lower $k_p$ is exhibited as early as around 50 % to 60 % conversion rate. At lower temperatures like 298.6 K and 301.0 K, deviation of linearity towards a higher $k_p$ is observed after around 70 % of the monomers are consumed. Very similar deviation of linearity behavior is observed in the $\ln[M_0]/[M]$ vs $t$ graphs of the anionic polymerization of 1.7.

**Figure 2.14** Graphs of $\ln ([M_0]/[M])$ vs $t$ (h) up to 80 % conversion for the polymerization of 2.5 with 2 mol % $n$BuLi at ca. 5 K temperature intervals between 298 K and 322 K.
It has been discussed in Part 2.2.2 and 2.2.3 that there is C-H activation of an \( \alpha \)-CH\(_3\) group during the polymerization of 2.5. Therefore, the propagation step is not as simple as the mechanism shown in Scheme 2.6. A more plausible mechanism of the propagation step is shown in Scheme 2.7. According to the NMR analysis results of 2.6 shown in Part 2.2.2, microstructure 2.6' dominates the polymer chain. Therefore, it should be species 2.11, not 2.10, that mainly propagates the polymerization. The presence of the isomerization between 2.10 and 2.11 should lead to the special kinetic behavior of the anionic polymerization of 2.5.

**Scheme 2.6** Mechanism (I) of the propagation step of the anionic polymerization of 2.5.

**Scheme 2.7** Mechanism (II) of the propagation step of the anionic polymerization of 2.5.
First of all, the isomerization between 2.10 and 2.11 slows down the polymerization because species 2.10 is the resting species (dormant species) and the concentration of the active species 2.11 is speculated to be lower than that of 2.10, i.e., the concentration of the active propagating species is much lower than calculated. Secondly, this equilibrium makes the mechanism of anionic polymerization of 2.5 more complicated. The mechanism and kinetics of the anionic polymerization of olefins have been well-studied in the last several decades. For the anionic polymerization of olefins like styrene, when the polymerization is initiated by alkyllithium, the propagating species PLi+ can exist as dormant associated species and active dissociated species. The associated species may exist as dimers, tetramers or hexamers, and the active dissociated species may be present as free-ions and ion-pairs including contact ion-pairs and solvent-separated ion-pairs. The relative concentrations of all these different species depend on the solvent, temperature, initiator concentration and monomer concentration. The mechanism of anionic polymerization of olefins is actually very complicated due to the presence of many different species in the polymerization system. When polar solvents are used, the propagating species are mainly considered as free-ions and ion-pairs with $k_{free-ion}$ being much larger than $k_{ion-pair}$. The formation of ion-pair is favored at higher temperatures and the formation of free-ion is favored at lower temperatures because it is easier for anions and cations to get desolvated and collide with each other at higher temperatures.

Similar to the anionic polymerization of olefins, it is speculated that during the anionic polymerization of 2.5, both dormant species and active species can be present in the
polymerization system, whereas the dormant species include not only associated species but also species like 2.10. Potentially, in polar solvents like glyme both dormant species 2.10 and active species 2.11 can exist as free-ions and ion-pairs (Scheme 2.8). Both $2.11_{\text{free-ion}}$ and $2.11_{\text{ion-pair}}$ may propagate the chain growth. Therefore, the rate law of the anionic polymerization of 2.5 could be at least modified to:

$$-\frac{d[M]}{dt} = (k_{\text{free-ion}}[2.11_{\text{free-ion}}] + k_{\text{ion-pair}}[2.11_{\text{ion-pair}}])[M] \quad \text{(Equation 2.2)}$$

Scheme 2.8  Mechanism (III) of the propagation step of the anionic polymerization of 2.5.

The equilibrium constants of reactions A, B, C, and D, and rate constants of reactions A, B, C, D, E, and F shown in Scheme 2.8 are all temperature dependent. Therefore, it is plausible that the relative concentrations of the two propagating species $2.11_{\text{free-ion}}$ and $2.11_{\text{ion-pair}}$ can
change slowly during the polymerization at different temperatures. Since \( k_{\text{free-ion}} \) may be much larger than \( k_{\text{ion-pair}} \), a small change in the concentration of \( 2.11_{\text{free-ion}} \) will make a difference in the observant \( k_p \) value. Thus, it is speculated that at lower temperatures, the formation of \( 2.11_{\text{free-ion}} \) is favoured, causing the value of \( k_{\text{free-ion}}[2.11_{\text{free-ion}}] \) to increase as the reaction proceeds, \( i.e. \), a deviation of the linearity towards a higher \( k_p \) is observed. Whereas at higher temperatures, it is plausible that the formation of \( 2.11_{\text{ion-pair}} \) is favoured, causing the value of \( k_{\text{free-ion}}[2.11_{\text{free-ion}}] \) to decrease as the reaction proceeds. Hence, a deviation of the linearity towards a lower \( k_p \) is observed.

Furthermore, if the rate constant of the isomerization between \( 2.10 \) and \( 2.11 \) (Scheme 2.7a) is much larger than that of the reaction shown in Scheme 2.7b, the isomerization reaction is the rate-limiting step, suggesting the propagation step may not follow pseudo-first-order kinetic behavior. A novel mathematic model and investigation on the kinetics of the isomerization between \( 2.10 \) and \( 2.11 \) will be helpful in better clarifying the kinetic behavior of the anionic polymerization of phosphaalkenes like \( 2.5 \) and \( 1.7 \).

The software COPASI is one of the tools that can be used to model chemical reactions. When a chemical reaction is modeled accurately, \( k \) values of all the steps involved can be calculated from the input kinetic data. However, a good model of the anionic polymerization of phosphaalkenes has not been obtained, probably due to the complicated mechanism of the polymerization. The presence of the propagating species in different forms as active species like free-ions and ion-pairs (including solvent-separated ion-pairs and contact ion-pairs), and dormant
species (such as associated dimers, tetramers or hexamers), the isomerization between dormant species 2.10 and active species 2.11, the potential coordination between phosphorus and metal cations, and the presence of chain transfer or termination reactions caused by impurities in the system may all make it too difficult to model the polymerization.

All the polymers isolated from the reactions for kinetic studies are finally analyzed by triple-detection GPC (Figure 2.15, Table 2.5). It is found that the observed $M_n$ values of the polymers are all lower than the calculated $M_n$ values and that the PDIs of the polymers obtained are relatively broad, ranging between 1.14 and 1.31. This is unexpected because all the monomers 2.5 have been converted to polymer 2.6 according to the NMR data collected. If there is any impurity that may quench part of the active ends during the anionic polymerization before all the monomers are consumed, the observed $M_n$ values should be higher than the calculated $M_n$ values. Two mechanisms may account for this unexpected observation.

First, although it is not very common, unexpected chain transfer has been observed in the anionic polymerization. When the polymerization of styrene is initiated by $\text{^nBuLi}$, chain transfer to toluene has been reported. The acid-base exchange between the active end of the growing chain and toluene terminates one growing chain first, and subsequently, the freshly-formed benzyl-lithium initiates a new chain. At high molecular weights, the chain transfer step leads to a broad PDI and a decreased molecular weight of the polymer compared to the calculated value.
Figure 2.15  Refractive index traces of 2.6 prepared at various temperatures (Table 2.5).

Table 2.5  $M_n$ and $M_p$ values of polymers isolated from the polymerization of 2.5 with 2 mol % $n$BuLi as initiator at various temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$M_n$ calcd. (g mol$^{-1}$)</th>
<th>$M_n$ obsd. (g mol$^{-1}$)</th>
<th>$M_p$ obsd. (g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.6</td>
<td>15100</td>
<td>9700</td>
<td>13100</td>
<td>1.14</td>
</tr>
<tr>
<td>301.0</td>
<td>15100</td>
<td>8200</td>
<td>10400</td>
<td>1.18</td>
</tr>
<tr>
<td>306.2</td>
<td>15100</td>
<td>7300</td>
<td>9700</td>
<td>1.22</td>
</tr>
<tr>
<td>311.3</td>
<td>15100</td>
<td>7500</td>
<td>10200</td>
<td>1.19</td>
</tr>
<tr>
<td>316.6</td>
<td>15100</td>
<td>6600</td>
<td>10200</td>
<td>1.28</td>
</tr>
<tr>
<td>321.9</td>
<td>15100</td>
<td>7500</td>
<td>11900</td>
<td>1.31</td>
</tr>
</tbody>
</table>
It is speculated that a similar chain transfer step takes place in the anionic polymerization of 2.5. Trace amount of impurities containing protons with $\delta_{\text{H}} = 3.50, 3.29,$ and $2.94$ are found in the glyme used as solvent for the polymerization (Figure 2.16). Although the assignments of the impurities are unknown, an unexpected chain transfer reaction similar to the chain transfer to toluene may happen due to the presence of these impurities in the reaction mixture. The active end of the growing chain may be quenched by the “unknown impurity”, affording a polymer chain shorter than expected. Subsequently, one monomer molecule is initiated by the “lithiated-impurity” and a new polymer chain starts to grow. Thus, although all the monomer 2.5 have been consumed, lower $M_n$ values and broad PDIs are observed.

**Figure 2.16** $^1\text{H}$ NMR spectrum (C$_6$D$_6$, 162 MHz, 298 K) of glyme used as solvent for the polymerization of 2.5.

Secondly, it is difficult to measure precisely the exact amount of effective initiator used for the polymerization (e.g., 15.4 $\mu$L). A small experimental error in the measurement will lead to
a significant change in the initiator-to-monomer ratio. If the amount of the initiator added to the monomer solution is more than expected, a lower $M_n$ will be obtained. As shown in Table 2.3, all the $k_p$ values of the polymerization of 2.5 are larger than the $k_p$ values of the polymerization of 1.7. This trend is in agreement with a higher amount of initiators added in. Therefore, further investigation in purifying the solvent and conducting the polymerization in a larger scale will provide more insight into the clarification of the unexpected $M_n$ values.

### 2.3 Summary

In conclusion, phosphaalkene 2.5 is prepared and polymerized by anionic polymerization. The microstructure of polymer 2.6 is analyzed by NMR spectroscopy. The C-H activation of the $\alpha$-CH$_3$ group of 2.5 during the polymerization is observed. An molecular model of the polymerization is built by using MeLi as the initiator and Ph$_3$CCl as the terminator. The molecular structure of 2.9 is confirmed by single-crystal X-ray crystallography, which supports the C-H activation of the $\alpha$-CH$_3$ group. Kinetic studies of the anionic polymerization of 2.5 are performed to investigate its mechanism.

### 2.4 Experimental section

**Materials and general procedures.** All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. $^1$H, $^{31}$P and $^{13}$C{$^1$H} NMR spectra were recorded at room temperature otherwise
specified on Bruker Avance 300 MHz, 400 MHz or 600 MHz spectrometers. Chemical shifts are reported relative to: residual CHCl₃ (δ = 7.26 for ¹H), C₆D₅H (δ = 7.16 for ¹H); 85% H₃PO₄ as an external standard (δ = 0.0 for ³¹P); CDCl₃ (δ = 77.0 for ¹³C{¹H}). Mass Spectra were acquired using Kratos MS 50 instrument in EI mode (70 eV). Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Polymer molecular weights were determined by triple detection gel permeation chromatography (GPC–MALs) using an Agilent liquid chromatograph equipped with n Agilent 1200 series isocratic pump, Agilent 1200 series standard autosampler, Phenomenex Phenogel 5 μm narrow bore columns (4.6 x 300 mm) 10⁴ Å (5000-500000), 500 Å (1000-15000), and 10³ Å (1000-75000), Wyatt Optilab T-rEx (refractive index detector, λ = 658 nm, 40 °C), Wyatt miniDAWN (laser light scattering detector, λ = 690 nm) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min⁻¹ was used and samples were dissolved in THF (ca. 1.5 mg ml⁻¹). The dn/dc of 2.6 was determined to be 0.2538 using a Wyatt Optilab T-rEx refractive index detector (λ = 658 nm).

Hexanes and toluene were deoxygenated with nitrogen and dried by passing through a column containing activated basic alumina. THF was freshly distilled from sodium/benzophenone ketyl before use. Glyme was distilled from sodium/benzophenone ketyl twice and was stored in the glovebox with activated molecular sieves. Methanol was degassed prior to use. Benzophenone (Aldrich) was sublimed prior to use. MeLi (1.6M in diethyl ether), nBuLi (1.6 M in hexanes) and trimethylsilyl chloride were purchased from Aldrich and used as received. BuLi was titrated by using N-benzylbenzamide before use. XylP(SiMe₃)₂ was
Prepared following literature procedures.\textsuperscript{84}

**Preparation of XylP=CPh\textsubscript{2} (2.5).** Phospha-Peterson reaction was used for the preparation of 2.5.\textsuperscript{84} To a stirred solution of XylP(SiMe\textsubscript{3})\textsubscript{2} (6.35 g, 22.5 mmol) dissolved in THF (30 mL) was added MeLi in Et\textsubscript{2}O (14.8 mL, 1.6 M, 23.6 mmol). An immediate color change of the solution from colorless to yellow was observed. The reaction mixture was heated to 55 °C for 1.5 h. Subsequently, the reaction mixture was cooled to -78 °C and a solution of benzophenone (4.10 g, 22.5 mmol) in THF (20 mL) was added. Upon addition of benzophenone, the yellow solution turned to dark red. After stirring for 30 min, the reaction mixture was warmed up to room temperature while being stirred for an additional 30 min. Trimethylsilyl chloride (3.7 mL, 29 mmol) was added to the reaction mixture after cooling to -78 °C. After stirring for 30 min, the solution was warmed up to room temperature while being stirred for an additional 30 min. The color of the solution turned from dark red to yellow. The volatiles were removed \textit{in vacuo}, leaving a yellow oil. To the oil was added hexanes (3 × 30 mL) and the suspension was filtered and the solvent was removed \textit{in vacuo}, leaving a yellow oil. The crude product was distilled under vacuum and subsequently recrystallized from hexanes. Yield: 2.86 g (42.1 %).

\textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): \(\delta\) 231.2 (s); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.62-6.91 (m, 13H, aryl H), 2.36 (s, 6H, o-CH\textsubscript{3}); Anal. Calcd. for C\textsubscript{21}H\textsubscript{19}P: C, 83.44; H, 6.29. Found: C, 83.65; H, 6.36. Characterization of 2.5 agreed with those reported previously in the literature.\textsuperscript{55}
Preparation of polymer 2.6. To a stirred solution of phosphaalkene 2.5 (0.488 g, 1.62 mmol) in THF (1.5 mL) was added "BuLi (45.0 μL, 64.6 μmol, 1.44 M). An immediate color change of the solution from yellow to dark red was observed upon addition of "BuLi. The reaction mixture was stirred and the reaction progress was monitored by $^{31}$P NMR spectroscopy. After 22 h the signal assigned to phosphaalkene monomer 2.5 ($\delta_{^{31}P} = 231.3$) was consumed and replaced by a broad signal ($\delta_{^{31}P}$ centered at -10.9). Subsequently, the reaction was quenched by 5 drops of degased methanol and the dark red solution turned to yellow. A pale yellow powder was isolated after precipitation with dry hexanes (50 mL) and filtration. After repeated precipitations from concentrated THF solution (1.5 mL) of "crude polymer" with dry hexanes (2 × 50 mL), the pale yellow polymer is isolated by filtration and dried in vacuo. Yield: 0.351g (71.9 %).

GPC (THF): $M_n = 6700$ g mol$^{-1}$, PDI = 1.14. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ -10.9 (br); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.2 (br, aryl H), 5.0 (br, -CHPh$_2$), 3.5 (br, -CH$_2$), 2.7 (br, o-CH$_3$); $^{13}$C{$^1$H} NMR (600 MHz, CDCl$_3$): $\delta$146.7 (br, aryl H), 142.3 (br, aryl H), 129.3 (br, aryl H), 128.2 (br, aryl H), 126.2 (br, aryl H), 51.6 (br, -CHPh$_2$), 31.5 (br, -CH$_2$), 24.6 (br, o-CH$_3$), 23.1 (br, o-CH$_3$).

