SYNTHESIS AND CHARACTERIZATION OF NEW π-CONJUGATED MOLECULES AND POLYMERS CONTAINING PHOSPHORUS

by

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Abstract

In this thesis, the synthesis and characterization of a new class of \( \pi \)-conjugated polymers is reported. In these new macromolecules, poly(\( p \)-phenylenephosphaalkene)s, the main chain consists of alternating aromatic rings and \( P=C \) groups. Several model compounds (Ph-\( P=C(\text{OSiMe}_3)\)-Mes, Ph-\( P=C(\text{OSiMe}_3)\)-\( C_6\text{Me}_4\)-C(\( \text{OSiMe}_3 \))=P-Ph, Mes-C(\( \text{OSiMe}_3 \))=P-\( C_6\text{H}_4\)P=C(\( \text{OSiMe}_3 \))-Mes) are reported for comparison to the polymer. This comparison illustrates that the polymer exhibits a degree of extended \( \pi \)-conjugation throughout the backbone of the material.

The effects of using thiophene (Tp) as an aromatic spacer in a poly(\( p \)-thiénylenephosphaalkene) are investigated, and reveal an increase in the UV/Vis maximum absorbance compared to phenylene systems. Two compounds (Tp-\( P=C(\text{OSiMe}_3)\)-Mes, Mes-C(\( \text{OSiMe}_3 \))=P-Tp-P=C(\( \text{OSiMe}_3 \))-Mes) are described as model compounds for the polymer. Mes-\( P=C(\text{OSiMe}_3) \)-Tp shows a significant increase in the UV/Vis maximum absorbance wavelength compared to the conformational isomer discussed above.

If the sterically demanding substituent resides on the phosphorus atom of the phosphaalkene bond in phenylene systems, a single isomer of the phosphaalkene forms selectively. Solid state structures of Mes-\( P=C(\text{OSiMe}_3) \)-Ph, Mes-\( P=C(\text{OSiMe}_3) \)-\( C_6\text{H}_4\)-C(\( \text{OSiMe}_3 \))=P-Mes, and Ph-C(\( \text{OSiMe}_3 \))=P-\( C_6\text{Me}_4\)-P=C(\( \text{OSiMe}_3 \))-Ph were determined. The corresponding polymer was synthesized and characterized.

Due to the synthetic route to the \( P=C \) bond which forms a siloxy group, these compounds are quite sensitive to protonolysis. Preliminary results towards preparing more robust poly(\( p \)-phenylenephosphaalkene)s are discussed.
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List of Abbreviations

Tp ........................................... Thiophene
Mes ........................................... 2,4,6-trimethylphenyl or mesityl
Mes* ........................................... 2,4,6-tri(tert-butyl)phenyl or supermesityl
Trip .......................................... 2,4,6-tri(isopropyl)phenyl
Ad ........................................... Adamantyl
'Bu ............................................. tertiary-butyl
'nBu ........................................... straight chain butyl
Cp ........................................... cyclopentadienyl
UV ........................................... Ultraviolet
UV/Vis ...................................... Ultraviolet-visible
HOMO ...................................... Highest Occupied Molecular Orbital
LUMO ...................................... Lowest Unoccupied Molecular Orbital
$\bar{X}_n$ ...................................... Number Average Degree of Polymerization
M ........................................... Moles/Litre
$p$ ........................................... Fraction of Reaction Conversion
ROP .......................................... Ring-opening Polymerization
PPV .......................................... Poly(p-phenylenevinylene)
$M_w$ .......................................... Weight Average Molecular Weight
$M_n$ .......................................... Number Average Molecular Weight
MW .......................................... Molecular Weight
GPC .......................................... Gel Permeation Chromatography
PDI .......................................... Polydispersity Index
AIBN ........................................ 2,2’-azobisisobutyronitrile
$\lambda_{\text{max}}$ ................................ UV/Vis Maximum Absorbance
TGA ........................................................ Thermogravimetric Analysis
TMEDA .................................................. \( N,N' \)-tetramethylethylenediamine
NMR ...................................................... Nuclear Magnetic Resonance
DBU ....................................................... \( 1,5 \)-diazabicyclo[5.4.0]undec-5-ene
Na ........................................................ Sodium metal
\( ^\circ \) C ....................................................... degrees Celcius
K .............................................................. degrees Kelvin
\( T_c \) ........................................................ Superconductivity temperature
\( \phi_P \) ....................................................... Dihedral angle between plane of \( P=C \) bond
and the aryl substituent at the phosphorus atom of the phosphaalkene
\( \phi_C \) ....................................................... Dihedral angle between plane of \( P=C \) bond
and the aryl substituent at the carbon atom of the phosphaalkene

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Statement of Co-Authorship

Chapter One

Chemistry at the Crossroads: An Introduction to the Challenges of Combining Inorganic, Organic, and Polymer Chemistry

1.0 Introduction

Throughout the entirety of chemical literature, research involving organic, or carbon containing compounds has been the predominant focus. This attention has ensured that the chemistry of carbon is well known and quite predictable. Since the 1920’s there has been considerable interest in generalizing the chemistry of carbon to other elements in the p-block. The initial search for a carbon analogue led to investigation of the element below carbon in the periodic table, silicon. F. S. Kipping, a pioneer of silicon chemistry, carried out extensive attempts to prepare compounds with Si=C, Si=O, and Si=Si bonds. At one point, he claimed to have successfully synthesized a disilene, Ph(Et)Si=Si(Et)Ph (1).\(^1\) Unfortunately, later studies proved all of the compounds Kipping prepared were not multiply bonded systems but singly bonded oligomers or polymers. Kipping later concluded that it was impossible to form multiple bonds to silicon.\(^2\)

![Chemical Structures](image)

Attempts to prepare compounds with multiple bonds between heavier p-block elements by a variety of chemists were met with similarly negative results. Of particular interest, in 1877 Köhler and Michaelis reported the synthesis of phosphobenzene (2), the phosphorus analogue of azobenzene.\(^3\) Thirty years after this report, Erlich attempted to prepare a compound with an As=As bond.\(^4\) The molecules thought to contain double

