LIVING ANIONIC POLYMERIZATION OF PHOSPHAALKENES. CONTROLLED ROUTES TO
HOMOPOLYMERS AND BLOCK COPOLYMERS WITH PHOSPHORUS ATOMS IN THE
POLYMER MAIN CHAIN

by

KEVIN JOSEPH TAAFFE NOONAN

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Abstract

In this thesis, the living anionic polymerization of the phosphaalkene MesP=CPh₂ is reported. The polymer backbone consists of alternating phosphorus and carbon atoms. Several experiments have been conducted to illustrate the living nature of P=C bond polymerization including: controlling the polymer chain length by varying the concentration of initiator, determining that molecular weight increases linearly with conversion and showing that the polymerization follows pseudo first order kinetics. Investigations into the mechanism of the n-butyllithium initiated MesP=CPh₂ polymerization allowed for the experimental determination of the activation energy of propagation for the growing polymer chain, $E_a = 14.0 \pm 0.9$ kcal mol⁻¹.

Several new block copolymer species have been prepared by sequential anionic polymerization including polystyrene-block-poly(methylene phosphine) and polyisoprene-block-poly(methylene phosphine). The polyisoprene-block-poly(methylene phosphine) was coordinated to AuCl and dissolved in n-heptane to prepare micellar Au(1) spherical and wormlike nanostructures visible by transmission electron microscopy.

Further evidence for the chemical functionality of the poly(methylene phosphine) species is reported in this thesis. Poly(methylene phosphine) was treated with several main group electrophiles to form a polymeric BH₃ coordination complex and a partially methylated phosphonium ionomer.

Finally, several P=C compounds bearing functional groups (i.e, C₁₀H₁₀Fe, 4-Cl-C₆H₄, 4-NEt₂-C₆H₄) on the carbon substituent have been synthesized. Several of these systems have been investigated as monomers for the anionic polymerization P=C bonds. Not all of the monomers polymerize by anionic methods and studies to better understand this behavior are underway.
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<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>A</td>
<td>preexponential factor</td>
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<td>sec-BuLi</td>
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<td>n-butyllithium or CH₃CH₂CH₂CH₂Li</td>
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<td>t-BuLi</td>
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<td>charge-coupled device</td>
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<td>CCDC</td>
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<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
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<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
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<td>THF</td>
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<td>Tf</td>
<td>triflate or $-$SO$_2$CF$_3$</td>
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<tr>
<td>Triple detection GPC</td>
<td>gel permeation chromatography equipped with light scattering instrument, viscometer and differential refractometer</td>
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<td>th</td>
<td>thiophene or C$_4$H$_4$S</td>
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δ  chemical shift in parts per million (ppm)
λ  wavelength (nm)
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Chapter 1

Applying Living Polymerization Techniques to Inorganic Polymers, a Route to Diversify Structure and Function of Macromolecules.

1.1 Introduction

The advent of synthetic polymer chemistry has been of paramount importance in shaping our modern world. Hermann Staudinger first proposed that macromolecules were not colloids but actually consisted of large numbers of covalently bonded atoms linked together in a long chain. This was a controversial topic, as researchers did not believe that molecules of such high molecular weights could exist. Some support for Staudinger's macromolecular theory was provided by Meyer and Mark who employed x-ray crystallographic analysis to elucidate the structures of several naturally occurring macromolecules: cellulose, chitin, and natural rubber. These discoveries, in conjunction with the pioneering work on polymerization by Carothers and co-workers, led to the general acceptance of the macromolecular theory. Staudinger was awarded the Nobel prize for his contribution to the field of polymer chemistry in 1953. Since the 1930's, both synthetic and naturally occurring polymeric materials have had a profound impact on our civilization and they are ever-present commodities in our society. Macromolecules are used in a variety of applications such as clothing, car tires, packaging, televisions, pharmaceuticals, medical devices and computers. In general, synthetic polymers are produced industrially for their mechanical properties, such as their tensile strength, flexibility, lightweight nature and photonic properties.

In contrast to synthetic polymers, naturally occurring macromolecules not only exhibit desirable mechanical properties but they also boast chemical functionality with the ability to mediate chemical processes. For example, deoxyribonucleic acid (DNA) is a polymer composed of only four nucleotide subunits (cytosine, guanine, adenine, and thymine). These
nucleotides can be arranged in a limitless number of combinations on a sugar phosphate backbone with the resultant DNA macromolecule being responsible for the transmission and storage of genetic information in the human body. Another example of functional biological polymers are proteins, which consist of covalently linked amino acids. Proteins are essential for the human body to function, for instance, actin and tubulin form strong fibers which are essential components for cytoskeleton mobility. The question remains whether humans can potentially synthesize polymers that can mimic the chemical complexity that biological polymers have already achieved. When we consider how biological polymers are prepared, it begins with two monomers being connected to form a dimer, the dimer is then combined with another monomer to form a trimer and this monomer incorporation will continue until high molecular weight polymer is reached. Impeccable control over both the chain length and polymer microstructure are observed during this process. When polymers are prepared synthetically, not all of the macromolecules have the same chain length; in fact, they generally consist of many polymer molecules of varying lengths.

1.2 Determination of Polymer Molecular Weights

The chain length of a polymer is directly related to its molecular weight. As the length of a polymer chain increases, more monomer units are being incorporated into the chain and, as a consequence, the molecular weight of the macromolecule increases. For example, a polystyrene chain which is 100 repeat units weighs approximately 10,406 g mol⁻¹ whereas a polystyrene chain with 200 repeat units has a molecular weight double that value (Figure 1.1). Throughout this thesis, the discussion of chain length and molecular weight will be, in many cases, used interchangeably.
Figure 1.1 Comparison of two polystyrene chains with different chain lengths. A doubling of the polymer chain length is consistent with a doubling in the polymer molecular weight.

Since all polymer samples are comprised of many macromolecules with varying chain lengths, the characterization of polymers must involve an average or statistical distribution. Conventional macromolecular science deals mainly with two statistical measurements,\textsuperscript{16} number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$). The $M_n$ term is simply a mean, the total weight of all the molecules divided by the total number of molecules in the sample (Equation 1.1). Weight-average molecular weight ($M_w$) however, is biased towards larger macromolecules since these contribute more to the overall weight of the sample (Equation 1.1).\textsuperscript{16} It is important to realize that high molecular weight macromolecules ($M_w$) are desired as this is a crucial characteristic of materials with useful physical properties.\textsuperscript{16} Finally, the distribution of molecular weights in a polymer sample is defined as the polydispersity index (PDI) and is equal to the weight-average molecular weight divided by the number-average molecular weight (PDI = $M_w/M_n$).\textsuperscript{16} Most biologically relevant macromolecules are monodisperse and have PDI's equal to one (PDI = 1), since all of the polymer molecules have the same chain length. Polymer samples prepared using synthetic protocols often possess broad molecular weight distributions with PDI's approximately equal to two (PDI ~ 2).\textsuperscript{16}

\[
M_n = \frac{\sum N_i \times M_i}{\sum N_i} \quad M_w = \frac{\sum N_i \times M_i^2}{\sum N_i \times M_i}
\]

Equation 1.1 Description of number average molecular weight $M_n$ and weight average molecular weight $M_w$. $N_i$ represents a polymer molecule and $M_i$ represents the molecular weight of that polymer molecule. Each equation is described as a sum of the polymer molecules that make up a sample.
Carothers was the first to classify synthetic polymers according to their mechanism of formation; he called the two synthetic routes addition and condensation polymerization. However, these definitions are no longer sufficient to appropriately describe all known polymerization processes with so many advances in macromolecular science since the 1930's. Currently, a polymerization is defined as either a step-growth or chain-growth process. Chain-growth polymerization requires a reactive species (radical, cationic or anionic initiator) that successfully adds many monomer molecules to itself (Scheme 1.1 Route A and B) forming a macromolecule (−[E−E]$_n$− where E = element). Chain-growth polymerization can proceed with either a vinylic monomer (addition polymerization) or a strained cyclic species (ROP – ring-opening polymerization). In contrast, step-growth polymerization is a process by which monomers come together and repeatedly eliminate a small molecule (XY) to form a macromolecule. Step-growth necessitates two species that possess different functional groups (Scheme 1.1 Route C). A self-condensation is also possible, where two different functional groups are present in one molecule and intermolecular elimination occurs forming the desired polymer (Scheme 1.1 Route D). The key difference between these polymerization mechanisms is that in a chain growth process, the intermediate formed during polymerization is much more reactive than the monomer and relatively high molecular weight polymers can be obtained even at low conversion. In step-growth processes, the intermediates formed are equally as reactive as the monomeric species and the size of the polymer chain grows relatively slowly with a high degree of conversion being necessary to achieve high molecular weight. For the purposes of this thesis, step polymerization techniques will not be discussed further.
Scheme 1.1  General polymerization routes to \([-\{E-E\}\text{- polymers (E = element). Chain-growth processes, require an initiator to polymerize either a multiple bond (A) or a strained cyclic species (B). Step growth polymerization involves loss of a small molecule XY to form the desired polymer (C and D).}

Addition polymerization of C=C bonds is an important synthetic route to industrially relevant polymers. The polymerization proceeds with an initiator (usually a radical, cationic or anionic species – denoted as \(R^*\)) adding across the double bond of an olefin (Scheme 1.2).\(^{16}\)

The propagation step involves the initiated species (\(RCH_2-CH_2^*\)) consuming many monomer units and forming a long chain until, a termination step destroys the active chain end (Scheme 1.2). The monomer depicted in Scheme 1.2 is ethylene; however, using other monomers such as \(CH_2=CH(\text{Ph})\) (styrene), \(CH_2=CH(\text{Cl})\) (vinyl chloride) or \(CH_2=CH(\text{Me})\) (propylene) can impart different and potentially useful properties to the synthesized polymer. As stated earlier, high molecular weight macromolecules are desired from these polymerization processes as this is a crucial characteristic of materials with useful properties.\(^{16}\)

Scheme 1.2  Polymerization of ethylene using a generic initiator \(R^*\).
The termination step depends completely on the type of initiator used to induce polymerization. When analyzing the synthesis of biological macromolecules such as proteins, one realizes that no unwanted termination step occurs! Upon achievement of the desired molecular weight for the macromolecule, the polymerization is terminated. Thus, is it possible to conduct synthetic polymerization without an unwanted termination step? Moreover, is this possible not only for organic C=C bond polymerizations but also for inorganic multiply bonded species?

1.2.1 Research objectives for this thesis

Recent work in the Gates group has focused on extending addition polymerization, an industrially important reaction for C=C bonds, to inorganic multiple bonds for the first time. In particular, the extension of addition polymerization to phosphaalkenes (MesP=CPh₂ where Mes = 2,4,6-trimethylphenyl) was a recent synthetic achievement to prepare poly(methylene phosphine)s which have a backbone of alternating phosphorus and carbon atoms. The three coordinate phosphine moiety has been exploited to form metal containing polymers, and the oxidation of the polymeric phosphine with H₂O₂ or S₈ to form P(V) polymers has also been reported. This thesis describes the application of living polymerization techniques to the MesP=CPh₂ phosphaalkene. Several block copolymers incorporating poly(methylene phosphine)s were prepared to illustrate how living polymerization can be used to prepare new macromolecules. Furthermore, several compounds containing P=C bonds were synthesized and polymerized to expand upon the generality of addition polymerization for phosphaalkenes. The next sections will outline the requirements of living polymerization and how they can lead to controlled architectures such as block copolymers. The upcoming sections will also detail why inorganic multiple bonds are interesting candidates for addition polymerization.
1.3 Living Polymerization – Characteristics and Challenges

Szwarc was the first to discover that the anionic polymerization of styrene initiated with sodium naphthalide can proceed without termination (Scheme 1.3).\textsuperscript{22,23} He described this behavior, as a "living" polymerization and this subject will be prevalent throughout the thesis. In Scheme 1.3, the polymer chain is equipped with a reactive species at the polymer chain end. This carbanion can be exploited to promote further chemistry and is the key feature of a living polymerization. This landmark discovery by Szwarc provided a unique avenue to more complex macromolecular architectures some of which are displayed in Figure 1.2.\textsuperscript{24} The reactive chain end can be replaced by a functional group, it can be used to initiate polymerization of a second monomer forming block copolymers (see Section 1.3.1) or multifunctional initiators can be employed to fabricate star polymers. These synthetic architectures illustrated in Figure 1.2 are not as complex as those observed with biological polymers but they are starting to further our advancement towards macromolecules with higher order structure and function. The following seven features are requirements of a living polymerization.\textsuperscript{24}

1. Over the course of the polymerization the monomer is completely consumed.
2. The molecular weight increases linearly with conversion.
3. The reaction follows pseudo-first order kinetics.
4. Once the polymerization is complete and the monomer is entirely consumed, the addition of more monomer to the reaction will result in a molecular weight increase for the polymer.
5. The synthesis of two covalently linked polymer chains should be possible.

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6. Control of the polymer chain length can be employed by varying the concentration of initiator.

7. Polydispersities should be very narrow (i.e., PDI = 1.00 - 1.10).

Scheme 1.3  Living polymerization of styrene upon combination with sodium naphthalide.

Figure 1.2  Schematic of accessible architectures using living polymerization techniques.²⁴
1.3.1 Block copolymers

This section will focus on the advantages and potential applications of block copolymers which are synthesized by sequential polymerization of two chemically different monomer units affording two polymer chains linked by a covalent bond (Figure 1.3). In contrast, random copolymers consist of a statistical mixture of two monomer units and polymer blends are physical mixtures of two homopolymers. Each of these different copolymers offer different physical properties but several unique physical features of block copolymers will be discussed briefly.

Block copolymers normally exhibit two separate glass transition temperatures ($T_g$) based on the two chemically linked polymer chains. Glass transition temperature is known as the temperature at which the onset of conformational mobility occurs in a polymer sample. AB block copolymers also exhibit microphase separation in the bulk when the A and B segments are incompatible. The degree of separation is limited by the covalent bond between them and this leads to block copolymers undergoing self-organization on the nanometer and micrometer scale.

If a block copolymer has two segments which exhibit different solubility properties and the polymer is dissolved in a solvent selective for only one block, organized structures such as micelles, rods and vesicles can be obtained. The most common form of solution separation behavior observed is the spherical micelle (Figure 1.4). The insoluble block forms the core of the spherical micelle and the soluble block forms the surrounding corona. However, depending on solubility conditions and the size of the block copolymers, a variety of organized structures may be observed. Applications for polymers that form ordered assemblies include: surfactants, drug-delivery systems, and nanoreactors. With these unique chemical properties, block copolymers offer a wide range of potential applications.

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copolymers have exploded into a major field of study and continue to attract a great deal of attention today.\textsuperscript{27-29}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{micelle.png}
\caption{Spherical micelles formed by solution self-assembly of AB block copolymers. Insoluble blocks form the core of the micelle and the soluble blocks form the corona on the periphery.}
\end{figure}

1.3.2 Different techniques employed to prepare polymers in a controlled or living fashion

The early advances in living polymerization were limited to anionic polymerizations of styrenic and butadiene type monomers.\textsuperscript{24} In the 1980's, research detailing living cationic polymerization strategies for monomers such as vinyl ethers and isobutylene appeared.\textsuperscript{30} In 1995, the first controlled radical polymerization as a route to access polyolefins was reported.\textsuperscript{31} Since more monomers will polymerize by radical methods as compared to cationic and anionic strategies, this stunning development has led to a wealth of new polymer chemistry, particularly in the area of block copolymers.\textsuperscript{32,33} This ability to access a wide variety of olefinic monomers such as methacrylates and acrylates has increased the potential to tune the properties of the resultant block copolymers and access unique macromolecules.

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Controlled radical polymerization involves a dormant species (R-X) such as an alkyl halide being activated by a metal complex (Figure 1.5).\textsuperscript{32, 33} The oxidized metal results in the formation of the desired radical species (R\(^{-}\)) which will consume monomer repeatedly until the equilibrium process results in reduction of the metal complex forming a dormant polymer chain. However, because this process is in equilibrium, the dormant polymer chain can reoxidize the metal and actively consume monomer once again. This process will continue until the monomer is quantitatively converted to polymer with fairly narrow polydispersities (\(\sim\)1.2).

\[
R-X + M^n \xrightarrow{k_{act}} R^* + X-M^{n+1}
\]

Monomer

\[
k_{deact}
\]

Termination

\[
k_t
\]

Figure 1.5 A simplified representation of controlled radical polymerization. \(R\) represents an alkyl group, \(X\) represents a halide, and \(M\) represents a metallic species.

When compared to conventional cationic, radical or anionic polymerization methodologies, coordination-insertion polymerization has always been the superior method to control the stereochemistry of synthetic polymers. Combining the excellent degree of stereochemical control of insertion polymerization with controlled molecular weights has become a growing field of interest.\textsuperscript{34, 35}

There are several reasons to research new living polymerization methodologies. There is the desire to control the structure and function of macromolecules such that the properties of new materials can be tailored. It is also of interest to prepare polymer systems that display chemical functionality and can mediate chemical processes. When preparing macromolecules in a controlled fashion, synthetic protocols have been limited to C=C bond polymerization, or ROP of strained cyclics (i.e., lactides, lactones).\textsuperscript{24} The preparation of inorganic polymers has attracted attention for synthesizing materials with unique features imparted by \(p\)-block or \(d\)-block elements.\textsuperscript{36-40} Moreover, the application of living techniques to inorganic monomers could allow for the preparation of more complex macromolecular architectures incorporating inorganic elements.

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1.4 Living Inorganic Polymers — Introducing Chemical Functionality In a Controlled Fashion

The development of controlled or living polymerization techniques for inorganic monomers remains in its infancy, but there have been several developments in this area which are outlined below. Some interesting structural features of the polymers will also be discussed.

Ring-opening polymerization of the cyclic compound, hexamethylcyclotrisiloxane (D₃ - 1.1) to form poly(dimethylsiloxane) was the first living polymerization of an inorganic molecule. Upon treatment of D₃ with an organolithium reagent such as sec-BuLi in a coordinating solvent (i.e., THF), controlled molecular weight poly(dimethylsiloxane) 1.2 was obtained with narrow polydispersity. The living polymerization must be carried out in coordinating solvents because in non-coordinating media two competing mechanistic pathways are observed: cyclic oligomer formation and acyclic polymer formation. The strongly coordinating ligand will complex the Li⁺ counterion during the polymerization process, impeding cyclic oligomer formation. Compounds such as THF and cryptands have been shown to effectively coordinate the Li⁺ counterion in living poly(dimethylsiloxane) preparation, these solvents effectively inhibit the cyclic oligomerization process.

Polysiloxanes, which consist of repeating Si–O linkages, are an extremely important class of inorganic polymer and have found a variety of commercial applications including oils, lubricants and synthetic skin. They have an exceptionally low T₆ (− 123 °C) and high thermooxidative stability making them incredibly versatile macromolecules.
Another inorganic system which was found to polymerize in a living fashion was the silicon-bridged [1]ferrocenophane 1.3. The poly(ferrocenylsilane) (1.4) is of considerable interest because of its fascinating magnetic, optical and electrochemical properties (Scheme 1.5). Treating a solution of [1]ferrocenophane 1.3 in THF with $^n$BuLi at room temperature affords poly(ferrocenylsilane)s with controlled molecular weights. Molecular weight control was confirmed by decreasing the initiator concentration ($^n$BuLi) which resulted in an increase of the polymer molecular weight ($M_n$). The living poly(ferrocenylsilane) species was also used to initiate $D_3$ polymerization yielding the desired poly(ferrocenylsilane)-block-poly(dimethylsiloxane). This remarkable achievement marked the first living polymerization of a macromolecule incorporating transition metal atoms in the polymer main chain. Recent developments involving monomer 1.3 include a photolytic living polymerization using weakly nucleophilic, functional group-tolerant initiators such as Na(C₅H₅). The living anionic polymerization of 1.3 has led to a variety of different block copolymers that have been investigated for their solution self assembly properties and for their bulk state organization capabilities.

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One recent highlight of poly(ferrocenylsilane) block copolymer studies was the solution self assembly of poly(ferrocenylsilane)-block-poly(dimethylsiloxane) and polyisoprene-block-poly(ferrocenylsilane) both of which formed "wormlike" cylindrical micelles upon slow evaporation from non-polar solvents. In both cases, the core of the micellar structures was the poly(ferrocenylsilane) block and the corona surrounding the core was either the poly(dimethylsiloxane) or the polyisoprene. This past year, the formation of spherical micelles upon oxidation of the ferrocenyl moiety in polystyrene-block-poly(ferrocenylsilane)s was reported. The Fe²⁺ centre of the poly(ferrocenylsilane) is oxidized using the one electron oxidant, tris(4-bromophenyl) ammoniumyl, which results in spherical micelles. The core is composed of the poly(ferrocenylsilane) block and the corona is composed of polystyrene; the authors attribute the self assembly behavior to an induced polarity change in the poly(ferrocenylsilane) block. This micelle formation can be reversed by one electron reduction of the Fe³⁺ using decamethylcobaltocene.

Two years after the discovery of living poly(ferrocenylsilane)s, a significant achievement in the development of phosphorus containing polymers was realized with the living anionic polymerization of a phosphorus-bridged [1]ferrocenophane (1.5) to form
poly(ferrocenylphosphine)s (1.6). This work was analogous to the polymerization chemistry of compound 1.3 and block copolymers containing poly(ferrocenylphosphine)s have been investigated in earnest. Remarkably, poly(ferrocenylphosphine) oligomerization was first reported in 1982 with oligomers up to five repeat units (1.6 where \( n=5 \)) being observed (mass spectrometry).

![Scheme 1.6](image)

**Scheme 1.6** Living anionic polymerization of phosphorus bridged [1]ferrocenophane at ambient temperature using \( n \)-butyllithium.

An important development for living inorganic polymerization was reported in 1995 by Allcock, Manners and co-workers. They reported the living cationic polymerization of phosphoranimine 1.7 to prepare controlled polyphosphazene (1.8) structures. Polyphosphazenes are a very important class of inorganic polymer and have been well studied. They consist of an alternating phosphorus nitrogen backbone as illustrated in Scheme 1.7, where the phosphorus atom has an oxidation state of five with two pendant chloro substituents. The versatility of this polyphosphazene system lies in the ability to chemically substitute the two chloro groups very easily. In Scheme 1.7, the poly(dichlorophosphazene) 1.8 is treated with NaOCH₂CF₃ to yield macromolecule 1.9. A wide range of substitution reactions are known for reactive P–Cl bonds and therefore a broad range of different polymer properties can be accessed from macromolecule 1.8. Moreover, since this pioneering development describing living phosphoranimine polymerization, a wide range of block copolymer architectures have been synthesized. Investigations in the field of polyphosphazenes are ongoing and the potential to use polyphosphazenes as drug delivery systems, flame retardant materials and fuel cell membranes continues to attract attention.

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Another significant synthetic achievement for living inorganic polymer preparation occurred in 1995 when Matsumoto and Yamaoka discovered that 1,1-dimethylsilacyclobutane 1.10 could be polymerized in the presence of $^n$BuLi or PhLi to prepare polycarbosilane 1.11 with controlled chain lengths.\(^7\) The use of THF-hexane solvent mixtures at low temperatures (−48 °C) were employed for the polymerization of 1.10 in a living manner. This remarkable report has resulted in some limited block copolymer work,\(^72-74\) and the use of silacyclobutanes as "carbanion pumps".\(^75-76\) This carbanion pump reaction involves using the cyclic ring system 1.10 to prepare block copolymers from two incompatible monomers. Normally, in order to covalently link AB block copolymers, the reactive chain end of living polymer A must be a better nucleophile than the living chain end formed for the B block. The silacyclobutane ring-opening reaction is thermodynamically driven by the release of ring strain and therefore, ring-opening can proceed with weak nucleophiles to afford the strong nucleophile RCH\(_2\)Li (Scheme 1.8).

\begin{center}
\begin{align*}
\text{Scheme 1.7 Living cationic polymerization of } &\text{Cl}_3\text{P=N-SiMe}_3 \text{ using catalytic PCl}_5 \text{ resulting in the elimination of SiMe}_3\text{Cl.} \\
\text{Scheme 1.8 Top - 1,1-dimethylsilacyclobutane living polymerization was initiated using } n\text{-butyllithium in THF/hexane mixtures. The polymerization was conducted at low temperatures. Bottom - The 1,1-dimethylsilacyclobutane being utilized as a carbanion pump for block copolymer preparation.}
\end{align*}
\end{center}
Finally, in 1997, the living anionic polymerization of vinyl ferrocene (compound 1.12) was reported.\textsuperscript{77} Polymerization of ferrocene-containing monomers by radical polymerization has attracted a great deal of attention for many years. Arimoto and Haven were the first to describe the radical polymerization of vinyl ferrocene and, since their work, the incorporation of the ferrocenyl organometallic moiety into polymers has become a fascinating point of study.\textsuperscript{78, 79} Nuyken and co-workers followed this original work with the successful living anionic polymerization of vinyl ferrocene (Scheme 1.9). Studies outlining the synthesis of block copolymers using vinyl ferrocene and isobutylene as monomers have appeared recently.\textsuperscript{80, 81}

![Scheme 1.9](image)

**Scheme 1.9** Vinyl ferrocene living polymerization conducted at low temperature, in THF and initiated using $n$-butyllithium.