Preparation of 2.9. To a stirred solution of phosphaalkene 2.5 (1.51 g, 5.00 mmol) dissolved in toluene (30 mL) at -78 °C was slowly added MeLi in Et$_2$O (3.4 mL, 1.6 M, 5.4 mmol). An immediate color change of the solution from yellow to dark red was observed. The reaction mixture was stirred for 30 min at -78 °C and subsequently warmed up to room
temperature while being stirred for an additional 1 h. The reaction mixture was cooled down to –78 °C again and triphenylmethyl chloride (1.62 g, 5.81 mmol) in toluene (5 mL) was added dropwise. The solution was stirred for 30 min at –78 °C and warmed up to room temperature while being stirred for an additional 1 h. A milky orange solution with white suspension was formed. The suspension was filtered through glasspaper and the solution obtained was left undisturbed for several days to allow the lithium salts to precipitate. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation. Yield: 2.21 g (78.9%).

$^{31}$P NMR (162 MHz, C$_6$D$_6$): δ -23.6 (s); $^1$H NMR (400 MHz, C$_6$D$_6$): δ 7.49 (d, $J = 7.2$ Hz, 2H, aryl H), 7.34-7.05 (m, 23H, aryl H), 6.90 (d, $J = 7.2$ Hz, 1H, aryl H), 6.75 (t, $J = 7.5$ Hz, 1H, aryl H), 6.61 (d, $J = 3.7$ Hz, 1H, aryl H), 5.01 (dd, $^2J_{HH} = -15.4$ Hz, $^1J_{PH}$ = 9.9 Hz, 1H, -CH$_2$-trityl), 4.67 (d, $^2J_{PH} = 3.7$ Hz, 1H, P-CHPh$_2$), 3.66 (d, $^2J_{HH} = -13.6$ Hz, 1H, -CH$_2$-trityl), 2.56 (s, 3H, o-CH$_3$), 0.90 (d, $^2J_{PH} = 4.5$ Hz, 3H, P-CH$_3$); $^{13}$C{$^1$H} NMR(100 MHz, C$_6$D$_6$): δ 147.1 (s, aryl C), 142.1 (d, $J = 26.0$ Hz, aryl C), 143.3 (s, aryl C), 142.8 (s, aryl C), 142.7 (s, aryl C), 142.1 (d, $J = 12.3$ Hz, aryl C), 136.1 (s, aryl C), 135.9 (s, aryl C), 130.7 (s, aryl C), 130.3 (s, aryl C), 129.6 (s, aryl C) 129.5 (s, aryl C), 129.2 (s, aryl C), 129.1 (s, aryl C), 128.7 (s, aryl C), 128.5 (s, aryl C), 128.5 (s, aryl C), 128.3 (d, $J = 6.1$ Hz, aryl C), 128.1 (s, aryl C), 127.5 (s, aryl C), 126.6 (s, aryl C), 126.5 (s, aryl C), 126.2 (s, aryl C), 125.9 (s, aryl C), 58.6 (s, trityl), 51.8 (d, $^1J_{PC} = 33.7$ Hz, P-CHPh$_2$), 44.0 (d, $J_{PC} = 16.9$ Hz, -CH$_2$-trityl), 23.4 (d, $J_{PC} = 4.6$ Hz, o-CH$_3$), 9.7 (d, $^1J_{PC} = 21.4$ Hz, P-CH$_3$); MS (low res EI) : m/z 560 [M$^+$]; Anal. Calcd. for C$_{41}$H$_{37}$P: C, 87.86; H, 6.61. Found: C,87.94; H,6.75.
Kinetic studies of the anionic polymerization of 2.5. To a stirred solution of phosphaalkene 2.5 (0.364g, 1.21 mmol) in glyme (3.0 mL) was added a solution of "BuLi (15.4 μL, 1.57 M, 0.0236 mmol) in hexanes in the glovebox. An aliquot of the reaction mixture was transferred to a NMR tube after stirring for 1 min. The sample was loaded in the NMR spectrometer ($T = 298.6$ K) and $^{31}$P NMR spectra were recorded in every 15 min interval with 72 scans for each spectrum until the reaction was complete. The relaxation delay ($d_1$) was set to 3s and tip angle was set to 30° to permit reliable integration of the spectra.\(^{87}\) Five drops of degassed methanol was added to the reaction mixture to terminate the living polymer after the polymerization was complete. A pale yellow powder is isolated after precipitation with dry hexanes (50 mL) and filtration. After repeated precipitations from concentrated THF solution of “crude polymer” with dry hexanes ($2 \times 50$ mL), the pale yellow polymer is isolated by filtration and dried \textit{in vacuo}. Similar experimental procedures were followed at different temperatures. The isolated yields are between 30 % and 50 %. The reproducibility of the NMR data collected was confirmed by repeating every experiment for at least twice at each temperature. Line broadening settings of LB = 10 and baseline correction were applied when raw NMR data was processed. Integration ranges for phosphaalkene 2.5 ($\delta_{^{31}P} = 231.3$) and polymer 2.6 ($\delta$ centered at $\delta_{^{31}P} = -10.9$) were chosen between 250 ppm and 210 ppm, and between 30 ppm and -75 ppm respectively.

\textbf{X-ray crystallography.} Crystal data and refinement parameters of 2.9 are listed in Table 2.6. The single crystal was immersed in oil and mounted on a glass fiber. All
measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Mo-Kα radiation. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using the multi-scan technique (SADABS) and corrected for Lorentz and polarization effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but not refined. All refinements were performed using the SHELXL-2013 crystallographic software package from Bruker AXS.
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<tr>
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<td>Temperature (K)</td>
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<td>c (Å)</td>
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<td>γ (°)</td>
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</tr>
<tr>
<td>Final R indexes [all data]^a</td>
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<tr>
<td>Largest diff. peak/hole (e Å^{-3})</td>
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</tr>
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</table>

^a R_1 = \sum \frac{|F_o| - |F_c|}{\sum |F_o|}, \quad wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}
Chapter 3 Chemistry of Phosphaalkenes Bearing Substituents Smaller Than Mes or Ph Group

3.1 Introduction

As discussed in Chapter 2, XylP=CPPh (2.5) can be polymerized by anionic polymerization, and the microstructure of the PMPs obtained (2.6) is similar to the PMPs (1.8') obtained by the polymerization of MesP=CPPh (1.7), i.e., 2.6 does not contain alternating phosphorus and carbon atoms in the main chain. Since the absence of alternating “P-C-P-C” bonds is caused by the C-H activation of the o-CH₃ group, it is tempting to hypothesize that the expected PMPs with alternating “P-C-P-C” bonds can be obtained if the polymerization starts with phosphaalkenes without any o-CH₃ group on the substituents, e.g., phosphaalkenes with smaller groups like Ph (Scheme 3.1).

Scheme 3.1 Possible phosphaalkenes that may generate PMPs with alternating “P-C-P-C” bonds in the main chain.
However, the polymerization of these phosphaalkenes is challenged by their difficult isolation. In the past, it was thought impossible to synthesize PhP=CHPh (3.1) or o-TolP=CHPh (2-MeC₆H₄P=CHPh) (3.9), since only “polymeric materials” were generated when PhPClC(H)Ph₂ or o-TolPCIC(H)Ph₂ was treated with DBU to eliminate HCl (Scheme 3.2).\(^{55}\) However, when Becker and co-workers studied the synthesis of phosphaalkenes by the phospha-Peterson reaction in 1981 (Scheme 3.3), they found that the formation of 3.1 could be detected by \(^{31}\)P NMR spectroscopy \textit{in situ} and that 3.1 had the tendency to dimerize upon formation.\(^{75}\) The dimer was characterized by mass spectroscopy and elemental analysis. Its structure was proposed to be a “P-C-P-C” four-membered ring (1,3-diphosphetane) formed by “head-to-tail” cycloaddition, although no X-ray analysis was performed to decisively confirm this proposal. Therefore, the reported “polymeric materials” in the past might be oligomers rather than polymers.
Scheme 3.3  Synthesis of 3.1 by the phospha-Peterson reaction reported by Becker and co-workers.  

Becker’s report provides support to the feasibility of synthesizing 3.1, but to our knowledge, no further work has been done on the isolation of 3.1 or on the chemistry of its dimer. In Chapter 3, further investigation on the synthesis and dimerization of 3.1 is described, followed by studies on the thermodynamic equilibrium between the monomeric and dimeric forms of 3.1. Subsequently, the coordination chemistry of 3.1 to metal complexes is discussed. Attempts on the synthesis of other phosphaalkenes, *i.e.*, o-TolP=CPh₂ (3.9) and MesP=C(H)Ph (3.14) are mentioned at last.

3.2  Results and discussion

3.2.1  Synthesis of PhP=CPh₂ (3.1) and its dimer (3.2)

The phospha-Peterson reaction is chosen to synthesize 3.1 following precedent literature and the starting material PhP(SiMe₃)₂ is obtained by following literature procedures shown in Scheme 3.4.  

In contrast to the results of the synthesis of phosphaalkene 2.5, three types of phosphorus with δₓ₃₁P = 231.9, 4.1, and -119.7 are detected when the crude reaction mixture is analyzed by ³¹P{¹H} NMR spectroscopy (Figure 3.1). The chemical shift of the
signal at $\delta_{31P} = 231.9$ is similar to the chemical shifts of many phosphaalkenes reported in the literature (MesP=CPh: $\delta_{31P} = 233.0$, MesP=C(4-FC₆H₄): $\delta_{31P} = 234.3$, E-2,6-(CF₃)₂C₆H₃P=CMePh: $\delta_{31P} = 209.3$). Thus, this signal is consistent with the desired formulation of the product as 3.1.

**Scheme 3.4** Synthetic route to 3.1 by the phospha-Peterson reaction.

**Figure 3.1** $^{31}P\{^1H\}$ NMR spectrum (THF, 122 MHz, 298 K) of an aliquot removed from the crude product mixture of the synthesis of 3.1 by the phospha-Peterson reaction.
After the removal of all the volatiles *in vacuo*, the remaining yellow oil-like products are extracted into hexanes and filtered. Upon standing, a white precipitate is formed and filtered. Surprisingly, both $^{31}$P{$^{1}$H} NMR spectra of the products remaining in the hexanes solution and the white precipitate filtered show only one type of phosphorus with $\delta_{31P} = -119.1$ (3.3) and 4.8 (3.2), respectively (Figure 3.2 and 3.3). The chemical shift of the signal at $\delta_{31P} = -119.1$ is similar to the chemical shift of 1,2-diphenyl-3,3-dimethyl-diposphirane reported in the literature ($\delta_{31P} = -122$). Furthermore, a signal at 382 $m/z$, which corresponds to the $M^+$ of 1,2-diphenyl-3,3-diphenyl-diphosphirane, is observed on the mass spectrum of the products left in the hexanes solution. Thus, it is speculated the signal at $\delta_{31P} = -119.1$ may be assigned to 3.3. Additionally, a signal with $\delta_{13C} = 196.6$ is observed in the $^{13}$C{$^{1}$H} NMR spectrum of the products left in the hexanes solution. This signal is assigned to the unreacted benzophenone. Based on the stoichiometry of the reactants, the existence of unreacted benzophenone is in agreement with the formulation of the product as 3.3.

![Figure 3.2](image-url)  
**Figure 3.2**  $^{31}$P{$^{1}$H} NMR spectrum (hexanes, 122 MHz, 298 K) of an aliquot removed from the product mixture of the synthesis of 3.1 remaining in the hexanes solution.
Figure 3.3 $^{31}$P NMR spectrum (CDCl$_3$, 122 MHz, 298 K) of the white precipitate (3.2) filtered from the hexanes solution upon standing for 15 h.

The white precipitate (3.2) filtered is further characterized by $^1$H NMR spectroscopy, which shows that only aryl protons exist in the isolated product (Figure 3.4). White crystals suitable for single-crystal X-ray crystallography were obtained by recrystallization from hexanes. According to Becker’s report, this compound should be the 1,3-diphosphetane.$^{75}$ However, in contrast to the original formulation proposed by Becker, the molecular structure determined by single-crystal X-ray crystallography shows that dimer 3.2 is 1,2-diphosphetane, which contains a “P-P-C-C” four-membered ring other than a “P-C-P-C” four-membered ring (Figure 3.5).

Figure 3.4 $^1$H NMR spectrum (CDCl$_3$, 300 MHz, 298 K) of the white precipitate (3.2) filtered from the hexanes solution upon standing for 15 h.
Figure 3.5  Molecular structure of 3.2 by ORTEP 3.86 Ellipsoids are drawn at the 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): P(1)-P(2) 2.1911(12), P(1)-C(7) 1.959(3), P(1)-C(1) 1.826(3), P(2)-C(26) 1.937(3), P(2)-C(20) 1.826(3), C(7)-C(8) 1.531(4), C(7)-C(14) 1.536(4), C(7)-C(26) 1.614(4); C(7)-P(1)-P(2) 79.38(9), C(7)-P(1)-C(1) 108.54(13), C(1)-P(1)-P(2) 101.68(11), C(7)-C(26)-P(2) 96.41(18), C(27)-C(26)-P(2) 110.8(2), C(33)-C(26)-P(2) 109.6(2).
Compound 3.2 is not the first example of 1,2-diphosphetanes obtained from the dimerization of phosphaalkenes. When there is insufficient thermodynamic or (and) kinetic stabilization in the phosphaalkenes, it is well-known that 1,2-diphosphetanes or 1,3-diphosphetanes can be formed by the dimerization of the phosphaalkenes through either “head-to-head” or “head-to tail” [2+2] cycloaddition.\textsuperscript{46,75,76,80,81,85} However, as discussed in Chapter 1, in phosphaalkenes, the $\pi_{\text{P-C}}$ bond is the HOMO and the $\pi^*_{\text{P-C}}$ bond is the LUMO. At first glance, the [2+2] cycloaddition of two P=C bonds is thermally symmetry forbidden, since the unmatched phases of HOMO and LUMO prohibit the $\sigma$ bond formation (Scheme 3.5a). One plausible mechanism of the formation of 3.2 is that the dimerization is a thermally allowed concerted process through $[\pi_2^s + \pi_2^a]$ cycloaddition (Scheme 3.5b).\textsuperscript{103,104}

\begin{center}
\textbf{Scheme 3.5} Mechanism of the formation of 3.2 by the [2+2] cycloaddition of 3.1.
\end{center}
It is speculated that both electronic and steric factors affect the structure of the dimer. The formation of 1,3-diphosphetane is favored when the P=C bond is more polar (1.11, 1.17, 1.20 in Figure 3.6).\textsuperscript{75,76,81} Whereas the formation of 1,2-diphosphetane is favored when the substituents on the phosphorus is larger than the substituents on the carbon, since the long P-P bond can better reduce the steric repulsions between the large substituents (1.13, 3.4 in Figure 3.6).\textsuperscript{76,85,105} In the case of 3.2, the substituents on the phosphorus and carbon are identical, therefore the formation of 1,2-diphosphetane should be mainly attributed to the low polarity of the P=C bond.

\begin{equation}
\text{Figure 3.6} \quad \text{Examples of 1,3-diphosphetanes or 1,2-diphosphetanes can be formed by the dimerization of the phosphaalkenes.} \textsuperscript{75,76,81,85}
\end{equation}

The \textit{trans}- configuration of the two phosphorus atoms is as expected for a more thermodynamically stable structure. The bond lengths of P-C\textsubscript{Ph2} bonds [P(1)-C(7): 1.959(3) Å,
P(2)-C(26): 1.937(3) Å and C_{Ph2} - C_{Ph2} [C(7)-C(26): 1.614(4) Å] are longer than a typical P-C single bond (1.85 Å) and a typical C-C single bond (1.53 Å), respectively. The bond length of P(1)-P(2) [2.1911(12) Å] is shorter than a typical P-P single bond (2.25 Å). The sum of bond angles for C(7)-P(1)-P(2), P(1)-P(2)-C(26), C(7)-C(26)-P(2) and C(26)-C(7)-P(1) is 351.74 °, which is less than 360 °, displaying the slightly off-plane of the “P-P-C-C” ring. The distances of the two carbon atoms [C(7) and C(26)] from the best plane of the “P-P-C-C” ring are 0.198 Å and 0.200 Å, respectively, whereas the distances of the two phosphorus atoms [P(1) and P(2)] from the best plane of the “P-P-C-C” ring are 0.143 Å and 0.145 Å, respectively. The two carbon atoms deviate more from the best plane. The P-C, C-C bond elongation, P-P bond shortening and the larger deviation of carbon atoms from the best plane should be caused by the intramolecular steric repulsion between the phenyl groups. In order to reduce the steric repulsion, the phenyl groups on the two carbon atoms or on one carbon atom and its adjacent phosphorus atom need to push away each other. Thus, the P-C, C-C bonds are elongated and the P-P bond is shortened. Since there are two phenyl groups on each carbon atom, they need to twist more to reduce the steric crowding. Thus, the four-membered ring is off-plane with the two carbon atoms deviating more from the best plane.