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bonds between phosphorus, arsenic, antimony, and germanium were later proven to be cyclic oligomers in most cases. Several landmarks occurred in 1981, when reports of compounds with a Si=Si bond by West et al. (3), and a Si=C bond by Brook et al. (4), appeared to justify the thought of using silicon as an analogue of carbon. However, further exploration of these systems revealed that the difficulty of synthesis and the high reactivity of these bonds made it exceedingly difficult to parallel alkene chemistry. Also in 1981, Yoshifuji et al. were able to synthesize and crystallographically characterize a diphosphene, the first compound to contain a phosphorus-phosphorus double bond (5).!

\[
\begin{array}{ccc}
\text{Mes} & \text{Mes} & \text{Mes} \\
\text{Si}=	ext{Si} & \text{Ad} & \text{P}=	ext{P} \\
\text{Mes} & \text{Mes} & \text{Mes} \\
\text{Me}_3\text{Si} & \text{O} & \\
\end{array}
\]

The family trends in the periodic table would suggest that silicon would be the element that most closely resembles carbon. These trends reflect the number of valence electrons of the element, and thus the valency of the central atom. In terms of valency however, there are some important differences between carbon and nitrogen, and their heavier congeners silicon and phosphorus. The latter can expand to six coordinate (hypervalence) due in part to their greater covalent radii (Si 1.11, P 1.10 versus C 0.77, N 0.70 Å) and possibly access to low-lying 3d orbitals. Recently, a diagonal relationship between carbon and phosphorus has been noted due to the similarities in electronegativity (C 2.5 versus P 2.2). In support of the phosphorus-carbon parallel, a number of striking similarities between the chemistry of low coordinate phosphorus and carbon are documented. This relationship is examined more closely in section 1.5.

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1.1 Research Objectives of this Thesis

The research goal of this project was to develop a synthetic route to incorporate phosphorus(III)-carbon double bonds into the main chain of a formally \( \pi \)-conjugated polymer. This effectively combines three separate fields:

1) **Multiple Bonds between Main Group Elements.** In the late 1970's, several examples of stable neutral compounds possessing acyclic \( (p-p)\pi \) bonds between heavier \( p \)-block elements were discovered.\(^{13}\) The bonding in these compounds is a subject of scientific debate, and continues to generate current interest.\(^ {14, 15} \)

2) **\( \pi \)-Conjugated Organic Polymers.** Organic \( \pi \)-conjugated polymers have attracted significant attention in recent years due to their interesting properties.\(^ {16-18} \) Of note, the Nobel prize in chemistry for the year 2000 was awarded to Heeger, MacDiarmid, and Shirakawa for their work on the electrically conducting organic \( \pi \)-conjugated polymer, polyacetylene, originally reported in 1977.\(^ {19} \)

3) **Inorganic Polymers.** The incorporation of inorganic elements into a polymer backbone is synthetically challenging and often results in materials with unique properties.\(^ {20} \)

Therefore, the development of methods to prepare \( \pi \)-conjugated polymers containing heavier main-group \( (p-p)\pi \) bonds is of fundamental interest, and may ultimately lead to materials with novel properties. In this thesis, the synthesis and characterization of some poly(arylenephosphaalkene)s, a new class of \( \pi \)-conjugated macromolecules, which contain phosphorus(III)-carbon double bonds in the polymer backbone is disclosed. It could be said that these polymers reside at an intersection of the three established fields of chemistry mentioned above. Thus, selected examples from each of these areas are touched upon during this introduction.
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1.2 Phosphorus – A Brief History

This thesis deals primarily with the chemistry of the element phosphorus. Phosphorus is a fascinating main group element with an extensive inorganic chemistry and likewise, innumerable organic phosphorus compounds are known. Phosphorus also plays important roles in many biochemical processes and is a critical component of all living things since DNA could be considered a phosphate macromolecule. Phosphorus has arguably one of the most intriguing histories of all the elements known, and a brief summary is given. In 1669, a German physician and alchemist named Hennig Brandt isolated phosphorus in an elemental form by distilling the residue of putrified urine making it the only element discovered from a human/animal source. The story of the differing reports of its discovery from a variety of people, is quite interesting. In its most common elemental form, \( P_4 \), phosphorus is a white, waxy substance which glows in the dark when exposed to air. In 1680, Robert Boyle improved the process, and referred to the material as “aerial noctiluca”, however the name phosphorus (Greek \( phos \), light; Greek \( phorus \), bringing) became generally accepted over time. Remarkably, it was not until a century later, in 1779 when Gahn discovered the first mineral source of phosphorus, a lead phosphate mineral called pyromorphite. Bergman and Proust subsequently found that the more abundant mineral apatite could also be a phosphorus source.

The pyrophoric nature of the element lead to its first uses in technology as Dérosne invented a phosphorus containing striking match in 1812. In 1848, Schrötter discovered a less reactive allotrope called “red phosphorus” which led to the Lundström brothers inventing “safety matches” in 1855. Just before the turn of the century Sévène and Cahen developed “strike anywhere” matches in France. In 1952, detergents based on polyphosphates overtook soap as the main washing agent in the USA, and heavy-duty

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liquid polyphosphate detergents were introduced in 1955. It is disturbing to note that whilst phosphorus is an essential element for life, and is present in all fertilizers, it is also an important component in weapons such as incendiary bombs and nerve gases.

The biological importance of phosphorus was revealed when phosphorus was first detected in plants by Albino in 1688. It was not until 1929 that Fiske and Subbarow discovered adenosine triphosphate (ATP) in muscle fibers, where it was found to be a chemical energy source used in biological cells. In the early 1940’s it was established that highly polymeric phosphate esters (nucleic acids) are present in all cells, and recognized as essential constituents of chromosomes. Some twenty years after its discovery in the body, Todd synthesized ATP garnering the Nobel Prize in 1957. In 1953, Crick, Watson, and Wilkins (with the help of Rosalind Franklin) established the now famous double helix structure of nucleic acids (DNA), a key component being phosphorus, for which they were awarded the Nobel Prize in chemistry in 1962.