Masked disilenes 1.13 have been polymerized in a living fashion but,\textsuperscript{82} cyclic tetrasilanes 1.14 have not been polymerized with a sufficiently narrow polydispersity to be considered strictly living.\textsuperscript{83, 84} Both of these methods are significant improvements upon the commonly employed Wurtz coupling to prepare polysilanes. The Wurtz strategy involves $R_2SiCl_2$ being treated with Na metal but it does not result in high yields of polysilane nor does it afford control over the molecular weight of the macromolecule. The efficient, high yielding methods to polysilanes outlined in Scheme 1.10 offer a degree of control and can be used to incorporate polysilanes into more complex macromolecular architectures. A significant development was reported on helical polysilanes, as chirality is important for molecular recognition. Polysilane-	extit{block}-poly(triphenylmethyl methacrylate) was synthesized (1.15) where the poly(triphenylmethyl methacrylate) block was prepared in the presence of (−) sparteine as this is known to induce helicity in polymers.\textsuperscript{85} Interestingly, below $−20 °C$ the helical methacrylate component induces chirality in the polysilane block. This behavior was cycled reversibly using temperature.\textsuperscript{85}
To the best of my knowledge, no other living polymerizations of inorganic monomers have been reported. Thus far, research in the area of controlled inorganic polymer synthesis has been primarily focused on ROP (ring-opening polymerization) or condensation polymerization. The controlled addition polymerization of vinyl ferrocene was a significant advance and it begs the question, can addition polymerization be expanded to multiple bonds other than C=C bonds? A potential route to inorganic polymers which has yet to be significantly explored is the addition polymerization of heavier element multiple bonds of the type \( R_2E=E'R_2 \) where one of either element \( E \) or \( E' \) has \( N \geq 3 \) \((N = \text{principal quantum number})\). In order to utilize these molecules as monomers for macromolecular synthesis, an investigation into their structure and bonding must be employed.

![Scheme 1.10 Anionic polymerization of masked disilenes and cyclic tetrasilanes using organolithium reagents. Block copolymerization of a masked disilene with triphenyl methyl methacrylate in the presence of sparteine induces helicity in the polymethacrylate segment.](image)
1.5 Inorganic Multiple Bonds

Species containing multiple bonds have been of longstanding interest in chemistry. However, the preparation of multiple bonds with inorganic elements (principal quantum number greater than two) have been more difficult to synthesize than their organic counterparts. These compounds display different physical and chemical properties than multiply bonded species involving lighter elements. They also display new and different bonding motifs that further the understanding of chemical bonding and structure. Many of the stable species isolated in the past 30 years with multiple bonds between heavy main group elements were originally thought to be unattainable because of the classical double bond rule. This rule implies that heavier element multiple bonds are not isolable because the (p-p)\(\pi\) interactions for E=E bonds (E has N > 2) are too weak. However, many species containing inorganic multiple bonds have been synthesized in the last 30 years, Figure 1.6 illustrates a few recent examples. 

\[
\text{Si}=\text{C} \quad \text{P}=\text{C} \quad \text{Ge}=\text{Ge} \\
\text{Si}=\text{Si} \quad \text{P}=\text{P} \quad \text{Sn}=\text{Sn} \\
\text{Si}=\text{Si} \quad \text{P}=\text{C} \quad \text{B}=\text{B}
\]

**Figure 1.6** Some of the recent achievements in heavier element main group multiple bonds.

Much of the recent work on heavier element multiple bonds centers around establishing parallels to the well-known chemistry of olefins. Our research group is interested in extending addition polymerization protocols, a common route to polyolefins, to heavier element multiple bonds. This is an attractive route to introduce inorganic functionalities into macromolecular structures with the potential to discover materials exhibiting unique properties. However, one of the main reasons that widespread interest in polymerization of \(R_2E=ER_2\) bonds has been lacking are the large bulky substituents (R groups) normally required to render these monomers isolable. The (p-p)\(\pi\) interactions of heavier element multiple bonds are generally fairly weak making them thermodynamically unstable. Consequently, to make heavier element multiply-

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bonded species isolable, a sterically encumbering R group surrounding the \( \pi \) bond is necessary to provide kinetic stabilization (Figure 1.7). Thus, increasing the steric congestion around the \((p-p)\pi\) bond results in a higher activation barrier \( (E_a) \) for these metastable species and allows for the isolation of \( R_2E=ER_2 \). From a polymer perspective, using big bulky R groups to prepare isolable \( R_2E=ER_2 \) molecules is also problematic as the activation barrier could be increased to a point which partially or completely inhibits any further reactivity of these compounds. In order to tap this vast resource of new monomers, a delicate balance where the R group supplies sufficient steric congestion to render isolation of \( E=E \) bonds possible but does not impede further reactivity must be obtained. From this standpoint, the potential to explore phosphorus containing double bonds (i.e, phosphaalkenes) seemed attractive, as these compounds have already been thoroughly investigated and exhibit some similarities to the reactivity of olefins.\(^9\) So the potential to expand this \( P=C, C=C \) analogy to polymer science seemed an intriguing possibility.
Figure 1.7 A reaction coordinate diagram representing the effect of a sterically unencumbered substituent versus a sterically bulky group on the activation barrier of $R_2E=ER_2$ molecules.

### 1.5.1 The analogy between P=C and C=C bonds

Köhler and Michaelis were the first to report their attempt at the isolation of phosphorus-containing multiple bonds. They described the isolation of $\text{PhP=PPh}$ (phosphobenzene) in 1877 but this was later shown to be the cyclic oligomer $(\text{PhP})_5$ or $6$. The first discovery of a stable P=C bond was 2,4,6-triphenylphosphabenzene (1.16), discovered by Markli in 1966. However, this compound was isolable based not only on kinetic stabilization but also on thermodynamic stability imparted by the $\pi$-delocalized ring structure. Becker and co-workers were the first to prepare a stable acyclic phosphaalkene in 1976 using silatropic migration as the driving force for the preparation of compound 1.17. Since this work, a number of different routes have been utilized to prepare a host of kinetically stabilized phosphaalkenes.
The isolation of stable phosphaalkenes has prompted investigation into their reactivity and it was discovered that the phosphaalkenes mimic the chemistry of olefins in many respects. These similarities have led to phosphorus being dubbed “the carbon copy”. There are some limitations to this analogy which generally arise from interference of the lone pair located on the phosphorus atom or from the higher energy $\text{P} = \text{C}$ bond as compared to the $\text{C} = \text{C}$ bond. However, coordination of the lone pair to metal fragments such as $\text{W} (\text{CO})_5$ can circumvent some of these limitations. Several interesting examples where $\text{P} = \text{C}$ bonds mimic the behavior of olefins are discussed below.

A 1,2-addition reaction has been described where electrophiles such as $\text{HBr}$ can be added across the $\text{P} = \text{C}$ bond of compound 1.18 (Scheme 1.12 - Top). Because P is slightly electropositive compared to C ($\text{P}_\sigma = \text{C}_\sigma$), the proton becomes attached to the C atom of the $\text{P} = \text{C}$ bond and the Br is bound to the phosphine moiety, as expected. Another interesting parallel between $\text{P} = \text{C}$ and $\text{C} = \text{C}$ bonds is the Diels-Alder reaction. This [4+2] cycloaddition has been used to trap unstable phosphaalkenes generated in situ, for example, $\text{ClP} = \text{C(TMS)}_2$ (1.19) can be prepared and will go on to act as the dienophile in the cycloaddition with 1.20 forming the cyclic phosphine 1.21 (Scheme 1.12 - Middle). The formation of these cyclic structures using phosphaalkenes is not limited to [4+2] reactions, and many other cyclizations have been reported. Another illustration of the $\text{P} = \text{C}$, $\text{C} = \text{C}$ parallel involves a 1,2 elimination to prepare phosphaalkynes. The treatment of compound 1.22 with hydroxide results in the elimination of hexamethyldisiloxane to prepare phosphaalkyne 1.23. The tert-butyl phosphaalkyne displays fascinating parallels to the chemistry of alkynes but this is beyond the scope of this thesis and will not be discussed further.
Scheme 1.12 Phosphaalkenes mimicking the reactivity of olefins. Top – 1,2-addition of HBr across the P=C bond of the sterically hindered Mes*P=CBr₂. Middle – Diels-Alder reaction to trap the unstable compound ClP=C(SiMe₃)₂ resulting in the formation of a cyclic phosphine. Bottom – 1,2-elimination of the Me₃SiP=C(OSiMe₃)(tBu) phosphaalkene to form the tbutyl phosphaalkyne.

Treatment of the four-coordinate phosphaalkene 1.24 with m-chloroperoxybenzoic acid (m-CPBA) will induce an epoxidation-type reaction forming the 3-membered cyclic ring structure 1.25. Interestingly, this reaction will not occur without the presence of the W(CO)₅ moiety to complex the lone pair of the phosphorus atom. All of the examples described in this section illustrate the close reactivity mimic which exists between P=C bonds and C=C bonds. Can this P=C/C=C bond analogy be extended to polymer science? Proper selection of monomer would be crucial in the potential success of this research.

Scheme 1.13 Formation of epoxide analogs by reaction of a complexed P=C compound with m-chloroperoxybenzoic acid.
1.6 Previous Research into the Addition Polymerization of P=C Bonds

Initially, efforts in the Gates' group were focused on the cationic polymerization of \( \text{Mes}^*\text{P}=\text{CH}_2 \) (1.26). This phosphaalkene (1.26) is synthesized by combining \( \text{Mes}^*\text{PH}_2 \) and \( \text{CH}_2\text{Cl}_2 \) in the presence of KOH.\(^{103}\) Cationic initiators such as GaCl\(_3\) and HOTf were employed to prepare polymers but unfortunately, stoichiometric combination of \( \text{Mes}^*\text{P}=\text{CH}_2 \) with GaCl\(_3\) resulted in C-H activation of a methyl group on \( \text{Mes}^* \) and the formation of compound 1.27.\(^{104,105}\) The combination of phosphaalkene 1.26 with HOTf yielded positive results with oligomers up to six repeats units being observed, however, larger molecular weight materials could not be obtained.

\[
\begin{align*}
\text{Mes}^*\text{P}=\text{CH}_2 & \xrightarrow{\text{GaCl}_3} \text{Mes}^*\text{P}^{+}\text{CH}_2^- \text{GaCl}_3
\end{align*}
\]

Scheme 1.14 Intramolecular C-H activation of \( \text{Mes}^*\text{P}=\text{CH}_2 \) in the presence of the Lewis acidic GaCl\(_3\) species.

Given the tendency of compound 1.26 to C-H activate, we turned our attention to the \( \text{MesP}=\text{CPh}_2 \) (1.28) phosphaalkene. Compound 1.28 has been synthesized using two different synthetic routes: by a phospha-Peterson reaction and by a 1,2-elimination reaction.\(^{106,107}\) The base catalyzed phospha-Peterson reaction involves treatment of \( \text{MesP(SiMe}_3\text{)_2} \) with benzophenone in the presence of catalytic NaOH or KOH to form the desired 1.28.\(^{106,108}\) The \( \text{MesP(SiMe}_3\text{)_2} \) compound is prepared from literature procedures starting from commercially available PCl\(_3\) (Scheme 1.15).\(^{109,110}\) The 1,2-elimination procedure outlined by Bickelhaupt and co-workers is illustrated in Scheme 1.16, where, compound 1.29 is treated with the basic 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) to afford phosphaalkene 1.28. Importantly, in the same paper, the attempted isolation of a \( \text{P}=\text{C} \) bond where the mesityl (2,4,6-trimethylphenyl) group was replaced by \( \text{o-methylphenyl (o-C}_6\text{H}_4\text{Me}) \) did not yield phosphaalkene but led to the isolation of polymeric material. This suggested that \( \text{MesP}=\text{CPh}_2 \) may be reactive enough to polymerize under appropriate conditions.

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Scheme 1.15 Preparation of the MesP=CPh₂ phosphaalkene from commercially available PCl₃. The phospha-Peterson reaction is employed as the final step to prepare the desired MesP=CPh₂ phosphaalkene.

Further evidence to support the theory of P=C bond polymerization was provided when stoichiometric combination of compound 1.28 and MeLi followed by combination with MeOH and air oxidation afforded compound 1.30. These results suggest that nucleophilic attack is possible at the P=C bond of the phosphaalkene (Scheme 1.17). Following this important study to prepare compound 1.30, treatment of 1.28 with substoichiometric amounts of either anionic or radical initiators resulted in the synthesis of the remarkable —[MesP—CPh₂]ᵣ—macromolecule 1.31 with alternating phosphine and carbon moieties (Scheme 1.17).

Scheme 1.17 Reaction of MesP=CPh₂ phosphaalkene with anionic MeLi and subsequent oxidation to afford a methyl mesityl phosphine oxide. Polymerization of MesP=CPh₂ using radical or anionic initiators at high temperature (ca. 150 °C).
The functional phosphine moiety of the poly(methylene phosphine) can be oxidized, sulfurized and it can be used as a ligand for metal-catalyzed Suzuki cross-coupling\textsuperscript{20,112} To polymerize phosphaalkene \textsuperscript{1.28}, high temperatures (up to 150 °C), long reaction times (ca. 24 h) and minimal solvent were employed. Under these conditions, low monomer conversions and several unidentified phosphorus byproducts were observed which resulted in poor isolated yields of the poly(methylene phosphine). It was of interest for our group to expand upon this work and search for cleaner, milder routes to these phosphine polymers.

Recently, addition polymerization of inorganic multiple bonds has seen a significant step forward with the polymerization of Ge=C bonds (1.32) using \textsuperscript{1}BuLi to afford polycarbogermanes \textsuperscript{1.33}.\textsuperscript{113} The polymer was isolated as an air stable material, in reasonable yield (45 \%), with modest molecular weight ($M_n = 36,000 \text{ g/mol}^{-1}$, PDI =1.5). The potential to form a variety of new copolymers incorporating Ge atoms is an exciting synthetic target within this research.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{Mes}};
\node at (0.5,0) {\text{H}};
\node at (1,0) {\text{Ge=C}};
\node at (1.5,0) {\text{Mes}};
\node at (2,0) {\text{CH}_2};
\node at (2.5,0) {\text{Bu}};
\node at (3,0) {1. \text{BuLi}};
\node at (3.5,0) {2. \text{MeOH}};\end{tikzpicture}
\end{center}

\textbf{Scheme 1.18} Polymerization of a Ge=C compound using tert-butyllithium as the anionic initiator to form polycarbogermanes.

\section*{1.7 Outline of Thesis}

With the discovery of addition polymerization of P=C bonds by Gates and co-workers, the application of living polymerization techniques to these inorganic multiple bonds is a logical extension for expanding upon the class of copolymers which could be prepared incorporating functional phosphine units. The application of living techniques to control the preparation of poly(methylene phosphine)s is outlined in Chapter Two. To illustrate the potential of this powerful polymerization technique, the preparation of a block copolymer, polystyrene-\textit{block}-poly(methylene phosphine) is also described in that same chapter. Chapter Three describes kinetic investigations into the living polymerization of P=C bonds. Apparent rate constants and an apparent activation energy of polymerization were extracted. Chapter Four details the

\textit{References start on page 28}
synthesis and solution self-assembly properties of polyisoprene-block-poly(methylene phosphine) copolymers which have been coordinated to a AuCl moiety. Chapter Five describes some of the developments surrounding poly(methylene phosphine)s and their chemistry with several isoelectronic main group electrophiles (CH3+ and BH3). Chapter Six outlines the synthesis and polymerization of a ferrocene-containing phosphaalkene. Chapter Seven, details the preparation and polymerization of several new phosphaalkenes in an attempt to expand upon the generality of P=C bond polymerization. Chapter Eight provides a synopsis of the thesis findings and describes some possible research directions in the future.

1.8 Contributions by Other Researchers to This Work

Several projects in this thesis were done in collaboration with other researchers and these people are listed in the Statement of Co-Authorship (xxi). For Chapters Two, Three and Six all synthetic work was completed by myself. Chapter Four was a collaborative effort between myself, Bronwyn Gillon and Dr. Vittorio Cappello. Two of the copolymers were prepared solely by myself and one was prepared in collaboration with Dr. Cappello, the Au(I) coordination to the polymer was realized by Bronwyn and Dr. Cappello whilst the TEM images were a collective effort of all three researchers. Chapter Five was also a collaborative effort between myself, Bastian Feldscher and Justin Kingsley. Bastian was under my direct supervision during his tenure at UBC and Justin Kingsley was in the Gates' lab prior to myself. Finally, Chapter Seven was my own work with the exception of the MesP=C(4-Cl-C6H4)(Ph) compound which was synthesized by Kam Zhi Ming. Kam was an exchange student under my supervision for 6 months while at UBC.
1.9 References


http://nobelprize.org/nobel_prizes/chemistry/laureates/1953/


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*References start on page 28*


*References start on page 28*
References start on page 28


Chapter 2

Ambient-Temperature Living Anionic Polymerization of Phosphaalkenes: Homopolymers and Block Copolymers with Controlled Chain Lengths*

The material pertaining to this Chapter has been removed due to copyright restrictions.
The Chapter describes the extension of living anionic polymerization techniques to P=C bonds. Experiments performed to confirm the living polymerization behavior of MesP=CPh₂ include: kinetic investigations of P=C bond polymerization, molecular weight versus conversion plots to confirm that molecular weight increases linearly with conversion and control of the polymer chain length by controlling the concentration of initiator. This new methodology has been used to prepare unprecedented polystyrene-block-poly(methylene phosphine) copolymers with narrow polydispersities and controlled molecular weights. This material is available at

http://www3.interscience.wiley.com

Chapter 3

Studying a Slow Polymerization: A Kinetic Investigation of the Living Anionic Polymerization of P=C bonds*

3.1 Introduction

In establishing the living nature of P=C bond polymerization as described in Chapter 2, an apparent rate constant of polymerization at room temperature using 2 mol % initiator was determined. Further investigations to extract kinetic parameters of this slow polymerization are described in this Chapter. Some background information on C=C bond polymerization kinetics is also presented for comparison.

Detailed kinetic investigations of living anionic olefin polymerization, particularly with styrene, have allowed for the determination of activation parameters for propagation. The effects of solvent (coordinating and non-coordinating), counterion (i.e., Li+, Na+, etc) and temperature on the rates of propagation of styrenic monomers have formed the basis for the textbook models of the mechanism of living anionic polymerization. The living anionic polymerization of alkenes proceeds via a two-step mechanism. The initiation step involves addition of a nucleophilic species, such as n-butyllithium, to the C=C bond of monomer A forming the propagating species B (Scheme 3.1). Compound B, which resembles n-butyllithium in terms of its nucleophilicity, then repeatedly adds to the C=C bond of another monomer A forming polymer C. In the absence of monomer, living polymer C will rest indefinitely but can be terminated by controlled addition of an electrophile (i.e., H*). When the rate of initiation is much faster than the rate of propagation, the rate equation can be expressed as shown below (Equation I). Typically, this equation is followed when the polymerization experiment is conducted in polar solvents. The rate constant of propagation is represented by k_p, [living ends]

stands for the concentration of the propagating polymer species that remains constant throughout the polymerization, and [M] represents the concentration of monomer A.

\[
\frac{-d[M]}{dt} = k_p \cdot \text{[living ends]} \cdot [M] 
\]

The development of synthetic routes to main chain phosphorus polymers is a vibrant area of research due to the potential applications of phosphorus materials as sensors, catalyst-supports, ceramic precursors, and biomedical materials.\(^{13-23}\) The successful extension of addition polymerization to P=C bonds \(^{24}\) (Scheme 3.2) forming poly(methylene phosphine)s \(^{E}\) and the subsequent ambient temperature living anionic polymerization of MesP=CPh\(_2\) \(^{1}\) are new contributions to the growing research on phosphorus-containing polymers. The living anionic polymerization of P=C bonds necessitates further investigation as this tool will enable the preparation of new macromolecules incorporating phosphorus atoms. In order to further understand this living polymerization, kinetic experiments were conducted to analyze the propagation step of P=C bond polymerization.

We propose that both the initiation and propagation steps in the anionic polymerization of P=C bonds involve nucleophilic addition of a lithium carbanion (i.e. \(^{n}\)BuLi or 3.2) to the P=C bond in a regioselective fashion (Scheme 3.3).\(^{1,26}\) This postulate is supported by molecular model studies where addition of MeLi to compound 3.1 affords Mes(Me)P–CHPh\(_2\) after

References start on page 62
In this chapter, the first kinetic studies of the living anionic polymerization of P=C bonds are described. Apparent rate constants of propagation are measured and estimated by following the consumption of [3.1] and formation of [3.3] using $^{31}$P NMR data collected over a 9 h period. Moreover, kinetic experiments were conducted at several temperatures to elucidate the activation energy for polymerization propagation.

References start on page 62
3.2 Results and Discussion

3.2.1 Procedure employed to conduct kinetic studies of MesP=CPh₂ phosphaalkene polymerization

To study the kinetics of the living anionic polymerization of C=C bonds, specialized capillary tube stop flow techniques are often employed to measure the rates of these rapid reactions. In contrast to olefin polymerizations, which have half lives of seconds to minutes, the half life of phosphaalkene polymerization is several hours. Consequently, the anionic polymerization of 3.1 can be conveniently monitored using $^{31}$P NMR spectroscopy. All kinetic experiments performed in this Chapter were conducted as follows:

1. Monomer 3.1 was dissolved in glyme in an inert atmosphere
2. $^t$BuLi was added to this solution and an immediate color change from yellow to red was observed upon initiation (50:1 monomer to initiator ratio).
3. The reaction mixture was transferred to an NMR tube and $^{31}$P NMR spectra were recorded at 15 min intervals.

The two acquisition parameters of the NMR spectrometer, (i) relaxation delay and (ii) tip angle, were set to ensure that the integration of the $^{31}$P NMR spectra were reliable ($d_1$ = 2 s and 30° tip angle). The relaxation time ($T_1$) of the phosphorus atom in the MesP=CPh₂ monomer was measured prior to conducting this kinetic analysis to ensure adequate delay time for complete relaxation between data acquisition ($T_1$ = 1.33 s). This ensures that integrations are reliable. Relaxation times ($T_1$) for polymer 3.3 is not a concern as macromolecules relax much faster on the NMR timescale than molecular compounds. Representative $^{31}$P NMR spectra from the $^t$BuLi polymerization of 3.1 at 296.3 K are shown in Figure 3.1. In each spectrum, the signals assigned to the monomer 3.1 ($\delta_{31P} = 233$) and the growing polymer 3.3 ($\delta_{31P} = -7$ ) were integrated separately and, using the known initial concentration of 3.1, the percent conversion was calculated. Under otherwise identical conditions, $^{31}$P NMR experiments were performed at 296.3 K, 301.8 K, 307.4 K, 313 K, 318.6 K, 324.2 K. Upon completion of the polymerization as...
determined by $^{31}$P NMR spectroscopy, the polymer 3.3 was quenched with methanol (0.1 mL), precipitated with hexanes (2 x 40 mL), and analyzed by triple-detection GPC. The molecular weights, which are listed in Table 3.1, were used to confirm that the polymer chain length correlated closely with the initiator concentration. Each experiment was repeated at least twice to ensure reproducibility. Although there was some variation in the observed molecular weights, the propagation rate constants determined were reproducible, within error, at each temperature.

![Figure 3.1](image-url)  

**Figure 3.1** Selected $^{31}$P NMR spectra (glyme; 296.3 K) of the $^n$BuLi initiated polymerization mixture showing the conversion of 3.1 to 3.3 over time ([Monomer]:[Initiator] = 50:1). $[M_0] = 0.394$ mol L$^{-1}$.

### 3.2.2 Determination of rate constant of propagation ($k_p$) at different temperatures for MesP=CPh$_2$ polymerization

The living polymerization of C=C bonds follows pseudo first order reaction kinetics (equation I) with [living ends] remaining constant throughout the polymerization and [M] decreasing over time.$^{12}$ Therefore, if the living anionic polymerization of 3.1 is analogous to that of C=C bonds, a plot of ln $[M]_0/[M]$ vs. time should be linear. At all temperatures, the propagation data collected is linear up to ca. 50% conversion (Figure 3.2). The rate constant of propagation ($k_p$) was determined by least-squares fitting the data at each temperature and the results are given in Table 3.1. Remarkably, the $k_p$ for 3.1 ($k_p = 21.0 \pm 2.5$ L mol$^{-1}$ h$^{-1}$ at 296.3 K) is several
orders of magnitude smaller than that observed for the sodium naphthalide initiated polymerization of styrene in THF at room temperature ($k_p = 1.4 \times 10^6 - 2.2 \times 10^6$ L mol$^{-1}$ h$^{-1}$).

Since MesCH=CPPh$_2$ has not been polymerized, the closest steric comparison for 3.1 that we have come across is vinylmesitylene. Importantly, the rate constant for polymerization of H$_2$C=CHMes in THF using sodium naphthalide ($k_p = 1.2 \times 10^3$ L mol$^{-1}$ h$^{-1}$) is several orders of magnitude slower than styrene,$^6,29$ which is attributed to larger steric constraints imposed by a mesityl group as compared to a phenyl group.

Figure 3.2 A graph showing ln [M]$_0$/[M] versus time (h) up to ~50% conversion for the polymerization of 3.1 with 2% $^t$BuLi at approximately 5 K temperature intervals between 296 and 324 K. These plots of ln [M]$_0$/[M] versus time (h) were fitted to a linear least squares function to determine rate constants illustrated in Table 3.1.

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### Table 3.1
Determination of $k_p$ at different temperatures for MesP=CPh$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M]:[I]$^a$</th>
<th>Temperature (K)</th>
<th>$k_p^b$ (L mol$^{-1}$ h$^{-1}$)</th>
<th>$M_n$ calculated$^c$ (g mol$^{-1}$)</th>
<th>$M_n$ observed$^d$ (g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50:1</td>
<td>296.3</td>
<td>$21.0 \pm 2.5$</td>
<td>15 900</td>
<td>13 500</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>50:1</td>
<td>301.8</td>
<td>$32.7 \pm 3.9$</td>
<td>15 900</td>
<td>15 100</td>
<td>1.02</td>
</tr>
<tr>
<td>3</td>
<td>50:1</td>
<td>307.4</td>
<td>$41.8 \pm 4.9$</td>
<td>15 900</td>
<td>13 800</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>50:1</td>
<td>313.0</td>
<td>$70.7 \pm 8.9$</td>
<td>15 900</td>
<td>14 400</td>
<td>1.09</td>
</tr>
<tr>
<td>5</td>
<td>50:1</td>
<td>318.6</td>
<td>$125 \pm 15$</td>
<td>15 900</td>
<td>12 300</td>
<td>1.07</td>
</tr>
<tr>
<td>6</td>
<td>50:1</td>
<td>324.2</td>
<td>$150 \pm 17$</td>
<td>15 900</td>
<td>13 600</td>
<td>1.05</td>
</tr>
<tr>
<td>7</td>
<td>50:2</td>
<td>296.3</td>
<td>$15.3 \pm 1.9$</td>
<td>8 000</td>
<td>8 800</td>
<td>1.09</td>
</tr>
</tbody>
</table>

$^a$[MesP=CPh$_2$]:["BuLi]. $^b$rate constant of propagation. $^c$Calculated using the monomer to initiator ratio. $^d$Molecular weights were determined using triple detection GPC.