Since there is not sufficient steric protection in 3.1, it has the tendency to dimerize upon standing. It is speculated that phosphaalkene 3.1 converts to 3.2 slowly in hexanes solution, and 3.2 precipitates out due to its low solubility. Thus, no 3.1 is detected after 15 h and only 3.3 is observed in the solution.
3.2.2 Thermodynamic equilibrium between PhP=CPh$_2$ (3.1) and its dimer (3.2)

When 3.2 is dissolved in THF, a colorless solution is formed, but the solution turns yellow after a couple hours. It is shown that 3.1 is reformed in THF solution by $^{31}$P{$^1$H} NMR spectroscopy. The ratio of 3.1 to 3.2 changes at various temperatures, indicating an equilibrium between 3.1 and 3.2 can form in solution (Equation 3.1). This equilibrium is monitored by $^{31}$P NMR spectroscopy at different temperatures (Figure 3.7). As shown below, at higher temperatures, the equilibrium shifts to give more of 3.1.

![Equation 3.1]

\[
2 \text{PhP}=\text{CPh}_2 \rightleftharpoons \text{PhP=Ph} \rightleftharpoons \text{PhP-Ph} \rightleftharpoons \text{Ph-Ph}
\]

(Figure 3.7) $^{31}$P NMR spectra (THF, 162 MHz) of an aliquot removed from 3.1 and 3.2 mixture in solution at various temperatures.
Based on the concentration of the original 3.2 solution, accurate integration of $^3$P NMR spectra, $K$ values of Equation 3.1 and $\Delta G^\circ$ values of the forward reaction in Equation 3.1 can be determined by the following equation:

$$\Delta G^\circ = -RT\ln K$$  \hspace{1cm} (Equation 3.2)

The $K$ and $\Delta G^\circ$ values determined are listed in Table 3.1. The $\Delta H^\circ$ and $\Delta S^\circ$ values of the forward reaction of Equation 3.1 are extracted from $\ln K$ vs $1/T$ graph (Figure 3.8) based on the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$$  \hspace{1cm} (Equation 3.3)

**Table 3.1** $K$ values of Equation 3.1 and $\Delta G^\circ$ values of the forward reaction of Equation 3.1 in THF at different temperatures.

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<thead>
<tr>
<th>$T$(K)</th>
<th>$K$</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>298.6</td>
<td>55.8</td>
<td>-10.0</td>
</tr>
<tr>
<td>300.9</td>
<td>37.5</td>
<td>-9.06</td>
</tr>
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<td>304.5</td>
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</tr>
<tr>
<td>311.3</td>
<td>11.4</td>
<td>-6.32</td>
</tr>
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</table>

The negative $\Delta H^\circ$ value ($-94.6 \pm 14.6$ kJ mol$^{-1}$) obtained indicates that the forward reaction shown in Equation 3.1 is exothermic, which is consistent with the formation of more
phosphaalkenes at higher temperatures. The negative value of $\Delta S^o (-284 \pm 48 \text{ J mol}^{-1} \text{K}^{-1})$ is in agreement with the formation of one dimer molecule from two phosphaalkene molecules in the forward reaction. For comparison, the $\Delta H^o$ value of the forward reaction of Equation 3.1 is also calculated from the estimated bond dissociation energies reported in the literature:\textsuperscript{12,13,46}

$$\Delta H^o (\text{calcd.}) = 2 \times 483 \text{ kJ mol}^{-1} (\text{P=C bond}) - 2 \times 264 \text{ kJ mol}^{-1} (\text{P-C bond}) - 308 \text{ kJ mol}^{-1} (\text{P-P bond}) - 241 \text{ kJ mol}^{-1} (\text{C-C bond}) = -111 \text{ kJ mol}^{-1}$$

The experimental value ($-94.6 \pm 14.6 \text{ kJ mol}^{-1}$) is close to the calculated value ($-111 \text{ kJ mol}^{-1}$), but it is noteworthy that the four-membered ring strain is not included in the calculation and that estimated bond dissociation energies are used. For example, the bond energy of the P=C bond is retrieved from the calculated value for HP=CH\textsubscript{2}.\textsuperscript{45} Therefore, the use of the calculated value ($-111 \text{ kJ mol}^{-1}$) is limited for orientation.

**Figure 3.8** $\ln K$ vs $1/T$ graph of the forward reaction of Equation 3.1. Error bars are reported with 95% confidence.
3.2.3 Coordination chemistry of PhP=CH2 (3.1)

As introduced in Part 1.4.3, coordinating phosphaalkenes to metal complexes acts as a good way to stabilize and isolate phosphaalkenes without enough steric protection. Since there is equilibrium between 3.1 and 3.2 in solution, it is expected that W(CO)$_5$(PhP=CH$_2$) (3.5) can form when 3.2 is treated with W(CO)$_5$(MeCN). The monomeric phosphaalkene 3.1 generated from 3.2 in solution may replace the MeCN ligand and coordinate to the tungsten center. Subsequently, the equilibrium shifts to generate more 3.1 for the coordination reaction. Finally, all the 3.2 may be consumed and afford 3.5.

![Scheme 3.6 Coordination reaction of 3.2 and W(CO)$_5$(MeCN).](image)

However, after dimer 3.2 is treated with W(CO)$_5$(MeCN) in DCM solution and stirred for 3 d (Scheme 3.6), the $^{31}$P-$^1$H NMR spectrum of an aliquot removed from the reaction mixture shows that the signal assigned to 3.2 is almost quantitatively consumed and replaced by two new signals with $\delta_{31p} = 197.3$ and 188.1, respectively (Figure 3.9). By referring to literature, the signal with $\delta_{31p} = 188.1$ is assigned to the expected product W(CO)$_5$(PhP=CH$_2$) (3.5), which has been synthesized via an alternative route by the reaction of 2-phosphanorbornadiene tungsten...
complex and Ph₂C=W(CO)₅.⁷⁸ The signal with δ₃¹P = 197.3 should also be assigned to a tungsten-phosphaalkene complex because the observation of $^{183}$W satellites ($^1J_{PW} = 265.7$ Hz) supports the coordination of the phosphorus center to the tungsten center. Both the chemical shift and the P-W coupling constant are similar to other tungsten-phosphaalkene complexes reported in the literature [cis-W(CO)₄(MesP=CPh₂)₂: δ₃¹P = 195, $^1J_{PW} = 264$ Hz; W(CO)₅(PhP=CMe₂): δ₃¹P = 176, $^1J_{PW} = 261$ Hz; W(CO)₅(PhP=CHCHMe₂): δ₃¹P = 186/191, $^1J_{PW} = 259$ Hz; Z-W(CO)₅(’BuP=CH’Bu): δ₃¹P = 228, $^1J_{PW} = 245$ Hz].⁷⁷,⁸²,¹⁰⁶ Furthermore, the low-field $^{3¹}$P NMR chemical shift is consistent with the conservation of P=C double bond.

**Figure 3.9** $^{3¹}$P NMR spectrum (DCM, 162 MHz, 298 K) of an aliquot removed from the reaction mixture of Scheme 3.6 after 3 d.

The structure of 3.6 is characterized by single-crystal X-ray crystallography. Dark red crystals suitable for X-ray diffraction were obtained by recrystallization of the product mixture
from diethyl ether at -30 °C. The molecular structure is shown in Figure 3.10 with metrical parameters included in the figure caption. The molecular structure determined by single-crystal X-ray crystallography shows that the main product 3.6 \((\delta_{31p} = 197.3)\) is cis-W(CO)\(_4\)(PhP=CPh\(_2\))².

**Figure 3.10** Molecular structure of 3.6 by ORTEP 3.\(^8\) Ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)-P(1) 2.4775 (12), W(1)-P(2) 2.4437(13), W(1)-C(40) 2.039(5), W(1)-C(41) 1.988(5), P(1)-C(1) 1.687(5), P(1)-C(14) 1.813(5), P(2)-C(20) 1.673(5), P(2)-C(34) 1.826(6), O(1)-C(41) 1.170(5), O(3)-C(40) 1.148(6); P(1)-W(1)-P(2) 90.17(5), C(41)-W(1)-P(1) 177.79(15), C(41)-W(1)-P(2) 87.92(15), C(1)-P(1)-W(1) 130.99 (17), C(1)-P(1)-C(14) 107.8 (2), C(14)-P(1)-W(1) 121.02 (16), C(20)-P(2)-W(1) 134.26 (18), C(20)-P(2)-C(34) 107.7 (2), C(34)-P(2)-W(1) 118.07(18).
Besides the low-field chemical shift ($\delta_{31P} = 197.3$) of 3.6 in the $^{31}$P NMR spectrum, the conservation of the P=C double bond is indicated by the short phosphorus-carbon bond length (1.687 Å and 1.673 Å) compared with typical P-C single bond length (1.85 Å). This bond length is close to the P=C double bond length (1.65 – 1.70 Å) found in similar phosphaalkenes reported in the literature. The octahedral geometry of tungsten is maintained and the 90.17° angle of P(1)-W(1)-P(2) shows that the two phosphaalkene ligands adopt cis geometry to each other.

It is intriguing to observe the formation of both 3.5 and 3.6, with 3.6 being the main product. There is only one MeCN ligand in the tungsten source, thus only the formation of 3.5 was expected. Two synthetic pathways were proposed at first (Scheme 3.7), but they are not very likely to account for the formation of 3.6. This is because the displacement of a CO ligand usually requires high temperatures or UV light, but neither of these conditions is provided during the reaction of W(CO)$_5$(MeCN) and 3.2. In a similar reaction reported in the literature, a mixture of disubstituted cis-W(CO)$_4$(MesP=CPh)$_2$ and monosubstituted W(CO)$_5$(MesP=CPh$_2$) were also obtained when MesP=CPh$_2$ (1.7) was treated with W(CO)$_5$(THF). However, no discussion was made on the cis-W(CO)$_4$(MesP=CPh$_2$)$_2$ to W(CO)$_5$(MesP=CPh$_2$) ratio or on the mechanism of the formation of the disubstituted product. Therefore, it is of interest to investigate on how 3.6 is formed.
After careful examining, it turns out that the formation of 3.6 may follow two possible mechanisms. First of all, the tungsten source W(CO)$_5$(MeCN) is synthesized by treating W(CO)$_6$ with Et$_4$NBr at reflux in dioxane solution for 2 h, followed by treating the resultant (Et$_4$N)[BrW(CO)$_3$] with excess acetonitrile.$^{110,111}$ It is possible that compounds like W(CO)$_4$(MeCN)$_2$ form as a side product due to the high temperature and excess acetonitrile provided in the synthesis. The result of low resolution EI-MS suggests that the tungsten source is not pure W(CO)$_5$(MeCN). Signals at 365 $m/z$, which is assigned to the W(CO)$_5$(MeCN)$^+$ fragment, is observed. This is consistent with the existence of W(CO)$_5$(MeCN). Whereas besides the signal at 365 $m/z$, signals at 350, 322, 294, and 266 $m/z$ are observed. They are assigned to W(CO)$_3$(MeCN)$_2^+$, W(CO)$_2$(MeCN)$_2^+$, W(CO)(MeCN)$_2^+$ and W(MeCN)$_2^+$ fragments. A signal at 352 $m/z$ is also detected. This signal is assigned to W(CO)$_6^+$. These results suggest that the
tungsten source may be a mixture of W(CO)$_5$(MeCN), W(CO)$_4$(MeCN)$_2$, and W(CO)$_6$. The elemental analysis result of the tungsten source used (C 23.22 %, H 1.14 %, N 3.88 %) is close to the calculated result of pure W(CO)$_5$(MeCN) (C 23.04 %, H 0.83 %, N 3.84 %). This elemental analysis result is reasonable if the molar amounts of W(CO)$_4$(MeCN)$_2$, and W(CO)$_6$ in the mixture are close. Disubstituted tungsten complex 3.6 can form if W(CO)$_4$(MeCN)$_2$ is present in the reaction mixture.

Secondly, the presence of dimer 3.2 may also contribute to the formation of 3.6. In order to clarify the function of dimer 3.2, monomeric phosphaalkene XylP=CPh$_2$ (2.5) is treated with the same tungsten source, *i.e.*, a mixture of W(CO)$_5$(MeCN), W(CO)$_4$(MeCN)$_2$, and W(CO)$_6$, for comparison (Scheme 3.8). The $^{31}$P NMR spectrum of an aliquot removed from the reaction mixture shows that after 3 d the signal assigned to phosphaalkene 2.5 ($\delta_{31p} = 232.3$) is replaced by two new signals ($\delta_{31p} = 185.0, 193.5$) (Figure 3.11b). These two signals are assigned to the monosubstituted tungsten complex 3.7 and the disubstituted tungsten complex 3.8 respectively, based on their similar chemical shifts to 3.5 ($\delta_{31p} = 188.1$) and 3.6 ($\delta_{31p} = 197.3$). The main product monosubstituted tungsten complex 3.7 should be formed by the reaction of 2.5 and W(CO)$_5$(MeCN), and the smaller amount of the disubstituted tungsten complex 3.8 should be formed by the reaction of 2.5 and W(CO)$_4$(MeCN)$_2$. However, the main product of this reaction is different from the main product of the reaction of W(CO)$_5$(MeCN) and 3.2. When the coordination reaction starts with dimer 3.2, the main product is the disubstituted tungsten complex 3.6 ($\delta_{31p} = 197.3$). The formation of the disubstituted tungsten complex 3.6 is favoured
indicates the role of dimer 3.2 in this coordination reaction is more than the generation of phosphaalkene 3.1.

Scheme 3.8  Coordination reaction of 2.5 and W(CO)$_3$(MeCN).

Figure 3.11  $^{31}$P NMR spectra (DCM, 162 MHz, 298 K) of an aliquot removed from a) reaction mixture of Scheme 3.6 after 3 d; b) reaction mixture of Scheme 3.8 after 3 d. Delay time ($d_I$) is set to 5 s to permit reliable integration.
A proposed mechanism of the formation of \textbf{3.6} by the reaction of \textbf{3.2} and W(CO)$_5$(MeCN) is shown in Scheme 3.9. One of the phosphorus centers of \textbf{3.2} may first replace the MeCN ligand and coordinate to the tungsten center through its lone pair. Subsequently, the other phosphorus center coordinates to the tungsten center and replaces the CO group at the \textit{cis} position, with the breakage of the P-P bond and C-C bond, and the formation of P=C bonds. This mechanism is in agreement with the \textit{cis} geometry of the two phosphaalkene ligands in compound \textbf{3.6}. It usually takes days for this coordination reaction to complete, so some monomeric phosphaalkene \textbf{3.1} can be generated from the unreacted dimer \textbf{3.2} in solution. The monomeric phosphaalkenes \textbf{3.1} are only able to substitute the MeCN ligand in W(CO)$_5$(MeCN), so a small amount of compound \textbf{3.5} is formed. When the starting material is the monomeric phosphaalkene \textbf{2.5}, this mechanism cannot be followed due to the absence of dimerized phosphaalkenes, therefore the monosubstituted tungsten complex \textbf{3.7} dominates the product.
3.2.4 Synthesis of o-TolP=CPh$_2$ (3.9)

Motivated by the successful polymerization of 2.5 and the isolation of 3.2, research is conducted to synthesize o-TolP=CPh$_2$ (3.9). Although it has been reported that 3.9 cannot be obtained by reacting o-TolPClC(H)Ph$_2$ with DBU,\textsuperscript{55} based on our studies on PhP=CPh$_2$ (3.1), the use of the phospha-Peterson reaction is expected to make a difference (Scheme 3.10).

**Scheme 3.10** Synthetic route to 3.9 by the phospha-Peterson reaction.

![Scheme 3.10](image)

**Figure 3.12** $^{31}$P{$^{1}$H} NMR spectrum (THF, 122 MHz, 298 K) of an aliquot removed from the crude product mixture of the synthesis of 3.9 by the phospha-Peterson reaction.