Phosphorus has only one naturally occurring isotope, $^{31}$P, which has a nuclear spin quantum number of $\frac{1}{2}$, and is of great utility in NMR spectroscopy. Dickinson measured the first $^{31}$P NMR chemical shifts (for POCI$_3$, PCl$_3$, etc. versus aqueous H$_3$PO$_4$) in 1951. In 1960 the concept of “pseudo-rotation” was introduced by Berry to rationalize the equivalence of the five fluorines in trigonal bipyramidal PF$_5$. In 1979, G. Wittig shared the Nobel prize in chemistry for the development of the Wittig reaction for olefin synthesis (Scheme 1), first reported in 1953. Wittig showed that a methylenetriphenylphosphine (6) would react with benzophenone (7) to produce triphenylphosphine oxide (8) and 1,1-diphenylethene (9).

$$\begin{align*}
\text{Ph}_3\text{P}=\text{C}=\text{H} & \quad + \quad \text{O}=\text{C}=\text{Ph} & \quad \rightarrow & \quad \text{Ph}_3\text{P}=\text{O} & \quad + & \quad \text{C}=\text{C}=\text{C}=\text{C} \quad \text{H} \quad \text{Ph} \\
6 & \quad 7 & \quad & 8 & \quad 9
\end{align*}$$
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Scheme 1.

It should now be evident that phosphorus has played a key role in chemistry and life. Recently, the chemistry of phosphorus in low coordinate environments has generated significant interest. This topic is discussed in more detail in the next section.

1.3 Heavier Main Group Element Multiple Bonds

1.3.1. The Classic “Double Bond Rule”

Although structures with low coordinate phosphorus atoms were postulated at the beginning of the 20th century, during this time the focus of phosphorus chemistry was on the synthesis and properties of three- (10), four- (11, 12), and five-coordinate (σ*) compounds (13) with three- (10), four- (11), or five-valent (λ*) phosphorus (12, 13). Examples of advances during this time are the Michaelis-Arbusov and Wittig reactions.

\[ \begin{align*}
\text{R}^3 & , \sigma^3, \lambda^3 \\
\text{R}^+ & , \sigma^4, \lambda^4 \\
\text{R}^- & , \sigma^4, \lambda^5 \\
\text{P}^{-} & , \sigma^5, \lambda^5 \\
10 & \\
11 & \\
12 & \\
13 & 
\end{align*} \]

For quite some time, a target of synthetic chemists around the world has been the preparation of molecules containing heavier main group elements with (p-p)\(\pi\) bonds. The first row of elements, carbon, nitrogen, and oxygen all readily form multiple bonds, thus making the lack of heavier congeners conspicuous. Indeed, Dasent dedicated an entire chapter to heavier main group element multiple bonding in his book entitled “Nonexistent Compounds – Compounds of Low Stability” in 1965.26 The “phosphobenzene,” (2),3 a phosphorus containing analogue of azobenzene (14) was later re-examined by J. J. Daly et al. in a series of papers during the 1960’s. The reported compound 2 was found to consist of five or six membered rings (15) which were structurally characterized.27-30

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Similarly, molecules thought to contain As=As,$^4$ Si=Si,$^{31}$ and Si=C double bonds were also later shown to be cyclic oligomeric species consisting of single bonds.$^{32,33}$ These experimental observations were supported by some theoretical papers by Pitzer$^{34}$ and Mulliken$^{35}$ which predicted that $\pi$ bonds between heavier main group elements would be very weak. These results led to the classic "double bond rule," which stated that elements of principal quantum number $n$ greater than or equal to three could not form stable (p-p)$\pi$ bonds.$^{34-39}$

\[
\begin{align*}
\text{Ph} & \quad \text{P} = \text{P} \quad \text{Ph} \\
\text{Ph} & \quad \text{N} = \text{N} \\
\text{Ph} & \quad \text{P} \text{-} \text{P} \text{-} \text{Ph} \\
\text{Ph} & \quad \text{P} \text{-} \text{P} \text{-} \text{Ph}
\end{align*}
\]

Around the time that many of the compounds initially thought to contain heavier main group element double bonds were being re-examined, new molecules containing genuine multiple bonds were being prepared as transient species. In 1961, a new era of phosphorus chemistry began inauspiciously with the preparation of two compounds containing low coordinate phosphorus(III) (in which the number of substituents, $\sigma$, is smaller than the number of bonds, $\lambda$), an $(\sigma^2, \lambda^3)$ adduct 16$^{40}$ and a $(\sigma^1, \lambda^3)$ phosphaalkyne 17.$^{41}$ These compounds proved to be unstable at room temperature, and were characterized in the gas phase. Although these reports were greeted with skepticism due to the so called "double bond rule", it proved to be the starting point for the burgeoning field of low coordinate phosphorus chemistry. The parent diphosphene (18) was first detected in 1966 as a transient species produced by thermal decomposition of P$_2$H$_4$$^{42,43}$ and later photolysis of P$_2$H$_4$.$^{44}$

\[
\begin{align*}
\text{Me}_3\text{P} = \text{P} - \text{CF}_3 & \quad \text{H} - \text{C} = \text{P} \\
16 & \quad 17 & \quad 18
\end{align*}
\]

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1.3.2. (3p-2p)π-Bond Stability

It became apparent that molecules containing multiple bonds between heavier main group elements could be prepared but not isolated, as the (p-p)π bond was quite weak.\textsuperscript{10} Below the first row of the periodic table the π bond is not as strong as the σ bond, thus the double bond is thermodynamically unstable with respect to cyclodimerization or oligomerization (Y, in Figure 1.1). To access an isolable molecule with a heavier main group element multiple bond, the molecule must be stabilized either thermodynamically or kinetically. Thermodynamic stabilization can occur through incorporation of the E=E bond (where E is any p-block element) into a π-conjugated system, thereby lowering the energy of the double bond (X, in Figure 1.1). This lower energy of the E=E bond makes dimerization or oligomerization unfavourable because ΔH becomes positive. Using substituents that are sterically demanding imparts kinetic stabilization to the E=E multiple bond by increasing the activation energy of dimerization (ΔA).