#### 3.2.3 Determination of activation energy ($E_a$) of propagation for P=C bond polymerization

The rate constant data was used to prepare an Arrhenius plot (Arrhenius equation displayed below: Equation II) from which the apparent activation energy ($E_a$) of the polymerization was extracted (Figure 3.3). The $E_a$ for the anionic polymerization of 3.1 in glyme was calculated to be $14.0 \pm 0.9$ kcal mol$^{-1}$ and the preexponential factor ($A = 4.4 \times 10^{11}$) was also obtained. Interestingly, this activation barrier is much larger than the $E_a$ measured for styrene polymerization in THF with Na$^+$ counterion ($E_a = 5.9$ kcal mol$^{-1}$).$^2,30$ For comparison, bulky substituted olefins have higher activation barriers and, therefore, slower polymerization rates. For example, the sterically hindered monomer $\alpha$-methylstyrene ($E_a = 7.2$ kcal mol$^{-1}$) has a higher activation energy than styrene.$^3$ The high activation barrier in the anionic polymerization of 3.1 is almost certainly a consequence of the high degree of steric bulk surrounding the P=C bond and, in addition, the propagating polymer species 3.3 is highly resonance stabilized, lowering its nucleophilicity.

$$k_p^{app} = Ae^{-E_a/RT}$$ (II)
Figure 3.3 An Arrhenius Plot was constructed from the linear least squares fit of $\ln k_p$ versus $1/T$ ($K^{-1}$). Error bars are reported to $3\sigma$. The linear least squares function ($y = -7051.5x + 26.811$) had an $R^2$ value of 0.9841.

3.2.4 Rate behavior changes observed above 50% conversion

Although rate constant data may be extracted, the plots of $\ln [M]_f/[M]$ vs. time in the anionic polymerization of 3.1 only exhibit pseudo first order kinetics up to ca. 50% conversion. Thereafter, a deviation from linearity is observed (Figure 3.4). For comparison, the anionic polymerization of styrene and $\alpha$-methylstyrene exhibit linear behavior up to 90% conversion.\textsuperscript{8,10} Although for styrene the conversion rate decreases as the monomer is consumed, the rate of propagation actually increases above 50% conversion for 3.1. Interestingly, at higher polymerization temperatures the expected behavior is observed and the rate of propagation for 3.1 slows above 50% conversion. Particularly striking is the experiment conducted at 324.2 K that appears almost linear up to $\sim$80% conversion. To our knowledge, an increase in rate at high conversion has not been observed for the living anionic polymerization of C=C bonds and suggests a more complex mechanism for the P=C system.\textsuperscript{31}

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Figure 3.4 A plot of ln[M]₀/[M] vs. time (h) up to ~90% conversion for the polymerization of MesP=CPh₂ with 2% "BuLi at ca. 5 K temperature intervals between 296 – 324 K.

In the polymerization of olefins, the observed or apparent rate constant \( k_p \) in polar solvents is actually composed of two different rate constants (equation III).\(^\text{12} \) Due to solvation phenomena, the rate equation must be rewritten in terms of, the free-ion rate constant (\( k_p^{\text{free}} \)) and the ion-pair rate constant (\( k_p^{\text{ion-pair}} \)). Both rate constants are expected to contribute to the rate of propagation for unsaturated bonds, however this contribution is not equal, especially in polar solvents. Consequently, increasing the number of ions in solution (i.e. increasing [living ends]) will affect the ion-pair free-ion equilibrium (i.e. [free-ion chain ends] and [ion-pair chain ends]) and alter the apparent rate of propagation \( k_p \). A preliminary experiment was conducted to test whether this applies to the polymerization of 3.1 in glyme. Under otherwise identical conditions, the anionic polymerization of 3.1 was conducted with double the concentration of "BuLi ([M]:[I] = 50:2) than that used in all other experiments (Table 3.1, entry 7). If only equation I applied, the reaction rate should be identical for both experiments. However, as predicted by equation III, polymerizations with a higher concentration of living ends results in a lower propagation rate constant (\( k_p = 15.3 \pm 1.9 \text{ L mol}^{-1} \text{ h}^{-1} \)) as compared to the experiment with 2%
initiator \( k_p = 21.0 \pm 2.5 \text{ L mol}^{-1} \text{ h}^{-1} \) at 296.3 K. Future work will focus on determining \( k_p^{\text{free}} \) and \( k_p^{\text{ion-pair}} \) by conducting polymerizations with excess counterion (Li\(^+\)).

\[
- \frac{d[M]}{dt} = k_p^{\text{free}} [\text{free-ion chain ends}] \cdot [M] + k_p^{\text{ion-pair}} [\text{ion-pair chain ends}] \cdot [M] \quad (\text{III})
\]

3.3 Conclusions

In summary, a kinetic investigation of the \( n \)-butyllithium initiated living anionic polymerization of MesP=CPh\(_2\) has been completed. Rate constants over a 25 K range were obtained and used to determine an activation energy for the anionic polymerization of MesP=CPh\(_2\) \((14.0 \pm 0.9 \text{ kcal mol}^{-1})\). This activation energy is significantly higher than that of styrene \((5.9 \text{ kcal mol}^{-1})\) and \(\alpha\)-methylstyrene \((7.2 \text{ kcal mol}^{-1})\). This large activation energy is most likely a product of the bulky substituents (Mes and Ph) surrounding the P=C bond and the doubly stabilized carbanion formed during polymer propagation. Future work will focus on collecting kinetic data for other P=C monomers which polymerize in a living fashion.

3.4 Experimental

3.4.1 Materials and General Procedures

Hexanes was dried by passing through activated alumina columns.\(^{32}\) 1,2-Dimethoxyethane (glyme) was distilled from sodium/benzophenone and was degassed under vacuum at \(-196 \, ^\circ\text{C}\) prior to use.\(^{33}\) MeOH was degassed by passing nitrogen through the solvent for 1 h prior to use.\(^{34}\) \(^6\)BuLi \((1.6 \text{ M in hexane})\) was purchased from Aldrich and was titrated with \(n\)-benzylbenzamide prior to use.\(^{34}\) MesP=CPh\(_2\) was prepared according to literature procedures.\(^{35}\) All manipulations of air and/or water sensitive compounds were performed under pre-purified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology glovebox.\(^{31}\) \(^31\)P NMR \((121.5 \text{ MHz})\) spectra were recorded at room temperature on a Bruker

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Avance 300 MHz spectrometer. Chemical shifts are reported relative to 85% $\text{H}_3\text{PO}_4$ as an external standard $\delta = 0.0$ for $^{31}\text{P}$. The relaxation time ($T_1$) for 3.1 is 1.33 s. To ensure accurate integrations, a relaxation delay of 2 s with a 30° tip angle was employed for all $^{31}\text{P}$ NMR experiments. Temperature was calibrated for NMR experiments using standard Bruker samples: 4% MeOH in MeOH-d$_4$ for the 194-283 K range and 80% ethylene glycol in DMSO-d$_6$ for the 300-400 K range. Molecular weights were estimated by triple detection gel permeation chromatography (GPC - LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 x 300 mm) HR5E (2 000 – 4 000 000), HR4 (5 000 – 500 000) and HR2 (500 – 20 000), Waters 2410 differential refractometer ($\lambda = 920$ nm), Wyatt tristar miniDAWN (laser light scattering detector operating at $\lambda = 690$ nm), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min$^{-1}$ was used and samples were dissolved in THF (ca. 2 mg mL$^{-1}$). The refractive index increment of poly(methylenephosphine) 3.4 ($dn/dc = 0.223$ mL g$^{-1}$) was determined by plotting the refractive index vs. concentration for six solutions of 3.4 in THF (1 – 6 mg mL$^{-1}$). Aqueous NaCl was used to calibrate the Waters 410 Differential Refractometer.

### 3.4.2 Purification of MesP=CPh$_2$ (3.1)

Crude 3.1 was transferred to a short path distillation apparatus and was heated under vacuum with an oil bath (190 °C, 0.01 mm Hg). The yellow liquid distilled between 150 – 160 °C and the distillate was recrystallized from hexanes. The crystalline solid was ground up into a fine powder using a mortar and pestle and was subsequently dried in vacuo for 12 h at 60 °C. $^1\text{H}$ NMR was used to confirm purity.

### 3.4.3 Anionic polymerization of MesP=CPh$_2$ for kinetic studies.

A solution of $^\text{tBuLi}$ (12 µL, 1.37 M, 0.016 mmol) in hexanes was added to a stirred solution of 3.1 (0.250 g, 0.790 mmol) in glyme (2 mL) in the glovebox. Immediately after mixing, an aliquot was removed from the reaction mixture and was transferred to an NMR tube. The sample was

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loaded into the spectrometer ($T = 296.3 \text{ K}$) and $^{31}\text{P}$ NMR spectra were recorded every 15 min
(72 scans) until the reaction was complete. At completion, the living polymer was terminated by
the addition of one drop of degassed MeOH (0.1 mL) and the polymer was isolated by
precipitation into hexanes ($2 \times 40 \text{ mL}$) under N$_2$. The purified polymer was dried in vacuo (4 h at
100 °C). GPC (absolute): $M_n = 13500 \text{ g mol}^{-1}$, PDI = 1.07. Experiments were repeated at least
two times at each temperature to ensure reproducibility.

3.4.4 General procedure for processing $^{31}\text{P}$ NMR spectra.

The raw NMR data, obtained as described above, were processed using line broadening
settings of ($LB = 10$) and a baseline correction was applied. The sharp signal for 3.1 ($\delta_{31\text{P}} = 233$)
and the broad signal for 3.2 and 3.3 ($\delta_{31\text{P}} = -7$) were integrated using approximate ranges
between 250 and 210 ppm and between 30 and $-75$ ppm, respectively. The relative
integrations, after phasing, were used to determine the percent conversion of monomer to
polymer and, consequently, the average concentration of monomer [$M$] during the acquisition of
each spectrum. In each case, the first NMR experiment was started 13.5 min after initiation.
Since the acquisition time for 72 scans requires 3 min, the time ($t$) for the first data point is 15
min (0.25 h). The delay time between NMR experiments was 12 min which results in data points
at $t = 30, 45, 60$ min, etc. The data is tabulated in Appendix B.
Chapter 3

3.5 References

5. Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. Polymer 1964, 5, 54.
29. A report with the rate constant \( k_p = 3.3 \times 10^3 \text{ L mol}^{-1} \text{ h}^{-1} \) for vinyl mesitylene has been reported. Bhattacharyya, D. N.; Smid, J.; Szwarc, M. J. Polym. Sci.: Part A: Polym. Chem. 1965, 3, 3099.
30. The activation energy reported was determined for free polystyryl anions in THF. Solvent has a significant affect on the activation energy as it affects the free-ion to ion-pair equilibrium discussed in the text. For example, in a solvent such as dioxane, the polymerization of styrene proceeds with a much lower rate constant \( k_p \approx 4 \text{ L mol}^{-1} \text{ s}^{-1} \) and has a higher activation energy \( E_a = 9 \text{ kcal/mol} \). This slower rate is likely due to lower concentration of free-ions than in a polar solvent such as THF. Szwarc, M., Carbanions, Living Polymers, and Electron Transfer Processes. Interscience: New York, 1968.
31. Upon careful examination of the \(^{31}\text{P} \text{NMR spectra of the} \ ^\text{tBuLi-initiated polymerization of 3.1 in glyme reveals two unassigned signals (} \delta = -29 \text{ and } -102 \text{). By comparison to the chemical shift of the anion model Mes(}^\text{tBu})P\text{-CPh}_2\text{Li which resonates at } -31.1 \text{ ppm in THF, (ref 34) we speculate that the resonance observed at } -29 \text{ ppm corresponds to species 3.3. The high field signal at } -102 \text{ ppm is much more difficult to rationalize. However, based on the high field chemical shift observed, we tentatively assign this}}

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species to the phosphide moiety of Me[MesP=CPH₂]nCPH₂–PMesLi which would result from that reverse addition of 3.3 to 3.1 during propagation. NOTE: This species is <<1% of total phosphorus. For comparison, Mes*P(H)Li has been previously prepared by Cowley and coworkers and resonates at -110 ppm (THF) in the ³¹P NMR spectrum (Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. J. Am. Chem. Soc. 1982, 104, 5820).


Chapter 4

Self-Assembly of Amphiphilic Block Copolymers Containing Phosphorus in the Main Chain: A Block Copolymer Approach to Defined Gold Nanostructures

4.1 Introduction

Living polymerization offers the unique possibility to tailor the size and properties of macromolecules.\(^1\)\(^-\)\(^3\) The most important feature of this synthetic tool is the preparation of controlled macromolecular architectures, such as block copolymers, which consist of two chemically different polymer chains linked by a covalent bond (see Section 1.3.1). These copolymers are prepared through sequential polymerization of two monomers (A and B in Figure 4.1) and they are attracting a great deal of attention as these materials display unique properties.\(^1\)\(^-\)\(^4\)\(^-\)\(^15\)

![Figure 4.1 Schematic representations of diblock and triblock copolymers.](image)

As discussed in Section 1.3.1, block copolymers can display phase separation in solution with appropriate solvent selection promoting aggregated structures such as micelles, rods and vesicles.\(^16\) The spherical micelle (Figure 1.4) is a commonly observed morphology but solubility conditions, block copolymer sizes and the chemical nature of the two different segments (A and B – Figure 4.1) can promote different organizational behavior.\(^16\) Many applications in nanoelectronics are being envisioned for block copolymers. The recent discovery of living
phosphaalkene polymerization offers the possibility of preparing block copolymer architectures with phosphine segments along the polymer backbone.\textsuperscript{17} These phosphine units could be exploited for metal coordination. There has been fairly extensive work on using block copolymers to stabilize and organize pre-formed metal (CdSe, Au and Ag) nanoparticles.\textsuperscript{13, 18-26} There has also been investigation into main chain iron copolymers which form ordered architectures by solution self-assembly.\textsuperscript{5, 27-36} However, to my knowledge, there have been no block copolymer systems used to stabilize Au(I) assemblies. The Au(I) moiety may be useful in catalysis, or it may be reduced \textit{in situ} to form Au(0) structures templated by the poly(methylene phosphine).

The polystyrene-bl\textit{ock}-poly(methylene phosphine) macromolecule discussed in Chapter 2 was not a suitable candidate for solution self assembly as the polystyrene and poly(methylene phosphine) homopolymers are both soluble in polar solvents (CH\textsubscript{2}Cl\textsubscript{2}, glyme, THF) and insoluble in non-polar solvents (hexanes, pentane).\textsuperscript{17} In an effort to prepare amphiphilic block copolymer structures, selecting a monomer amenable to living anionic polymerization that also forms a polymer which is soluble in nonpolar media, was imperative. Isoprene was selected as a co-monomer for polymerization with MesP=CH\textsubscript{2} since isoprene readily polymerizes in a living fashion. Moreover, polyisoprene is soluble in both polar and non-polar solvents.\textsuperscript{37-41} In this chapter, the preparation of polyisoprene-bl\textit{ock}-poly(methylene phosphine) copolymers (PI-\textit{b}-PMP) and their coordination to Au(I) is described. The solution self-assembly properties of these PI-\textit{b}-PMP-Au copolymers was investigated using transmission electron microscopy (TEM) and dynamic light scattering (DLS).

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4.2 Results and Discussion

4.2.1 Preparation of PI–b–PMP block copolymers through successive anionic polymerization of isoprene and MesP=CPh₂

Three different copolymer samples of polyisoprene-block-poly(methylene phosphine) were prepared and these are labeled as entries a, b and c in Table 4.1. Throughout the Results and Discussion section in this Chapter, the discussion of a polymer sample i.e., 4.2 will be followed by an a, b or c to indicate the appropriate macromolecule. Each copolymer was synthesized from successive anionic polymerization of isoprene and MesP=CPh₂ (Scheme 4.1).

Treatment of an isoprene solution in THF with substoichiometric °BuLi resulted in a pale yellow solution. The reaction mixture was stirred for 0.75 h at room temperature after which, a drop of the living polyisoprene (4.1) solution was removed from the reaction vessel, precipitated from MeOH, and analyzed by triple-detection GPC. The molecular weight determination indicated isoprene polymerization had proceeded successfully ($M_n = 27500 \text{ g mol}^{-1}$ $\text{PDI} = 1.05$). Then a MesP=CPh₂ solution in THF was rapidly added to the reaction mixture producing an immediate color change from yellow to red. This color change is consistent with the previously reported living MesP=CPh₂ polymerization using °BuLi.¹⁷ Complete consumption of the MesP=CPh₂ monomer was confirmed using $^{31}$P NMR spectroscopy ($\delta_{31P} = 233$). The reaction mixture was precipitated using methanol ($2 \times 100 \text{ mL}$) and the desired PI–b–PMP polymer (4.2a) was isolated as a white solid. Removal of the volatiles in vacuo yielded the desired copolymer 4.2a ($M_n = 38500 \text{ g mol}^{-1}$ $\text{PDI} = 1.12$). A $^{31}$P NMR spectrum of the copolymer displays only one signal at $-7 \text{ ppm}$ which confirms the synthesis of the poly(methylene phosphine) block.⁴² A small amount of quenched polyisoprene was detected in the GPC trace of copolymer 4.2a. The microstructure of the PI block is dependent on the polymerization solvent and previous studies have determined that PI formation in THF produces the microstructure illustrated in Scheme 4.1.⁴³ Unfortunately, this could not be confirmed using
$^1$H NMR spectroscopy as the spectrum of copolymer 4.2a displays very broad overlapping signals for the PI and PMP segments.

Table 4.1 Selected characterization data for polyisoprene-block-poly(methylenephosphine)s (PI$_r$-$b$-PMP$_m$) prepared by the successive living anionic polymerization of isoprene and MesP=CPH$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>PDI</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>PDI</th>
<th>n:m$^a$ expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>27 500</td>
<td>1.05</td>
<td>38 500</td>
<td>1.12</td>
<td>404:32</td>
</tr>
<tr>
<td>(b)</td>
<td>15 100</td>
<td>1.06</td>
<td>39 400</td>
<td>1.06</td>
<td>222:77</td>
</tr>
<tr>
<td>(c)</td>
<td>11 200</td>
<td>1.09</td>
<td>38 200</td>
<td>1.24</td>
<td>164:85</td>
</tr>
</tbody>
</table>

$^a$The estimated chain lengths for each block ($n$ and $m$) are determined from the absolute $M_n$ of each homo- and copolymer samples.

Since molecular weight correlates directly to polymer chain length, we can use the molecular weights determined from triple-detection GPC analysis to estimate the chain length of each block copolymer segment. Sample 4.2a has a PI block with a molecular weight of 27 500 g mol$^{-1}$, if this is divided by the molecular weight of the repeating isoprene unit (68.12 g mol$^{-1}$) then we can estimate that the block copolymer has a PI segment with 404 repeat units. Copolymer 4.2a has a total molecular weight of 38 500 g mol$^{-1}$ which corresponds to a 10,000 g mol$^{-1}$ molecular weight for the PMP segment. If we divide this weight by the molecular weight of the repeating phosphine unit (316.38 g mol$^{-1}$) then this leads to a chain length of approximately 32 repeat units. Two other copolymer samples 4.2b and 4.2c were prepared with different chain lengths for the PI and PMP blocks (Table 4.1). Analysis of samples 4.2b and 4.2c by GPC chromatography revealed a small signal assigned to quenched polyisoprene homopolymer. The polyisoprene could be removed by washing each sample with hexanes. A stack plot of the GPC chromatograms for H-terminated 4.1b and copolymer 4.2b is shown in Figure 4.2 to illustrate the observed increase in molecular weight from the polyisoprene homopolymer to the polyisoprene-block-poly(methylenephosphine).

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Scheme 4.1 Polymerization of isoprene in THF at room temperature using \(^n\)BuLi followed by
addition of MesP=CPh\(_2\) to the living polyisoprene forming polyisoprene–block–
poly(methylene phosphine).

Figure 4.2 GPC chromatograms (refractive index traces) collected for 4.1b and 4.2b. Red
trace – macromolecule 4.1b. Blue trace – macromolecule 4.2b.
4.2.2 Preparation of gold complexes of the PI–b–PMP

The self-assembly of block copolymer 4.2a should be possible using non-polar solvents because the polyisoprene is soluble in non-polar media whereas the poly(methylene phosphine) is not. In addition, the potential to exploit the three coordinate phosphine moiety in the polymer backbone for transition metal coordination is a potential route to self-assembled metal nanostructures. Using gold(I) was an attractive starting point to synthesize metallated phosphorus polymers because several phosphine-containing polymers in the literature have been shown to form coordination complexes with AuCl moieties.44,45

The metallation of nBu [MesP-CPh2]nH with AuCl has been reported previously, and a similar procedure was followed for the coordination of the block copolymer 4.2a to AuCl.45 Sample 4.2a was treated with a (tetrahydrothiophene)AuCl solution in CH2Cl2 under N2 atmosphere. The reaction mixture was stirred for several hours before removal of the volatiles in vacuo. Analysis of the sample using 31P NMR spectroscopy revealed only one resonance at 25 ppm, this has been assigned to the coordination compound PI–b–PMP-AuCl (4.3a). The observed resonance in the 31P NMR spectrum for macromolecule 4.3a is in close agreement with the previously reported signal for the poly(methylene phosphine) Au(I) coordination complex (δ31P = 25).

![Scheme 4.2](image)

Scheme 4.2 Treatment of polyisoprene-block-poly(methylene phosphine) with (tetrahydrothiophene)gold(I) chloride to form a polyisoprene-block-poly(methylene phosphine) gold(I) coordination complex.

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The metallated copolymer 4.3a was also characterized by triple detection GPC-LLS and a significant increase in the molecular weight is observed (Table 4.2 - entry (a): $M_n = 43500 \text{ g mol}^{-1}$; PDI = 1.18) as compared to 4.2a (Table 4.1 entry (a): $M_n = 38500 \text{ g mol}^{-1}$; PDI = 1.12). This behavior is consistent with the addition of a heavy AuCl moiety to the polymer microstructure. Copolymers 4.3b and 4.3c were prepared following an analogous procedure to 4.3a (Table 4.2). Representative $^{31}$P NMR spectra are displayed in Figure 4.3 for compounds 4.2b and 4.3b to illustrate the observed shift upon coordination of copolymer 4.2b ($\delta_{31P} = -7$) to AuCl (4.3b: $\delta_{31P} = 25$).

Table 4.2  
GPC data for polyisoprene-block-poly(methylene phosphine) coordinated to AuCl.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>PDI</th>
<th>$R_n$ (THF)$^a$</th>
<th>$R_n$ (C$<em>7$H$</em>{16}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>43500</td>
<td>1.18</td>
<td>5 nm</td>
<td>82 nm</td>
</tr>
<tr>
<td>(b)</td>
<td>44800</td>
<td>1.10</td>
<td>5 nm</td>
<td>75 nm</td>
</tr>
<tr>
<td>(c)</td>
<td>57900</td>
<td>1.15</td>
<td>5 nm</td>
<td>ca. 1400 nm</td>
</tr>
</tbody>
</table>

(a) hydrodynamic radius was determined using viscometer data from the triple detection GPC analysis; (b) hydrodynamic radius was determined from dynamic light scattering (DLS) data on the solutions used to prepare TEM samples.

Figure 4.3  
$^{31}$P NMR spectra for compounds 4.2b and 4.3b. Top – macromolecule 4.3b and bottom – macromolecule 4.2b.
4.2.3 Formation of PI–b–PMP–AuCl nanostructures

To determine whether self-assembly was feasible, transmission electron microscopy (TEM) and dynamic light scattering (DLS) were employed. Good contrast for TEM requires the presence of large atoms in specific domains and the scattering power of the phosphine-gold moiety compared to the organic PI block provided sufficient contrast for TEM imaging and thus no TEM staining was required.

Suitable solvent conditions for the polymers to self-assemble into macromolecular structures were crucial. Both PMP and PI are soluble in polar solvents but only PI is soluble in aliphatic solvents. Dilute solutions of 4.3a (0.5 mg mL⁻¹) in n-heptane were dropcast onto a copper TEM grid coated with Formvar. The sample was loaded into the transmission electron microscope and analyzed. The formation of well-defined nanospheres (Figure 4.4a) are clearly visible in the TEM images, it seems the assemblies are small spherical structures with fairly uniform shape and size. From the 197 spheres on the TEM image (Figure 4.4a – 100 nm resolution), 20 were taken and measured; the diameter of the structures is on average 28 – 32 ±11 - 15 nm. To ensure that sphere formation was not simply an aggregation effect from solvent evaporation, dynamic light scattering of the dilute n-heptane solution was employed. The hydrodynamic radius ($R_h$) of copolymer 4.3a in THF is approximately 5 nm whereas in dilute n-heptane, a 15-fold increase is observed ($R_h = 82$ nm), supporting the hypothesis that the copolymer sample is forming assemblies in solution. The potential to access morphologies other than spheres was of interest and the two block copolymers with longer PMP segments, 4.3b and 4.3c, were investigated.