Similar to the results of the synthesis of phosphaalkene 3.1, three types of phosphorus with $\delta_{31p} = 233.8$, -13.7, and -117.7 are detected in the crude reaction mixture (Figure 3.12). The chemical shift of the signal at $\delta_{31p} = 233.8$ is similar to the chemical shifts of
phosphaalkenes both reported in the literature \([\text{MesP=CPh}_2; \delta_{31P} = 233.0, \text{MesP=C(4-FC}_6\text{H}_4)_2; \delta_{31P} = 234.3, E-2,6-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{P}=\text{CMePh}; \delta_{31P} = 209.3] \) and reported in this thesis (2.5: \( \delta_{31P} = 231.2, 3.1: \delta_{31P} = 231.9 \)). Thus, this signal is consistent with the desired formulation of the product as 3.9. The chemical shift of the signal at \( \delta_{31P} = -117.7 \) is similar to the chemical shift of 1,2-diphenyl-3,3-dimethyl-diphosphirane reported in the literature (\( \delta_{31P} = -122 \)) and 3.3 (\( \delta_{31P} = -119.7 \)). Thus, it is speculated this signal may be assigned to 3.11. A signal at 410 \( m/z \), which corresponds to the M+ of 3.11, is observed on the mass spectrum of the product mixture. Thus, the assignment of the signal (\( \delta_{31P} = -117.7 \)) to 3.11 is further supported. Additionally, a signal with \( \delta_{13C} = 196.5 \) is observed in the \( ^{13}\text{C}\{^1\text{H}\} \) NMR spectrum of the product mixture. This signal is assigned to the unreacted benzophenone. Based on the stoichiometry of the reactants, the existence of the unreacted benzophenone is in agreement with the formulation of the product as 3.11.

The chemical shift of the signal at \( \delta_{31P} = -13.7 \) is close to the chemical shift of 3.2 (\( \delta_{31P} = 4.1 \)). So this signal may be assigned to the product as 3.10. In order to justify this assignment, the product mixture is heated at 50 °C for 5 h. By comparison to the \( ^{31}\text{P} \) NMR spectrum of the product mixture before heating (Figure 3.13), an increase of the signal at \( \delta_{31P} = 233.8 \) to the signal at \( \delta_{31P} = -13.7 \) ratio is observed. As shown in Part 3.2.2, the 3.1 to 3.2 ratio is also increased upon heating (Figure 3.7). The similar temperature dependent ratio change is consistent with the assignment of the signal at \( \delta_{31P} = -13.7 \) to 3.10.
Figure 3.13 $^{31}$P NMR spectra (CDCl$_3$, 162 MHz, 298 K) of an aliquot removed from a) the crude product mixture of the synthesis of 3.9 by the phospha-Peterson reaction; b) the crude product mixture after being heated at 50 °C for 5 h. Delay time ($d_I$) is set to 5 s to permit reliable integration.

3.2.5 Coordination chemistry of o-TolP=CPh$_2$ (3.9)

Unfortunately, efforts to isolate 3.9 or 3.10 by distillation or crystallization were fruitless. Distillation of the reaction mixture results in a mixture of phosphaalkene 3.9 and side products, which might be formed from the decomposition of phosphaalkene 3.9 at high temperatures. Crystallization from hexanes at -30 °C affords no crystal of the products.

In order to isolate 3.9, efforts are undertaken to coordinate 3.9 to tungsten complexes. The crude product mixture of 3.9, 3.10 and 3.11 is treated with a small portion of W(CO)$_5$(MeCN) in DCM solution (Scheme 3.11). The reaction is monitored by $^{31}$P{${^1}$H} NMR
spectroscopy with more W(CO)$_5$(MeCN) being added to the solution in small portions until both the signals assigned to 3.9 (δ$_{31P}$ = 234.0) and 3.10 (δ$_{31P}$ = -13.2) are almost consumed. As shown by the $^{31}$P($^1$H) NMR spectra, upon addition of W(CO)$_5$(MeCN), both the signals assigned to 3.9 (δ$_{31P}$ = 234.0) and 3.10 (δ$_{31P}$ = -13.2) are consumed and replaced by new signals with δ$_{31P}$ = 192.4 and 185.3 (Figure 3.14b). With the addition of more W(CO)$_5$(MeCN), the signal assigned to 3.10 (δ$_{31P}$ = -13.2) is replaced completely by the new signals and the signal assigned to 3.9 (δ$_{31P}$ = 234.0) is much weaker than before (Figure 3.14c). No change of the signal assigned to 3.11 (δ$_{31P}$ = -118.3) is observed even if more W(CO)$_5$(MeCN) is added to the reaction mixture.

**Scheme 3.11** Coordination reaction of 3.9 and W(CO)$_5$(MeCN).
Figure 3.14 $^{31}$P{'^1}$H NMR spectra (DCM, 122 MHz, 298 K) of an aliquot removed from a) the crude product mixture of the synthesis of 3.9 by the phospha-Peterson reaction; b) the reaction mixture after a small portion of W(CO)$_5$(MeCN) is added and stirred for 5 h; c) the reaction mixture after more W(CO)$_5$(MeCN) is added and stirred for 3 d.

The signal at $\delta_{31p} = 185.3$ is assigned to 3.12 and the signal at $\delta_{31p} = 192.4$ is assigned to 3.13 due to their similar chemical shifts to 3.5 ($\delta_{31p} = 188.1$) and 3.6 ($\delta_{31p} = 197.3$) respectively, which are formed by treating 3.2 with W(CO)$_5$(MeCN). The low-field $^{31}$P NMR
chemical shifts are consistent with the conservation of P=C double bond. The observation of $^{183}$W satellites of the signal with $\delta_{31P} = 185.3$ ($J_{PW} = 268.5$ Hz) and 192.4 ppm ($J_{PW} = 263.9$ Hz) supports the coordination of the phosphorus center to the tungsten center. These chemicals shifts of signals and P-W coupling constants are similar to other tungsten-phosphaalkene complexes reported in the literature [cis-W(CO)$_4$(MesP=CPh)$_2$]: $\delta_{31P} = 195$, $J_{PW} = 264$ Hz; W(CO)$_5$(PhP=CM$_2$): $\delta_{31P} = 176$, $J_{PW} = 261$ Hz; W(CO)$_5$(PhP=CHCHMe$_2$): $\delta_{31P} = 186/191$, $J_{PW} = 259$ Hz; Z-W(CO)$_5$(tBuP=CHC'tBu): $\delta_{31P} = 228$, $J_{PW} = 245$ Hz].$^{77,82,106}$

Additionally, the observation that similar products (disubstituted tungsten phosphaalkene complex and monosubstituted tungsten phosphaalkene complex) are obtained from the reaction of W(CO)$_5$(MeCN) and 3.9, 3.10, 3.11 mixture, and the reaction of W(CO)$_5$(MeCN), and 3.2 lends more support to the assignment of the signal at $\delta_{31P} = -13.2$ as 3.10. The disubstituted tungsten-phosphaalkene complex 3.13 may be formed following a similar mechanism to the formation of complex 3.6 (Scheme 3.9), i.e., after one of the phosphorus on the four-membered ring replaces the MeCN ligand and coordinates to the tungsten center, the P-P and C-C bonds break, P=C bonds form and the other phosphorus coordinates to the tungsten center. Unfortunately, no crystal was obtained from the product mixture.
3.2.6 Synthesis of MesP=C(H)Ph (3.14)

Thus far, it has been shown that interesting chemistry is discovered in phosphaalkenes bearing Ph or $o$-Tol groups on the phosphorus side. It will also be of interest if P-mesityl phosphaalkenes bearing substituents smaller than Ph on the carbon side can be synthesized. So attempts are made to synthesize MesP=C(H)Ph (3.14) by phospha-Peterson reaction and base-catalyzed phospha-Peterson reaction. The MesP(SiMe$_3$)$_2$Li or MesP(SiMe$_3$)$_2$ in THF solution is treated with benzaldehyde (Scheme 3.12 and 3.13). An aliquot is removed from the reaction mixture for $^{31}$P NMR spectroscopy, but no signal ($\delta_{31P} > 200$) that can be assigned to the expected phosphaalkene is detected (Figure 3.15 and 3.16).

![Scheme 3.12](image)

**Scheme 3.12** Attempted synthesis of 3.14 by the phospha-Peterson reaction.

![Figure 3.15](image)

**Figure 3.15** $^{31}$P{$^1$H} NMR spectra (THF, 122 MHz, 298 K) of an aliquot removed from the reaction mixture of the synthesis of 3.14 by the phospha-Peterson reaction.
Scheme 3.13  Attempted synthesis of 3.14 by the base-catalyzed phospha-Peterson reaction.

Figure 3.16  $^{31}P\{^1H\}$ NMR spectra (THF, 122 MHz, 298 K) of an aliquot removed from the reaction mixture of the synthesis of 3.14 by the base-catalyzed phospha-Peterson reaction.

When the Lewis acid-mediated phospha-Peterson reaction is used (Scheme 3.14), the formation of both $E + Z$ isomers of 3.14 is detected by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 3.17). The chemical shifts of the signals observed ($\delta_{31p} = 247.1, 231.5$) are similar to the chemical shifts of similar phosphaalkenes reported in the literature ($E$-{EtBu}$P=CH'$Bu: $\delta_{31p} = 275.0$, $E$-Ph$P=CH'$Bu: $\delta_{31p} = 221.7$, $E$-Ad$P=CH'$Bu: $\delta_{31p} = 268.4$, $E$-Mes$P=CH'$Bu: $\delta_{31p} = 228.4$, $E$-Cy$P=CH'$Bu: $\delta_{31p} = 257.8$).$^{107,112,113,114}$ Thus, these signals are consistent with the desired formulation of the product as 3.14. The doublet observed with $\delta_{1H} = 9.08$ ($^2J_{PH} = 25.2$ Hz) in the $^1H$ NMR spectrum of the crude product mixture also supports the formulation of the product as 3.14 (Figure 3.18). Both the chemical shift and the P-H coupling constant are similar to
other similar phosphaalkenes reported in the literature \((E^-BuP=CH^tBu): \delta_{1H} = 8.66,\)
\(^2J_{PH} = 24.6\) Hz; \(E^-PhP=CH^tBu): \delta_{1H} = 9.01, \(^2J_{PH} = 25.2\) Hz; \(E^-AdP=CH^tBu): \delta_{1H} = 8.65,\)
\(^2J_{PH} = 24.9\) Hz; \(E^-MesP=CH^tBu): \delta_{1H} = 8.43, \(^2J_{PH} = 25.3\) Hz; \(E^-CyP=CH^tBu): \delta_{1H} = 8.64,\)
\(^2J_{PH} = 24.8\) Hz).\(^{107,112,113,114}\)

Scheme 3.14 Synthetic route to 3.14 by the Lewis acid-mediated phospha-Peterson reaction.

Figure 3.17 \(^{31}P\) NMR spectra (DCM, 162 MHz, 298 K) of an aliquot removed from the reaction mixture of the synthesis of 3.14 by the Lewis acid-mediated phospha-Peterson reaction.
Figure 3.18 $^1$H NMR spectra (CDCl$_3$, 162 MHz, 298 K) of an aliquot removed from the crude product mixture of the synthesis of 3.14 by the Lewis acid-mediated phospha-Peterson reaction.

However, phosphaalkene 3.14 is not stable enough to isolate. Decomposition takes place soon after 3.14 is formed in solution (Figure 3.19). The small broad signals centered around -5 ppm and -20 ppm in the $^{31}$P NMR spectrum may indicate the formation of polymers since they are close to the chemical shifts of PMPs 1.8' and 2.6, the signals of which both center around -10 ppm in the $^{31}$P NMR spectra. Further characterizations like GPC analysis and mass spectroscopy are needed to confirm the formulation of these “polymers”.
Figure 3.19  $^{31}$P NMR spectra (DCM, 162 MHz, 298 K) of an aliquot removed from the reaction mixture of the synthesis of 3.14 by the Lewis acid-mediated phospha-Peterson reaction over time.

3.3 Summary

Phosphaalkene 3.1 was synthesized through the phospha-Peterson reaction and detected by NMR spectroscopy in situ. Its dimer 3.2 was isolated and the structure of 3.2 was confirmed by single-crystal X-ray crystallography. It was discovered that 3.2 is 1,2-diphosphetane with a “P-P-C-C” four-membered ring structure, which was in contrast to the 1,3-diphosphetane with a “P-C-P-C” four-membered ring structure proposed in the literature. Monomeric phosphaalkene 3.1 and its dimer 3.2 could form equilibrium in solution. The equilibrium constants ($K$) were measured at various temperatures. The $\Delta H^\circ$ and $\Delta S^\circ$ values were determined to be $-94.6 \pm$...
14.6 kJ mol\(^{-1}\) and -284 ± 48 J mol\(^{-1}\) K\(^{-1}\) respectively, from the lnK vs 1/T plot. In order to isolate 3.1, tungsten-phosphaalkene complexes were synthesized by treating 3.2 with W(CO)\(_5\)(MeCN). Both monosubstituted (3.5) and disubstituted tungsten complexes (3.6) were formed. The structure of 3.6 was determined by single-crystal X-ray crystallography, which showed that the two phosphaalkene ligands adopt cis- geometry to each other. The existence of W(CO)\(_4\)(MeCN)\(_2\) and the four-membered dimer ring structure of 3.2 both accounted for the formation of the disubstituted tungsten complex 3.6. Attempted synthesis of phosphaalkene 3.9 and its coordination to W(CO)\(_5\)(MeCN) were conducted as well. It was discovered that phosphaalkene 3.9 could be synthesized by the phospha-Peterson reaction and that it also tended to dimerize upon formation. Phosphaalkene 3.14 was synthesized by Lewis-acid mediated phospha-Peterson reaction and the formation of both Z + E isomers were detected by NMR spectroscopy in situ, although 3.14 was not stable enough for isolation and had the tendency to polymerize upon standing.

3.4 Experimental section

**Materials and general procedures.** All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. \(^1\)H, \(^{31}\)P and \(^{13}\)C\({}^\{\text{1H}\}\) NMR spectra were recorded at room temperature otherwise specified on Bruker Avance 300 MHz or 400 MHz spectrometer. Chemical shifts are reported relative to: residual CHCl\(_3\) (\(\delta = 7.26\) for \(^1\)H); 85% H\(_3\)PO\(_4\) as an external standard (\(\delta = 0.0\) for \(^{31}\)P);
CDCl$_3$ ($\delta = 77.0$ for $^{13}$C$\{^1$H$\}$). Mass Spectra were acquired using Kratos MS 50 instrument in EI mode (70 eV). Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Hexanes, diethyl ether and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated basic alumina.$^{96}$ THF was freshly distilled from sodium/benzophenone ketyl before use. Benzophenone (Aldrich) was sublimed prior to use. KOH was recrystallized from EtOH and heated in vacuo following a modified literature procedure for the purification of sodium hydroxide.$^{97}$ Benzaldehyde was purified following literature procedures.$^{97}$ MeLi (1.6 M in diethyl ether and trimethylsilyl chloride were purchased from Aldrich and used as received. AlCl$_3$ was sublimed before use. Methanol was degassed prior to use. PhP(SiMe$_3$)$_2$ and $\alpha$-TolP(SiMe$_3$)$_2$ were prepared following literature procedures.$^{84}$

**Preparation of PhP=CPh$_2$ (3.1) and (PhP=CPh$_2$)$_2$ (3.2).** Phospha-Peterson reaction was used for the preparation of 3.1.$^{84}$ To a stirred solution of PhP(SiMe$_3$)$_2$ (1.96 g, 7.72 mmol) dissolved in THF (10 mL) was added MeLi in Et$_2$O (4.8 mL, 1.6 M, 7.7 mmol). An immediate color change of the solution from colorless to yellow was observed. The reaction mixture was heated to 55°C for 1.5 h. Subsequently, the reaction mixture was cooled to -78°C and a solution of benzophenone (1.44 g, 7.91 mmol) in THF (6 mL) was added. Upon addition of benzophenone, the yellow solution turned to dark red. After stirring for 30 min, the reaction mixture was warmed up to room temperature while being stirred for an additional 30 min. Trimethylsilyl chloride (1.5 mL, 12 mmol) was added to the reaction mixture after cooling to
-78 °C. After stirring for 30 min, the solution was warmed up to room temperature while being stirred for an additional 30 min. The color of the solution turned from dark red to yellow. The volatiles were removed *in vacuo* leaving a yellow oil. To the oil was added hexanes (3 × 20 mL) and the suspension was filtered and the solvent was removed *in vacuo* leaving a yellow oil. To the yellow oil was added dry hexanes (3 × 20 mL). The suspension was filtered and a yellow solution was obtained. An aliquot was removed from the solution for $^{31}$P NMR spectroscopy. It was shown that a mixture of 3.1, 3.2 and 3.3 was in the solution. White solids formed upon standing for more than 15 h. The white solids were filtered, washed with hexanes (3 × 5 mL), and dried *in vacuo*. White crystals suitable for single-crystal X-ray crystallography were obtained by recrystallization from hexanes. The single-crystal X-ray crystallography confirms the white solid product was 3.2. Yield: 0.651 g (30.8 %).