\textbf{Figure 1.1.} Reaction Coordinate diagram showing the reaction of a multiple bond to single bonded species.
1.3.3. Low Coordinate Phosphorus Compounds

In 1964 Dimroth and Hoffman reported the first isolable (σ², λ³) phosphorus compound, the phosphamethine cyanine cation 19. 2,4,6-Triphenylphosphabenzene (20) was prepared by Märkl in 1966, and the parent phosphabenzene (21) was characterized by Ashe in 1971. These compounds depend mostly on thermodynamic stabilization of the phosphorus-carbon double bond through π-delocalization. In the study of heavier main group element multiply bonded compounds, the structures grew smaller and simpler as the limits of kinetic and thermodynamic stabilization required to obtain an isolable molecule were pushed.

In 1976, Becker prepared the first isolable, acyclic compound containing a localized phosphorus-carbon double bond (22), known as a phosphaalkene, as shown in Scheme 2. This phosphaalkene was kinetically and thermodynamically stabilized by sterically demanding substituents at carbon.

![Phosphorus Compounds](image)

Scheme 2.

Slightly before the report of the first phosphaalkene, a low coordinate amino(imino)phosphine (23) was prepared by Niecke and Flick in 1973. Both Niecke and Scherer reported the (σ³, λ⁵) metaphosphate derivative (24) in 1974, featuring a trigonal planar coordinated phosphorus atom.

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In 1981, two independent research groups headed by Appel and Becker reported phosphaalkynes, a (\(\sigma^1,\lambda^3\)) compound containing a localized phosphorus-carbon triple bond. The trimethylsilylphosphaalkyne (25) reported by Appel et al. was not stable at room temperature.\(^{52}\) In contrast, the tert-butylphosphaalkyne (26) reported by Becker et al. was distilled as a clear liquid.\(^{53}\) More recently, a bisphosphaalkyne (27) was crystallographically characterized.\(^{54}\) 1981 was a year of unprecedented advances in heavier main group element multiple bond chemistry. A disilene, a compound with a genuine silicon-silicon double bond, was reported by West et al. (4).\(^{6}\) The silicon-carbon double bond was prepared by Brook et al. (5).\(^{7}\) Also in the same year, Yoshifuji et al. characterized the first compound with a localized phosphorus-phosphorus double bond, the trans-diphosphene (6).\(^{8}\) Niecke et al. was able to characterize the iminophosphenium cation (28), a compound isoelectronic with a phosphaalkyne, a few years later.\(^{55}\) In 1993, Burford and coworkers reported \(\eta^6\)-arene complexation to a similar iminophosphenium cation, and extensively studied these systems.\(^{56-59}\)

1.3.4. Heavier Group 15 Element-Carbon Multiple Bonds

Compounds with multiple bonds between heavier group 15 elements such as the phosphaarsenes (29) and (30) were reported in 1983 by the groups of Cowley\(^{60}\) and
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Escudie, respectively. Escudie and co-workers also prepared some compounds containing double bonds to some heavier group 14 elements, namely germanium (31) and tin (32).

![Chemical structures]

Arsaalkenes, compounds containing arsenic-carbon double bonds, are more rare than phosphaalkenes. In an interesting parallel to phosphaalkene chemistry, shortly after Becker reported the first arsaalkene (33) in 1977, Bickelhaupt and co-workers reported a tri-aryl substituted arsaalkene (34). Approximately two dozen arsaalkene species have been isolated. Weber has recently reviewed this topic. Three compounds containing Sb-C double bonds have been reported (35-37).

![Chemical structures]

1.3.5. Heavier Group 14 Element-Pnictogen Multiple Bonds

Several compounds featuring double bonds between heavier group 14 elements and group 15 (also known as the pnictogens) have been reported. The silaimines (Si=N) with a silicon substituent on nitrogen possess almost linear (170-178°) Si=N=Si bond.
angles due to electronic effects \(^{38}\). Stable germaimines (Ge=N) and stannaimines (Sn=N) can be obtained by reacting Ge(II) and Sn(II) precursors with azides.\(^{13}\) Several molecules have been structurally characterized.\(^{74-79}\) The germaimines feature planar geometries at germanium and bent geometries at the nitrogen, and Ge-N distances ranging 1.681(8)-1.704(5)Å. Similarly the stannaimines have a planar geometry at tin, and an even more bent geometry at nitrogen than germaimines.

\[
\text{Bu}_3^t\text{Si} = \text{N} = \text{Si}^{t\text{Bu}}
\]

\(38\)

### 1.3.6. Recent Advances in Heavier Main Group Element Multiple Bonding

Multiple bonding in heavier main group elements has been and is an area of active research.\(^5,^{13,80}\) Advances in this field are a challenge to both the synthetic and theoretical chemist as the preparations are difficult, and bonding descriptions are not straightforward.\(^{13,15,81}\) A long time goal in this area, an isolable compound with a silicon-silicon triple bond, was recently realized (Scheme 3).\(^{82}\) A tetrabromotetrasilane (39) was reduced to the structurally characterized 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyl-2-tetrasilyne (40).

\[
\text{(Me}_3\text{Si})_2\text{HC}^t\text{Pr} = \text{Si}^t\text{Si}^t\text{Si}^t\text{Si}^t\text{Pr} \quad \text{(Me}_3\text{Si})_2\text{HC}^t\text{Pr} = \text{Si}^t\text{Si}^t\text{Si}^t\text{Si}^t\text{Pr}
\]

\(39\)

\[
\text{KC}_8 (4 \text{ eq}) \quad \text{THF} \quad \text{(Me}_3\text{Si})_2\text{HC}^t\text{Pr} = \text{Si}^t\text{Si}^t\text{Si}^t\text{Si}^t\text{Pr} \quad \text{(Me}_3\text{Si})_2\text{HC}^t\text{Pr} = \text{Si}^t\text{Si}^t\text{Si}^t\text{Si}^t\text{Pr}
\]

\(40\)

**Scheme 3.**

### 1.4 Synthetic Routes to Phosphaalkenes

There are several different methods of preparing a phosphorus-carbon double bond. The incorporation of various metal complexes as phosphaalkene substituents,
termed metallophosphaalkenes, has been recently reviewed, as well as fluorine containing phosphaalkenes. These types of phosphaalkenes will not be discussed in any detail, merely noted.