Both macromolecules 4.3b and 4.3c were not soluble in n-heptane. Polymer 4.3b was dissolved in a minimal amount of THF after which, n-heptane was added (10% THF: 90% heptane). The cloudy solution was dropcast onto a Formvar coated TEM grid and analyzed using transmission electron microscopy (Figure 4.3b). The shapes observed in this case were significantly different than 4.3a. The morphologies varied along the grid; some spherical species were present (diameter = 22 - 25 nm) and some cylindrical or "wormlike" structures were

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observed. The sizes of the cylinders vary in length from 60 to 250 nm and the thickness was in the range of 15 - 25 nm. The oblong structures were more difficult to measure as the lengths varied quite a bit and thus a range is reported rather than an average. The solution of 4.3b in THF:heptane was analyzed using DLS experiments and the hydrodynamic radius ($R_h = 75 \text{ nm}$) was similar to that of 4.3a. Once again, the $R_h$ of 4.3b in THF:heptane was significantly higher than the $R_h$ of 4.3b in THF (4.3b: $R_h = 5 \text{ nm}$). The increase in the poly(methylene phosphine) chain length while decreasing the length of the polyisoprene block results in a change from well defined nanospheres to “wormlike” structures. To confirm this hypothesis, analysis of macromolecule 4.3c was necessary. It has the shortest PI length and longest PMP segment of the three block copolymer samples and the expected trend is that longer cylindrical structures will result from solution self-assembly.

Macromolecule 4.3c was not completely soluble in n-heptane and was dissolved in a THF n-heptane mixture (20% THF: 80% heptane). Upon drop-casting the solution of 4.3c onto a TEM grid for analysis, ordered cylinders were observed. These structures are long connected networks on the order of hundred’s of nm but are extremely difficult to measure. DLS measurements revealed the large micelle size (ca. 1400 nm) to corroborate the TEM analysis. Importantly, the expected behavior was observed from 4.3b to 4.3c, that the decrease in PI length coupled with the increase in the PMP segment resulted in a size increase for the self-assembled nanostructures.

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Figure 4.4 TEM images at 500 nm and 100 nm resolution which were formed from slow evaporation of a dilute n-heptane solution containing polyisoprene-block-poly(methyleneephosphine-gold(I)). (a) – 4.3a, (b) – 4.3b, (c) – 4.3c.

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4.3 Conclusions

New polyisoprene-block-poly(methylene phosphine) copolymers have been synthesized by sequential anionic polymerization of isoprene and MesP=CH2 using 0.6BuLi. As polyisoprene is soluble in non-polar solvents and poly(methylene phosphine) is not, I hypothesized that self-assembly would be feasible with these systems. Three copolymer samples were prepared with different polyisoprene and poly(methylene phosphine) chain lengths. Each block copolymer was combined with (tht)AuCl to form a phosphine-AuCl coordination complex. These metal-containing copolymers were then dissolved in n-heptane and their solution self-assembly properties were analyzed by TEM and DLS. The TEM images indicated that morphology control is possible with nanospheres and cylinders both being accessible simply by altering the length of the polyisoprene and poly(methylene phosphine) chain lengths in the copolymer samples. Further work will focus on attempting different solvents for self-assembly, and trying to exert more control over the self-assembled structures.

4.4 Experimental

4.4.1 Materials and General Procedures

All manipulations of air and/or water sensitive compounds were performed under pre-purified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology Inc. glovebox. Hexanes, toluene and CH2Cl2 were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. Methanol was degassed prior to use. CD2Cl2 was purchased from Cambridge Isotope Laboratories and dried over molecular sieves (3 Å). 0.6BuLi (1.6 M in hexanes) and n-heptane (spectrophotometric grade) were purchased from Aldrich used as received. Alkyl lithium reagents were titrated prior to use. Isoprene was purchased from Aldrich and distilled prior to use. MesP=CH2 and (tht)AuCl were prepared following literature procedures.

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$^{31}$P NMR spectra were recorded on Bruker AV300 or AV400 spectrometers at room temperature. Chemical shifts for $^{31}$P NMR spectra are reported relative to H$_3$PO$_4$ as an external standard (85% in H$_2$O, δ = 0).

Molecular weights were estimated by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm) HR5E (2000-4 000 000), HR4 (5000-500 000), and HR2 (500-20 000), Waters 2410 differential refractometer (λ = 940 nm, 40 °C), Wyatt tristar miniDAWN (laser light scattering detector operating at 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. 2 mg mL$^{-1}$). The dn/dc of polyisoprene has been previously reported (dn/dc = 0.129 mL g$^{-1}$). TEM images were collected at the UBC Biol Imaging Facility on a Hitachi H7600 TEM (120 kV tungsten filament) equipped with a side mount AMT Advantage (1 mega-pixel) CCD camera (Hamamatsu ORCA). The sample solutions were deposited on a Formvar-coated TEM grid and evaporated to dryness.

DLS experiments were performed with a Coulter N4 Plus DLS instrument equipped with a 10-mW helium-neon laser (λ = 632.8 nm) and thermoelectric temperature controller. Measurements were taken at a 90° scattering angle in a 3 × 3-mm quartz cuvette on solutions that had been equilibrated at 25 °C. Particle sizes were estimated by SDP weight and intensity analyses.

### 4.4.2 Preparation of PI$_{404}$—b—PMP$_{32}$

To a stirred solution of isoprene (2.0 g, 29 mmol) in THF (1.0 mL) was added 45 μL of $^n$BuLi (1.36 M, 0.061 mmol) in hexanes via 100 μL syringe. The reaction mixture turned yellow immediately and was stirred for approximately 45 min. A drop of the reaction mixture was removed and added to 50 mL of methanol. The polymer 4.1a precipitated out of solution as a white solid. After isolation, H-terminated polyisoprene was dried in vacuo and analyzed using GPC-LLS ($M_n = 27 500$ g mol$^{-1}$, PDI = 1.05). To the reaction mixture containing the living

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polyisoprene, a solution of MesP=CPh₂ (0.430 g, 1.36 mmol) in a minimal amount of THF was added. The solution immediately turned red and was allowed to stir for several days at which point the reaction mixture was almost black in colour. The solution was added dropwise into methanol (2 x 100 mL) and filtered. Volatiles were removed \textit{in vacuo} at 60 °C for several hours. The product was isolated as a yellow powder. Yield = 1.69 g (70%). δ\textsubscript{p}(121.5 MHz; THF; H\textsubscript{3}PO\textsubscript{4}) – 7 ppm (br s). GPC-LLS (THF): \(M_n = 38\ 500\ \text{g mol}^{-1}\), PDI = 1.12, dn/dc = 0.129.

4.4.3 Preparation of Pl\textsubscript{222–b–PMP\textsubscript{77}}

To a stirred solution of isoprene (0.68 g, 10 mmol) in THF (0.5 mL) was added 20 μL of \textsuperscript{6}BuLi (1.36 M, 0.027 mmol) in hexanes via 100 μL syringe. The reaction mixture turned yellow immediately and was stirred for approximately 45 min. A drop of the reaction mixture was removed and added to 50 mL of methanol. The H-terminated polyisoprene precipitated out of the solution as a white solid and was analyzed using GPC-LLS (\(M_n = 15\ 100\); PDI = 1.06). To the living polyisoprene was added a solution of MesP=CPh₂ (0.520 g, 1.6 mmol) in a minimal amount of THF. The solution immediately turned red and was allowed to stir for 24 h at which point the reaction mixture was almost black in colour. The solution was added dropwise into methanol (2 x 100 mL) and filtered. Volatiles were removed \textit{in vacuo} at 60 °C for several hours. The product was isolated as a yellow powder. Yield = 0.86 g (72%). δ\textsubscript{p}(162 MHz; THF; H\textsubscript{3}PO\textsubscript{4}) – 7 ppm (br s). GPC-LLS (THF): \(M_n = 39\ 400\ \text{g mol}^{-1}\), PDI = 1.06, dn/dc = 0.157.

4.4.4 Preparation of Pl\textsubscript{164–b–PMP\textsubscript{85}}

To a stirred solution of isoprene (0.68 g, 10 mmol) in THF (0.5 mL) was added 35 μL of \textsuperscript{6}EuLi (1.36 M, 0.048 mmol) in hexanes via 100 μL syringe. The reaction mixture turned yellow immediately and was stirred for approximately 45 min. A drop of the reaction mixture was removed and added to 50 mL of methanol. H-terminated polyisoprene precipitated out of the solution as a white solid and was analyzed using GPC-LLS (\(M_n = 11\ 200\); PDI = 1.09). A solution of MesP=CPh₂ (1.29 g, 4.1 mmol) in a minimal amount of THF was added to the living
polyisoprene. The solution immediately turned red and was allowed to stir for 24 h after which, the mixture was added dropwise into methanol (2 × 100 mL) and filtered. Several washings of the polymer with hexanes (2 × 100 mL) removed quenched polyisoprene homopolymer. Volatiles were removed in vacuo at 60 °C for several hours. The product was isolated as a yellow powder. Yield = 0.99 g (51%). δₚ(162 MHz; THF; H₃PO₄) = 7 ppm (br s). GPC-LLS (THF): $M_n = 38200$ g mol⁻¹, PDI = 1.24, dn/dc = 0.190.

4.4.5 Preparation of Pl₄₀₄—b—(PMP·AuCl)₃₂

A solution of (tht)AuCl (9 mg, 0.028 mmol) in CH₂Cl₂ (5 mL) was added to a solution of (Pl₄₀₄—b—PMP₃₂) (50.0 mg, $M_n = 38500$, PDI = 1.12) in CH₂Cl₂ (5 mL) and stirred for 1 h. The solvent was removed in vacuo resulting in a white solid. Toluene (2 × 3 mL) followed by hexanes (2 × 5 mL) were added to the product and subsequently removed in vacuo to ensure the removal of tht. The product was dried overnight in vacuo. Yield = 52 mg (93%). δₚ(121.5 MHz; THF; H₃PO₄) 25 (br s). GPC-LLS (THF): $M_n = 43500$, PDI = 1.18, dn/dc = 0.129.

4.4.6 Preparation of Pl₂₂₂—b—(PMP·AuCl)₇₇

To a stirring solution of copolymer Pl₂₂₂—b—PMP₇₇ (50 mg, $M_n = 39400$, PDI = 1.06) in CH₂Cl₂ (3 mL) was added (tht)AuCl (25 mg, 0.078 mmol) in CH₂Cl₂ (2 mL). After stirring for 1 h, the reaction was monitored by $^{31}$P NMR spectroscopy ($δ = 25$ br). The solvent was removed in vacuo resulting in a yellow solid. The product was dissolved in a minimal amount of CH₂Cl₂ and precipitated from hexanes. Toluene (2 × 3 mL) followed by hexanes (2 × 5 mL) were added to the product and subsequently removed in vacuo to ensure the removal of tht. The product was dried overnight in vacuo. Yield = 54 mg (79 %). δₚ(121.5 MHz; THF; H₃PO₄) 25 (br s). GPC-LLS (THF): $M_n = 44800$ g mol⁻¹, PDI = 1.10, dn/dc = 0.157.
4.4.7 Preparation of \( \text{PI}_{164-b}-(\text{PMP-AuCl})_{85} \)

To a stirring solution of copolymer \( \text{PI}_{164-b} \)-\( \text{PMP}_{85} \) (68 mg, \( \text{M}_n = 38200 \), PDI = 1.24) in \( \text{CH}_2\text{Cl}_2 \) (5 mL) was added (tht)AuCl (51 mg, 0.16 mmol) in \( \text{CH}_2\text{Cl}_2 \) (5 mL). After stirring for 1 h, the reaction was monitored by \( ^{31}\text{P} \) NMR spectroscopy (\( \delta = 25 \text{ br} \)). The solvent was removed \textit{in vacuo} resulting in a yellow solid. Toluene (2 x 3 mL) followed by hexanes (2 x 5 mL) were added to the product and subsequently removed \textit{in vacuo} to ensure the removal of tht. The product was dried overnight \textit{in vacuo}. Yield = 104 mg (99%). \( \delta_{\text{p}}(121.5 \text{ MHz;} \text{THF}; \text{H}_3\text{PO}_4) 25 \text{ (br s). GPC-LLS (THF): } M_n = 57900 \text{ g mol}^{-1}, \text{PDI} = 1.15, \text{dn/dc} = 0.190. \)

4.4.8 Preparation of spherical structure from \( \text{PI}_{404-b}-(\text{PMP-AuCl})_{32} \)

To polymer 4.3a (2.9 mg) was added \( n \)-heptane (4 mL). The solution was sonicated for approximately 10 min to assure complete dissolution of the polymer sample. The solution was dropcast on a Formvar-coated TEM grid. Solution was filtered through 0.2 \( \mu \text{m} \) filter before DLS analysis. DLS: \( R_h = 82 \text{ nm.} \)

4.4.9 Preparation of wormlike structure from \( \text{PI}_{222-b}-(\text{PMP-AuCl})_{77} \)

Macromolecule 4.3b (3.1 mg) was dissolved in THF (0.5 mL) and to this solution was added \( n \)-heptane (3.5 mL). The opaque solution was sonicated for approximately 10 min to ensure complete dissolution of the polymer sample. The solution was dropcast on a Formvar-coated TEM grid. Solution was filtered through 0.2 \( \mu \text{m} \) filter before DLS analysis. DLS: \( R_h = 75 \text{ nm.} \)
4.4.10 Preparation of long cylindrical structure from PI\textsubscript{164-b-(PMP-AuCl)}\textsubscript{85}

Macromolecule 4.3c (2.9 mg) was dissolved in THF (2.0 mL) and to this solution was added \textit{n}-heptane (6.0 mL). The opaque solution was sonicated for approximately 10 min to ensure complete dissolution of the polymer sample. The solution was dropcast on a Formvar-coated TEM grid. Solution was filtered through 0.2 \textmu m filter before DLS analysis. There is potentially some aurophilic interactions which are partially responsible for the large value of $R_h$. DLS: $R_h = \text{ca.} 600$ nm.
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Chapter 5

Chemical Functionality of Poly(methylene phosphine): Phosphine-Borane Adducts and Methylphosphonium Ionomers*

5.1 Introduction

Main-group-element-containing macromolecules have garnered considerable attention in recent years. In the quest for polymers exhibiting unusual properties, the poly(methylene phosphine) is an attractive starting material. The phosphine segments of this homopolymer, which are present at every second atom along the polymer backbone, could be exploited for facile polymer modification. There are several possibilities to functionalize the —[MesP—CPh₂]— polymer: either through coordination chemistry, or perhaps by an oxidation reaction of the three coordinate phosphine to afford phosphorus(V) polymers. Some previous work in this area has already been reported by our group; polymeric phosphine oxides and phosphine sulfides were synthesized by treatment of —[MesP—CPh₂]— with H₂O₂ and S₈, respectively (Scheme 5.1). Although a well-defined metal complex was not isolated, Dr. Chi-Wing Tsang illustrated that the poly(methylene phosphine) prepared from monomer 5.1 is an effective support for Pd-catalyzed Suzuki cross-coupling. More recently, Bronwyn Gillon prepared well-defined phosphine gold coordination complexes of [MesP—CPh₂]ₙ upon treatment of poly(methylene phosphine) with tetrahydrothiophene gold(I) chloride (Scheme 5.1).

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Scheme 5.1  Functionalization of poly(methylene phosphine) using H$_2$O$_2$, S$_8$ and AuCl. What will occur if the poly(methylene phosphine) is treated with common electrophiles.

Although macromolecules possessing trivalent phosphorus atoms in the main chain are common,\textsuperscript{6,7,10,13,17-19} polymer 5.2 is the only polymer with an alternating phosphorus carbon backbone. As described in Chapter 2, the living anionic polymerization of 5.1 provides a mild route to controlled molecular weight poly(methylene phosphine) 5.2 and the phosphine moieties in 5.2 can be treated with some simple main group electrophiles to access polymers possessing unique features. In particular, phosphine-borane adducts are of interest as potential protecting groups for the slightly air-sensitive phosphine environments in 5.2 and for their potential use as pre-ceramic materials.\textsuperscript{3} In addition, alkylation of the phosphine moieties would provide a convenient route to novel phosphonium ionomers.\textsuperscript{20} Ionomers or polymers with ionic groups, are of interest in applications ranging from drug delivery to fuel cell membranes.\textsuperscript{21,22} The successful methylation of 5.2 would also provide access to polymers with a high ion density in the main chain due to the close proximity of phosphorus atoms.

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In this Chapter, work on the chemical functionalization of phosphine polymer 5.2 through boronation and methylation reactions is described. To simplify polymer characterization, the potential reactivity of the high molecular weight polymer is first assessed by comparison to molecular model systems. Although borane functionalities may be incorporated at every atom along the main chain in 5.2, only ca. 50% of the phosphine units could be methylated by MeOTf.

### 5.2 Results and Discussions

#### 5.2.1 Synthesis of molecular model compounds

Phosphines 5.3a and 5.3b were prepared from 5.1 following the literature procedures.\textsuperscript{23, 24} These molecular compounds function as useful models to evaluate the chemical functionality of polymer 5.2. In an attempt to form a phosphine-borane adduct, a pale yellow solution of 5.3a in THF was treated with BH\textsubscript{3}-SMe\textsubscript{2} in Et\textsubscript{2}O at \(-78\) °C. Analysis of the reaction mixture using \textsuperscript{31}P NMR spectroscopy revealed that the signal for free phosphine 5.3a (\(\delta = -24.0\)) was replaced by a new signal (\(\delta = 18.3\)). Likewise, treating silyl-terminated 5.3b with BH\textsubscript{3}-SMe\textsubscript{2} affords a single product as judged by its \textsuperscript{31}P NMR spectrum (\(\delta = 24.8\) cf. 5.3b: \(\delta = -23.9\)). Crystals of each product were obtained directly from the reaction solutions. Analysis of the crystals by x-ray crystallography confirmed that phosphine-boranes 5.4a and 5.4b had been formed successfully (see Figures 5.1 and 5.2). Compounds 5.4a and 5.4b were further characterized using \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy. Interestingly, the borane can conveniently be removed to regenerate 5.3 by treating either phosphine-borane with amines such as diethylamine.

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Scheme 5.3 Model compound preparation from MesP=CPh₂ phosphalkene. The three-coordinate phosphine (5.3) is coordinated reversibly to BH₃.

We are also interested in the functionalization of poly(methylene phosphine) with CH₃⁺, which is isoelectronic to BH₃. From a polymer perspective, this would provide access to novel methylphosphonium polyelectrolytes. We chose MeOTf as the methylating agent rather than milder agents due to the anticipated difficulty fully alkylating the closely spaced phosphorus atoms in 5.2. Thus, a solution of 5.3a in CH₂Cl₂ was treated with excess MeOTf to give compound 5.5 (δ₃¹P = 29.8) Slow evaporation of the solvent afforded large colorless crystals of the air-stable phosphonium salt 5.5. A single crystal of compound 5.5 was analyzed using x-ray diffraction (Figure 5.3). The analytically pure crystals were further characterized by ³¹P, ¹H, ¹³C and ¹⁹F NMR spectroscopy. The ¹H NMR spectrum for compound 5.5 (in DMSO-d₆) is consistent with the proposed product, although it is not possible to assign the overlapping signals for the methyl protons (i.e. P–CH₃, α–CH₃ and ρ–CH₃). In the ¹⁹F NMR spectrum, a sharp signal is observed at −77.5 ppm, which is typical of uncoordinated triflate.

Scheme 5.4 Methyl phosphonium model compound preparation from the three-coordinate phosphine (compound 5.3a)

5.2.2 X-ray crystallography

Compounds 5.4a, 5.4b and 5.5 were characterized crystallographically and the molecular structures are shown in Figures 5.1, 5.2 and 5.3, respectively. Important metrical parameters are found in the figure captions and details of the structure solution and refinement are found in Table 5.1. Interestingly, the P(1)–B(1) bond [1.831(6) Å] in 5.4a is shorter than the

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analogous bond in 5.4b [1.977(2) Å]. For comparison, the typical range for P-B bonds is 1.90 to 1.95 Å$^{25}$ and the bond length in Ph$_3$P–BH$_3$ [1.917 Å].$^{26}$ We speculate that the apparent shortening of the P–B bond in 5.4a results from difficulty modelling the disorder in the crystal rather than providing chemical insight into the bonding in 5.4a (see Experimental Section for details).

The P–C bonds in 5.4a [avg. 1.815(8) Å] and 5.4b [avg. 1.853(3) Å] are in the range typical for P–C bonds (1.85 – 1.90 Å).$^{25}$ For comparison, the analogous bonds in 5.3a [avg. 1.858(2)] and 5.3b [avg. 1.853(3) Å] are similar in length to those in 5.4a and 5.4b. Interestingly, the longest P–C bond is the P–CPh$_2$R bond [5.4a: P(1)–C(11) = 1.837(4) Å, 5.4b: P(1)–C(11) = 1.894(1) Å]. These P–CPh$_2$R bonds in 5.4a and 5.4b are shorter than in the free phosphines [5.3a: 1.882(1) Å, 5.3b: 1.902(1) Å].$^{24}$ The shortening is less significant between 5.3b and 5.4b.

Figure 5.1 Solid state molecular structure of 5.4a (ORTEP). Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)–C(1) = 1.814(4), P(1)–C(10) = 1.795(5), P(1)–C(11) = 1.837(4), P(1)–B(1) = 1.831(6); C(1)–P(1)–C(11) = 105.0(2) C(2)–C(1)–P(1) = 120.4(4), C(8)–C(1)–P(1) = 121.0(3), C(12)–C(11)–P(1) = 111.6(3), C(18)–C(11)–P(1) = 112.0(3), C(10)–P(1)–B(1) = 102.6(3), B(1)–P(1)–C(11) = 115.1(3), C(1)–P(1)–B(1) = 121.1(3).

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than between 5.3a and 5.4a. Presumably, this reflects the increased steric congestion in the former [-CPh₂(SiMe₂H) vs -CPh₂(H)]. Similarly, in methylphosphonium 5.5 the P–Me bonds (avg. 1.794(3) Å) and P–Mes [P(1)–C(1) = 1.809(2) Å] bonds are significantly shorter than the P–CPh₂H [P(1)–C(12) = 1.854(2) Å]. The P–C bonds in 5.5 are all shortened considerably with respect to the analogous bonds in 5.3a [P–Me: Δ(P–C) = 0.046(3); P–Mes: Δ(P–C) = 0.043(2); P–CPh₂H: Δ(P–C) = 0.030(2) Å].

For the most part, the bond angles in compounds 5.4a, 5.4b and 5.5 are unremarkable with the exception of the Mes–P–CPh₂R angles. In particular, this angle expands significantly upon coordination. For example, Mes–P–CPh₂R angle is between 105 and 108° in 5.4a, 5.4b and 5.5 whereas the analogous angle in 5.3a is just 100°. This is likely a consequence of increased s-character in the phosphorus bonds upon quaternization of the phosphorus lone pair.

![Figure 5.2](image.png)

**Figure 5.2** Solid state molecular structure of 5.4b (ORTEP). Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)–C(1) = 1.846(2), P(1)–C(10) = 1.819(2), P(1)–C(11) = 1.894(2), P(1)–B(1) = 1.977(2), C(11)–Si(1) = 1.941(2), C(24)–Si(1) = 1.857(2); C(1)–P(1)–C(11) = 107.8(1), C(2)–C(1)–P(1) = 117.6(1), C(8)–C(1)–P(1) = 124.1(1), C(12)–C(11)–P(1) = 106.6(1), C(18)–C(11)–P(1) = 112.0(1), C(10)–P(1)–B(1) = 100.7(1), C(11)–P(1)–B(1) = 122.9(1), C(1)–P(1)–B(1) = 110.6(1).
Figure 5.3  Solid state molecular structure 5.5 (ORTEP). Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°).

\[
\begin{align*}
\text{P}(1)–\text{C}(1) & = 1.809(2), \text{P}(1)–\text{C}(10) = 1.797(2), \text{P}(1)–\text{C}(11) = 1.790(2), \text{P}(1)–\text{C}(12) = 1.854(2); \\
\text{C}(1)–\text{P}(1)–\text{C}(12) & = 107.2(1), \text{C}(2)–\text{C}(1)–\text{P}(1) = 124.1(2), \text{C}(8)–\text{C}(1)–\text{P}(1) = 116.5(2), \text{C}(12)–\text{P}(1)–\text{C}(11) = 109.0(1), \text{C}(12)–\text{P}(1)–\text{C}(10) = 110.5(1).
\end{align*}
\]

5.2.3 Chemical functionalization of poly(methylenephosphine)

Following the synthesis and characterization of the model compounds, the preparation of phosphine-borane and methyl phosphonium polymers was attempted. The anionic polymerization of 5.1 in glyme using \(^{6}\text{BuLi}\) as the initiator afforded poly(methylenephosphine) 5.2 ($M_n$ of $3.89 \times 10^4$ g mol\(^{-1}\); PDI = 1.34).\(^{27}\) The polymerization was not conducted using the rigorous standards required for a living polymerization and, consequently, the molecular weight distribution (PDI) is greater than 1.1. In an attempt to prepare poly(methylenephosphine borane) 5.6, the phosphine polymer 5.2 was treated with BH\(_3\)-SMe\(_2\) (1.4 equiv). Polymer 5.6 was isolated as a colorless solid after the volatiles were removed \textit{in vacuo}. The $^{31}$P NMR spectrum

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of 5.6 is shown in Figure 5.4(b) and the chemical shift for the borane polymer is similar to models 5.4a and 5.4b ($\delta = 18.3$ and $24.8$, respectively). The spectrum shows no evidence for the presence of uncoordinated phosphine moieties [cf. Figure 5.4(a)].