When 3.2 was dissolved in THF solution, a colorless solution was formed. After 3 h, the color of the solution turned from colorless to yellow. An aliquot was removed from the solution for $^{31}$P NMR spectroscopy. It was shown that part of 3.2 dissociated to form 3.1 in solution.

$^{31}$P NMR (162 MHz, CDCl$_3$): δ 232.5 (s, 3.1), 4.8 (s, 3.2); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.17-6.60 (m, aryl H); $^{13}$C{$_^1$H} NMR(100 MHz, CDCl$_3$): δ 195.0 (d, $^1$J$_{PC}$ = 41.8 Hz, P=C, 3.1), 145.2 (t, $J$ = 13.2 Hz, aryl C), 142.7 (s, aryl C), 137.6 (t, $J$ = 10.7 Hz, aryl C), 133.4 (d, $J$ = 13.8 Hz, aryl C), 132.2 (d, $J$ = 13.8 Hz, aryl C), 132.0 (s, aryl C), 131.5 (s, aryl C), 131.0 (t, $J$ = 15.3 Hz, aryl C), 130.2 (d, $J$ = 7.7 Hz, aryl C), 129.5 (s, aryl C), 128.7 (s, aryl C), 128.5 (s, aryl C), 128.1 (s, aryl C), 128.0 (s, aryl C), 127.6 (s, aryl C), 127.5 (s, aryl C), 127.2 (s, aryl C),
126.3 (s, aryl C), 126.1 (s, aryl C), 124.7 (s, aryl C), 68.7 (s, -P-P-C-, 3.2); MS (low res EI) : 
\[m/z\] 548 [M⁺] (3.2); Anal. Calcd. for C₃₈H₃₀P₂ (3.2): C, 83.20; H, 5.51. Found: C,83.29; H,5.55.

**Preparation of W(CO)₄(PhP=CHPh)₂ (3.6).** To a stirred solution of 3.2 (0.230 g, 0.420 mmol) dissolved in DCM (2 mL) was added W(CO)⁵(MeCN) (0.308 g, 0.843 mmol). An immediate color change of the solution from colorless to dark brown was observed. The reaction was monitored by \(^{31}\text{P}\{^{1}\text{H}\} \text{NMR spectroscopy} until it reached completion after 3 d. The solvent was removed in vacuo leaving a dark red solid. To the solid was added diethyl ether (2 mL). Dark red crystals formed after being stored in the freezer for 5 d. The crystals were filtered and washed with hexanes (3 × 0.5 mL). The volatiles were removed and the dark red crystals were dried in vacuo. Yield: 0.205 g (29.0%).

\(^{31}\text{P}\) NMR (162 MHz, CDCl₃): \(\delta\) 197.2 (s, \(J_{PW} = 265.7\) Hz); \(^{1}\text{H}\) NMR (400 MHz, CDCl₃): \(\delta\) 7.45-6.78 (m, 30H, aryl H); \(^{13}\text{C}\{^{1}\text{H}\} \text{NMR}(100 MHz, CDCl₃): \(\delta\) 203.2 (t, \(J_{PC} = 10.7\) Hz, CO), 198.3 (t, \(J_{PC} = 9.2\) Hz, CO), 182.7 (q, \(J_{PC} = 26.4\) Hz, \(J_{PC} = 18.4\) Hz, P=C), 144.0 (t, \(J = 14.0\) Hz), 143.6 (t, \(J = 12.0\) Hz), 140.9 (t, \(J = 20.0\) Hz), 133.7 (s, aryl C), 130.7 (s, aryl C), 130.3 (t, \(J = 6.0\) Hz, aryl C), 129.6 (s, aryl C), 128.6 (s, aryl C), 128.4 (s, aryl C), 128.0 (s, aryl C), 127.7 (s, aryl C), 127.4 (s, aryl C); MS (low res EI) : \[m/z\] 844 [M⁺]; Anal. Calcd. for C₄₂H₃₀P₂O₄W: C, 59.72; H, 3.55. Found: C,58.98; H,3.58. The deviation between the calculated and observed elemental analysis results is caused by the traces of W(CO)⁵(MeCN) present in 3.6, despite three times of recrystallization was performed. The presence of W(CO)⁵(MeCN) was detected by \(^{1}\text{H}\) NMR spectroscopy.
Preparation of \( o\text{-TolP=CPh}_2(3.9) \). Phospha-Peterson reaction was used for the preparation of 3.9.\(^8\) To a stirred solution of \( o\text{-TolP(SiMe}_3)_2 \) (3.07 g, 11.5 mmol) dissolved in THF (30 mL) was added MeLi in Et\(_2\)O (7.2 mL, 1.6 M, 12 mmol). An immediate color change of the solution from colorless to yellow was observed. The reaction mixture was heated to 55 °C for 1.5 h. Subsequently, the reaction mixture was cooled to -78 °C and a solution of benzophenone (2.17 g, 11.9 mmol) in THF (10 mL) was added. Upon addition of benzophenone, the yellow solution turned to dark red. After stirring for 30 min, the reaction mixture was warmed up to room temperature while being stirred for an additional 30 min. Trimethylsilyl chloride (1.5 mL, 12 mmol) was added to the reaction mixture after cooling to -78 °C. After stirring for 30 min, the solution was warmed up to room temperature while being stirred for an additional 30 min. The color of the solution turned from dark red to yellow. The volatiles were removed \( \text{in vacuo} \) leaving a yellow oil. To the oil was added hexanes (3 × 20 mL) and the suspension was filtered and the solvent was removed \( \text{in vacuo} \) leaving a yellow oil. The \( ^{31}\text{P} \) NMR spectrum of the product mixture showed that the product was a mixture of 3.9, 3.10 and 3.11.

\(^{31}\text{P} \) NMR (162 MHz, CDCl\(_3\)): \( \delta \) 233.8 (s, 3.9), -13.7 (s, 3.10), -117.2 (s, 3.11); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.26-6.74 (m, aryl H), 2.52 (s, \( o\text{-CH}_3 \)), 2.51 (s, \( o\text{-CH}_3 \)), 2.39 (s, \( o\text{-CH}_3 \)); \(^{13}\text{C}(^1\text{H}) \) NMR(100 MHz, CDCl\(_3\)): \( \delta \) 194.9 (d, \( ^1J_{PC} = 42.3 \) Hz, P=C, 3.9); 144.5 (d, \( J = 24.5 \) Hz, aryl C), 142.9 (s, aryl C), 140.7 (d, \( J = 23.0 \) Hz, aryl C), 133.2 (d, \( J = 6.1 \) Hz, aryl C), 132.3 (s, aryl C), 131.2 (s, aryl C), 130.0 (s, aryl C), 129.5 (s, aryl C),
129.0 (d, $J = 4.6$ Hz, aryl C), 128.6 (s, aryl C), 128.2 (s, aryl C), 127.5 (s, aryl C), 127.3 (d, $J = 6.0$ Hz, aryl C), 127.1 (s, aryl C), 126.0 (s, aryl C), 125.7 (d, $J = 13.8$ Hz, aryl C), 125.2 (d, $J = 3.1$ Hz, aryl C), 124.7 (s, aryl C), 67.5 (s, $OCH_3$); MS (low res EI): $m/z$ 288 [M$^+$] (3.9); $m/z$ 410 [M$^+$] (3.11).

Preparation of 3.12 and 3.13: The crude product mixture of 3.9, 3.10 and 3.11 was synthesized by phospha-Peterson reaction as described above. To a stirred solution of the mixture of 3.9, 3.10 and 3.11 dissolved in DCM (3 mL) was added a small amount of W(CO)$_5$(MeCN). An immediate color change of the solution from yellow to dark brown was observed. The reaction was monitored by $^{31}$P{${^1}$H} NMR spectroscopy with continuous addition of W(CO)$_5$(MeCN) in small portions until it reached completion. The $^{31}$P NMR spectrum of the crude product showed that the product was a mixture of 3.12 and 3.13.

$^{31}$P NMR (162 MHz, DCM): $\delta$ 192.4 (s, $^{1}J_{PW} = 263.9$ Hz, 3.13), 185.4 (s, $^{1}J_{PW} = 268.5$ Hz, 3.12); MS (low res EI): $m/z$ 872 [M$^+$] (3.13), 612 [M$^+$] (3.12).

Preparation of MesP=C(H)Ph (3.14). To a suspension of AlCl$_3$ (0.563 g, 4.22 mmol) in DCM (5 mL) was added a mixture of MesP(SiMe$_3$)$_2$ (1.25 g, 4.22 mmol) and benzaldehyde (0.448 g, 4.23 mmol) in DCM (5 mL). The light pink solution turned to yellow after being stirred for 1 min. The mixture was stirred for 40 min and an aliquot of the reaction mixture was removed for $^{31}$P NMR spectroscopy. The $^{31}$P NMR spectrum showed that the signal assigned to MesP(SiMe$_3$)$_2$ was all consumed. The volatiles were removed in vacuo, leaving a yellow residue. An aliquot of the product mixture was removed for NMR spectroscopy.
$^{31}$P NMR (162 MHz, DCM): $\delta$ 247.1 (d, $^2J_{PH} = 25.2$ Hz, E-isomer), 231.5 (d, $^2J_{PH} = 35.2$ Hz, Z-isomer); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.08 (d, $^2J_{PH} = 25.2$ Hz, P=C(H)Ph), 7.67-7.15 (m, aryl H), 6.96 (s, Mes), 2.41 (s, o-CH$_3$), 2.34 (s, p-CH$_3$); $^{13}$C{^1}H NMR (100 MHz, CDCl$_3$): $\delta$ 184.5 (d, $^1J_{PC} = 35.3$ Hz, P=C(H)Ph), 140.3 (s, aryl C), 140.3 (s, aryl C), 138.5 (s, aryl C), 137.9 (s, aryl C), 128.9 (s, aryl C), 128.8 (s, aryl C), 128.7 (s, aryl C), 128.6 (s, aryl C), 126.5 (s, aryl C), 125.9 (s, aryl C), 125.7 (s, aryl C), 23.0 (s, o-CH$_3$), 22.9 (s, o-CH$_3$), 21.1 (s, p-CH$_3$).

Measurement of $K$ of Equation 3.1. All the experiments are conducted under the identical way at different temperatures. In a typical experiment, i) 150 mg dimer 3.2 was dissolved in 6.0 mL THF in an inert atmosphere and an aliquot was transferred to an NMR tube; ii) the solution in the NMR tube was heated at 298.6 K overnight to ensure the complete formation of the equilibrium; iii) $^{31}$P NMR spectra of the mixture solution were collected at 298.6 K for at least 3 times to confirm the complete formation of the equilibrium. The delay time ($d_1$) was set to 15s to permit reliable integration of $^{31}$P NMR spectra. In each spectrum, signals assigned to phosphaalkene 3.1 ($\delta_{31P} = 231.9$ ppm) and the dimer 3.2 ($\delta_{31P} = 4.1$ ppm) were integrated respectively with ranges between 250 ppm and 210 ppm, and between 25 ppm and -15 ppm. Each experiment was conducted at least twice to ensure the reproducibility of the $K$ values obtained.

X-ray crystallography. Crystal data and refinement parameters are listed in Table 3.2. All single crystals were immersed in oil and mounted on a glass fiber. All measurements were
made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using the multi-scan technique (SADABS) and corrected for Lorentz and polarization effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but not refined. All refinements were performed using the SHELXL-2013 crystallographic software package from Bruker AXS.
Table 3.2 X-ray crystallographic data of 3.2 and 3.6.

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<th>Crystal</th>
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<td>3512.2(2)</td>
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<td>Final R indexes [all data]^a</td>
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<td>Largest diff. peak/hole (e Å^{-3})</td>
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<td>1.59/-0.75</td>
</tr>
</tbody>
</table>

^a R_1 = \sum ||F_o|| - ||F_c|| / \sum ||F_o||, wR_2 = \{\sum[w(F_{o}^2 - F_{c}^2)^2] / \sum[w(F_{o}^2)] \}^{1/2}
Chapter 4 Facile Synthesis of “Masked Phosphaalkenes”

4.1 Introduction

As discussed in previous chapters, the smaller the substituents are, the more difficult it is to isolate phosphaalkenes in large scales with sufficient purity to make them suitable for polymerization studies. Therefore, it will be of great help if alternative synthetic pathways to PMPs, which do not require isolated monomeric phosphaalkenes as starting materials, can be developed. In the synthesis of polysilanes, one novel route starts with 7,8-disilabicyclo[2.2.2]octa-2,5-dienes (“masked disilenes”, 4.1, 4.2, and 4.3). These “masked disilenes” can be synthesized by treating radical anion of anthracene, naphthalene, or biphenyl with 1,1,2,2-tetramethyl-1,2-dichlorodisilane (Scheme 4.1).\(^{115}\)

![Scheme 4.1](image)

Scheme 4.1 Synthetic route to 7,8-disilabicyclo[2.2.2]octa-2,5-dienes.\(^{115}\)
These “masked disilenes” can release tetramethyldisilene upon heating. Due to the high reactivity of the Si=Si bond, the formation of tetramethyldisilene was proved by chemical trapping with dienes via a Diels-Alder reaction (Scheme 4.2). In the absence of suitable dienes, the pyrolysis of “masked disilenes” afforded a white oil, which was proposed to be “a polymer resulting from the polymerization of rearranged tetramethyldisilene”\textsuperscript{115}. Motivated by the potential of making silicon-containing polymers from “masked disilenes”, scientists finally discovered polysilanes could be obtained by anionic polymerization of 4.3 (Scheme 4.3).\textsuperscript{116,117}

![Scheme 4.2](image)

**Scheme 4.2** Chemical trapping of tetramethylsilene by the Diels-Alder reaction.\textsuperscript{115}

![Scheme 4.3](image)

**Scheme 4.3** Synthetic route to polysilanes by addition polymerization of 4.3.\textsuperscript{116}

Similar compounds 2-phosphabicyclo[2.2.2]octa-5,7-dienes (“masked phosphaalkenes”, 4.4 and 4.5 shown in Figure 4.1) and dibenzo-7\(\lambda^3\)-phosphanorbornadienes (4.6 shown in Figure 4.1) have also been reported in the literature.\textsuperscript{118,119} “Masked phosphaalkenes” were synthesized...
by Pete and his co-workers in the 1980s. These “masked phosphaalkenes” are not very stable and 4.5 requires preservation at low temperatures. It was reported that they could extrude MeP=CH$_2$ and PhP=CH$_2$ by thermolysis (Scheme 4.4). However, little work has been followed up since these “masked phosphaalkenes” were introduced. Probably it results from the difficult and time-consuming ten-step synthetic route (Scheme 4.5), which presents a barrier for other researchers to further study these compounds.

![Chemical structures](image)

**Figure 4.1** Examples of compounds with similar structures to “masked disilenes”.

![Scheme 4.4](image)

**Scheme 4.4** Generation of MeP=CH$_2$ and PhP=CH$_2$ by the thermolysis of 4.4 and 4.5.
Although research done on the synthesis and chemistry of “masked phosphaalkenes” is very limited, their capability of generating phosphaalkenes suggests the possibility of synthesizing PMPs via anionic polymerization of these “masked phosphaalkenes” in a similar way to the synthesis of polysilanes (Scheme 4.6). In order to study the anionic polymerization of “masked phosphaalkenes”, a facile synthetic pathway is required.