1.4.1 Silatropic Migrations

Phosphorus bound silyl groups can undergo facile migration to an α-positioned, doubly bonded element such as N, O, or S (Scheme 4). This migration is thermodynamically favourable due to the formation of a strong silicon-element bond. The relative weakness of the phosphorus-silicon bond compared to the strength of this silicon-element bond often leads to an irreversible migration. This preference can be used in conjunction with condensation and addition reactions as a versatile method of preparing phosphaalkenes.

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{P} - \text{C} \\
R & \quad X \quad R_1
\end{align*}
\xrightarrow{} \quad \begin{align*}
X - \text{SiMe}_3 & \quad \text{R} - \text{P} &= \text{C} \\
R_1 & \quad R_1
\end{align*}
\]

\(X = \text{N, O, S}\)

Scheme 4.

For example, reacting bis(trimethylsilyl)phosphines with carboxylic acid chlorides, imide chlorides, and related molecules such as phosgene (COCl₂) or isocyanide dichlorides, a phosphorus-carbon bond forms via condensation reaction. The initial condensation reaction affords an acylphosphine intermediate which usually undergoes a quick, irreversible [1,3] silyl group migration to form the phosphaalkene as shown in Scheme 5.

\[
\begin{align*}
\text{R} - \text{SiMe}_3 & \quad \text{Cl} \quad \text{C} - \text{R}^1 \\
\text{SiMe}_3 & \quad \text{O} \quad \text{R}^1
\end{align*}
\xrightarrow{} \quad \begin{align*}
\text{Me}_3\text{Si} & \quad \text{P} - \text{C} \\
\text{R} & \quad \text{R}^1
\end{align*}
\xrightarrow{} \quad \begin{align*}
\text{R} - \text{P} &= \text{C} \\
\text{O} - \text{SiMe}_3 & \quad \text{R}^1
\end{align*}
\]

Scheme 5.
The silatropic migration can also be coupled with addition reactions to molecules with cumulated hetero double bonds such as carbon disulfide, carbodiimides, or carbon dioxide.\textsuperscript{88-91} The first step is the migration of the silyl group to the heteroatom attached to the central carbon atom, followed by the 1,3-silatropic migration to prepare the P=C bond as shown in Scheme 6.

\begin{center}
\begin{tikzpicture}
\t\node at (0,0) {\text{SiMe}_3};
\t\node at (1,0) {\text{Me}_3\text{Si}};
\t\node at (2,0) {\text{O-SiMe}_3};
\t\node at (0,-1) {\text{Me}_3\text{Si}};
\t\node at (1,-1) {\text{Me}_3\text{Si}};
\t\node at (2,-1) {\text{R-P=C}};
\t\node at (1,-2) {\text{SiMe}_3};
\end{tikzpicture}
\end{center}

Scheme 6.

1.4.2. 1,2-Eliminations

Analogous to the chemistry to form olefins, suitable organophosphines can undergo 1,2 eliminations to form phosphaalkenes with release of a thermodynamically favourable molecule XY (i.e. HCl, Me\textsubscript{3}SiCl, etc.) as shown in Scheme 7. The formation of XY was initiated thermally by strong bases or metals.\textsuperscript{52,92-97} This synthetic route was one of the most utilized in the initial exploration of phosphaalkene chemistry. The removal of by-products or catalyst can sometimes prove to be difficult.

\begin{center}
\begin{tikzpicture}
\t\node at (0,0) {X};
\t\node at (1,0) {Y};
\t\node at (2,0) {P-C-R\textsuperscript{1}};
\t\node at (1,-1) {R\textsuperscript{1}};
\t\node at (0,-2) {R\textsuperscript{1}};
\t\node at (1,-2) {R\textsuperscript{2}};
\t\node at (2,-2) {R\textsuperscript{2}};
\end{tikzpicture}
\end{center}

Scheme 7.

1.4.3. Condensation Reactions

Another well-studied synthetic route to the phosphorus-carbon double bond involves condensation reactions that form disiloxane (route A, Scheme 8),\textsuperscript{98} halosilane (route B, Scheme 8), and water (route C, Scheme 8).\textsuperscript{99,100} A bis(trimethylsilyl)phosphine can react with a ketone or a difluoromethane to produce a phosphaalkene and a
corresponding condensation molecule. Similarly, a phosphine with a bulky aryl group such as supermesitylene can react with an aldehyde in the presence of dehydrating agents. The small molecule elimination makes the reaction entropically and thermodynamically favourable due to the formation of stronger bonds in the condensation molecule.

\[
\begin{align*}
\text{A} & : \quad \begin{array}{c}
\text{SiMe}_3 R^1 \quad \text{SiMe}_3 R^1 \\
\end{array} + \begin{array}{c}
O=C R^2 \\
\end{array} \rightarrow \begin{array}{c}
R^1 \text{-P=}\!C R^2 \\
- (\text{SiMe}_3)_2 \text{O}
\end{array}
\end{align*}
\]

\[R^1 = \text{alkyl, aryl} \]
\[R^2 = \text{H; } R^3 = \text{Me}_2 \text{N, Ph}\]

\[
\begin{align*}
\text{B} & : \quad \begin{array}{c}
\text{SiMe}_3 R^1 \quad \text{SiMe}_3 R^1 \\
\end{array} + \begin{array}{c}
\text{F}_2 C=O R^2 \\
\end{array} \rightarrow \begin{array}{c}
R^1 \text{-P=}\!C R^2 \\
- 2 \text{FSiMe}_3
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{C} & : \quad \begin{array}{c}
\text{Ar-PH}_2 + \text{O=C} \\
\end{array} \rightarrow \begin{array}{c}
\text{Ar-P=}\!C \\
- \text{H}_2 \text{O}
\end{array}
\end{align*}
\]

\[R = \text{H, Ph}\]

Scheme 8.