![Scheme 5.5 Borane protection of poly(methylene phosphine) using BH$_3$SMe$_2$. The BH$_3$ group can be removed by treatment of the polymer with amine.](image)

Interestingly, the signals observed for 5.6 are much sharper and are better resolved than those observed for 5.2. For example, the $^{31}$P NMR spectrum of phosphine-borane polymer 5.6 exhibits two signals at $32.4$ ppm (minor) and $26.8$ ppm (major). In addition, a small shoulder is observed on the high field end of the signal at $26.8$ ppm. In contrast, uncomplexed poly(methylene phosphine) 5.2 shows broad unresolved signals that likely encompass the different environments which are resolved in 5.6. We speculate that the observation of multiple signals in the $^{31}$P NMR spectrum of macromolecule 5.6 may be an indication of the tacticity in poly(methylene phosphine)s. Unfortunately, this hypothesis cannot be confirmed until control over the tacticity can be obtained (i.e. isotactic or syndiotactic).

![Figure 5.4 Stack plot of $^{31}$P NMR spectra of (a) poly(methylene phosphine) 5.2 in THF, (b) poly(methylene phosphine borane) 5.6, (c) and poly(methylene phosphonium triflate) 5.7.](image)

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The absolute number average molecular weight \((M_n)\) of 5.6 was determined using triple detection GPC \((M_n = 4.13 \times 10^4 \text{ g mol}^{-1}; \text{PDI} = 1.26)\), very similar to that of 5.2 \((M_n = 3.89 \times 10^4 \text{ g mol}^{-1}; \text{PDI} = 1.34)\). The molecular weight data of 5.2 and 5.6 confirms that no backbone degradation occurs during the BH\(_3\) protection. Notably, the molecular weight distribution is much narrower for 5.6 than for 5.2. This is surprising since the polydispersity indices should not change upon complexation. We postulate that the larger PDI for 5.2 is due to some interaction of the phosphine moieties in the main chain with the GPC columns. Problems with separation of phosphine polymers using GPC has been observed previously for phosphine polymers.\(^{28}\) This is an important consideration for the entire thesis and it may be more appropriate to run the polymers as oxidized samples. The reaction of polymer 5.6 with excess amine such as NEt\(_3\) results in the clean deprotection of the BH\(_3\) group to form poly(methylene phosphine) 5.2. The reformation of 5.2 was confirmed by \(^{31}\)P NMR spectroscopy and GPC analysis \((M_n = 3.71 \times 10^4 \text{ g mol}^{-1}; \text{PDI} = 1.36)\). Thus, borane may be a useful protecting group for the mildly air sensitive polymer.

\[ \text{PHPhMePh} \]
\[ \text{n.Bu-P-C=H} \]
\[ \text{MesPh} \]

\[ \xrightarrow{\text{MeOTf (excess)}} \]
\[ \text{CH}_2\text{Cl}_2 \]

\[ \text{n.Bu-P-C=H} \]
\[ \text{MeOTf} \]
\[ \text{MePh} \]
\[ \text{MesPh} \]

\[ \xrightarrow{\text{OTf}} \]

\[ \text{CH}_2\text{Cl}_2 \]

**Scheme 5.6** Methylation of poly(methylene phosphine).

The synthesis of poly(methylene phosphonium triflate) proved to be more difficult than the borane polymer. A solution of 5.2 in CH\(_2\)Cl\(_2\) was treated with MeOTf (excess) and was heated to 50 °C. The reaction mixture was monitored by \(^{31}\)P NMR spectroscopy and signals for free phosphine were still observed even after several days. The \(^{31}\)P NMR spectrum of the product after precipitation is shown in Figure 5.4(c). Importantly, a signal is observed at 31 ppm which is consistent with methylphosphonium moieties by comparison to the chemical shift of 5.5 \((\delta_{31P} = 29.8)\). Integrating the signals for the methylated \((\delta_{31P} = 31)\) and unmethylated \((\delta_{31P} = -7)\) phosphorus atoms in 5.7 suggests that approximately 50 % of the phosphorus atoms are methylated. This experiment was repeated several times and, even after several days of heating.

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5.2 with excess MeOTf, the degree of methylation never exceeded 50%. Complete methylation would require a formal positive charge at every second atom in the polymer backbone. We speculate that phosphorus atoms are methylated in a roughly alternating fashion rather than in a completely random fashion as shown in Figure 5.5. For both steric and electronic reasons the alternating addition would be favourable and would lead to ca. 50% methylation.

\[ \text{--P}^+ \text{P} -- \text{P}^+ \text{P} -- \text{P}^+ \text{P} \]

\[ \text{--P} \text{P} \text{P}^+ \text{P}^+ \text{P}^+ \text{P}^+ \text{P}^+ \text{P}\]

**Figure 5.5** The possibilities for methylation of P chain. (a) alternating positive charge, (b) random distribution of positive charge.

Polymer 5.7 was characterized by $^1$H, $^{31}$P, $^{19}$F and $^{13}$C NMR spectroscopy. The $^{13}$C NMR spectrum of poly(methylene phosphonium triflate) 5.7 in DMSO-d$_6$ is shown in Figure 5.6 (bottom) and, although the signals are broadened significantly, the spectrum shows signals in the same regions with that for model compound 5.5 [Figure 5.6 (top)]. Of note, are the signals assigned to P-CH$_3$ ($\delta$$_{13}$C = 13.2) and O$_2$SCF$_3$ ($\delta$$_{13}$C = 120.7, $q$, $^1$J$_{CF}$ = 322 Hz). Macromolecule 5.7 is soluble in DMSO and, consequently GPC analysis in THF could not be obtained. Static light scattering experiments were attempted with this ionic polymer but reliable molecular weight data could not be attained.
5.3 Conclusions

In closing, we have investigated the chemical functionality of poly(methylenephosphine) 5.2 through phosphine coordination to main group Lewis acids. The chemical functionality of 5.2 was examined by reacting Mes(Me)P—CPh₂R [R = H (5.3a) or SiMe₂H (5.3b)], molecular model compounds for the polymer, with BH₃·SmMe₂ or MeOTf. Three new functionalized model systems were prepared and characterized crystallographically; namely, Mes(Me)P(BH₃)—CPh₂H (5.4a), Mes(Me)P(BH₃)—CPh₂SiMe₂H (5.4b) and [Mes(Me)₂P—CPh₂H]⁺ OTf⁻ (5.5). The analogous reactions were successful when polymer 5.2 was used. Specifically, we report a new

![Figure 5.6](image)

Figure 5.6 ¹³C{¹H} NMR spectra of compound 5.5 (top) and macromolecule 5.7 (bottom). * DMSO—d⁶.
phosphine-borane polymer \( n\text{-}Bu[\text{MesP}(\text{BH}_3)\text{CPh}_2]H \) (5.6) and a methylphosphonium polymer \( n\text{-}Bu[\text{MesP} \text{CPh}_2]_\sim \text{C}[\text{MesP(Me)}\text{CPh}_2]H^+\text{OTf}^- \) (5.7: \( x:y = \text{ca.} 1:1 \)). These new polymers were fully characterized spectroscopically and absolute molecular weights were determined for 5.6.

Future work will focus on studying the properties of the phosphine-borane and methylphosphonium polymers reported herein. The prospect of preparing water soluble phosphorus homo- or copolymers by post polymerization modification of 5.2 is an exciting synthetic target.

5.4 Experimental

| Table 5.1 X-ray crystallographic data of 5.4 and 5.5 |
|----------------|----------------|----------------|
| Crystal        | 5.4a           | 5.4b           |
| Formula        | \( \text{C}_{23}\text{H}_{28}\text{PB} \) | \( \text{C}_{25}\text{H}_{34}\text{PSi} \) |
| Formula Weight | 346.23         | 404.39         |
| Crystal System | monoclinic     | triclinic      |
| Space Group    | \( P 2_1/n \)  | \( P 1 \)      |
| Color          | colourless     | colourless     |
| \( a \) (Å)    | 8.342(5)       | 10.128(5)      |
| \( b \) (Å)    | 13.896(5)      | 10.750(5)      |
| \( c \) (Å)    | 16.931(5)      | 12.890(5)      |
| \( \alpha \) (°) | 90.000(5)    | 108.324(5)     |
| \( \beta \) (°) | 99.909(5)     | 93.499(5)      |
| \( \gamma \) (°) | 90.000(5)     | 117.089(5)     |
| \( V \) (Å³)   | 1933.4(15)     | 1151.0(9)      |
| \( Z \)        | 4              | 2              |
| \( T \) (K)    | 173(2)         | 173(2)         |
| \( \mu \) (Mo Kα) (cm⁻¹) | 1.45       | 1.80           |
| Crystal Size (mm) | 0.20×0.60×0.90 | 0.40×0.20×0.10 |
| \( D_{\text{calc}} \) (g cm⁻³) | 1.189     | 1.167          |
| \( 2\theta \) (°) | 47.3        | 56.0           |
| No. of Reflections | 26106     | 23770          |
| No. of unique data | 2889       | 5485           |
| \( R_{\text{int}} \) | 0.077       | 0.029          |
| Reflections/parameters ratio | 12.45    | 14.10          |
| \( R_1 \), \( wR_2 \) (all data)° | 0.073; 0.190 | 0.036; 0.091  |
| \( R_1 \), \( wR_2 \) (all data)° | 0.110; 0.222 | 0.045; 0.097  |
| \( GOF \) | 1.10          | 1.04           |

° \( R_1 = \sum |F_o| - |F_c| / \sum |F_o| \), \( wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}} \)

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5.4.1 Materials and general procedures

All manipulations of air and/or water sensitive compounds were performed under pre-purified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology glovebox. Hexanes, and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. CDCl₃ was distilled from P₂O₅ and degassed. CD₂Cl₂ and DMSO-d⁶ were purchased from Cambridge Isotope Laboratories and were used as received. Methanol was degassed prior to use. NEt₃, HNEt₂, DBU, MeLi (1.6 M in Et₂O) ⁷BuLi (1.6 M in hexanes), BH₃-SMe₂ (2 M in Et₂O) and MeOTf were purchased from Aldrich and used as received. Alkyl lithium reagents were titrated prior to use. MesP=CPh₂ (5.1), Me(Mes)P=CPH₂(H) (5.3a) and Me(Mes)P=CPH₂(SiMe₂H) (5.3b) were prepared using literature methods. ²³ ²⁴ Polymer 5.2 was prepared according to literature procedure. ²⁷

¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported relative to residual CHCl₃ (δ = 7.26 for ¹H and and 77.23 for ¹³C), CHDCI₂ (δ = 5.32 for ¹H and and 54.00 for ¹³C) and DMSO-d⁶ (δ = 2.50 for ¹H and 39.51 for ¹³C). CFCl₃ was used as an external standard δ = 0.0 for ¹⁹F. 85% H₃PO₄ was used as an external standard δ = 0.0 for ³¹P. Molecular weights were determined by triple detection gel permeation chromatography (GPC – LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 x 300 mm; HR5E, HR4 and HR2), Waters 2410 differential refractometer, Wyatt tristar 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. 2 mg mL⁻¹). Elemental analysis was conducted at the University of British Columbia.

5.4.2 Preparation of Mes(Me)P(BH₃)–CHPh₂ (5.4a)

An ethereal solution of BH₃-SMe₂ (1.4 mL, 2 M, 2.8 mmol) was added dropwise by syringe to a cooled solution (−78 °C) of compound 5.3a (0.94 g, 2.8 mmol) in THF (40 mL). The

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reaction mixture was allowed to warm slowly to room temperature and an aliquot was removed for analysis by $^{31}$P NMR spectroscopy ($\delta = 18.3$, br). After removal of the volatiles in vacuo, an oil was obtained which crystallized slowly over a period of 10 h. Yield: 0.72 g, 74%. $\delta_P$(121.5 MHz; CDCl$_3$; H$_3$PO$_4$) 18.3 (1 P, br s). $\delta_H$(300.1 MHz, CDCl$_3$; SiMe$_4$) 7.69 – 7.17 (10 H, m, aryl H), 6.86 (2 H, s, m–H of Mes), 4.86 (1 H, d, $^2$J$_{PH}$ = 17 Hz, CHPh$_2$), 2.40 (6 H, s, o–CH$_3$), 2.27 (3 H, s, p–CH$_3$), 2 – 0.5 (3H, br q, BH$_3$), 1.69 (3 H, d, $^2$J$_{PH}$ = 9 Hz, PCH$_3$). $\delta_C$(75.5 MHz; CDCl$_3$; SiMe$_4$) unassigned) 143.9 (d, $J_{PC}$ = 9 Hz), 140.9 (d, $J_{PC}$ = 2 Hz) 137.2 (d, $J_{PC}$ = 3 Hz), 131.1 (d, $J_{PC}$ = 9 Hz), 129.9 (d, $J_{PC}$ = 5 Hz), 129.4 (d, $J_{PC}$ = 5 Hz), 128.6, 128.1 (d, $J_{PC}$ = 2 Hz), 127.4 (d, $J_{PC}$ = 2 Hz), 127.1 (d, $J_{PC}$ = 3 Hz), 123.4 (d, $J_{PC}$ = 46 Hz), 51.8 (d, $J_{PC}$ = 26 Hz), 24.4 (d, $J_{PC}$ = 4 Hz), 20.8, 15.7 (d, $J_{PC}$=39 Hz).

5.4.3 Reaction of 5.4a with Et$_2$NH

A solution of compound 5.4a (0.72 g, 2.1 mmol) in THF (5 mL) was combined with Et$_2$NH (7 mL). The reaction mixture was stirred for 4 h and an aliquot was removed for analysis by $^{31}$P NMR spectroscopy. Complete conversion to 5.3a (–24 ppm) was observed and the solvent was removed in vacuo. The resultant oil was dissolved in CH$_2$Cl$_2$ and washed with water. The aqueous phase was then extracted with CH$_2$Cl$_2$ (3 x 20 mL). The collected extracts were combined and dried over MgSO$_4$. Filtration of the CH$_2$Cl$_2$ solution and removal of the solvent in vacuo afforded 5.3a as an oil. Yield: 0.22 g, 31%.

5.4.4 Preparation of Mes(Me)P(BH$_3$)–CPh$_2$SiMe$_2$H (5.4b)

An ethereal solution of BH$_3$SMe$_2$ (0.6 mL, 2 M, 1.2 mmol) was added dropwise to a cooled solution (–78 °C) of phosphine 5.3b (0.47 g, 1.2 mmol) in THF (20 mL). The reaction mixture was slowly warmed to room temperature. After evaporation of the solvent in vacuo a white solid was obtained. The solid was recrystallized by slow evaporation in an inert atmosphere from a concentrated THF solution. Yield: 0.11 g, 22%. $\delta_P$(121.5 MHz; CDCl$_3$; H$_3$PO$_4$) 24.8 (1P, br s). $\delta_H$(300.1 MHz, CDCl$_3$; SiMe$_4$) 7.55 – 7.19 (10 H, m, aryl H), 6.69 (2 H, br

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s, m-Mes), 4.77 (1 H, m, Si-H), 2.5-0.5 (3H, br q, BH₃), 2.37 (6 H, br, o-CH₃), 2.22 (3 H, s, p-CH₃), 1.88 (3 H, d, ²Jph = 8 Hz, PCH₃), 0.12 (3 H, d, J = 3 Hz, SiCH₃), 0.0 (3 H, d, J = 3 Hz, SiCH₃). δc(75.5 MHz, CD₂Cl₂: SiMe₄) 145.2, 140.4 (d, Jpc = 2 Hz), 139.0 (d, Jpc = 4 Hz), 138.4 (d, Jpc = 4 Hz), 131.9, 131.8, 131.1 (d, Jpc = 9 Hz), 127.8, 127.5, 126.7, 125.7 (47 Hz), 48.4, 25.4 (br), 20.8, 16.8 (d, Jpc = 39 Hz), −3.5, −3.6.

5.4.5 Preparation of [Mes(Me)₂P—CPh₂H]OTf (5.5)

To a solution of compound 5.1 (2.00 g, 6.3 mmol) in THF (20 ml), was added MeLi (5.4 mL., 1.4 M, 7.6 mmol). The reaction mixture was stirred for 1 h and then solvent was removed in vacuo. Extraction of the reaction mixture with hexanes (3 × 10 mL) provided compound 5.3a as an oil. This yellow oil was dissolved in CH₂Cl₂ and added to MeOTf (2 eq.) in the glovebox. The reaction mixture was placed in a vial and slow evaporation afforded the crystalline salt. The crystals were dried for 72 h. Yield: 0.60 g, 19 %. δp(121.5 MHz; DMSO-d⁶; H₃PO₄) 29.8 (1 P, s). δH(300.1 MHz, DMSO-d⁶; SiMe₄) 7.57—7.39 (10 H, m, aryl H), 7.06 (2 H, s, m—H of Mes), 5.68 (1 H, d, ²Jph = 18 Hz, CPh₂), 2.33-2.27 (15 H, m, o—CH₃, p—CH₃, P—CH₃). δc(75.5 MHz; DMSO-d⁶; SiMe₄) (unassigned) 144.0 (d, Jpc = 3 Hz), 143.6 (d, Jpc = 10 Hz), 133.4 (d, Jpc = 4 Hz), 131.8 (d, Jpc = 12 Hz), 129.7 (d, Jpc = 6 Hz), 129.2 (d, Jpc = 2 Hz), 128.6 (d, Jpc = 2 Hz), 120.7 (q, ¹Jpc = 322 Hz), 114.7 (d, Jpc = 77 Hz), 49.1 (d, Jpc = 43 Hz), 23.7(d, Jpc = 4 Hz), 20.4, 13.2 (d, Jpc = 52 Hz): δF(282.4 MHz; DMSO-d⁶; CFCl₃) −77.5 (s, CF₃). Anal. Calcd. for C₂₅H₂₈PSO₃F₃: C, 60.47; H, 5.68. Found: C, 60.41; H, 5.66.

5.4.6 Preparation of n-Bu[MesP(BH₃)—CPh₂]ₙH (5.6)

Poly(methylenephosphine) 5.2 (0.35 g, 1.1 mmol) (Mₙ = 3.89 × 10⁴ g/mol, PDI = 1.34) was dissolved in THF (20 ml) and BH₃SMe₂ (0.75 ml, 2 M, 1.5 mmol) was added dropwise via syringe at −78 °C. The reaction mixture was allowed to slowly warm up to room temperature. After evaporation of the volatiles in vacuo a solid was obtained. Yield: 0.25 g, 68 %. Mₙ = 4.13 × 10⁴ g/mol, PDI = 1.26. δp(121.5 MHz; CDCl₃; H₃PO₄) 32.4 (1 P, br s), 26.8 (1 P, br s).

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5.4.7 Reaction of 5.6 with amines

A solution of the poly(methylenephosphine-borane) 5.6 (0.25 g) in THF was treated with excess amine (DBU, NEt₃, NEt₂H). The reaction was stirred for 12 h and an aliquot of the reaction was removed and analyzed using ³¹P NMR spectroscopy (δ₃¹P = −7). Upon removal of the solvent in vacuo, the polymer was dissolved in CH₂Cl₂ (15 ml) and washed with degassed water (2 x 5 ml). The organic layer was dried over MgSO₄ and solvent was removed in vacuo, affording 5.2. Yield: 0.22 g, 91 %. Mₙ = 3.71 x 10⁴ g/mol. PDI = 1.36.

5.4.8 Preparation of n-Bu[MesP—CPh₂]—[MesP(Me)—CPh₂]H (5.7)

To a solution of polymer 5.2 (0.40 g, 1.3 mmol) in CH₂Cl₂ (10 ml) was added excess methyl triflate (10 eq.). The reaction mixture was stirred overnight. Analysis of the mixture by ³¹P NMR spectroscopy exhibited two broad singlets with one signal at 31 ppm and the other at −7 ppm. Integration of the two signals revealed an approximate 1:1 ratio of the two signals. The polymer was isolated by precipitating a concentrated CH₂Cl₂ solution (ca. 1 mL) with hexanes (20 mL) (x3). The yellow solid was dried in vacuo at 80 °C overnight. Yield: 0.23 g, 46 %.

δ₁P(121.5 MHz; DMSO-d⁶; H₃PO₄) 31 (1P, br s), −7 (1P, br s). δ₁H(300.1 MHz, DMSO-d⁶; SiMe₄) 7.2 (12 H, br, m-Mes-H, Ph-H), 2.2 (15 H, o,p-CH₃, P-CH₃); δ₁C(75.5 MHz; DMSO-d⁶; SiMe₄) (unassigned), 145, 140, 133, 129, 120.7 (q, 1JCF = 320 Hz), 114, 49, 23, 20, 12; δ₁F(282.4 MHz; DMSO-d⁶;CFCl₃) −78.7 (s, CF₃).

5.4.9 X-ray crystallography

Crystal Data and refinement parameters are listed in Table 5.1. All single crystal were immersed in oil and mounted on a glass fiber. Data were collected at 173 ± 0.1K on a Bruker X8 APEX 2 diffractometer with graphite-monochromated Mo Ka radiation. Data was collected and integrated using the Bruker SAINT²⁹ software package. All structures were solved by direct methods⁰ and subsequent Fourier difference techniques and refined anisotropically for all non-
hydrogen atoms using the SHELXTL\textsuperscript{31} crystallographic software package from Bruker-AXS. All data sets were corrected for Lorentz and polarization effects.

Compounds 5.4\textbf{b} and 5.5 did not exhibit any crystallographic complexity. Data collection for compound 5.4\textbf{a} was attempted to $2\theta = 56^\circ$, however, due to poor quality crystals, no significant reflections were observed beyond $2\theta = 40^\circ$. We attribute this lack of long-range reflections to disorder in the crystal lattice. Although efforts to model the disorder have been thus far unsuccessful, we hypothesize the incorporation of non-boronated phosphine into the crystal lattice is responsible. The consequence of this lattice defect would be increased electron density near the phosphorus atom from the lone pair. Our efforts to model the location of the boron atom are thus complicated as software compensates for the electron density by shortening the P-B distance to the observed bond length.

CCDC reference numbers 668085 – 668087
5.5 References


20. Recently, an example of a methylated phosphole ionomer has been reported. Durben, S.; Dienes, Y.; Baumgartner, T. Org. Lett., 2006, 8, 5893.


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Chapter 6

Redox-Active Iron-Containing Polymers: Synthesis and Anionic Polymerization of a C-Ferrocenyl Substituted Phosphaalkene *

6.1 Introduction

Macromolecules containing transition metals are known to possess unique redox, magnetic, optical and electronic properties. These materials are attractive as potential ceramic precursors, catalyst supports and for specialty applications. The ferrocenyl moiety has played an integral role in the growth of metal-containing polymer science; many polymers are known where ferrocene is incorporated into the main chain, side-chain and even into dendrimers. The earliest ferrocene-containing polymers were prepared from radical polymerization of vinyl ferrocene.

The chemical functionality of the three-coordinate phosphine moiety in poly(methylene phosphine)s has already been demonstrated by utilizing these polymers as effective ligands for Pd-catalyzed Suzuki cross-coupling reactions. The preparation of macromolecules composed of phosphines and ferrocenes is an attractive synthetic target with the prospect of accessing well-defined bimetallic polymers exhibiting interesting electronic, magnetic or catalytic properties. There are very few effective synthetic routes to phosphine-ferrocene hybrid polymers, as of now, only a few examples have been reported. In this Chapter, the synthesis and addition polymerization of C-ferrocenyl phosphaalkene 6.1 to afford a new redox-active, poly(methylene phosphine) (6.2) is described.

*A version of this chapter has been published. Kevin J. T. Noonan, Derek P. Gates and Brian O. Patrick. Redox-active iron-containing polymers: synthesis and anionic polymerization of a C-ferrocenyl-substituted phosphaalkene. Chem Commun. 2007, 3658.
Although metalla-phosphaalkenes are quite common, the target monomers, ferrocenyl-substituted phosphaalkenes, are not widely available. Some Becker-type phosphaalkenes \([\text{RP} = \text{C(OSiMe}_3\text{)} \text{R'}]\) possessing \(\text{C-Fc}\) and \(\text{P-Fc}\) substituents are known; however, very few reported non-heteroatom-substituted \(\text{P=C}\) systems have been reported. A rare example, \(\text{tBuP=CHFc}\), was detected in solution but dimerized upon attempted isolation. For polymerization studies, monomers with no heteroatoms directly attached to the \(\text{P=C}\) bond are desired to avoid possible side reactions during initiation. Consequently, methods to access new ferrocene-substituted phosphaalkenes are needed. The phospha-Peterson reaction is a general and convenient route to phosphaalkenes. This remarkable reaction involves the condensation of a silyl phosphide \(\text{Li}[\text{RP(SiMe}_3\text{)}]\) with a ketone and affords phosphaalkenes with a variety of substituents. However, suitably bulky substituents must be employed to render the desired \(\text{P=C}\) compound isolable.

### 6.2 Results and Discussion

#### 6.2.1 Synthesis of \(\text{MesP=C(Ph)(Fc)}\)

In order to prepare C-ferrocenyl phosphaalkene 6.1, benzoylferrocene was first synthesized according to a modified literature procedure and sublimed at 120 °C \textit{in vacuo}. An ethereal solution of MeLi was added to the air-sensitive \(\text{MesP(SiMe}_3\text{)}_2\) in THF under \(\text{N}_2\) and this mixture was stirred for ca. 1 h at 60 °C. Removal of an aliquot from the reaction mixture for analysis using \(\text{P}^{31}\) NMR spectroscopy revealed that \(\text{MesP(SiMe}_3\text{)}_2\) (\(\delta_{31\text{P}} = -162\)) had been completely consumed. A new signal was observed (\(\delta_{31\text{P}} = -187\)) which was assigned to \(\text{Li}[\text{MesP(SiMe}_3\text{)}]\). The reaction mixture was then treated with benzoylferrocene at 60 °C and

*References start on page 116*
stirred for approximately 30 min. The deep red reaction mixture was analyzed using $^{31}$P NMR spectroscopy and two new signals at 218 and 211 ppm (70:30 ratio) had appeared and were consistent with the formation of E/Z-6.1. Notably, the Li[MesP(SiMe$_3$)] ($\delta_{31P} = -187$) had been completely consumed. Crystals suitable for X-ray diffraction were obtained from the slow evaporation of a hexanes solution of E/Z-6.1. The solid-state molecular structure of phosphaalkene 6.1 is shown in Figure 6.1 and, interestingly, the Fc substituent is cis to the bulky P-Mes substituent (i.e. Z-6.1). Dissolution of the crystals of Z-6.1 in $^7$C$_6$D$_6$, followed by $^{31}$P NMR analysis revealed signals consistent with both E-6.1 and Z-6.1 isomers in solution and is indicative of interconversion (ca. 85:15 ratio). Selective $^1$H NMR NOE experiments provided confirmation that the major isomer in solution is Z-6.1. Irradiating at the resonance frequency of the ortho CH$_3$ groups on the mesityl ring ($\delta_H = 2.30$) of the major isomer leads to enhancement of signals assigned to the ortho hydrogens of the substituted Cp ring ($\delta_H = 4.61$), of the major isomer. This signal enhancement is consistent with the Mes and Fc substituents being cis configured and therefore the Z-6.1 isomer was concluded to be the major isomer (85%) in solution.