**Scheme 4.5** Synthetic route to 4.5.

**Scheme 4.6** Proposed synthetic route to PMPs by addition polymerization of “masked phosphaalkenes”.
In contrast to the tedious synthesis of “masked phosphaalkenes”, a facile synthetic pathway to dibenzo-7\(\lambda^3\)-phosphanorbornadienes has been developed by Cummins and co-workers.\(^\text{119}\) Direct reaction between Mg\(\text{A} \cdot 3\text{THF} (\text{A} = \text{anthracene})\) and dichlorophosphines leads to the formation of unprotected dibenzo-7\(\lambda^3\)-phosphanorbornadienes with about 20 % to 30 % yield (Scheme 4.7). Similar to “masked phosphaalkenes”, which are not stable at high temperatures and extrude phosphaalkenes,\(^\text{118}\) dibenzo-7\(\lambda^3\)-phosphanorbornadienes also decompose upon heating, although it gives rise to anthracene and highly reactive phosphinidene species other than phosphaalkenes.

\[
\text{MgA} \cdot 3\text{THF} + \text{RPCl}_2 \rightarrow 4.6
\]

\(\text{A}: \text{anthracene}, \text{R}: \text{tBu}, (\text{Me}_3\text{Si})_2\text{N}, \text{Pr}_2\text{N}\)

**Scheme 4.7** Facile synthesis of 4.6 by direct reaction of Mg\(\text{A} \cdot 3\text{THF} (\text{A} = \text{anthracene})\) and dichlorophosphines.\(^\text{119}\)

This facile synthetic pathway provides the motivation of synthesizing “masked phosphaalkenes” from the reaction of Mg\(\text{A} \cdot 3\text{THF}\) and (chloromethyl)arylphosphinyl chloride, although there may be drawbacks like low yields and the difficult isolation of products from the crude product mixture in this method. In this chapter, preliminary research on the facile synthesis of “masked phosphaalkenes” starting from PCl\(_3\) is described. Results of mass spectroscopy and NMR spectroscopy are shown to support the formation of dibenzo-7-mestily-7-phospha-bicyclo[2.2.2]octa-2,5-diene (4.13).
4.2 Results and discussion

4.2.1 Synthesis of dichloro(chloromethyl)phosphine (4.9)

The proposed synthetic route to “masked phosphaalkenes” is shown in Scheme 4.8. Precedent research on the preparation of dichloro(chloromethyl)phosphine (4.9) was conducted by Patrick Werz.\textsuperscript{120} In a typical reaction, (chloromethyl)phosphonic dichloride (4.7) is prepared following modified literature procedures by treating PCl₃ with AlCl₃ (1.0 equiv) and CH₂Cl₂ (1.0 equiv).\textsuperscript{121,122} Compound 4.7 is then converted to (chloromethyl)phenyl-phosphonothioic dichloride (4.8) by being refluxed with P₄S₁₀ at 175 °C for 6 h. Purification of 4.8 is accomplished by distillation. By being refluxed with PhPCl₂ at 175 °C for 6 h, compound 4.8 is reduced to dichloro(chloromethyl)phosphine (4.9). Careful distillation at atmospheric pressure under N₂ is required to purify the product. Since 4.7, 4.8, and 4.9 are all known compounds, their collected NMR data (Figure 4.2) is compared to the reported NMR data in the literature. The collected NMR data is in agreement with the NMR data reported, so the formation of 4.7, 4.8, and 4.9 has been confirmed.\textsuperscript{121,123,124}

Scheme 4.8 Proposed synthetic route to “masked phosphaalkenes” (4.13).\textsuperscript{120}
4.2.2 Synthesis of (chloromethyl)mesitylphosphinyl chloride/bromide (4.10a/b)

Compound 4.9 in THF solution is treated with freshly made Grignard reagent MesMgBr (1.0 equiv) (Scheme 4.9). The $^{31}$P<sup>1</sup>H NMR spectrum of an aliquot removed from the reaction mixture shows that the signal assigned to 4.9 is almost quantitatively replaced by a new signal ($\delta_{31P} = 73.3$) (Figure 4.3). The chemical shift of this new signal ($\delta_{31P} = 73.3$) is similar to the chemical shifts of dialkylchlorophosphines, diarylchlorophosphines or alkylarylchlorophosphines reported in the literature (Me<sub>2</sub>PCl: $\delta_{31P} = 92$, Ph<sub>2</sub>PCl: $\delta_{31P} = 82$, PhMePCI: $\delta_{31P} = 84$)<sup>125,126,127</sup> so it may be assigned to (chloromethyl)mesitylphosphinyl chloride (4.10a).
Scheme 4.9  Synthetic route to 4.10a.

Figure 4.3  $^{31}$P{$^1$H} NMR spectra (THF, 122 MHz, 298 K) of a) 4.9; b) an aliquot removed from the reaction mixture of Scheme 4.9 after MesMgBr (1.0 equiv) is slowly added in small portions.

The solvent THF is removed in vacuo, leaving a yellow oil. The yellow oil is extracted with hexanes and filtered. Interestingly, another signal ($\delta_{31p} = 58.0$) is detected by $^{31}$P{$^1$H} NMR spectroscopy (Figure 4.4a). After addition of PCl$_3$ to the mixture, only the signal ($\delta_{31p} = 218.7$) assigned to PCl$_3$ and the signal ($\delta_{31p} = 73.1$) assigned to 4.10a are observed (Figure 4.4b). Therefore, the new signal ($\delta_{31p} = 58.0$) is assigned to 4.10b, which may be formed by the
halogen exchange between chlorine and bromine in the reaction mixture.

Figure 4.4 $^{31}$P($^1$H) NMR spectra (hexanes, 122 MHz, 298 K) of an aliquot removed from a) the crude product mixture of Scheme 4.9 after removal of THF and extraction into hexanes; b) the reaction mixture after PCl$_3$ is added.

However, 4.10b is formed again with a reduced amount after all the volatiles are removed in vacuo. A mixture of 93 % 4.10a and 7 % 4.10b (Figure 4.5) is obtained after five rounds of addition and removal of PCl$_3$ in the product mixture.
These products are further characterized by $^1$H NMR spectroscopy. In general, four different types of protons are detected, which are assigned to the protons of $p$-CH$_3$ group, $o$-CH$_3$ group, methylene group and the aryl ring, respectively (Figure 4.6). Four types of carbons are also detected in the $^{13}$C\{$^1$H\} NMR spectrum and they are assigned to $p$-CH$_3$ carbon, $o$-CH$_3$ carbon, methylene carbon and aryl carbon, respectively (Figure 4.7). The integration of the $^1$H NMR spectrum shows that there are two protons attached to the methylene carbon, further supporting the formulation of the product as 4.10a/b. Interestingly, the two protons of –CH$_2$– are diastereotopic. Therefore, the chemical environments of these two protons are slightly different. These two protons are coupled to each other, resulting in two doublets detected in the $^1$H\{$^{31}$P\} NMR spectrum (Figure 4.6). The coupling constant ($^2$J$_{HH}$) is -12 Hz, which is consistent with the proton-proton geminal coupling constants.$^{128,129}$ These two protons are also coupled to the phosphorus, so two doublets of doublets are present in the $^1$H NMR spectrum ($^2$J$_{PH}$ = 8.3 Hz, 13.3 Hz), although the signals with $\delta_{1H}$ around 4.25 overlap with each other.

Figure 4.5  $^{31}$P NMR spectrum (CDCl$_3$, 162 MHz, 298 K) of the 4.10a and 4.10b mixture.
Figure 4.6 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of the 4.10a and 4.10b mixture.

Figure 4.7 $^{13}$C($^1$H) NMR spectrum (CDCl$_3$, 100 MHz, 298 K) of the 4.10a and 4.10b mixture.
4.2.3  **Synthesis of benzylmesitylphenylphosphine (4.12)**

In order to study the reactivity of the two different chloro groups on 4.10a, the 4.10a and 4.10b mixture in THF solution is treated with PhMgBr (2.0 equiv) (Scheme 4.10). The reaction is monitored by $^{31}$P NMR spectroscopy (Figure 4.8). It is shown that the signals ($\delta_{31P} = 73.3, 57.0$) assigned to 4.10a and 4.10b are quantitatively replaced by a new signal ($\delta_{31P} = -16.7$) after PhMgBr (1.0 equiv) is added to the solution. The chemical shift of the new signal is similar to the chemical shifts of tertiary phosphines reported in the literature (PMe$_3$: $\delta_{31P} = -62$, MePh$_2$P: $\delta_{31P} = -28$, PPh$_3$: $\delta_{31P} = -6$). Consequently, the new signal is assigned to (chloromethyl)mesitylphenylphosphine (4.11) based on both the stoichiometry of the reactants and the chemical shift of the signal observed in the $^{31}$P{$^1$H} NMR spectrum.

$$
\text{Mes} \quad \text{Cl} \quad \text{P} \quad \text{Cl} \quad \text{PhMgBr} \quad \text{Cl} \quad \text{P} \quad \text{Mes} \quad \text{PhMgBr} \quad \text{Ph} \quad \text{P} \quad \text{Mes}
$$

**Scheme 4.10**  Synthetic route to 4.12.
Figure 4.8  $^{31}$P\text{\text{\texttt{H}}} NMR spectra (THF, 122 MHz, 298 K) of an aliquot removed from the reaction mixture after PhMgBr is added to the 4.10a and 4.10b mixture in small portions.

No immediate change in the $^{31}$P\text{\texttt{H}} NMR spectrum is observed after the addition of a second equiv of PhMgBr to the reaction mixture, indicating the chloro group on the phosphorus is much more reactive than the chloro group on the carbon. A new signal ($\delta_{31P} = -18.8$) is detected after the reaction mixture is stirred for 3 h at room temperature. This new product dominates the product mixture after the reaction time is extended to 15 h (Figure 4.9b). The final product is purified by precipitation from absolute ethanol and dried \textit{in vacuo}. This product is proposed to be benzylmesitylphenylphosphine (4.12) based on the stoichiometry of the reactants.
Figure 4.9 $^{31}$P{H} NMR spectra (THF, 122 MHz, 298 K) of an aliquot removed from the reaction mixture of Scheme 4.10 after PhMgBr (2.0 equiv) is added and being stirred for a) 3 h; b) 15 h.

Benzylmesitylphenylphosphine is a known compound and has been synthesized by the reaction of the mesitylphenyl phosphide anion ($\text{Li}^+\text{PMesPh}^-$) and benzyl chloride.\textsuperscript{131} The NMR data of the isolated product (Figure 4.10 and 4.11) is in agreement with the NMR data of benzylmesitylphenylphosphine reported in the literature. A signal at 318 $m/z$, which is assigned to the fragment of $M^+$ of 4.12, is observed in the mass spectrum. Therefore, the formulation of the product as benzylmesitylphenylphosphine is supported.
Figure 4.10 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of 4.12.

Figure 4.11 $^{31}$P{$^1$H} NMR spectrum (CDCl$_3$, 162 MHz, 298 K) of 4.12.

4.2.4 Preliminary study on the facile synthesis of “masked phosphaalkenes” (4.13)

The formation of 4.12 proves the feasibility of the reaction of organomagnesium reagents and (chloromethyl)phosphinyl chloride (4.10a). Attempts are made towards the synthesis of dibenzo-7-mesityl-7-phosphabicyclo[2.2.2]octa-2,5-diene by direct reaction of MgA•3THF and 4.10a/b. To the mixture of 4.10a and 4.10b in THF solution cooled to -78 °C is added MgA•3THF in small portions (Scheme 4.11). The light yellow solution turns orange immediately
upon the addition of \( \text{MgA} \cdot 3\text{THF} \), and subsequently it turns colorless when the reaction mixture is warmed up to room temperature. The reaction is monitored by \(^{31}\text{P}\) NMR spectroscopy. After around 1 h, almost all the 4.10a and 4.10b are consumed. After removal of THF, the white residue is dissolved in diethyl ether and filtered. The products obtained are extracted into \( n \)-pentane and stored in the freezer. Many different types of phosphorus are detected by \(^{31}\text{P}\{^1\text{H}\} \) NMR spectroscopy (Figure 4.12), suggesting a mixture of different phosphorus containing products is obtained.

**Scheme 4.11** Synthetic route to 4.13.

**Figure 4.12** \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum (\( \text{C}_6\text{D}_6 \), 162 MHz, 298 K) of an aliquot removed from the crude product mixture of Scheme 4.11.
Due to the overlapping of $^1$H NMR signals from various products in the mixture, the formation of 4.13 is mainly proved by $^1$H-$^{31}$P HMBC spectroscopy and mass spectroscopy. The results of $^1$H-$^{31}$P HMBC spectroscopy analysis of the product mixture is shown in Figure 4.13. Correlations between the phosphorus signal at $\delta_{^{31}P} = -25.2$ and the proton signals at $\delta_{^1H} = 1.66, 2.19, 2.61, 2.72, 4.00, 4.15, 6.82, 6.91$ and $7.00$ are observed. Correlations between proton signals at $\delta_{^1H} = 4.15, 2.19, 1.66$ are also observed in the $^1$H-$^1$H COSY NMR spectrum of the product mixture (Figure 4.14).

![Figure 4.13](image)

**Figure 4.13**  $^1$H-$^{31}$P HMBC spectrum ($C_6D_6$, 400 MHz for $^1$H, 298 K) of an aliquot removed from the crude product mixture of Scheme 4.11.
Figure 4.14 \(^1\text{H}-^1\text{H}\) COSY spectrum (C\(_6\)D\(_6\), 400 MHz, 298 K) of an aliquot removed from the crude product mixture of Scheme 4.11.

Selected \(^1\text{H}\) NMR data of 4.5, 4.13 and 4.14 are shown in Table 4.1.\(^{118,119}\) Chemical shifts of protons in 4.13 are similar to the chemical shifts of protons in 4.5 and 4.14 reported in the literature.\(^{118,119}\) Furthermore, the chemical shift of the phosphorus (\(\delta_{^31\text{P}} = -25.2\)) is close to the chemical shift of the phosphorus in 4.5 (\(\delta_{^31\text{P}} = -29.0\)).\(^{118}\) Both the \(^1\text{H}\) and \(^{31}\text{P}\) NMR data are consistent with the desired formulation of the product as 4.13.
Table 4.1  Selected NMR data of 4.5, 4.13 and 4.14.

<table>
<thead>
<tr>
<th>Chemical Shifts (ppm)</th>
<th>Proton</th>
<th>Compound</th>
<th>4.5</th>
<th>4.13</th>
<th>4.14</th>
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<tr>
<td>a</td>
<td>4.35</td>
<td>4.00</td>
<td>3.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>2.12</td>
<td>2.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>1.60</td>
<td>1.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>4.10</td>
<td>4.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aryl-H</td>
<td>6.82, 6.91, 7.00</td>
<td>6.74-6.77, 6.92-6.97, 7.16-7.21</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference 118 This thesis 119

However, it is noteworthy that the chemical shift of the protons of the \( p \)-CH\(_3\) group should also be around 2.2 ppm, thus, the NMR data alone is not informative enough. The product mixture is further characterized by mass spectroscopy. Because of the sensitivity of the products towards air and heat, mass spectroscopy is run immediately on the sample taken out of the freezer in the glovebox. A signal at 342 \( m/z \) is observed (Figure 4.15), which is assigned to the fragment of \( M^+ \) of 4.13. Importantly, the isotope distribution observed (342 : 343 : 344 = 1 : 0.267 : 0.043) is close to the calculated isotope distribution (342 : 343 : 344 = 1 : 0.263 : 0.033). Therefore, the formation of 4.13 is supported.
4.3 Summary

In conclusion, a novel synthetic pathway to “masked phosphaalkenes” is developed. The “masked phosphaalkene” 4.13 can be synthesized by direct reaction of organomagnesium reagents and (chloromethyl)mesitylphosphinyl chloride (4.12), which is more facile than the tedious route reported in the literature. The formation of 4.13 is preliminarily supported by NMR spectroscopy and mass spectroscopy, although studies on the purification of the product and the optimization of reaction conditions are needed in the future.

4.4 Experimental section

Materials and general procedures. All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. $^1$H, $^{13}$C{$^1$H} and $^{31}$P NMR spectra were recorded at room temperature on Bruker
Avance 300 MHz spectrometer or Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to: residual CHCl₃ (δ = 7.26 for ¹H), C₆D₅H (δ = 7.16 for ¹H); 85% H₃PO₄ as an external standard (δ = 0.0 for ³¹P); CDCl₃ (δ = 77.0 for ¹³C{¹H}). Mass Spectra were acquired using Kratos MS 50 instrument in EI mode (70 eV). Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Hexanes was deoxygenated with nitrogen and dried by passing through a column containing activated alumina, and n-pentane was dried by CaH₂ and distilled before use. THF was freshly distilled from sodium/benzophenone ketyl before use. Ethanol was degassed before use. Phosphorus trichloride (Aldrich), aluminum chloride (Acros Organics), phosphorus pentasulfide (Acros Organics), dichlorophenylphosphine (Aldrich), magnesium (Fisher Science Education), and 2-bromomesitylene (Alfa Aesar) were used as received. MgA•3THF (A = anthracene) was prepared following literature procedures.