1.4.4. Carbene Reactions

Phosphaalkenes with very bulky substituents on phosphorus can be prepared by combining a phosphine and di- or trichloromethane treated with a strong base (Scheme 9). Historically, it has been thought that these reactions proceed via a carbene addition mechanism,\textsuperscript{101,102} although some recent investigations in the Gates lab provide evidence from the spectroscopic detection of intermediates which question this theory.\textsuperscript{103}

\[
\begin{align*}
\text{Ar-PH}_2 + \text{HCX}_3 & \quad \begin{array}{c}
2 \text{KOH} \\
\end{array} \rightarrow \begin{array}{c}
\text{Ar-P=}\!C \quad \text{X} \\
\end{array}
\end{align*}
\]

\[X = \text{Cl, Br}\]

\[
\begin{align*}
\text{Ar-PH}_2 + \text{H}_2 \text{CCl}_2 & \quad \begin{array}{c}
2 \text{KOH} \\
\end{array} \rightarrow \begin{array}{c}
\text{Ar-P=}\!C \quad \text{H} \\
\end{array}
\end{align*}
\]

\[X = \text{Cl, Br}\]

Scheme 9.
1.4.5. Phospha-Wittig Reactions

Mathey and co-workers reported another process of generating P=C bonds.\textsuperscript{104-107} Initially, the phospha-Wittig reagents were stabilized by coordination to a metal centre such as [W(CO)\textsubscript{5}]. Protasiewicz’s group has also developed a method in which a bulky aryl dichlorophosphine is treated with zinc, and an excess of trimethylphosphine to generate the phospha-Wittig reagent \textit{in situ} (Scheme 10).\textsuperscript{108} The phospha-Wittig reagent then proceeds to react with an aldehyde in the second step, producing trimethylphosphine oxide as an energetically favourable by-product.\textsuperscript{109}

Scheme 10.

1.4.6. Rearrangement Reactions

Secondary vinylphosphines can undergo a concerted [1,3] hydrogen shift (route A, Scheme 11) similar to the well known allylic tautomerization (double bond migration) in alkenes.\textsuperscript{110,111} It is often difficult to isolate these phosphaalkenes in a pure form as the reaction is in equilibrium. Gates and co-workers have recently reported isolable examples containing CF\textsubscript{3} substituted phenyl groups (route B, Scheme 11).\textsuperscript{112} The electron withdrawing groups on phosphorus appear to increase acidity of P-H and the phosphaalkene is formed quantitatively.

\[
\text{X = Me, Ph, Mes} \\
\text{Y = H, Me}
\]
1.5 The Phosphorus-Carbon Analogy

During the initial studies of low-coordinate phosphorus chemistry it became clear that these species could mimic the chemistry of unsaturated carbon systems to a certain degree.\textsuperscript{11,12,13,14} The ability of phosphorus to act as an analogue of carbon in unsaturated systems and the small difference in electronegativity of phosphorus and carbon (C 2.5 versus P 2.2) has led to a diagonal relationship being proposed between the elements. Electronegativity is correlated strongly to reactivity as electrons in high-lying orbitals or accessible low-lying empty orbitals results in a high reactivity. Aromatic systems, $\pi$ bonds, strained rings and electron-deficient species are some examples of molecules following this pattern of high reactivity. Considering these systems whose reactivity mainly depends on electronegativity, it is not surprising that the phosphorus-carbon analogy is strongest in molecules containing phosphorus in coordination numbers 1 and 2.

A comparison of the parent compounds of the C=N, C=C, and C=P double bonds outlines the ability of low coordinate phosphorus to mimic the chemistry of alkenes. A study performed by UV photoelectron spectroscopy provides data for this comparison.\textsuperscript{115} The HOMO of each compound are shown in Figure 1.2, along with the second highest molecular orbital (HOMO-1) in the case of the imine and phosphaalkene.
The HOMO of the imine corresponds to the lone pair on nitrogen (-10.62 eV) and the π bond lies much lower in energy (-12.49 eV). From these energy levels, one would expect that the imine would react through its lone pair. In contrast, the HOMO of the alkene and the phosphaalkene is the π bond (-10.51 eV, -10.30 eV respectively), with the lone pair on the phosphorus of the P=C bond being only slightly lower in energy (-10.70 eV). From these observations one would expect the P=C π bond to be more reactive than the C=C in an alkene, however the lone pair on phosphorus may also have some reactivity. The relative reactivities of the alkene and phosphaalkene have been confirmed in a study of the heats of decomposition (\(D_{p-C} = 45\) versus \(D_{C-C} = 65\) kcal mol\(^{-1}\)).\(^{116}\) The π bond of the phosphaalkene has been calculated to be almost apolar,\(^{117}\) which means that the regioselectivity of the addition of a polar reagent should be able to be controlled by varying the substituents of the P-C bond as outlined in Scheme 12.\(^{118}\) Weber’s research group has studied a family of phosphaalkenes with “inverse electron density” on the P=C bond, where the polarization is \(\text{P}^\delta^-\) and \(\text{C}^\delta^+\).\(^{119}\) This inversion of polarity is a function of the substituents.
Scheme 12.

The ability of low coordinate phosphorus to mimic the chemistry of olefins is only limited by the higher reactivity of the P=C bond, and occasional interference of the lone pair on phosphorus. If the lone pair is coordinated to an inert metal fragment such as \([\text{W(CO}_5\text{]}\), reactions that will not proceed with uncomplexed phosphaalkene such as epoxidation\(^\text{120}\) and catalytic cis-hydrogenation of P=C bonds can be carried out.\(^\text{121}\) A phospha-Cope rearrangement was discovered for 1,3,4,6-tetraphosphahexa-1,5-dienes as outlined in Scheme 13.\(^\text{122}\) At room temperature the AA’XX’ \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum collapses to a broad singlet, indicating a facile equilibrium between the two and three coordinate phosphorus atoms in the phosphadiene. Similar phospha-Cope rearrangements have been reported for some 3-phospha and 3,4-diphosphahexa-1,5-dienes.}\(^\text{123, 124}\)

Scheme 13.