![Scheme 6.2 Preparation of ferrocenyl phosphaalkene from the MesP(SiMe$_3$)$_2$, methyllithium and benzoyl ferrocene.](image)

**Scheme 6.2** Preparation of ferrocenyl phosphaalkene from the MesP(SiMe$_3$)$_2$, methyllithium and benzoyl ferrocene.

### 6.2.2 Attempted synthesis of MesP=CFc$_2$ (6.3) and MesP=C(th)(Fc) (6.4)

Upon discovery that compound 6.1 was stable and isolable at room temperature, the synthesis of MesP=CFc$_2$ (6.3) and MesP=C(th)(Fc) (6.4) were attempted using the phospha-Peterson reaction. 1,1-Diferrocenyl ketone and 1-[2-thiophenecarbonyl]ferrocene were prepared according to literature procedures. A solution of Li[MesP(SiMe$_3$)] in THF was treated with diferrocenyl ketone. Unfortunately, upon analysis of the reaction mixture using $^{31}$P NMR spectroscopy, no signal was observed that could be assigned to P-Mes phosphaalkenes ($\delta_{31P} >$
Treatment of Li[MesP(SiMe₃)] in THF with 1-[2-thiophenecarbonyl]ferrocene resulted in the formation of the desired phosphaalkene (δ₃P = 221.8, 219.6 E/Z isomers in THF) along with several other unwanted side products. Neither recrystallization nor distillation could afford the pure product in appreciable quantities.

Scheme 6.3 Attempted synthesis of MesP=CFc₂ and MesP=C(th)(Fc) using the phospha-Peterson reaction.

6.2.3 X-ray crystallography

The molecular structure of Z-6.1 is shown in Figure 6.1 and the metrical parameters for this compound are displayed in Table 6.1. The P=C bond length in 6.1 (1.697(2) Å) is fairly long compared to typical C-substituted phosphaalkenes (1.61-1.71 Å); however, it is similar to the P=C bond length in MesP=CPh₂ (1.692(3) Å). Interestingly, the cis-Fc substituent shows a larger angle to the P=C bond than the ideal sp² angle (∠P=C–C_Fc = 130.7(1)°) and is significantly greater than the typical cis aryl substituent of P-mesityl phosphaalkenes (∠P=C–C_{cis} = 125 – 128°). We speculate that this is a consequence of increased steric repulsion between the cis configured Fc and Mes moieties in Z-6.1. Remarkably, the angle between the best planes of the C₅H₄ moiety and the P=C bond is just 13.2(1)°. For comparison, the analogous angle in the only other crystallographically characterized C-ferrocenyl phosphaalkene (Me₃SiP=C(OSiMe₃)Fc) is 36.6° whilst that in MesP=CPh₂ is 42.9°. This data suggests that significant π-conjugation is present between the Fc substituent and the P=C bond in Z-6.1.

Additional support for π-conjugation in Z-6.1 is provided by the shortening of C(1)–C(8) bond.
(1.468(2) Å) with respect to the typical C–C single bond length (ca. 1.54 Å) and by the intense red colour of 6.1 compared with pale yellow MesP=CH2.

Figure 6.1 Solid state molecular structure of Z-6.1. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P1–C1 = 1.697(2), P(1)–C(18) = 1.842(2), C(1)–C(2) = 1.512(2), C(1)–C(8) = 1.468(2); C(8)–C(1)–C(2) = 114.9(1), C(8)–C(1)–P(1) = 130.7(1), C(2)–C(1)–P(1) = 114.2(1), C(1)–P(1)–C(18) = 107.3(1).

6.2.4 Polymerization of ferrocenyl phosphaalkene monomer 6.1

To determine whether anionic initiation of the C-ferrocenyl phosphaalkene 6.1 was feasible, a stoichiometric combination of 6.1 with 7-BuLi (1 equiv) in glyme (1,2-dimethoxyethane) was undertaken. The 31P NMR spectrum of the reaction mixture showed only a singlet at -18.7 ppm which is consistent with the quantitative formation of Li[Mes(Bu)PC(Fc)Ph]. Once the feasibility of anionic initiation had been demonstrated, a solution of monomer 6.1 in glyme was treated with 7-BuLi (5 mol %). The progress of the polymerization was monitored by 31P NMR

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spectroscopy and, after seven days, 50 – 60 % of monomer 6.1 had been cleanly converted to polymer 6.2 (δ = 5 br). Quenching with methanol terminated the polymerization and polymer 6.2 was separated from 6.1 by precipitation from THF into methanol (x4). The golden coloured polymer was analyzed by triple detection GPC and an absolute number average molecular weight (Mn) was determined to be 9,500 with a polydispersity index (PDI) of 1.21. The identical experiment was repeated and the same Mn was achieved with a PDI of 1.18. Further studies are underway to ascertain whether this polymerization may be conducted in a living fashion.

In order to investigate the electronic properties of 6.1 and 6.2, both were analyzed by UV-Vis spectroscopy (Figure 6.2). Previous studies on phosphaalkenes have demonstrated that P=C bonds are capable of electronic communication through π conjugation.34-40 The deep red solution of 6.1 exhibited two broad absorbances at λmax = 512 nm and 331 nm which are assigned to the d-d transition of the ferrocenyl moiety and the π–π* transition for the P=C bond, respectively. Interestingly, the absorbance maximum at 512 nm is significantly red-shifted when compared to that for vinylferrocene (λmax = 442 nm) and ferrocene (λmax = 440 nm).8,41 The dramatic bathochromic shift is most likely attributed to some conjugation between the ferrocene group and the P=C bond. The second transition at 331 nm, assigned to the π–π* transition of the P=C bond, is similar to that observed for MesP=CPh2 (λmax = 324 nm).42 In contrast, the gold coloured macromolecule 6.2 exhibits only a weak transition at 448 nm, which is very similar to the d–d transition for ferrocene (440 nm).
The electrochemical properties of poly(methylenephosphine) 6.2 were analyzed by cyclic voltammetry (Figure 6.3). The observed quasi-reversible one electron oxidation of 6.2 is consistent with the expected ferrocene-ferrocenium couple. The detection of a single wave suggests that the Fc moieties are electronically isolated; analogous to the case of poly(vinylferrocene). The half-cell potential (vs SCE) for polymer 6.2 is (ΔE_{1/2} = 0.41 V) is slightly lower that for poly(vinylferrocene) (ΔE_{1/2} = 0.44 – 0.48 V). For comparison, FcCH₂PPh₂, a possible model compound for polymer 6.2, similarly exhibits a reversible oxidation slightly lower than that for ferrocene (ΔE = –0.04 V).
Finally, compound 6.2 was analyzed by thermal gravimetric analysis (Figure 6.4). The onset polymer degradation temperature was found ($T_{\text{onset}} = 290 ^\circ \text{C}$) to be slightly higher than that of the $-[\text{MesP-CPh}_2]_n-$ polymer ($T_{\text{onset}} = 265 ^\circ \text{C}$). This is a consequence of increased thermal stability imparted by the ferrocene moiety. Moreover, the ceramic yield upon polymer degradation was found to be $\sim 21 \%$ which is consistent with iron and phosphorus remaining. We suspect this polymer may be a useful precursor to iron-phosphide ceramic materials.

Figure 6.3  Cyclic Voltammogram of 6.2 in CH$_2$Cl$_2$ (scan rate 100mV/s) containing 0.1M [(n-Bu)$_4$N]PF$_6$. Referenced to decamethyl ferrocene. Concentration of 6.2 = 2.4 mM
6.3 Conclusions

In summary, a phosphaalkene analogue of vinyl ferrocene has been prepared and polymerized anionically to afford new redox active polymers. This development could be used to synthesize bimetallic polymers possessing both Fc moieties and AuCl moities which may have interesting optoelectronic, magnetic and pre-ceramic properties. The potential to polymerize these monomers in a living fashion would also be of interest for preparing new macromolecules.

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6.4 Experimental

Table 6.1 X-ray crystallographic data of 6.1.

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</table>

6.4.1 Materials and general procedures

All manipulations of air and/or water sensitive compounds were performed under prepurified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology glovebox. Hexanes and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. CD₂Cl₂ and C₆D₆ were purchased from Cambridge Isotope Laboratories and were used as received. Methanol was degassed prior to use. MeLi (1.5 M in Et₂O) °BuLi (1.6 M in hexanes), SiMe₂Cl were purchased from Aldrich and used as

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received. Alkyl lithium reagents were titrated prior to use. Benzoyl ferrocene was prepared according to literature procedures and sublimed in vacuo (120 °C). 29 1,1-Diferrocenyl ketone and 1-[2-thienophenecarbonyl]ferrocene were prepared according to literature procedures and sublimed in vacuo at 115 °C. 30 Air sensitive MesP(SiMe₃)₂ was prepared from literature procedures and distilled at 110 °C in vacuo. 45, 46

1H, 13C, 19F and 31P NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported relative to CHCl₃ (δ = 5.32 for 1H, 54.00 for 13C) or C₆H₅D₃ (δ = 7.16 for 1H). 85% H₃PO₄ was used as an external standard (δ = 0.0 for 31P).

Molecular weights were determined by triple detection gel permeation chromatography (GPC – LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 x 300 mm; HR5E, HR4 and HR2), Waters 2410 differential refractometer, Wyatt tristar 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. 2 mg mL⁻¹). Elemental analysis was conducted at the University of British Columbia.

6.4.2 Preparation of MesP=C(Ph)(Fc) (6.1):

To a stirred solution of MesP(SiMe₃)₂ (5.03 g, 17 mmol) in THF was added MeLi in Et₂O (12.2 mL, 1.4 M, 17 mmol) at 25 °C. The reaction mixture was heated to 60 °C for ca. 1 h and analysis of an aliquot by 31P NMR spectroscopy suggested quantitative formation of MesP(SiMe₃)Li (δ = –187). Subsequently, benzoylferrocene (4.94 g, 17 mmol) was added and the reaction mixture was stirred at 60 °C for ca. 30 min. The 31P NMR spectrum showed signals at 218 and 211 ppm (70:30 ratio) assigned to Z–6.1 and E–6.1, respectively. To the solution was added Me₃SiCl (2.15 mL, 17 mmol) to quench the LiOSiMe₃. The volatiles were removed in vacuo, the residue was extracted into hexanes (3 x 50 mL), filtered through Celite, and the solvent removed in vacuo. Single crystals of 6.1 (4.16 g, 58%) were obtained from slow evaporation of a hexanes solution of the crude product. δ(121.5 MHz; C₆D₆; H₃PO₄) 218 (s, 1P,

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Z - 85%), 211 (s, 1P, E - 15%). \( \delta_t(300.1 \text{ MHz, CD}_{2} \text{Cl}_2; \text{SiMe}_4) 7.5 \) (m, 5H, E-o,m,p -Ph), 7.10 (m, 5H, Z-o,m,p -Ph), 6.98 (s, 2H, E-m-Mes), 6.69 (s, 2H, Z-m-Mes), 4.61 (t, 2H, \( ^2J_{pH} = 1.2 \text{ Hz, Z-o-Fc} \)), 4.45 (s, 2H, Z-m-Fc), 4.23 (m, 5H, Z-Cp-Fc, 2H, E-m-Fc), 4.10(s, 5H, E-Cp-Fc), 3.79 (s, 2H, E-o-Fc), 2.44 (s, 6H, E-o-CH \(_{3}\)2), 2.37 (s, 3H, E-p-CH \(_{3}\)), 2.30 (s, 6H, Z-o-CH \(_{3}\)), 2.17 (s, 3H, Z-p-CH \(_{3}\)). \( \delta_c(75.5 \text{ MHz, CD}_{2} \text{Cl}_2; \text{SiMe}_4) 194.94 \) (d, \( ^1J_{pc} = 43 \text{ Hz, Z-P=C} \)) 190.23 (d, \( ^1J_{pc} = 45.6 \text{ Hz, E-P=C} \)) 144.64 (d, \( ^2J_{pc} = 27.5 \text{ Hz, E-i-Ph} \)) 143.30 (d, \( ^2J_{pc} = 14 \text{ Hz, Z-i-Ph} \)) 140.68 (d, \( ^2J_{pc} = 6.2 \text{ Hz, Z-o-Mes} \)) 140.57 (d, \( ^2J_{pc} = 6.5 \text{ Hz, E-o-Mes} \)) 139.34 (s, E-p-Mes) 138.44 (s, Z-p-Mes) 137.76 (d, \( ^1J_{pc} = 48.4 \text{ Hz, E-i-Mes} \)) 136.45 (d, \( ^1J_{pc} = 40 \text{ Hz, Z-i-Mes} \)) 129.93 (d, \( ^3J_{pc} = 14 \text{ Hz, E-o-Ph} \)) 129.27 (s, E-m-Mes) 128.46 (s, Z-m-Mes) 128.03 (d, \( ^3J_{pc} = 7.3 \text{ Hz, Z-o-Ph and E-m-Ph} \)) 127.55 (s, Z-m-Ph) 127.13 (s, Z-p-Ph) 89.81 (d, \( ^2J_{pc} = 31.2 \text{ Hz, Z-i-Fc} \)) 87.28 (d, \( ^2J_{pc} = 16.6 \text{ Hz, E-i-Fc} \)) 70.87 (s, Z-Cp-Fc) 70.76 (s, E-Z-m-Fc) 70.44 (s, E-Cp-Fc) 69.13 (d, \( ^3J_{pc} = 3.5 \text{ Hz, E-o-Fc} \)) 66.79 (d, \( ^3J_{pc} = 17.1 \text{ Hz, Z-o-Fc} \)) 21.59 (s, E-p-CH \(_{3}\)) 21.31 (s, Z-p-CH \(_{3}\)). MS (El, 70eV): 424 [8, 36; M\(^*\)]. UV/Vis (C\(_7\)H\(_8\)): \( \lambda_{max} (\varepsilon) = 331 \text{ (4600), 512 (930).} \) Anal. Calcd. For C\(_{26}\)H\(_{25}\)PFe: C, 73.60; H, 5.94. Found: C, 73.30; H, 6.04.

6.4.3 Attempted synthesis of MesP=CFC \(_2\) (6.3):

A solution of MesP(SiMe\(_3\))\(_2\) (0.2 g, 0.67 mmol) in THF (5 mL) was treated with MeLi (0.45 mL, 1.5 M, 0.67 mmol). Removal of an aliquot from the reaction mixture for analysis by \(^{31}\text{P NMR spectroscopy confirmed the formation of Li}[\text{MesP(SiMe}_3)] (\delta_{31P} = -187). \) To the reaction was added the 1,1'-diferocenyketone but phosphaalkene formation was not observed.

6.4.4 Attempted synthesis of MesP=C(th)(Fc) (6.4):

A solution of MesP(SiMe\(_3\))\(_2\) (1.0 g, 3.37 mmol) in THF (5 mL) was treated with MeLi (2.25 mL, 1.5 M, 3.4 mmol). Removal of an aliquot from the reaction mixture for analysis by \(^{31}\text{P NMR spectroscopy confirmed the formation of Li}[\text{MesP(SiMe}_3)] (\delta_{31P} = -187). \) To the reaction was added the 1-[2-thiophenecarbonyl]ferrocene and the mixture was stirred for ca. 1 h. Two References start on page 116
signals attributed to the E/Z isomers of MesP=C(th)(Fc) 6.4 were observed in the $^{31}$P NMR spectrum of the reaction mixture ($\delta_{31P} = 221.8, 219.6$ E/Z isomers in THF). The E/Z mixture could not be isolated by recrystallization or distillation.

6.4.5 Synthesis of $[P$(Mes)C(Fc)(Ph)$]_n$ (6.2):

A typical polymerization procedure is described. To a stirred solution of MesP=CPh(Fc) (1.00 g, 2.3 mmol) at room temperature in glyme (7 mL) was added $^7$BuLi (1.5 M, 80 µL, 0.12 mmol). The reaction was stirred at room temperature and monitored by $^{31}$P NMR spectroscopy. The growth of a broad signal in the $^{31}$P NMR spectrum was observed over 7 days and, subsequently, the reaction mixture was removed from the glovebox, quenched and precipitated using methanol (3 x 100 mL). Residual solvent was removed in vacuo. Yield = 250 mg (25 %). $\delta_P$(121.5 MHz; C$_6$D$_6$; H$_3$PO$_4$) –5 ppm (br, 1P). $\delta_H$(300.1 MHz, C$_6$D$_6$; SiMe$_4$) 8-6.5 (br, 7H, Aryl-H), 4.5-3.5 (br, 9H, Fc-H), 3-1.5 (br, (H, Mes-H). GPC-LLS (THF): $M_n = 9,500$ PDI = 1.21 $R_h = 1.5$ nm. UV/Vis (C$_7$H$_9$): $\lambda_{max}$ (c) = 448 (210). Anal. Calcd. for C$_{26}$H$_{25}$PFe: C, 73.60; H, 5.94. Found: C, 73.50; H, 6.29.

6.4.6 X-ray crystallography

Crystal Data and refinement parameters are listed in Table 6.1 for compound Z-6.1. The single crystal was immersed in oil and mounted on a glass fiber. Data was collected at 173±0.1K on a Bruker X8 APEX 2 diffractometer with graphite-monochromated Mo Ka radiation. Data collection and integration was completed using the Bruker SAINT$^{47}$ software package. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXT$^{48}$ crystallographic software package from Bruker-AXS. The data set was corrected for Lorentz and polarization effects.

CCDC reference numbers 642679

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6.5 References


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Polymerization of MesP=CPh₂ Derivatives, Functionalized Poly(methyleneephosphine)s

7.1 Introduction

Most work in the broad field of polymer chemistry has focused on synthesizing materials composed primarily of organic elements such as C, N and O.¹ However, there is growing interest in the preparation of macromolecules containing inorganic elements because of the potential to access materials with unique properties.²⁻¹⁸ The recent discovery of living anionic P=C bond polymerization afforded the first macromolecule with alternating phosphorus and carbon atoms in the main chain (Scheme 7.1).¹⁷⁻¹⁸ The incorporation of different functional groups offers a means to tailor the polymer properties. For example, the incorporation of metal centers into poly(methyleneephosphine)s described in Chapter Six of this thesis yielded a material with redox capabilities. In an attempt to expand on this work, the preparation of polymeric phosphines with different pendant functional groups is currently under investigation.¹⁹⁻²¹

\[ \text{Scheme 7.1 Living polymerization of phosphaalkenes.} \]

In order to expand upon the polymerization of MesP=CPh₂, several P=C containing monomers bearing electron donating and electron withdrawing groups have been synthesized and polymerized. The inspiration to modify the substituents surrounding the P=C bond is derived from olefins (i.e, styrene).²² The living anionic polymerization of styrenic monomers bearing functional groups has been investigated; however, the functional moiety can have
undesirable effects on the polymerization reactivity of the olefinic species.\textsuperscript{22, 23} Many functionalized styrenic monomers display different initiation and propagation behavior than styrene itself, which limits the generality of anionic polymerization.\textsuperscript{22}

In an effort to expand upon anionic P=C polymerization, an investigation into MesP=CPh\textsubscript{2} derivatives is presented in this chapter. The versatile phospha-Peterson reaction was selected as a suitable route to prepare a series of phosphaalkenes.\textsuperscript{24-33} There are two reactions that are both classified as phospha-Peterson condensations. One reaction, which is analogous to the Peterson olefination reaction,\textsuperscript{34} involves the \textit{in situ} formation of a RP(Li)SiMe\textsubscript{3} and subsequent treatment with a sterically hindered ketone to render the desired phosphaalkene (Scheme 7.2 – Route A). The base catalyzed phospha-Peterson reaction proceeds by combination of a bis(silyl) phosphine [of the type RP(SiMe\textsubscript{3})\textsubscript{2}] and a ketone in the presence of catalytic base (i.e., KOH or NaOH) to form the desired phosphaalkene along with the easily removable Me\textsubscript{3}SiOSiMe\textsubscript{3} (Scheme 7.2 – Route B).\textsuperscript{35} Utilizing this well-known methodology for synthesizing new phosphaalkenes bearing electron donating or electron withdrawing groups at the periphery of the P=C bond seemed attractive.

In this Chapter the synthesis and of four new phosphaalkenes (7.1a, 7.1b, 7.1c and 7.1f) is described and preliminary polymerization experiments for monomers 7.1a-7.1e have been conducted. Several of these newly prepared polymers offer the intriguing possibility of post-polymerization modification as the pyridyl moiety in 7.2 could be used to coordinate metal atoms or the chloro substituent of 7.5 could undergo substitution reactions to alter the polymer microstructure.

\begin{equation}
\begin{array}{c}
\text{Route A} \\
\text{Route B}
\end{array}
\end{equation}

\textbf{Scheme 7.2} Standard phospha-Peterson procedures as a route to phosphaalkene monomers.
Chapter 7

7.2 Results and Discussion

7.2.1 Synthesis of several new MesP=C(Ph)(Ar) phosphaalkenes using the phospha-Peterson methodology

Compounds 7.1a – 7.1e were all synthesized using the base catalyzed phospha-Peterson reaction (Scheme 7.3).36 Only two of these compounds, 7.1d and 7.1e, have been synthesized previously.33 All five molecules were purified by distillation at approximately 200 °C followed by recrystallization from either hexanes or toluene. The isolated yields for 7.1a-7.1e varied between ~20 and 40 %. These molecules all exhibit characteristic 31P NMR shifts for P-Mes phosphaalkenes (downfield at δ31P > 200). Compound Z–7.1a was obtained as a crystalline material from a concentrated hexanes solution. Upon dissolution of the Z–7.1a crystals in CD2Cl2 for analysis by 31P and 1H NMR spectroscopy, signals corresponding to both the E and the Z isomers were observed (δ31P = 211.0 and 209.8: E/Z–7.1a), suggesting facile E/Z isomerization in solution. A concentrated hexanes solution of E/Z–7.1b afforded crystalline E–7.1b in modest yield (Yield = 32%). NMR analysis of the crystals dissolved in CD2Cl2 did not reveal any E/Z isomerization (δ31P = 238.1: E–7.1b). Phosphaalkene 7.1c has only been obtained as a viscous yellow oil and solution phase NMR studies revealed the presence of two signals assigned to both the E and Z isomers (δ31P = 229.9 and 229.2 ppm). Cis/trans isomerization of phosphaalkenes has been investigated previously,25,37-39 and UV light was deemed necessary for interconversion between the two species in solution. Interestingly, studies in our laboratory have revealed that cis/trans isomerization for certain phosphaalkenes can occur even in the absence of light.33 Further investigations are currently underway to determine the mechanism of isomerization for compounds 7.1a and 7.1c. Inducing isomerization of compound 7.1b is also under investigation.

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Scheme 7.3 Synthesis of several substituted mesityl phosphaalkenes using the base catalyzed (NaOH) phospha-Peterson reaction. Varying the electronic properties of the P=\(\text{C}\) bond by altering the surrounding side groups.

Attempts to prepare the 4-pyridyl phosphaalkene 7.1f using the base catalyzed phospha-Peterson reaction were undertaken. Though phosphaalkene formation was confirmed by analysis of the reaction mixture using \(^{31}\text{P}\) NMR spectroscopy (7.1f: \(\delta_{31\text{P}} = 255\) and 246 in THF), several unidentified byproducts were observed in the region typical of trivalent phosphorus (\(\delta_{31\text{P}} = -20\)). Unfortunately, attempts to isolate compound 7.1f from this reaction mixture were unsuccessful. To circumvent, or at the very least, minimize the undesired side reactions, a classical phospha-Peterson reaction was employed where, MesP(Li)\(\text{SiMe}_3\) was prepared \textit{in situ} by addition of MeLi to a colorless MesP(SiMe\(_3\))\(_2\) solution in THF. The formation of MesP(Li)\(\text{SiMe}_3\) was confirmed by \(^{31}\text{P}\) NMR spectroscopy (\(\delta_{31\text{P}} = -187\) in THF) and the reaction mixture was then treated with 4-benzoylpyridine at 60 °C. Upon stirring for 1 h, followed by addition of \(\text{SiMe}_3\)\(\text{Cl}\) to quench the LiOSiMe\(_3\), compound 7.1f was extracted from the reaction mixture and successively recrystallized using hexanes (3x) to yield the pure product (Yield = 8%). The synthesis of phosphaalkene 7.1f was confirmed upon \(^{31}\text{P}\) NMR analysis of a solution of 7.1f in CD\(_2\)Cl\(_2\) that revealed two signals (\(\delta_{31\text{P}} = 255.2\) and 246.2 \(E/Z\) isomers) in the expected region (\(\delta_{31\text{P}}\) for P-Mes phosphaalkenes > 200). The \(^1\text{H}\) NMR spectrum of 7.1f in CD\(_2\)Cl\(_2\) exhibits a characteristic downfield doublet for the Aryl C-H bonds in the \textit{meta} position of the pyridyl.