Preparation of (chloromethyl)phosphonic dichloride (4.7). Dichloromethane (37.2 g, 0.438 mol, 28.0 mL) and phosphorus trichloride (58.8 g, 0.428 mol, 37.0 mL) were added to aluminum chloride (58.10 g, 0.4352 mol) in a 1 liter Schlenk flask under N₂. The reaction mixture was heated to reflux at 90 °C for 3 d until it turned to a clear colorless solution. The reaction mixture was cooled to room temperature before another 450 mL dichloromethane was added and the solution was then cooled in a water-ice bath to stay around 0 °C. Degassed water (87.1 mL, 4.84 mol) was then added in portions of 1 mL with vigorous stirring to avoid the generation of too much heat at once. White solids were formed with the addition of water, which
were supposed to be aluminum salts. The HCl generated was absorbed by NaOH solution. After the addition of water, the solution was filtered and all the volatiles were removed in vacuo. The light yellow residue was distilled at 75 °C under partial pressure (water pump) to give colorless liquid (chloromethyl)phosphonic dichloride. Yield: 18.95 g (26.0 %).

\[ ^{31}P \text{ NMR (162 MHz, CDCl}_3\] : δ 38.8 (s); \[ ^{1}H \text{ NMR (400 MHz, CDCl}_3\] : δ 4.15 (d, \[ ^{2}J_{PH} = 7.9 \text{ Hz, 2H, -CH}_2\] ); \[ ^{13}C \text{ NMR (100 MHz, CDCl}_3\] : δ 45.3 (d, \[ ^{1}J_{PC} = 116.5 \text{ Hz, -CH}_2\] ).

**Preparation of (chloromethyl)phosphonothioic dichloride (4.8).** Compound 4.7 (39.57 g, 0.2362 mol) was added to phosphorus pentasulfide (12.68 g, 0.02849 mol) under N₂. The reaction mixture was heated to reflux at 175 °C under N₂. The reaction mixture turned from yellow to black upon heating. The reaction mixture was cooled down to room temperature after being refluxed for 6 h and distilled at 70 °C under partial pressure (water pump) to give colorless liquid (chloromethyl)phosphonothioic dichloride. Yield: 24.37 g (56.23 %).

\[ ^{31}P \text{ NMR (162 MHz, CDCl}_3\] : δ 74.6 (s); \[ ^{1}H \text{ NMR (400 MHz, CDCl}_3\] : δ 4.28 (d, \[ ^{2}J_{PH} = 3.0 \text{ Hz, 2H, -CH}_2\] ); \[ ^{13}C \text{ NMR (100 MHz, CDCl}_3\] : δ 52.0 (d, \[ ^{1}J_{PC} = 87.4 \text{ Hz, -CH}_2\] ).

**Preparation of dichloro(chloromethyl)phosphine (4.9).** Dichlorophenylphosphine (29.02 g, 16.21 mmol) was added to 4.8 (25.18 g, 13.68 mol) under N₂. The reaction mixture was heated at 175 °C under nitrogen for 6 h. The reaction mixture stayed colorless during reflux. After cooled down to room temperature, the reaction mixture was distilled first under partial pressure (water pump) at 55 °C and then carefully distilled under atmospheric pressure (170 °C) to give colorless liquid dichloro(chloromethyl)phosphine.
Yield: 8.87 g (43.1 %).

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 157.9 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.07 (d, $^2$J$_{PH}$ = 16.0 Hz, 2H, -CH$_2$-); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 48.9 (d, $^1$J$_{PC}$ = 53.7 Hz, -CH$_2$-).

**Preparation of (chloromethyl)mesitylphosphinyl chloride/bromide (4.10a/b).** To a stirred suspension of magnesium (0.39 g, 16 mmol) in THF (40 mL) was slowly added 2-bromomestiylene (2.96 g, 14.9 mmol). The reaction mixture was refluxed at 70 °C for 2 h. This freshly made Grignard reagent was added dropwise to the solution of 4.9 (3.498 g, 23.11 mmol) in THF (20 mL) cooled to -78 °C. Transparent solution slowly turned to yellow. The solvent was removed *in vacuo*, leaving a pale yellow oil. To the oil was added dry hexanes (30 + 20 +20 mL) and the suspension was filtered and the solvent was removed *in vacuo*. The product was dissolved in 20 mL THF. Phosphorus trichloride was added to the light yellow solution in excess. The solution was stirred for 2 h and the volatiles were removed *in vacuo*. After five rounds of phosphorus trichloride addition and removal, a mixture of 93 % 4.10a and 7 % 4.10b was obtained. Yield: 2.210 g (40.2 %).

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 73.0 (s, 4.10a), 57.8 (s, 4.10b); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.94 (s, 2H, aryl H), 4.32 (dd, $^2$J$_{HH}$ = -12.0 Hz, $^2$J$_{PH}$ = 8.3 Hz, 1H, -CH$_2$-), 4.25 (dd, $^2$J$_{HH}$ = -11.5 Hz, $^2$J$_{PH}$ = 13.3 Hz, 1H, -CH$_2$-), 2.67 (d, $J_{PH}$ = 2.54 Hz, 6H, o-CH$_3$), 2.31 (s, 3H, p-CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.8 (s, aryl C), 144.6 (s, aryl C), 142.3 (s, aryl C), 130.6 (s, aryl C), 130.5 (s, aryl C), 127.0 (s, aryl C), 126.5 (s, aryl C), 42.4 (d, $^1$J$_{PC}$ = 41.4 Hz, -CH$_2$-), 22.4 (d, $J_{PC}$ = 21.5 Hz, o-CH$_3$), 21.1 (s, p-CH$_3$); MS (low res EI) : m/z 236,
Preparation of benzylmesitylphenylphosphine (4.12). To a stirred suspension of magnesium (0.09 g, 4 mmol) in THF (10 mL) was slowly added bromobenzene (0.30 g, 1.9 mmol). The reaction mixture was refluxed at 70 °C for 2 h. This freshly made Grignard reagent was added dropwise to the mixture of 4.10a and 4.10b (0.202 g, 0.786 mmol) dissolved in THF (5 mL) cooled to -78 °C. The reaction was monitored by $^{31}$P NMR spectroscopy. Light yellow solution slowly turned to colorless after stirring for 15 h. The solvent was removed in vacuo, leaving a white residue. To the residue was added degassed ethanol (5 mL) and the suspension was filtered. The white powder obtained was dried in vacuo. Yield: 0.087 g (35 %).

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ -19.9 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.27-7.19 (m, 10H, aryl H), 6.85 (s, 2H, Mes), 3.65 (dd, $^2J_{HH}$ = -13.3 Hz, $^2J_{PH}$ = 3.1 Hz, 1H, -CH$_2$-), 3.52 (dd, $^2J_{HH}$ = -13.4 Hz, $^2J_{PH}$ = 3.4 Hz, 1H, -CH$_2$-), 2.28 (s, 3H, p-CH$_3$), 2.22 (s, 6H, o-CH$_3$);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.4 (s, aryl C), 141.7 (d, $J$ = 16.9 Hz, aryl C), 138.4 (d, $J$ = 10.8 Hz, aryl C), 129.7 (s, aryl C), 129.6 (s, aryl C), 129.3 (s, aryl C), 129.2 (s, aryl C), 129.1 (s, aryl C), 128.3 (s, aryl C), 128.2 (s, aryl C), 126.5 (s, aryl C), 125.8 (s, aryl C), 32.9 (d, $^1J_{PC}$ = 18.4 Hz, -CH$_2$-), 23.3 (s, o-CH$_3$), 23.2 (s, o-CH$_3$), 21.0 (s, p-CH$_3$); MS (low res EI): m/z 318 [M$^+$].

Preparation of dibenzo-7-mesityl-7-phosphabicyclo[2.2.2]octa-2,5-diene (4.13). To a stirred mixture of 4.10a and 4.10b (0.401 g, 1.68 mmol) dissolved in THF (20 mL) cooled to
-78 °C was slowly added MgA•3THF (0.710 g, 1.68 mmol) in small portions. The light yellow solution turned orange immediately upon addition of MgA•3THF, and subsequently it turned colorless when the reaction mixture was warmed up to room temperature. The reaction was monitored by $^{31}$P NMR spectroscopy. After almost all the 4.10a and 4.10b were consumed, the solvent was removed in vacuo. To the white residue was added dry diethyl ether (50 + 50 mL) and the suspension was filtered and all the volatiles were removed in vacuo. To the white residue was added dry n-pentane and the suspension was filtered. The filtered solution was stored in the freezer of the glovebox. The product mixture was characterized by mass spectroscopy and NMR spectroscopy.

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ -25.2 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.00 (aryl H), 6.91 (aryl H), 6.82 (Mes H), 4.15 (bridge CH), 4.00 (P-CH), 2.72 ($o$-CH$_3$), 2.61 ($o$-CH$_3$), 2.19 (P-CH$_2$-$p$-CH$_3$), 1.66 (P-CH$_2$-$p$-CH$_3$), all the assignments are made by $^1$H-$^{31}$P HMBC data shown in Figure 4.14 and Table 4.1; MS (low res EI): $m/z$ 342 [M$^+$].
Chapter 5  Overall Conclusions and Future Work

5.1  Summary of thesis work

Since 2003, many achievements have been made by the Gates Group in addition polymerization of phosphaalkenes by both radical initiation and anionic initiation, especially the discovery of an alternative microstructure for PMPs (Scheme 5.1). The C-H bond on the o-CH$_3$ group of the mesityl group is activated during the polymerization, so the PMPs obtained does not contain alternating “P-C-P-C” bonds in the main chain. However this investigation was only done on the radical initiated polymerization of MesP=CPh$_2$ (1.7). The main contributions of this thesis are the further study on the C-H activation of the o-CH$_3$ group in anionic polymerization of a similar phosphaalkene XylP=CPh$_2$ (2.5), the preparation of phosphaalkenes bearing substituents smaller than Mes or Ph groups, and the facile synthesis of “masked phosphaalkenes” for the generation of new PMPs by anionic polymerization.

![Scheme 5.1](image-url)  

Scheme 5.1  Addition polymerization of 1.7.
In Chapter 2, phosphaalkene XylP=CPh \(_2\) (2.5) has been successfully prepared by phospha-Peterson reaction and polymerized by anionic polymerization with \(\text{^nBuLi}\) as the initiator (Scheme 5.2). The microstructure of polymer 2.6 was characterized by NMR spectroscopy. It has been shown that C-H activation of the \(o\)-CH\(_3\) also takes place during the anionic polymerization of 2.5. Molecular model of this anionic polymerization was made by treating 2.5 with Ph\(_3\)CCl (Scheme 5.3). The molecular structure of 2.9 confirms the C-H activation on the \(o\)-CH\(_3\) group. The kinetic studies on the anionic polymerization of 2.5 shows larger observant rates constant (\(k_p\)) than those of the polymerization of 1.7. Similar to the polymerization of 1.7, the propagation process speeds up at low temperatures, which is in contrast to the propagation process of olefins polymerization. A mechanism that may account for this rate constant increase has been proposed (Scheme 5.4), but more investigations are needed to model the polymerization accurately.

\[
\begin{align*}
\text{Xyl} & \quad \quad \text{Ph} \\
\text{P=CHPh}_2 & \quad \quad \text{Ph} \\
\text{Xyl} & \quad \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{2.5} & \quad \quad \text{2.6}
\end{align*}
\]

Scheme 5.2 Anionic polymerization of 2.5.

\[
\begin{align*}
\text{Me} & \quad \quad \text{P=CHPh}_2 \\
\text{Ph} & \quad \quad \text{Me} \\
\text{Ph} & \quad \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \quad \text{P=CHPh}_2 \\
\text{Ph} & \quad \quad \text{Me} \\
\text{Ph} & \quad \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{2.5} & \quad \quad \text{2.9}
\end{align*}
\]

Scheme 5.3 Synthetic route to the molecular model of the anionic polymerization of 2.5.
Work done on the synthesis and chemistry of PhP=CPh$_2$ (3.1), $o$-TolP=CPh$_2$ (3.9), and MesP=C(H)Ph (3.14) is described in Chapter 3. The results obtained demonstrated that 3.1 had the tendency to dimerize upon formation and the single-crystal X-ray crystallography showed the dimer formed (3.2) was 1,2-diphosphetane, not 1,3-diphosphetane proposed in the literature. Monomeric phosphaalkene 3.1 and the dimer 3.2 could form equilibrium in solution (Equation 5.1). The $\Delta H^0$ and $\Delta S^0$ values of the forward reaction of Equation 5.1 were determined to be $-94.6 \pm 14.6$ kJ mol$^{-1}$ and $-284 \pm 48$ J mol$^{-1}$ K$^{-1}$ respectively, from the ln$K$ vs $1/T$ plot. The monomeric phosphaalkene 3.1 was isolated by coordination to tungsten complexes, generating cis-W(CO)$_4$(PhP=CPh$_2$)$_2$ (3.6) (Scheme 5.5). Attempts were also made on the synthesis of 3.9 and 3.14. Their formation was detected by NMR spectroscopy. The NMR results
also showed that 3.9 had the tendency to dimerize upon formation, and phosphaalkene 3.14 had the tendency to polymerize upon standing.

\[
\begin{align*}
2 \text{Ph-P=CP=CPh} & \rightleftharpoons \text{Ph-P=PPh} \text{Ph-P=PPh} \\
\text{3.1} & \quad \text{3.2} \quad \text{(Equation 5.1)}
\end{align*}
\]

Scheme 5.5 Isolation of 3.1 by coordination to tungsten complex.

Chapter 4 outlines a facile synthetic route to dibenzophosphabicyclooctadienes (“masked phosphaalkenes”) starting from PCl₃ (Scheme 5.6). Further investigation is needed for the purification of the product and the reaction condition optimization, but the formation of 4.13 was preliminarily supported by NMR spectroscopy and mass spectroscopy. The facile synthesis of “masked phosphaalkenes” will contribute to future studies on phosphaalkenes bearing small substituents and pave the road to a novel method of making phosphorus-containing polymers by anionic polymerization (Scheme 5.7).
Scheme 5.6  Synthetic route to 4.13 from PCl₃.

Scheme 5.7  Proposed synthetic route to PMPs by the anionic polymerization of 4.13.

5.2 Future work

One of the long term purposes behind this project is to obtain new PMPs with alternating “P-C-P-C” bonds in the main chain by anionic polymerization. In order to achieve this goal, ground work on the synthesis of phosphaalkenenes bearing substituents smaller than Mes or Ph has been presented in this thesis. Their potentials to oligomerize or polymerize upon formation have also been illustrated. Preliminary research on the facile synthesis of “masked phosphaalkenenes” has also been conducted to develop a novel synthetic route to new PMPs by anionic polymerization.
The first short term future work for this project involves the isolation of phosphaalkenes bearing smaller substituents. One possible direction is to coordinate compounds 3.1, 3.2, 3.9, and 3.10 to a wider range of metals. Potential results will offer not only better chances to isolate these phosphaalkenes, but also more insight into their coordination chemistry. Besides coordination, it is also worthwhile to synthesize 3.1 and 3.9 by base-catalyzed and Lewis acid-mediated phospha-Peterson reactions at lower temperatures to prevent the formation of by-products such as 3.2, 3.3, 3.10, and 3.11.

The other short term goal is the reaction condition optimization of the preparation of “masked phosphaalkenes”. Factors including temperatures, solvents and ratios of the starting materials can be optimized to afford better yield of 4.13. Continuous crystallization may serve as a way to isolate 4.13 from by-products, especially from anthracene. Furthermore, another potential route (Scheme 5.8) mimicking the synthesis of “masked disilenes” (Scheme 5.9) also has the potential to afford 4.13.115

![Scheme 5.8](image)

**Scheme 5.8** Possible synthetic route to 4.13.

![Scheme 5.9](image)

**Scheme 5.9** Synthetic route to 4.1.115
After the fulfillment of short-term purposes, the ultimate goal can be achieved by the polymerization of the isolated phosphaalkenes or “masked phosphaalkenes” with the proper choice of initiators under suitable conditions. The PMPs obtained will be good materials for further microstructure studies. Importantly, “masked phosphaalkenes” are not limited to compound 4.13. A library of “masked phosphaalkenes” bearing different substituents (5.1-5.5 shown in Figure 5.1) are worthy of synthesis over a longer term. A set of modifications on phosphorus, carbon and bicyclo-ring could allow the study of the effects of sterics on the chemistry and stability of “masked phosphaalkenes”. New PMPs bearing different substituents can also be generated from these “masked phosphaalkenes”.