A widely accepted definition of heteroaromaticity has never been proposed, and this subject has always been somewhat controversial. Some correlations between structural, thermodynamic, and magnetic properties that might denote some heteroaromaticity have been noted in five-membered unsaturated heterocycles by Schleyer’s group.\(^\text{125}\) The six-membered phosphinine or phosphabenzene (21) reported by
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Ashe in 1971 was among the first aromatic species containing phosphorus to be well characterized. The phosphinine ring shows structural characteristics that one would expect from an aromatic system. The ring is planar, the phosphorus-carbon bonds are short at \( \approx 1.73 \text{ Å} \), and the carbon-carbon bonds show little alternation in length (ca. 1.40 Å). The aromaticity of this six-membered \( \pi \) system has been estimated at 88% of that of benzene. The phosphinine HOMO has \( \pi \) character, and the in-plane lone pair corresponds to the HOMO-3, and the phosphorus atom carries a positive charge of 0.55.

The ability of low-coordinate phosphorus to act as a carbon analogue in unsaturated systems has opened a new area of phosphorus chemistry termed “phospha-organic”. Assuming that one could tentatively state that \( \pi \)-conjugation should propagate through \( \text{P} = \text{C} \) bonds in the backbone of a conjugated polymer, how might one prepare such a macromolecule? Phosphorus and other main group elements have previously been incorporated into the main chain of polymers. However, as is detailed in section 1.7 which discusses inorganic polymers, creating long chains of inorganic elements is a synthetic challenge. As well, there are many types of organic \( \pi \)-conjugated polymers (outlined in section 1.8), but which would best serve as a framework for an attempt to prepare a new class of \( \pi \)-conjugated polymers? Clearly, there are many considerations, but first of all we must be cognizant of the unique requirements of polymer synthesis.

1.6 Background Polymer Chemistry

Macromolecules were originally classified by Carothers into condensation and addition polymers, based upon the mechanism of polymer formation. In the case of an addition or chain-growth polymerization, in many cases an unsaturated monomer is

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activated by an initiator (I; a radical, anionic, or cationic species, route A, Scheme 14), and a reactive moiety generated (denoted by *). This activated end subsequently attacks another unsaturated monomer, forming an identical reactive moiety, but at the new end of the propagating chain. Ring-opening polymerizations also proceed via a similar chain-growth mechanism (route B, Scheme 14) where $E$ is a $p$ block element. In some instances, an initiator is required, but reactions can also be initiated thermally. Such is the case for polyphosphazenes, which is discussed in more detail in section 1.7.1.

![Scheme 14.](image)

In a chain growth polymerization high molecular weight polymer is formed very early in the polymerization process even though unreacted monomer may still be present. In a living polymerization, the reactive moiety is still present at the chain end when all of the monomer has been consumed. At this point, more monomer may be added to the reaction, in which case the chain-growth will continue until all the monomer is consumed. Alternatively, a different unsaturated monomer could be added to produce a block co-polymer in which the first section of the backbone was produced from the first monomer, and the other section generated from the second monomer. In most examples of polymers prepared by an addition polymerization, the repeat unit of the resulting macromolecule has the same composition as the monomer. For example, in
polyethylene, the polymer produced in route A of Scheme 14, the monomer composition is \( \text{C}_2\text{H}_4 \), as is the case of the repeat unit.

A formally \( \pi \)-conjugated polymer is one whose backbone consists of alternating single and double bonds. To produce a formally \( \pi \)-conjugated polymer, from an unsaturated monomer, the degree of unsaturation of the monomer must be one higher than that desired in the backbone. For instance, the simplest \( \pi \)-conjugated polymer is polyacetylene, which is prepared from \( \text{H-C=CH} \) as the name implies. The attempted synthesis of a polyacetylene analogue, a poly(phosphaalkene) through the spontaneous polymerization of phenylphosphalkyne (\( \text{Ph-C=P} \)) has been reported. The resulting material contained mainly three coordinate phosphorus, as determined by \( ^{31}\text{P} \) NMR spectroscopy. Perhaps more investigation would reveal the correct amount of steric protection of the phosphaalkyne bond, which would allow polymerization without subsequent reaction of the phosphaalkene bonds in the polymer chain. It appears that a condensation approach might be better, as many of the synthetic routes to the phosphorus-carbon double bond can be classified as such, as illustrated in section 1.4.

Condensation or step growth polymerizations usually feature two types of bifunctional monomers (Scheme 15) with reactive functional groups. The end-groups react, usually condensing and eliminating some sort of small molecule (\( \text{M} \) in Scheme 15), and cause the chain to grow in a stepwise fashion. In the case of nylons, or polyamides, an amine condenses with a carboxylic acid, eliminating \( \text{H}_2\text{O} \). Any two molecules in the polymerization with differing functional groups can react with each other. In a typical step growth polymerization, the monomers initially react to form dimers, then trimers, and so on. The repeat unit of the resulting polymer consists of two structural units, one from each of the monomers. The repeat unit produced by a condensation polymerization
differs in composition from the monomers by the constituents of the small molecule that was eliminated.

\[
\begin{align*}
R & \quad R \\
\text{X-} & \quad \text{C-C-X} \\
R & \quad R \\
+ & \quad - M
\end{align*}
\]

\[
\begin{align*}
\text{Y-} & \quad \text{C-C-Y} \\
R' & \quad R' \\
\text{R' } & \quad \text{R'} \\
\text{R' } & \quad \text{R'}
\end{align*}
\]

\[\text{Scheme 15.}\]

The total number of structural units in any reaction equals the total number of bifunctional monomers initially present. The number-average degree of polymerization \((\bar{X}_n)\) is defined as the average number of structural units per polymer chain. \(\bar{X}_n\) is simply given as the total number of monomer molecules originally present \(N_o\) divided by the total number of molecules present at any time \(t\) \((N)\) as outlined in equation (1).

Alternatively, \(\bar{X}_n\) can also be expressed in terms of initial monomer concentration \(M_o\) and current monomer concentration \(M\) in an identical expression, also shown in equation (1). The monomer concentration can be written as a function of initial monomer concentration and the extent or fraction of conversion \(p\) as shown in equation (2).