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moiety as displayed in Figure 7.1 ($\delta_{1H} = 8.56$ and $8.32$ E/Z–7.1f). Attempts to purify compound 7.1f by distillation at $200^\circ C$ resulted in isolation of an orange-coloured solid ($M_n = 22300$, PDI = 1.22) in low yield (6%) from four successive precipitations into hexanes (200 mL). The polymer has been tentatively assigned as compound 7.2 but only GPC-LLS experiments have been conducted on the material and more structural characterization is needed to confirm the assignment. Both the base catalyzed phospha-Peterson and the conventional phospha-Peterson reactions seem well suited to form P-Mes phosphaalkenes. The versatility offered by simply changing the ketone in the preparative procedure results in the convenient side group modification and could be applied to synthesize a wide range of new phosphaalkenes.

![Scheme 7.4](image)

**Scheme 7.4** Preparation of 4-pyridyl phosphaalkene 7.1f using the phospha-Peterson reaction. The MesP(Li)(SiMe3)2 species is combined with 4-benzoyl pyridine. The resultant phosphaalkene can be purified by recrystallization.

![NMR spectrum](image)

**Figure 7.1** $^1H$ NMR spectrum of compound 7.1f in $\text{CD}_2\text{Cl}_2$. The diagnostic signals for the $m$-pyridyl C-H protons are assigned above.
7.2.2 X-ray crystallographic analysis of compounds 7.1a, 7.1b and 7.1f

X-ray structure determination of single crystals for compounds 7.1a, 7.1b, and 7.1f were conducted at low temperature. Unfortunately, compound 7.1c could not be crystallographically characterized since attempts to recrystallize this compound from hexanes and toluene resulted in viscous yellow oils. The solid-state molecular structures of 7.1a, 7.1b, and 7.1f are displayed in Figures 7.2, 7.3 and 7.4, respectively. Compound 7.1a crystallizes as the Z isomer, 7.1b crystallizes preferentially as the E isomer and 7.1f crystallizes as mixture of E/Z isomers (E isomer of 7.1f is displayed in Figure 7.4). The important metrical values of the crystallographically characterized phosphaalkenes are outlined in Table 7.1 and the cell constants and data collection values are displayed in Table 7.2.

Table 7.1 Important metrical parameters for crystallographically characterized phosphaalkenes 7.1a, 7.1b and 7.1f.

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<th>7.1a</th>
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<th>7.1f</th>
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<tr>
<td>Bond Lengths</td>
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<td>P=C</td>
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<td>P−C_{Mes}</td>
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<td>1.829(2)</td>
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<td>C−C_{trans}</td>
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<td>C−C_{cis}</td>
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<td>1.479(2)</td>
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<td>Bond Angles</td>
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<td>∠C_{Mes}−P=C</td>
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<td>107.1(1)</td>
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<td>∠P=C−C_{cis}</td>
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<td>39.9</td>
<td>48.9</td>
<td>55.7</td>
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</table>

*a* The angle between the mean plane of the specified aryl ring atoms to the mean plane C_{ipso}−P=C−(C_{trans})(C_{cis}) atoms.

Compounds with localized (p−p):π bonds between phosphorus and carbon normally exhibit P=C bond lengths in the range of 1.61 − 1.71 Å. The three compounds shown below have relatively long P=C bonds (1.69 − 1.71 Å) especially compound 7.1a (1.708(2) Å). The diethylamino moiety of compound 7.1a is extremely donating as evidenced by the short C_{Aryl}−NEt₂ bond (1.376(2) Å). Moreover, the angles around the N atom sum to 359.3° which is expected for an sp² hybridized N atom but not for an sp³ hybridized atom. These observations

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clearly support donation of the lone pair centered on the nitrogen atom into the π-cloud of the aryl ring. A possible rationale for the long P=C bond is that the 4-NEt₂-C₆H₄ moiety is donating electron density into the phosphaalkene bond causing the slight elongation observed (1.708(2) Å) when compared to MesP=CPh₂ (1.692(3) Å).²⁴ The P-Mes bond lengths in all three solid-state molecular structures are shorter than the expected P-C single bond length (1.85 – 1.90 Å)⁴¹ which suggests a slight degree of conjugation between the Mes group and P=C bond. However, the angles between the planes of the P=C bond and the mesityl groups are large (~70°) for all three compounds (7.1a, 7.1b, 7.1f) which is indicative of little to no conjugation between those moieties. The aryl substituents seem to have more π conjugation with the P=C bonds than the mesityl rings in all three cases. This is evidenced by the smaller angles between planes of the aryl rings and P=C bonds (Table 7.1).²⁰ The angles surrounding the C atom of the P=C bond are essentially planar for all three compounds (~360°), but the Ar_cis moieties of compounds 7.1a, 7.1b and 7.1f are bent further away from the P=C bond (∠ P=C–C_cis ~ 125 – 128°) than the Ar_trans (∠ P=C–C_trans ~ 115 – 117°) groups. This suggests some degree of steric repulsion between the Mes and Ar_cis moieties.
Figure 7.2  Solid state molecular structure of 7.1a. Crystallized preferentially as the Z isomer. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)–C(10) = 1.708(2), P(1)–C(1) = 1.839(2), C(10)–C(11) = 1.492(2), N(1)–C(20) = 1.376(2), N(1)–C(23) = 1.464; C(1)–P(1)–C(10) = 106.1(1), P(1)–C(10)–C(17) = 128.8(1), C(11)–C(10)–C(17) = 116.4(1), N(1)–C(20)–C(21) = 122.4(1), C(23)–N(1)–C(20) = 120.5(1), C(25)–N(1)–C(20) = 121.7(1), C(25)–N(1)–C(23) = 117.1(1).
Figure 7.3  Solid state molecular structure of 7.1b. Crystallized preferentially as the E isomer. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)—C(10) = 1.696(2), P(1)—C(1) = 1.829(2), C(10)—C(11) = 1.479(2), C(10)—C(17) = 1.483(2), C(20)—Cl(1) = 1.737(2); C(1)—P(1)—C(10) = 107.1(1), P(1)—C(10)—C(17) = 116.5(1), C(19)—C(20)—Cl(1) = 119.1(1), C(21)—C(20)—Cl(1) = 119.9(1).

Figure 7.4  Solid state molecular structure 7.1f. Crystallized as E/Z mixture. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)—C(10) = 1.700(2), P(1)—C(1) = 1.839(2), C(10)—C(11) = 1.496(2), C(19)—N(1) = 1.363(3), C(21)—N(1) = 1.359(3); C(1)—P(1)—C(10) = 107.8(1), P(1)—C(10)—C(17) = 117.4(1), P(1)—C(10)—C(11) = 125.1(1), C(21)—N(1)—C(19) = 117.0(2).
7.2.3 Preliminary investigations into the polymerization behavior of phosphaalkenes

7.1a – 7.1e.

Compounds 7.1a – 7.1e have all been investigated as potential monomers for anionic P=C bond polymerization. In an inert atmosphere glovebox at room temperature, compound 7.1a could not be polymerized in gylme using °BuLi as the initiator. The attempted polymerization was monitored after 13 days using 31P NMR spectroscopy and no signal corresponding to the expected poly(methylene phosphine) was observed. A small resonance at –40 ppm was visible in the 31P NMR spectrum which most likely results from addition of °BuLi across the P=C bond forming a carbanion. Stoichiometric combination of °BuLi with a solution of 7.1a in gylme was analyzed by 31P NMR spectroscopy and revealed nearly quantitative formation of the same species at –40 ppm. Further investigations are currently underway to ascertain why this monomer will not polymerize and to hopefully circumvent this undesired behavior. This is especially surprising since the CH2=C(Ph)(4-NMe2-C6H4) styrene analog does polymerize in the presence of anionic initiators.42

Compound 7.1d was combined with °BuLi in gylme at room temperature and the reaction was stirred for 7 days. An aliquot was removed from the reaction mixture and analyzed by 31P NMR spectroscopy which revealed only 10% conversion from the monomeric MesP=C(Ph)(4-F-C6H4) to poly(methylene phosphine). Precipitation of the mixture into 50 mL of hexanes did not yield any polymer. The electron-withdrawing fluoro group may stabilize the propagating carbanionic species by drawing electron density into the aryl ring and thus, slowing the rate of propagation considerably. To date, compound 7.1d has not been polymerized with sufficient conversion to isolate any polymeric material.

Compound 7.1e was also treated with °BuLi in an attempt to isolate a new poly(methylene phosphine). Surprisingly, no evidence for polymerization is observed. Upon addition of the initiator to a pale yellow solution of 7.1e in gylme, a noticeable color change from yellow to red was immediately observed. However, analysis of the reaction by 31P NMR spectroscopy after two days did not reveal any signal in the region typical of

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poly(methylenephosphine). This result was particularly striking when one considers the anionic polymerization of styrene (7.3) and 2-vinyl pyridine (7.4).

\[
\begin{align*}
\text{Scheme 7.5} & \quad \text{Anionic polymerization of styrene versus 2-vinyl pyridine.}
\end{align*}
\]

Styrene and 2-vinylpyridine differ at only one position where a CH moiety in the aryl ring is replaced by a N atom but this small difference has a large affect on polymerization behavior. Both the phenyl and pyridyl groups promote nucleophilic attack at the terminal CH\textsubscript{2} moiety because the carbanion that is formed is stabilized by electron delocalization onto the aryl rings (Scheme 7.5). However, when comparing the two monomers, the pyridyl moiety in 7.4 has an electronegative N atom, which inductively withdraws electron density from the olefinic bond. This polarization results in the CH\textsubscript{2} moiety being more electropositive and thus much more susceptible to nucleophilic attack when compared to 7.3\textsuperscript{23} In addition, the N atoms of the growing poly(2-vinylpyridine) chain can also coordinate the Na\textsuperscript{+} counterion which is responsible for creating more “free” or solvent separated cation/anion pairs in solution (Scheme 7.5). As discussed in Chapter 3, “free” or solvent separated ion pairs contribute more to the overall rate of polymerization than “tight” or contact ion pairs. Therefore, a growing poly(2-vinylpyridine) chain will have not only have more “free” ions than a growing polystyrene chain but the 2-vinyl pyridine monomer is also more susceptible to nucleophilic attack. This results in a much higher rate constant of propagation for 2-vinyl pyridine polymerization (7.4 – \( k_p = 7300 \text{ L mol}^{-1} \text{ s}^{-1} \)) when compared to styrene (7.3 – \( k_p = 950 \text{ L mol}^{-1} \text{ s}^{-1} \)) under otherwise identical conditions\textsuperscript{23}

One would expect MesP=C(Ph)(2-Py) to exhibit a significant increase in the rate of

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propagation relative to MesP=CPh₂ analogously to 2-vinylpyridine polymerizing faster than styrene. The N atom of the 2-pyridyl ring should inductively withdraw electron density from the P=C bond in compound 7.1e making it more electropositive and more susceptible to nucleophilic attack. Moreover, the N atom of the pyridyl moiety in compound 7.1e should be able to coordinate the Li⁺ counterion providing more “free” anions in solution to increase the rate of polymerization. The surprising lack of polymerization for the 2-pyridyl phosphaalkene 7.1e warrants further investigation to better understand this behavior.

Compounds 7.1b and 7.1c undergo anionic polymerization in ethereal solvents to afford the desired poly(methylene phosphine)s 7.5 and 7.6, respectively (Scheme 7.6). Polymerizations were conducted under inert atmosphere using n-BuLi as initiator at room temperature and the macromolecules were isolated with modest molecular weights (7.5: \( M_n = 17200, \text{ PDI} = 1.09; \)
7.6: \( M_n = 27600, \text{ PDI} = 1.25 \)). Each polymer exhibits a broad resonance at \(-7 \text{ ppm}\) in the \(^{31}\text{P} \) NMR spectrum. A representative \(^{31}\text{P} \) NMR spectrum of compound 7.5 is displayed in Figure 7.5. The polymerizations of 7.1b and 7.1c were not conducted with anionic polymerization grade monomer and consequently, the polymerizations did not proceed in a living fashion. Further investigations will focus on living polymerization of these monomers and chemically modifying the side groups to tune the properties of the resultant poly(methylene phosphine).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Mes} & \quad \text{R} \\
\text{P=C} & \quad \text{Li} \\
\text{Ph} & \quad \text{P-C} \\
\text{Mes} & \quad \text{R} \\
\end{align*}
\]

\text{Scheme 7.6} Synthesis of poly(methylene phosphines) 7.5 and 7.6 by combination of phosphaalkenes 7.1b and 7.1c with substoichiometric amounts of \( n \)-butyllithium in glyme at room temperature under inert atmosphere.

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7.3 Conclusions

Several new P-Mes phosphaalkenes have been prepared and crystallographically characterized. These exhibit similar structural features to other carbon substituted P=C bonds. The solid-state molecular structure of compound 7.1a indicated that the NEt₂ moiety was strongly electron donating and surprisingly, this species did not polymerize in the presence of anionic initiators. Compounds 7.1b and 7.1c polymerized using "BuLi as the initiator and the isolable polymer 7.5 has a functional group (Cl) which can be exploited for post-polymerization modification. Compounds 7.1a, 7.1d and 7.1e did not yield isolable poly(methylene phosphine)s by anionic polymerization and further studies are underway to determine suitable polymerization conditions for these monomers. Investigations to polymerize compound 7.1f will be conducted in the future.

Figure 7.5 $^{31}$P NMR spectrum of compound 7.5. * indicates a slight amount of poly(methylene phosphine oxide).
Chapter 7

7.4 Experimental

Table 7.2 X-ray crystallographic data of 7.1a, 7.1b and 7.1f

<table>
<thead>
<tr>
<th>Crystal</th>
<th>7.1a</th>
<th>7.1b</th>
<th>7.1f</th>
</tr>
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<tbody>
<tr>
<td>Formula</td>
<td>C_{52}H_{60}N_{2}P_{2}</td>
<td>C_{22}H_{20}PCl</td>
<td>C_{21}H_{20}NP</td>
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<td>Formula Weight</td>
<td>774.96</td>
<td>350.80</td>
<td>317.35</td>
</tr>
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<td>Crystal System</td>
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<td>triclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space Group</td>
<td>C 1 2/c 1</td>
<td>P1</td>
<td>Pbca</td>
</tr>
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<td>Color</td>
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<td>yellow</td>
<td>yellow</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>16.897(5)</td>
<td>8.578(5)</td>
<td>17.343(5)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>15.365(5)</td>
<td>10.737(5)</td>
<td>9.589(5)</td>
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<tr>
<td>(c) (Å)</td>
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<td>11.148(5)</td>
<td>20.860(5)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90.000(5)</td>
<td>68.773(5)</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>109.968(5)</td>
<td>73.306(5)</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90.000(5)</td>
<td>86.855(5)</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>(V) (Å³)</td>
<td>4412(2)</td>
<td>915.4(8)</td>
<td>3469(2)</td>
</tr>
<tr>
<td>(Z)</td>
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<td>2</td>
<td>8</td>
</tr>
<tr>
<td>(T) (K)</td>
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<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>(\mu) (Mo Kα) (cm⁻¹)</td>
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<td>2.96</td>
<td>1.58</td>
</tr>
<tr>
<td>Crystal Size (mm)</td>
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<td>0.40x0.45x0.65</td>
</tr>
<tr>
<td>(D) calcd. (g cm⁻³)</td>
<td>1.167</td>
<td>1.273</td>
<td>1.215</td>
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<tr>
<td>(2\theta) (max) (°)</td>
<td>56.2</td>
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<td>55.6</td>
</tr>
<tr>
<td>No. of Reflections</td>
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<td>26895</td>
<td>26119</td>
</tr>
<tr>
<td>No. of unique data</td>
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<td>4336</td>
<td>4085</td>
</tr>
<tr>
<td>(R) int</td>
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<td>0.025</td>
<td>0.036</td>
</tr>
<tr>
<td>Reflections/parameters ratio</td>
<td>20.54</td>
<td>19.71</td>
<td>19.27</td>
</tr>
<tr>
<td>(R_1, wR_2[l \geq 2\sigma(l)]^a)</td>
<td>0.038; 0.087</td>
<td>0.041; 0.110</td>
<td>0.041; 0.098</td>
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<tr>
<td>(R_1, wR_2) (all data)^a</td>
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<td>0.052; 0.122</td>
<td>0.066; 0.113</td>
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<tr>
<td>GOF</td>
<td>1.03</td>
<td>1.05</td>
<td>1.05</td>
</tr>
</tbody>
</table>

\(^a\)R₁ = \sum \left| F_{o} - |F_{c}| \right| / \sum |F_{o}|, \ wR_2 = \left[ \sum (w (F_{o} - F_{c})^2) / \sum w(F_{o})^2 \right]^{1/2}

7.4.1 Materials and general procedures

All manipulations of air and/or water sensitive compounds were performed under prepurified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology glovebox. Hexanes and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. CDC\(_3\) was distilled from P\(_2\)O\(_5\) and degassed. CD\(_2\)Cl\(_2\) and DMSO–d\(_6\) were purchased from Cambridge Isotope Laboratories and were used as received. Methanol was degassed prior to use. 4-benzoylpyridine, 4-methylbenzophenone, 4-chlorobenzophenone were purchased from Aldrich and sublimed prior to use. 4-diethylaminobenzophenone was used as received from Aldrich. Both "BuLi (1.45M in hexanes)

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and MeLi (1.5 M in Et2O) were purchased from Aldrich and used as received. Alkyl lithium reagents were titrated prior to use.

$^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on either a Bruker Avance 300 MHz or Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to residual CHCl$_3$ ($\delta = 7.26$ for $^1$H and and 77.16 for $^{13}$C), CHDCI$_2$ ($\delta = 5.32$ for $^1$H and and 54.00 for $^{13}$C). 85% H$_3$PO$_4$ was used as an external standard $\delta = 0.0$ for $^{31}$P. Molecular weights were estimated by triple detection gel permeation chromatography (GPC - LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 $\times$ 300 mm) HR5E (2 000 $-$ 4 000 000), HR4 (5 000 $-$ 500 000) and HR2 (500 $-$ 20 000), Waters 2410 differential refractometer ($\lambda = 920$ nm), Wyatt tristar miniDAWN (laser light scattering detector operating at $\lambda = 690$ nm), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min$^{-1}$ was used and samples were dissolved in THF (ca. 2 mg mL$^{-1}$).

Refractive index increments were estimated by comparison of the concentration of the prepared polymer solution to the concentration calculated by the Waters 2410 differential refractometer. Elemental analysis was conducted at the University of British Columbia.

7.4.2 Preparation of MesP=:C(Ph)(4-NEt$_2$-C$_6$H$_4$) 7.1a

Liquid MesP(SiMe$_3$)$_2$ (7 g, 0.024 mol) was added to a solution of 4-diethylaminobenzophenone (6.82 g, 0.024 mol) in dry THF (~ 20 mL) under inert atmosphere. A catalytic amount (~0.05 g) of dry NaOH was added to the reaction mixture and upon stirring for several hours, the mixture turned bright orange. The reaction was stirred under N$_2$ in an inert atmosphere glovebox for several days. Removal of an aliquot for analysis by $^{31}$P NMR spectroscopy revealed that the MesP(SiMe$_3$)$_2$ had been completely consumed ($\delta_{31P} = -162$) and replaced by 2 signals at ($\delta = 211$ and 209). Upon removal of the THF in vacuo, the mixture was transferred to a round bottom flask and fractionally distilled at high temperatures (> 200 °C). The distillate was recrystallized from hexanes and ground into a fine powder and dried in vacuo for several days at 55 °C. Yield (2.17 g, 23 %) $\delta_{P}$(121.5 MHz; CD$_2$Cl$_2$; H$_3$PO$_4$) 211.0 (1 P, s, E/Z

References start on page 139
isomer), 209.8 (1P, s, E/Z isomer). δH(300.1 MHz, CD2Cl2; SiMe4) 7.50 (2H, m, E/Z Aryl—H),
7.36 (4H, m, E/Z Aryl—H), 7.07 (4H, m, E/Z Aryl—H), 6.91 (2H, m, E/Z Aryl—H), 6.79 (2H, s, E/Z
Aryl—H), 6.70 (4H, m, E/Z Aryl—H), 6.59 (2H, d, JPH = 9 Hz, E/Z Mes—H), 6.32 (2H, d, JPH = 9 Hz,
E/Z Mes—H), 3.39 (4H, q, 3JHH = 7 Hz, E/Z NCH2CH3), 3.27 (4H, q, 3JHH = 7 Hz, E/Z NCH2CH3),
2.30 (6H, s, E/Z o–CH3), 2.27 (6H, s, E/Z o–CH3), 2.24 (3H, s, E/Z p–CH3), 2.17 (3H, s, E/Z p–
CH3), 1.17 (6H, t, 3JHH = 7.2 Hz, E/Z NCH2CH3), 1.09 (6H, t, 3JHH = 7.2 Hz, E/Z NCH2CH3). Low
Res El: m/z 387 [M+, MesP=C(Ph)(4-NEt2-C6H4)], Anal. Calcd. for C26H20NP: C, 80.59; H, 7.80;
N, 3.61. Found: C, 80.37; H, 7.86; N, 3.62.

7.4.3 Preparation of MesP=C(Ph)(4-Cl-C6H4) 7.1b

Liquid MesP(SiMe3)2 (9.87 g, 0.033 mol) was added to a solution of 4-
chlorobenzophenone (7.20 g, 0.033 mol) in dry THF (~20 mL) under inert atmosphere. A
catalytic amount (~0.05 g) of dry NaOH was added to the reaction mixture and upon stirring the
mixture turned a bright yellow. The reaction was stirred under N2 in an inert atmosphere
glovebox for several days. Removal of an aliquot for analysis by 31P NMR spectroscopy
revealed that the MesP(SiMe3)2 had been completely consumed (δ31P = -162) and replaced by 2
signals at (δ31P = 239 and 237). Upon removal of the THF in vacuo, the mixture was transferred
to a round bottom flask and fractionally distilled at high temperatures (> 190 °C). The distillate
was recrystallized from hexanes and ground into a fine powder and dried in vacuo for several
days at 55 °C. The E isomer (δ31P = 239) crystallized selectively. Yield (3.75 g, 32 %) δ31P(121.5
MHz; CD2Cl2; H3PO4) 238.1 (1P, E isomer, s). δH(300.1 MHz, CD2Cl2; SiMe4) 7.46 (2H, m, E
Aryl—H), 7.30 (2H, d, JPH = 8.6 Hz, E Aryl—H), 7.09 (3H, m, E Aryl—H), 6.86 (2H, d, E Aryl—H),
6.72 (2H, s, E Mes—H), 2.25 (6 H, s, E o–CH3), 2.19 (3 H, s, E p–CH3). δC(75.5 MHz, CD2Cl2;
SiMe4 - unassigned) 192.2 (d, JPC = 45 Hz) 143.7 (s). 143.3 (d, JPC = 8 Hz), 143.0 (s), 140.4 (d, 
JPC = 7 Hz), 138.8 (s), 136.1 (d, JPC = 42 Hz), 134.8 (d, JPC = 6 Hz), 129.1 (s), 128.8 (d, JPC = 7
Hz), 128.7 (s), 128.4 (d, JPC = 7 Hz), 127.7 (s) , 22.1 (s), 20.9 (s). Low Res El: m/z 350 [M+,
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MesP=C(Ph)(4-ClC₆H₄)]. Anal. Calcd. for C₂₂H₂₀ClP: C, 75.32; H, 5.75. Found: C, 75.41; H, 5.97.

7.4.4 Preparation of MesP=C(Ph)(4-Me-C₆H₄) 7.1c

Liquid MesP(SiMe₃)₂ (10.0 g, 0.034 mol) was added to a solution of 4-methylbenzophenone (6.62 g, 0.034 mol) in dry THF (~20 mL) under inert atmosphere. Catalytic (~0.05 g), dry NaOH was added to the reaction mixture. Over several hours, the mixture turned bright yellow. After several days of stirring under inert atmosphere, removal of an aliquot for analysis by ³¹P NMR spectroscopy revealed that the MesP(SiMe₃)₂ had been completely consumed (δ₃¹P = -162) and replaced by 2 signals at (δ₃¹P = 230 and 229). Upon removal of the THF in vacuo, the mixture was transferred to a round bottom flask and fractionally distilled at high temperatures (> 200 °C). The distillate was recrystallized from hexanes and ground into a fine powder and dried in vacuo for several days at 55 °C. Yield (4.61 g, 42%). An E/Z mixture was isolated after recrystallization. δₚ(121.5 MHz; CD₂Cl₂; H₂PO₄) 229.9 (1P, s) 229.2 (1P, s). δₚ(300.1 MHz, CD₂Cl₂; SiMe₄) 7.51 (2H, m, E/Z Aryl–H), 7.38 (4H, m, E/Z Aryl–H), 7.13 (6H, dd, E/Z Aryl–H), 6.92 (2H, d, JₗH = 7.2 Hz, E/Z Aryl–H), 6.82 (1H, s, E/Z Aryl–H), 6.79 (1H, s, E/Z Aryl–H), 6.77 (2H, s, E/Z Mes–H), 6.74 (2H, s, E/Z Mes–H) 2.39 (3H, s, E/Z C₆H₄ p–CH₃) 2.31 (6H, s, E/Z Mes o–CH₃), 2.30 (6H, s, E/Z Mes o–CH₃), 2.26 (3H, s, E/Z C₆H₄ p–CH₃), 2.24 (3H, s, E/Z Mes p–CH₃), 2.22 (3H, s, E/Z Mes p–CH₃). Low Res El: m/z 330 [M+, MesP=C(Ph)(4-MeC₆H₄)].