![Image of phosphaalkenes](image)

**Figure 5.1** Examples of “masked phosphaalkenes” bearing different substituents.

### 5.3 Closing remarks

Studies on the microstructure of PMPs bearing Xyl group on phosphorus were conducted. It was shown that the C-H bond on the o-CH₃ group of Xyl group was activated during the anionic polymerization of XylP=CPh₂. Investigations on the synthesis of phosphaalkenes bearing
substituents smaller than Mes or Ph showed these unsaturated inorganic molecules had the tendency to oligomerize or polymerize upon formation. A facile synthesis route to “masked phosphaalkenes” was designed. This thesis lays the foundation towards the synthesis of new PMPs by anionic polymerization. New materials made from these polymers will have novel applications in various areas. The journey with phosphorus-containing polymers is just at the beginning.
References


35 Kuran, W. *Principles of Coordination Polymerization*; John Wiley & Sons Ltd: West Sussex, 2001; Chapter 1.


Appendices

Appendix A  The determination of the $dn/dc$ of 2.6

Figure A.1  Graph of differential refractive index vs. concentration of 2.6 in THF (measured on Wyatt Optilab T-rEx refractive index detector). The slope of the best fit line is used to calculate the $dn/dc$. 
Appendix B  Monomer conversion data collected for the polymerization of 2.5

Table B.1  Monomer conversion data collected for the polymerization of 2.5 using 2 mol % \textsuperscript{a}BuLi as initiator at 298.6 K.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>Conversion percentage</th>
<th>$[M]^{a}$ (mol L$^{-1}$)</th>
<th>ln([M$_0$]/[M])</th>
</tr>
</thead>
<tbody>
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<td>0.0663</td>
<td>0.3567</td>
<td>0.0686</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1218</td>
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<td>0.1734</td>
<td>0.7899</td>
</tr>
<tr>
<td>3.5</td>
<td>0.5918</td>
<td>0.1559</td>
<td>0.8960</td>
</tr>
<tr>
<td>3.75</td>
<td>0.6102</td>
<td>0.1489</td>
<td>0.9421</td>
</tr>
<tr>
<td>4</td>
<td>0.6342</td>
<td>0.1397</td>
<td>1.0057</td>
</tr>
<tr>
<td>4.25</td>
<td>0.6678</td>
<td>0.1269</td>
<td>1.1020</td>
</tr>
<tr>
<td>4.5</td>
<td>0.6821</td>
<td>0.1214</td>
<td>1.1460</td>
</tr>
<tr>
<td>4.75</td>
<td>0.7159</td>
<td>0.1085</td>
<td>1.2584</td>
</tr>
<tr>
<td>5</td>
<td>0.7354</td>
<td>0.1011</td>
<td>1.3259</td>
</tr>
<tr>
<td>5.25</td>
<td>0.7637</td>
<td>0.0903</td>
<td>1.4427</td>
</tr>
<tr>
<td>5.5</td>
<td>0.7764</td>
<td>0.0854</td>
<td>1.4979</td>
</tr>
<tr>
<td>5.75</td>
<td>0.8091</td>
<td>0.0729</td>
<td>1.6560</td>
</tr>
<tr>
<td>6</td>
<td>0.8259</td>
<td>0.0665</td>
<td>1.7481</td>
</tr>
<tr>
<td>6.25</td>
<td>0.8540</td>
<td>0.0558</td>
<td>1.9241</td>
</tr>
<tr>
<td>6.5</td>
<td>0.8742</td>
<td>0.0481</td>
<td>2.0731</td>
</tr>
<tr>
<td>6.75</td>
<td>0.8939</td>
<td>0.0405</td>
<td>2.2434</td>
</tr>
<tr>
<td>7</td>
<td>0.9087</td>
<td>0.0349</td>
<td>2.3936</td>
</tr>
</tbody>
</table>

$^{a}$ $[M]$ = concentration of 2.5, $[M_0]$ = 0.382 mol L$^{-1}$. 
Table B.2 Monomer conversion data collected for the polymerization of 2.5 using 2 mol % "BuLi as initiator at 301.0 K.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>Conversion percentage</th>
<th>[M]$^a$ (mol L$^{-1}$)</th>
<th>ln([M$_0$]/[M])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.0709</td>
<td>0.3735</td>
<td>0.0735</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1528</td>
<td>0.3406</td>
<td>0.1658</td>
</tr>
<tr>
<td>0.75</td>
<td>0.1898</td>
<td>0.3257</td>
<td>0.2105</td>
</tr>
<tr>
<td>1</td>
<td>0.2615</td>
<td>0.2969</td>
<td>0.3031</td>
</tr>
<tr>
<td>1.25</td>
<td>0.3033</td>
<td>0.2801</td>
<td>0.3614</td>
</tr>
<tr>
<td>1.5</td>
<td>0.3540</td>
<td>0.2597</td>
<td>0.4370</td>
</tr>
<tr>
<td>1.75</td>
<td>0.4065</td>
<td>0.2386</td>
<td>0.5217</td>
</tr>
<tr>
<td>2</td>
<td>0.4512</td>
<td>0.2206</td>
<td>0.6000</td>
</tr>
<tr>
<td>2.25</td>
<td>0.5116</td>
<td>0.1963</td>
<td>0.7166</td>
</tr>
<tr>
<td>2.5</td>
<td>0.5440</td>
<td>0.1833</td>
<td>0.7853</td>
</tr>
<tr>
<td>2.75</td>
<td>0.5888</td>
<td>0.1653</td>
<td>0.8887</td>
</tr>
<tr>
<td>3</td>
<td>0.6419</td>
<td>0.1440</td>
<td>1.0269</td>
</tr>
<tr>
<td>3.25</td>
<td>0.6808</td>
<td>0.1283</td>
<td>1.1419</td>
</tr>
<tr>
<td>3.5</td>
<td>0.7219</td>
<td>0.1118</td>
<td>1.2798</td>
</tr>
<tr>
<td>3.75</td>
<td>0.7638</td>
<td>0.0950</td>
<td>1.4431</td>
</tr>
<tr>
<td>4</td>
<td>0.7971</td>
<td>0.0816</td>
<td>1.5950</td>
</tr>
<tr>
<td>4.25</td>
<td>0.8363</td>
<td>0.0658</td>
<td>1.8097</td>
</tr>
<tr>
<td>4.5</td>
<td>0.8508</td>
<td>0.0600</td>
<td>1.9025</td>
</tr>
<tr>
<td>4.75</td>
<td>0.8818</td>
<td>0.0475</td>
<td>2.1354</td>
</tr>
<tr>
<td>5</td>
<td>0.8950</td>
<td>0.0422</td>
<td>2.2538</td>
</tr>
<tr>
<td>5.25</td>
<td>0.9133</td>
<td>0.0349</td>
<td>2.4453</td>
</tr>
<tr>
<td>5.5</td>
<td>0.9408</td>
<td>0.0238</td>
<td>2.8268</td>
</tr>
</tbody>
</table>

$^a$ [M] = concentration of 2.5, [M$_0$] = 0.402 mol L$^{-1}$. 
Table B.3  Monomer conversion data collected for the polymerization of 2.5 using 2 mol % "BuLi as initiator at 306.2 K.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>Conversion percentage</th>
<th>[M]$^a$ (mol L$^{-1}$)</th>
<th>ln([M$_0$]/[M])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.0987</td>
<td>0.3623</td>
<td>0.1039</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1965</td>
<td>0.3230</td>
<td>0.2188</td>
</tr>
<tr>
<td>0.75</td>
<td>0.2689</td>
<td>0.2939</td>
<td>0.3132</td>
</tr>
<tr>
<td>1</td>
<td>0.3522</td>
<td>0.2604</td>
<td>0.4342</td>
</tr>
<tr>
<td>1.25</td>
<td>0.4384</td>
<td>0.2258</td>
<td>0.5770</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5048</td>
<td>0.1991</td>
<td>0.7028</td>
</tr>
<tr>
<td>1.75</td>
<td>0.5833</td>
<td>0.1675</td>
<td>0.8754</td>
</tr>
<tr>
<td>2</td>
<td>0.6390</td>
<td>0.1451</td>
<td>1.0189</td>
</tr>
<tr>
<td>2.25</td>
<td>0.7068</td>
<td>0.1179</td>
<td>1.2269</td>
</tr>
<tr>
<td>2.5</td>
<td>0.7500</td>
<td>0.1005</td>
<td>1.3863</td>
</tr>
<tr>
<td>2.75</td>
<td>0.7985</td>
<td>0.0810</td>
<td>1.6020</td>
</tr>
<tr>
<td>3</td>
<td>0.8304</td>
<td>0.0682</td>
<td>1.7743</td>
</tr>
<tr>
<td>3.25</td>
<td>0.8614</td>
<td>0.0557</td>
<td>1.9762</td>
</tr>
<tr>
<td>3.5</td>
<td>0.8829</td>
<td>0.0471</td>
<td>2.1447</td>
</tr>
<tr>
<td>3.75</td>
<td>0.8986</td>
<td>0.0408</td>
<td>2.2887</td>
</tr>
<tr>
<td>4</td>
<td>0.9079</td>
<td>0.0370</td>
<td>2.3849</td>
</tr>
</tbody>
</table>

$^a$ [M] = concentration of 2.5, [M$_0$] = 0.402 mol L$^{-1}$. 
Table B.4  Monomer conversion data collected for the polymerization of 2.5 using 2 mol % "BuLi as initiator at 311.3 K.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>Conversion percentage</th>
<th>$[\text{M}]^a$ (mol L$^{-1}$)</th>
<th>$\ln([\text{M}]_0/\text{[M]})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.1525</td>
<td>0.3568</td>
<td>0.1655</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2885</td>
<td>0.2995</td>
<td>0.3404</td>
</tr>
<tr>
<td>0.75</td>
<td>0.4294</td>
<td>0.2402</td>
<td>0.5611</td>
</tr>
<tr>
<td>1</td>
<td>0.5506</td>
<td>0.1892</td>
<td>0.7998</td>
</tr>
<tr>
<td>1.25</td>
<td>0.6517</td>
<td>0.1466</td>
<td>1.0547</td>
</tr>
<tr>
<td>1.5</td>
<td>0.7324</td>
<td>0.1127</td>
<td>1.3183</td>
</tr>
<tr>
<td>1.75</td>
<td>0.7884</td>
<td>0.0891</td>
<td>1.5531</td>
</tr>
<tr>
<td>2</td>
<td>0.8327</td>
<td>0.0704</td>
<td>1.7880</td>
</tr>
<tr>
<td>2.25</td>
<td>0.8650</td>
<td>0.0568</td>
<td>2.0025</td>
</tr>
<tr>
<td>2.5</td>
<td>0.8841</td>
<td>0.0488</td>
<td>2.1550</td>
</tr>
<tr>
<td>2.75</td>
<td>0.8945</td>
<td>0.0444</td>
<td>2.2490</td>
</tr>
<tr>
<td>3</td>
<td>0.9056</td>
<td>0.0397</td>
<td>2.3602</td>
</tr>
<tr>
<td>3.25</td>
<td>0.9171</td>
<td>0.0349</td>
<td>2.4901</td>
</tr>
<tr>
<td>3.5</td>
<td>0.9190</td>
<td>0.0341</td>
<td>2.5133</td>
</tr>
</tbody>
</table>

$^a$ $[\text{M}] = \text{concentration of 2.5}, [\text{M}]_0 = 0.421 \text{ mol L}^{-1}$. 
Table B.5  Monomer conversion data collected for the polymerization of 2.5 using 2 mol % BuLi as initiator at 316.6 K.

<table>
<thead>
<tr>
<th>t (h)</th>
<th>Conversion percentage</th>
<th>[M]a (mol L⁻¹)</th>
<th>ln([M₀]/[M])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.1631</td>
<td>0.3423</td>
<td>0.1781</td>
</tr>
<tr>
<td>0.5</td>
<td>0.3732</td>
<td>0.2564</td>
<td>0.4671</td>
</tr>
<tr>
<td>0.75</td>
<td>0.5319</td>
<td>0.1915</td>
<td>0.7591</td>
</tr>
<tr>
<td>1</td>
<td>0.6514</td>
<td>0.1426</td>
<td>1.0538</td>
</tr>
<tr>
<td>1.25</td>
<td>0.7317</td>
<td>0.1097</td>
<td>1.3156</td>
</tr>
<tr>
<td>1.5</td>
<td>0.7727</td>
<td>0.0930</td>
<td>1.4815</td>
</tr>
<tr>
<td>1.75</td>
<td>0.8015</td>
<td>0.0812</td>
<td>1.6170</td>
</tr>
<tr>
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<td>1.7401</td>
</tr>
<tr>
<td>2.25</td>
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<td>1.9092</td>
</tr>
<tr>
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</tr>
<tr>
<td>2.75</td>
<td>0.8707</td>
<td>0.0529</td>
<td>2.0456</td>
</tr>
</tbody>
</table>

a [M] = concentration of 2.5, [M₀] = 0.409 mol L⁻¹.

Table B.6  Monomer conversion data collected for the polymerization of 2.5 using 2 mol % BuLi as initiator at 321.9 K.

<table>
<thead>
<tr>
<th>t (h)</th>
<th>Conversion percentage</th>
<th>[M]a (mol L⁻¹)</th>
<th>ln([M₀]/[M])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.1945</td>
<td>0.3665</td>
<td>0.2163</td>
</tr>
<tr>
<td>0.5</td>
<td>0.4148</td>
<td>0.3250</td>
<td>0.5358</td>
</tr>
<tr>
<td>0.75</td>
<td>0.5705</td>
<td>0.2945</td>
<td>0.8451</td>
</tr>
<tr>
<td>1</td>
<td>0.6408</td>
<td>0.2609</td>
<td>1.0239</td>
</tr>
<tr>
<td>1.25</td>
<td>0.6932</td>
<td>0.2234</td>
<td>1.1816</td>
</tr>
<tr>
<td>1.5</td>
<td>0.7369</td>
<td>0.1942</td>
<td>1.3352</td>
</tr>
<tr>
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<td>0.7714</td>
<td>0.1621</td>
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<td>0.1405</td>
<td>1.5498</td>
</tr>
</tbody>
</table>

a [M] = concentration of 2.5, [M₀] = 0.401 mol L⁻¹.
Appendix C  Monomer to dimer ratio data collected for $K$ measurement of Equation 3.1

Table C.1  Concentration of 3.1 to concentration of 3.2 ratio data collected for $K$ measurement of Equation 3.1.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$[D_0]^a$ (mol L$^{-1}$)</th>
<th>$[P] : [D]$ ratio at equilibrium$^b$</th>
<th>$K$</th>
<th>$\Delta G^o$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.6</td>
<td>0.0456</td>
<td>1.00 : 1.341</td>
<td>54.4</td>
<td>-9.93</td>
</tr>
<tr>
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<td>0.0515</td>
<td>1.000 : 1.484</td>
<td>57.2</td>
<td>-10.1</td>
</tr>
<tr>
<td>300.9</td>
<td>0.0472</td>
<td>1.000 : 1.125</td>
<td>38.8</td>
<td>-9.16</td>
</tr>
<tr>
<td>300.9</td>
<td>0.0459</td>
<td>1.000 : 1.061</td>
<td>36.1</td>
<td>-8.98</td>
</tr>
<tr>
<td>304.5</td>
<td>0.0368</td>
<td>1.000 : 0.704</td>
<td>23.0</td>
<td>-7.95</td>
</tr>
<tr>
<td>304.5</td>
<td>0.0377</td>
<td>1.000 : 0.744</td>
<td>24.5</td>
<td>-8.10</td>
</tr>
<tr>
<td>306.2</td>
<td>0.0368</td>
<td>1.000 : 0.635</td>
<td>19.6</td>
<td>-7.56</td>
</tr>
<tr>
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<td>0.0368</td>
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</tr>
<tr>
<td>311.3</td>
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<td>11.8</td>
<td>-6.39</td>
</tr>
<tr>
<td>311.3</td>
<td>0.0310</td>
<td>1.000 : 0.387</td>
<td>11.1</td>
<td>-6.21</td>
</tr>
</tbody>
</table>

$^a$ $[D_0]$ = original concentration of 3.2 in THF solution;

Appendix D  NMR spectra of 4.9

Figure D.1  $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of 4.9.

Figure D.2  $^{13}$C{$^1$H} NMR spectrum (CDCl$_3$, 100 MHz, 298 K) of 4.9.