7.4.5 Preparation of MesP=C(Ph)(4-Pyr) 7.1f

An ethereal solution of MeLi (1.4 M, 4.8 mL) was added to a colorless solution of MesP(SiMe₃)₂ (2.0 g, 0.0067 mol) in THF (10 mL) at room temperature. The solution turned yellow upon addition of the MeLi and the reaction mixture was allowed to stir for 1 – 1.5 h at 60 °C. Analysis of the reaction mixture by ³¹P NMR spectroscopy revealed the in situ formation of MesP(Li)SiMe₃, which was treated with 4-benzoyl pyridine (1.23 g, 0.0067 mol) and

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subsequently the reaction mixture was allowed to stir for several hours. The formation of 7.1f was confirmed by $^{31}$P NMR spectroscopy with the appearance of two signals ($\delta_{31P} = 255$ and 246) in the $^{31}$P NMR spectrum. The solvent was removed in vacuo, and the product was extracted with hexanes (3 x 10 mL). Three successive recrystallizations from a minimal amount of hexanes produced the pure product in low yield. (Yield 0.160 g, 8 %) $\delta_{31P}(121.5$ MHz; CDCl$_3$; H$_3$PO$_4$) 255.2 (1P, s) 246.2 (1P, s). $\delta_{H}(300.1$ MHz, CDCl$_3$; SiMe$_4$) 8.56 (2H, dd, E/Z N–CH$_2$) 8.32 (2H, dd, E/Z N–CH$_2$) 7.51–7.48 (2H, m, E/Z Aryl–H) 7.42 – 7.31 (5H, m, E/Z Aryl–H), 7.16 – 7.05 (3H, m, E/Z Aryl–H), 6.83 (2H, m, E/Z Aryl–H), 6.76 (2H, m, E/Z Aryl–H), 6.71 (4H, s, E/Z Mes–H), 2.26 (6H, s, E/Z o–CH$_3$), 2.24 (6H, s, E/Z o–CH$_3$), 2.21 (3H, s, E/Z p–CH$_3$), 2.20 (3H, s, E/Z p–CH$_3$). Low Res El: m/z 317 (M+, MesP=C(Ph)-4-Pyr), Anal. Calcd. for C$_{21}$H$_{20}$PN: C, 79.47; H, 6.35; N, 4.41. Found: C, 79.15; H, 6.54; N, 4.32.

7.4.6 Isolation of poly(methylene phosphine) 7.2 from the distillation residue

The brown residue from the distillation was dissolved in THF (20 mL) and added to a hexanes (ca. 200 ml) which resulted in the precipitation of a yellow flaky solid. The polymer was precipitated four times from a concentrated THF solution with hexanes. The solid was dried in vacuo at 60° overnight. Yield = 0.589 g (6 %). GPC-LLS (THF): $M_n = 22 300$, PDI = 1.22.

7.4.7 Attempted Polymerization of MesP=C(Ph)(4-NEt$_2$-C$_6$H$_4$)

Reaction was conducted with M:I ratio of 33:1. Addition of 19 $\mu$L of 6 BuLi (1.45 M in hexanes) by microsyringe to a stirring yellow solution of 7.1a (0.350 g, 0.9 mmol) in glyme (5 mL) produced an immediate colour change from yellow to red. The reaction mixture was stirred for 13 days in an inert atmosphere glovebox and then an aliquot was removed for NMR analysis. A $^{31}$P NMR spectrum of the reaction mixture exhibited two signals for the E/Z isomers of the MesP=C(Ph)(4-NEt$_2$-C$_6$H$_4$) phosphaalkene but no broad signal corresponding to the desired poly(methylene phosphine) was observed.
7.4.8 Attempted polymerization of MesP=C(Ph)(4-F-C₆H₄)

Reaction was conducted with M:l ratio of 25:1. Addition of 23 μL of ⁹BuLi (1.36 M in hexanes) by microsyringe to a stirring yellow solution of 7.1d (0.275 g, 0.8 mmol) in glyme (2 mL) produced a colour change from yellow to red. The reaction mixture was stirred for 7 days in an inert atmosphere glovebox and an aliquot was removed for NMR analysis. A ³¹P NMR spectrum of the reaction mixture exhibited two signals for the E/Z isomers of the MesP=C(Ph)(4-F-C₆H₄) phosphaalkene and a small broad signal corresponding to the poly(methylenephosphine) was observed. Precipitation of the reaction mixture using hexanes (50 mL) did not yield any of the desired poly(methylenephosphine).

7.4.9 Attempted polymerization of MesP=C(Ph)(2-Py)

Reaction was conducted with M:l ratio of 25:1. Addition of 24 μL of ⁹BuLi (1.36 M in hexanes) by microsyringe to a stirring yellow solution of 7.1e (0.251 g, 0.79 mmol) in glyme (2 mL) produced a colour change from yellow to red. The reaction mixture was stirred for 2 days and ³¹P NMR analysis of the reaction mixture displays two signals for the E/Z isomers of the MesP=C(Ph)(2-Py) phosphaalkene and no signal corresponding to the poly(methylenephosphine) was observed.

7.4.10 Polymerization of MesP=C(Ph)(4-Cl-C₆H₄) to form 7.5

Addition of 50 μL of ⁹BuLi (1.45 M in hexanes) by microsyringe to a stirring yellow solution of 7.1b (0.600 g, 1.72 mmol) in THF (3.0 mL) produced an immediate colour change from yellow to red. Precipitation of the reaction mixture after 2 d into hexanes (2 x 70 mL) resulted in the isolation of the substituted poly(methylenephosphine). (Yield 0.071 g, 12 %). δp (121.5 MHz; CDCl₃; H₃PO₄) -7 (1P, br). GPC-LLS (THF): Mₙ = 17 200, PDI = 1.09;

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7.4.11 Polymerization of MesP=C(Ph)(4-Me-C₆H₄) to form 7.6

Addition of 13.5 μL of "BuLi (1.45 M in hexanes) by microsyringe to a stirring yellow solution of 7.1c (0.350 g, 1.1 mmol) in glyme (2 mL) produced an immediate colour change from yellow to red. The reaction was monitored by ³¹P NMR spectroscopy and proceeded to approximately 90% conversion after 2 days. Precipitation of the reaction mixture into hexanes (2 x 70 mL) resulted in the isolation of the substituted poly(methylenephosphine). (Yield 0.247 g, 71%). δₚ(121.5 MHz; CDCl₃; H₃PO₄)→7 (1P, br). δₚ(300.1 MHz, CDCl₃; SiMe₄) 8 – 6 (11H, br, Aryl–H), 3–0.5 (12H, br, Mes–CH₃, Ph–Me). GPC-LLS (THF): Mn = 27 600 PDI = 1.25.

7.4.12 X-ray crystallography

Crystal Data and refinement parameters are listed in Table 7.1. All single crystal were immersed in oil and mounted on a glass fiber. Data were collected at 173±0.1K on a Bruker X8 APEX 2 diffractometer with graphite-monochromated Mo Kα radiation. Data was collected and integrated using the Bruker SAINT software package. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXTL crystallographic software package from Bruker-AXS. All data sets were corrected for Lorentz and polarization effects.

Compounds 7.1a and 7.1b did not exhibit any crystallographic complexity. Compound 7.1f crystallized as a mixture of E/Z isomers that produced some disorder in modelling atoms N1, N2, C14 and C20. Though the E isomer is shown in Figure 7.4, the Z isomer could also have been displayed.

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7.5 References


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Chapter 8

Summary and Future Directions

8.1 Summary

The main theme of this thesis was two-fold: to develop controlled routes for the polymerization of phosphaalkenes and to expand upon the chemistry of functional polymers possessing phosphorus atoms in the main chain. Living polymerization of olefins has had a profound impact on the broad field of macromolecular chemistry.\textsuperscript{1-4} The expansion of living polymerization techniques to monomers containing inorganic elements in the quest for materials exhibiting unique properties is an exciting prospect.\textsuperscript{5,6} The similar reactivity of alkenes and phosphaalkenes and the previously reported addition polymerization of phosphaalkenes led us to attempt the living anionic polymerization of the MesP=CPh\textsubscript{2} phosphaalkene.\textsuperscript{7-9}

In Chapter 2, the ambient temperature living anionic polymerization of phosphaalkenes was described. Several experiments were conducted to ascertain whether the polymerization proceeded in a living fashion. Performing the polymerization reaction in the glovebox, while rigorously excluding moisture and impurities provided the desired poly(methylene phosphine) with modest molecular weights and low polydispersities. Using \textsuperscript{31}P NMR spectroscopy it was confirmed that the MesP=CPh\textsubscript{2} phosphaalkene was completely consumed and the living\textsuperscript{9}Bu[MesP=CPh\textsubscript{2}]\textsubscript{n}Li had formed quantitatively. Moreover, kinetic studies revealed the polymerization reaction follows pseudo 1\textsuperscript{st} order kinetics up to 50\% conversion with a small apparent rate constant of propagation (\(k_p = 21 \text{ L mol}^{-1} \text{ h}^{-1}\)). Two separate experiments were performed to confirm that the molecular weight of the growing polymer chain increases linearly with conversion. By varying the concentration of \textsuperscript{8}BuLi in the polymerization, precise control over the polymer chain length was achieved. This living methodology was also expanded to the MesP=C(Ph)(4-OME-C\textsubscript{6}H\textsubscript{4}) substituted monomer. Finally, to illustrate the living nature of the
A block copolymer was prepared from styrene and MesP=CPh₂. Treatment of a MesP=CPh₂ solution in glyme with living polystyryl anion resulted in the synthesis of the polystyrene-block-poly(methylene phosphine) 2.6. Two separate copolymer experiments were conducted and the expected molecular weights were in reasonable agreement with those determined using triple detection GPC analysis.

Upon confirmation of the living nature of phosphaalkene polymerization, the "BuLi initiated living anionic polymerization of MesP=CPh₂ was studied at a variety of temperatures (T = 296.3, 301.8, 307.4, 313, 318.6, and 324.2 K) with a fixed monomer to initiator ratio (50:1). The consumption of monomer and formation of polymer were monitored by ³¹P NMR spectroscopy and the conversion data obtained was analyzed using first order kinetics. Up to 50% conversion, the plot of ln [M]₀/[M] vs. time was linear and apparent propagation rate constants (kₚ) were extracted (kₚ = 21 – 150 L mol⁻¹ h⁻¹; T = 296.3 – 324.2 K, respectively). These rate constants were used to construct an Arrhenius Plot and the apparent activation energy for the polymerization of P=C bonds was estimated (Eₐ = 14.0 ± 0.9 kcal mol⁻¹).

The self-assembly of diblock copolymers is an area of current interest as their phase separation capabilities can result in the formation of controlled nanostructures. In particular, the potential to exploit block copolymer architectures as nanoscale tools to organize metals is attracting attention. Polysoprene-block-poly(methylene phosphine) copolymers (4.2) were synthesized by combination of living polyisopropenyl lithium with a MesP=CPh₂ solution in THF. These copolymers were then coordinated to AuCl by treatment of the PI–b–PMP copolymer with (tetrahydrothiophene)AuCl at room temperature. Both ³¹P NMR spectroscopy and GPC analysis confirmed the coordination of the AuCl moiety. Solution self-assembly of the metallated block copolymers from dilute solutions of heptane were analyzed using transmission electron microscopy revealing that both spherical and cylindrical morphologies of the Au-rich PMP domains were accessible simply by altering the chain lengths of the respective PI and PMP blocks.

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Chapter 5 described some coordination chemistry of the poly(methylene phosphine) with two isoelectronic species; namely, BH₃ and CH₃. The potential reactivity of the phosphine polymer is modeled by examining the reactivity of molecular phosphines bearing similar substituents as the polymer. In particular, the phosphine-borane adducts Mes(Me)P(BH₃)—CPh₂H (5.4a) and Mes(Me)P(BH₃)—CPh₂SiMe₃ (5.4b) are prepared from the reaction of BH₃·SMe₂ with either Mes(Me)P—CPh₂H (5.3a) or Mes(Me)P—CPh₂SiMe₂H (5.3b). Treating 5.3a with MeOTf affords methylated model compound, [Mes(Me)₂P—CPh₂H]OTf (5.5). Reacting the poly(methylene phosphine) with BH₃·SMe₂ affords the phosphine-borane polymer n-Bu[MesP(BH₃)—CPh₂]ₙH (5.6) (Mn = 4.13 x 10⁴, PDI = 1.26). In contrast, methylation of poly(methylene phosphine) gives n-Bu[MesP—CPh₂]ₙ—/[MesP(Me)—CPh₂]HOTf (5.7) where approximately 50% of the phosphine moieties are methylated (from ³¹P NMR).

In order to incorporate more functionality into the poly(methylene phosphine), Fe containing polymers were prepared. The ferrocenyl phosphaalkene Mes P=C(Ph)(Fc) (6.1) was prepared from MesP(Li)(SiMe₃) and FcC(O)(Ph). This phosphaalkene was polymerized by anionic methods yielding a redox-active polymer (6.2: Mn = 9500 g mol⁻¹, PDI = 1.21). One quasi-reversible oxidation was observed upon electrochemical oxidation of the polymeric species, this was assigned to the ferrocene-ferricinium redox couple. The monomer also exhibited some intense absorptions in the visible spectrum, which is indicative of π-conjugation between the P=C and ferrocenyl moiety.

Chapter 7 described the synthesis of four new phosphaalkenes bearing new functional groups using the phospha-Peterson reaction. The four new phosphaalkenes MesP=C(Ph)(4-NEt₂-C₆H₄), MesP=C(Ph)(4-Cl-C₆H₄), MesP=C(Ph)(4-Me-C₆H₄) and MesP=C(Ph)(4-Py) were characterized using NMR, x-ray analysis, mass spectrometry and elemental analysis. Some preliminary investigations to polymerize these new phosphaalkenes were conducted and not all of the monomers can be polymerized using anionic methods. This was somewhat surprising and further investigations must be undertaken to better probe this behavior.

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In conclusion, P=C bonds have been shown to polymerize in a controlled fashion. Several block copolymer architectures bearing functional phosphine units in the polymer backbone have been synthesized by sequential anionic polymerization. Several new P=C monomers have been synthesized and polymerized in an attempt to tailor the properties of the resultant poly(methylene phosphine).

8.2 Future Work

As this project has provided a controlled mild route to poly(methylene phosphine)s, the expansion of living polymerization techniques to other phosphaalkene monomers such as 6.1, 7.3b and 7.3c should be undertaken. These monomers have already been shown to polymerize by anionic methods and finding the optimal conditions for living polymerization seems to be a logical extension of this work. Expanding living polymerization to monomer 6.1 could provide access to redox active copolymers, perhaps forming micellar structures from simple redox chemistry, similar to the polystyrene-block-polyferrocenylsilane copolymers described in Chapter 1 (Section 1.4). Another crucial investigation in this work will be to investigate whether monomers MesP=C(Ph)(4-NeEt2-C6H4), MesP=C(Ph)(4-F-C6H4), MesP=C(Ph)(2-Py) and MesP=C(Ph)(4-Py) will polymerize by anionic methods if the polymerization conditions are modified. Why some of these monomers are not amenable to anionic polymerization is not yet understood and further investigation is necessary.

In terms of future directions for the MesP=CPh2 monomer there are many different copolymer architectures that should be synthesized for example, ABA triblock copolymers should be prepared. If styrene is initiated using the electron transfer reagent sodium naphthalide, it is known to polymerize in two directions forming two active chain ends (Scheme 8.1). These two Na stabilized ends could then be used to polymerize MesP=CPh2 and form the triblock copolymer illustrated in Scheme 8.1, poly(methylene phosphine)-block-polystyrene-block-poly(methylene phosphine).

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Another potentially accessible block copolymer that may possess intriguing self-assembly properties are poly(methyl methacrylate)-block-poly(methylene phosphine)s. Poly(methyl methacrylate) is known to form crystalline domains and in combination with the amorphous poly(methylene phosphine) interesting self-assembled structures should be accessible. Methyl methacrylate necessitates fairly special reaction conditions for polymerization to proceed in a living fashion.\textsuperscript{14-16} As outlined in Scheme 8.2, the low temperature (\(-78 \, ^\circ\text{C}\)) polymerization of methyl methacrylate using 1,1-diphenylhexyllithium proceeds in a living fashion. The living chain end of MesP=CPh\textsubscript{2} polymerization bears a strong resemblance to 1,1-diphenylhexyllithium in that the carbanion is doubly-benzylic. I propose that AB block copolymers where the A block is poly(methylene phosphine) and the B block is poly(methyl methacrylate) could be synthesized by initiating the methyl methacrylate polymerization at low temperature. This would potentially provide access to elastomeric polymers bearing phosphine functional groups.
Scheme 8.2  1,1-diphenylhexyllithium is prepared from 1,1-diphenylethylene and n-butyl lithium and used to initiate living methyl methacrylate polymerization. The living chain end formed by polymerization of MesP=CPh₂ resembles 1,1-diphenylhexyllithium in terms of its nucleophilicity as they are both doubly-benzylic. Thus, living poly(methylene phosphine) should be a suitable initiator to polymerize methyl methacrylate and synthesize poly(methyl methacrylate)-block-poly(methylene phosphine).

New monomers for anionic polymerization are also of interest within the Gates group. Currently, P-Mes phosphaalkenes possessing aryl substituents on the carbon have been shown to polymerize but MesP=CR₂ systems bearing alkyl substituents have not yet been polymerized (R = alkyl). Recently, our collaborators reported the synthesis of the MesP=C(H)(tBu) phosphaalkene, and I suspect that anionic polymerization of this monomer should be possible under the appropriate reaction conditions.¹⁷ The rate constant of propagation for this MesP=C(H)(tBu) polymerization should be much higher than 21 L mol⁻¹ h⁻¹ because the formed carbanion upon attack of the n-BuLi initiator across the P=C bond would be much less stabilized. The tBu and H groups would not provide any resonance stabilization which is in sharp contrast to the two phenyl groups of the doubly-benzylic carbanion from MesP=CPh₂ polymerization (Scheme 8.3).
Scheme 8.3  Reaction of MesP=CPh₂ with °BuLi forms a doubly benzylic carbanion. Addition of °BuLi across the MesP=C(H)(°Bu) phosphaalkene will form a less stabilized carbanion because the t-butyl and H groups do not provide any resonance stabilization.

The preparation of a thiophene-containing phosphaalkene could be of interest for preparing polymers with interesting optical or electronic properties (Scheme 8.4). The synthesis of this monomer should be possible using the base-catalyzed phospha-Peterson reaction. The polymer would possess not only a functional phosphine moiety but also a sulfur atom that could impart some interesting characteristics to the polymer. Possible avenues to further chemically functionalize the polymer include; exploring the coordination chemistry of the thiophene, forming bimetallic polymers by coordinating the phosphine and sulfur atoms to metals, or substitution of the 5-position on the thiophene ring to impart more functional groups to the polymer structure.

Scheme 8.4  Preparation of thiophene-containing phosphaalkene from the combination of Mes(SiMe₃)₂ and benzoyl thiophene using the base catalyzed phospha-Peterson reaction.

One of the earlier projects in the Gates group which was discussed in Chapter 1 involved the attempted cationic polymerization of the Mes*P=CH₂ phosphaalkene.¹⁸,¹⁹ This compound was combined with substoichiometric quantities of HOTf which produces oligomers of up to 6 repeat units as determined by ESI mass spectrometry. I propose that this compound will undergo anionic polymerization by combining Mes*P=CH₂ and °BuLi under identical reaction conditions for the MesP=CPh₂ phosphaalkene polymerization (Scheme 8.5). One reaction that

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Chi-Wing Tsang conducted in our laboratory prior to my arrival at UBC involved combination of Mes*P=CH₂ with MeLi in THF. As expected, the yellow Mes*P=CH₂ reaction solution turns deep red upon addition of the ethereal MeLi solution. However, the reaction was only stirred for 30 min and precipitation from hexanes yielded no polymer. From Chapters 2 and 3, the MesP=CPh₂ polymerization with 2% n-BuLi requires 9 h to quantitatively convert to poly(methylenephosphine), therefore I suspect that anionic Mes*P=CH₂ polymerization will necessitate longer than 30 min and this reaction should be revisited.

\[
\begin{align*}
\text{Mes}^*\text{P}=\text{CH}_2 & \xrightarrow{1,\text{n-BuLi}} \xrightarrow{2,\text{MeOH}} (\text{Mes}^*\text{P}=\text{CH}_2)_n \\
\end{align*}
\]

**Scheme 8.5** Polymerization of Mes*P=CH₂ using n-butyl lithium as the initiator. MeOH is employed as an electrophile to quench the reactive anions after polymerization.

The living anionic polymerization of phosphaalkenes has opened up new avenues of exploration for incorporating functional phosphine units into controlled macromolecular architectures. There remains much work to be done in this area, including making new block copolymer architectures such as the proposed poly(methylenephosphine)-block-poly(methylmethacrylate) or attempting to make ABA triblock copolymers. The preliminary research in controlling the size and morphology of self-assembled block copolymer architectures described in Chapter 4 must be expanded upon including studies to attempt bulk phase self-assembly of PS-PMP copolymers. The polymerization behavior of phosphaalkenes must be studied in further detail as well as expanding upon the monomers that form polymers. The potential to prepare functional polymers with unique properties is of significant interest and further exploration is needed into the area of phosphaalkene polymerization.

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8.3 References


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Figure A1. - Refractive index traces of 2.3a (Table 2.1 entries 1-4) with increasing $M_n$ (black trace – $M:l = 100:1$, blue trace – $M:l = 50:1$, pink trace – $M:l = 33:1$, green trace – $M:l = 25:1$.)
Figure A2. GPC trace of 2.3b (Table 2.1, entry 5). $M_n = 11500$ (red trace – viscometer signal, green trace – refractive index signal, black trace – laser light scattering signal).

Figure A3. GPC trace of 2.3b (Table 2.1, entry 6) $M_n = 14600$. (red trace – viscometer signal, green trace – refractive index signal, black trace – laser light scattering signal).
Appendix B

Table B1. Monomer conversion data collected for the polymerization of 3.1 using 2% BuLi as initiator at 296.3 K.

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<th>Time (h)</th>
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$^a$[M] = 3.1, [M$_0$] = 0.394 mol L$^{-1}$. Molecular weight of isolated polymer 3.4 after quenching with H$^+$ ($M_n = 13500$, PDI = 1.07).
Table B2. Monomer conversion data collected for the polymerization of 3.1 using 2% $^7$BuLi as initiator at 301.8 K.

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$^a[M] = 3.1. [M_0] = 0.392 \text{mol L}^{-1}$. Molecular weight of isolated polymer 3.4 after quenching with H$^+$ ($M_n = 15100$, PDI = 1.02).
Table B3. Monomer conversion data collected for the polymerization of 3.1 using 2% \( ^{\text{a}}\text{BuLi} \) as initiator at 307.4 K.

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<tr>
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<td>0.0327</td>
<td>2.4877</td>
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</tr>
</tbody>
</table>

\( ^a[M] = 3.1. [M]_0 = 0.394 \text{ mol L}^{-1}. \) Molecular weight of isolated polymer 3.4 after quenching with H\(^+ \) \((M_n = 13800, \text{PDI} = 1.05)\).
Table B4. Monomer conversion data collected for the polymerization of 3.1 using 2% \textsuperscript{6}BuLi as initiator at 313.0 K.

<table>
<thead>
<tr>
<th>Entry</th>
<th>percent conversion determined by (^{31}\text{P} \text{NMR} )</th>
<th>( [M]^{a} ) mol L(^{-1} )</th>
<th>( \ln [M_0]/[M] )</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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</tr>
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<td>0.2963</td>
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<tr>
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<td>2.8098</td>
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</table>

\(^{a}[M] = 3.1. [M_0] = 0.392 \text{ mol L}^{-1}. \text{ Molecular weight of isolated polymer } 3.4 \text{ after quenching with } H^+ (M_n = 14400, \text{ PDI } = 1.09).\)

Table B5. Monomer conversion data collected for the polymerization of 3.1 using 2% \textsuperscript{6}BuLi as initiator at 318.6 K.

<table>
<thead>
<tr>
<th>Entry</th>
<th>percent conversion determined by (^{31}\text{P} \text{NMR} )</th>
<th>( [M]^{a} ) mol L(^{-1} )</th>
<th>( \ln [M_0]/[M] )</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
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</tr>
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</tr>
<tr>
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<td>0.75</td>
</tr>
<tr>
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</table>

\(^{a}[M] = 3.1. [M_0] = 0.397 \text{ mol L}^{-1}. \text{ Molecular weight of isolated polymer } 3.4 \text{ after quenching with } H^+ (M_n = 12300, \text{ PDI } = 1.07).\)
Table B6. Monomer conversion data collected for the polymerization of 3.1 using 2% BuLi as initiator at 324.2 K.

<table>
<thead>
<tr>
<th>Entry</th>
<th>percent conversion determined by $^{31}$P NMR</th>
<th>[M]&lt;sup&gt;a&lt;/sup&gt; mol L&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>In [M&lt;sub&gt;0&lt;/sub&gt;]/[M]</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
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<tr>
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<tr>
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<tr>
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</tbody>
</table>

$^a$[M] = 3.1. [M<sub>0</sub>] = 0.397 mol L<sup>-1</sup>. Molecular weight of isolated polymer 3.4 after quenching with H<sup>+</sup> ($M_n = 13 600$, PDI = 1.05).

Table B7. Monomer conversion data collected for the polymerization of 3.1 using 4% BuLi as initiator at 296.3 K.

<table>
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<tr>
<th>Entry</th>
<th>percent conversion determined by $^{31}$P NMR</th>
<th>[M]&lt;sup&gt;a&lt;/sup&gt; mol L&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>In [M&lt;sub&gt;0&lt;/sub&gt;]/[M]</th>
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$^a$[M] = 3.1. [M<sub>0</sub>] = 0.395 mol L<sup>-1</sup>. Molecular weight of isolated polymer 3.4 after quenching with H<sup>+</sup> ($M_n = 8 800$, PDI = 1.09).
Inversion-Recovery($T_1$)

$I(t) = I(0)(1- e^{-t/T_1})$

Region 1 from 236.199 to 234.433 ppm
$T_1 = 1.329s$

**Figure B1.** $T_1$ Inversion Recovery Sequence recorded for compound MesP=CPh$_2$. 