Combining equation (1) and equation (2) allows us to express \(\bar{X}_n\), the degree of polymerization in terms of monomer conversion as shown in equation (3). This equation that relates the degree of polymerization to the extent of reaction was first proposed by Carothers,\(^{131}\) and is often referred to as the Carothers Equation.\(^{132}\)

\[
\bar{X}_n = \frac{N_o}{N} = \frac{[M]_o}{[M]} \quad (1)
\]

\[
[M] = [M]_o - [M]_o p = [M]_o (1-p) \quad (2)
\]

\[
\bar{X}_n = \frac{1}{(1-p)} \quad (3)
\]

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In a step-growth polymerization, if 90% of the monomers have reacted \( (p = 0.90) \), then from Carother’s equation, one can see that \( \bar{X}_n \) would be 10 as shown in equation (4). From this observation, one can deduce that high molecular weight polymer is produced only in the final stages of a step-growth polymerization, and only then if reaction has gone to close to 100% conversion.

\[
\bar{X}_n = \frac{1}{(1 - 0.9)} = \frac{1}{0.1} = 10
\]  

(4)

When the degree of polymerization depends upon the extent of reaction, having matching stoichiometry of both bifunctional monomers (X-X and Y-Y) is crucial. If one monomer is in slight excess, the chain growth is effectively terminated when the same functional group caps both end of the macromolecule, and none of the other functional group are left to continue the polymerization. The stoichiometric ratio of monomers \( r \) is defined by the ratio of the number of X and Y functional groups, \( N_X \) and \( N_Y \) as shown in equation (5), and is always defined to be less than one. \( N_X \) and \( N_Y \) are merely twice the number of X-X and Y-Y monomers respectively. This stoichiometric imbalance leads to the modification of the Carother’s equation to the form shown in equation (6).

If either or both of the monomers are not analytically pure, a stoichiometric imbalance will also occur.

\[
r = \frac{N_X}{N_Y}
\]  

(5)

\[
\bar{X}_n = \frac{1 + r}{(1 + r - 2rp)}
\]  

(6)

In the case \( r = 1 \), the formula simplifies to the Carother’s equation. If \( r \neq 1 \), a non-stoichiometric case, but \( p = 1 \), the result is equation (7). In reality, complete conversion is rarely achieved, so that \( p \) is seldom one. An example where \( r = 0.9 \), and \( p = 0.9 \) is detailed in equation (8).
In this case, the degree of polymerization is not quite seven units, which might be considered an oligomer, not a true polymer, depending on the system. Often a material is not considered to be a polymer until it possesses the desired properties (i.e. the ability to form films, etc.), which are a consequence of chain entanglement. It must be emphasized that the synthesis of a high molecular weight polymer via a step-growth polymerization is extremely difficult, as the stoichiometries of the monomers must be closely matched, and the monomers must be very pure, to try to ensure complete conversion.

1.7 Inorganic Polymers

The prevalence of organic polymers in almost every aspect of modern life can be attributed to their ease of preparation and fabrication. Organic polymers are macromolecules whose backbone consists solely of carbon, nitrogen, or oxygen atoms. The straightforward synthesis of these materials stems from the advanced state of organic chemistry, but also the availability of cheap petroleum derived monomers. The systematic functional group transformations of inorganic elements are often not as mature as those of organic chemistry. Indeed, there are many common organic functional groups that have no heavier congener. For example, the silicon analogue of a ketone, is still unknown as an isolable entity. The development of synthetic routes to long polymer chains constructed mainly, or entirely, of inorganic elements has been a monumental challenge for chemists. These macromolecules that contain inorganic elements (other than C, O, or N) in the main chain are referred to as inorganic polymers.
Due to the difficult syntheses associated with their preparation, inorganic polymer chemistry is not as developed as that of organic polymers. Despite these challenges, or perhaps because of them, there has been an increasing interest in inorganic polymers.\(^{133}\)

The inclusion of inorganic elements into the backbone of a polymer would likely change the bond angles and thus torsional mobilities along the chain when compared to carbon.\(^ {134}\) As well, inorganic elements may have different valencies than carbon, allowing a variation in the number of polymer chain side groups in a repeat unit. Presumably, these differences might affect chain flexibility, reactivity, and solubility, and lead to novel properties not achievable through organic modification or substitution of organic polymers.\(^ {134}\)

The transfer of polymer synthetic routes that work well for organic monomers to inorganic polymers is often problematic. For instance, it is difficult to generalize addition polymerization of C=C bonds to inorganic E=E bonds since suitably reactive, but stable multiple bonds between inorganic elements are a challenge to prepare.\(^ {135}\) As discussed in section 1.3, the isolation of inorganic compounds containing acyclic multiple bonds usually requires sterically demanding substituents that prevent oligomerization.\(^ {10}\)

Polycondensation reactions were used in early attempts at preparing inorganic polymers. Step-growth polymerizations have worked well for bifunctional organic monomers, as the purification of these compounds is usually straightforward, allowing the strict requirements for stoichiometry and conversion required for high molecular weight polymer to be met. In contrast, bifunctional inorganic monomers (such as dilithio species) are often difficult to purify due to their extreme reactivity. As detailed in the previous section, low monomer purity prevents exact stoichiometry reactions between two bifunctional monomers even if complete conversion of monomers is achieved. A variation of this condensation polymerization is to have both functional groups present in

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each monomer, removing the requirement for strict matching of stoichiometries, and allowing some of these reactions to proceed via a chain-growth mechanism which leads to higher molecular weight materials more naturally.\textsuperscript{136} Ring-opening polymerization (ROP), which also follows a chain-growth mechanism, is an attractive approach as inorganic ring chemistry is fairly well developed so that many potential monomers are available.\textsuperscript{137}

The polyphosphazenes (39), polysiloxanes or silicones (40), and polysilanes (41) are perhaps the most well known inorganic polymers. As is discussed in more detail in the next sections, the inorganic backbones of these macromolecules lead to very interesting properties. An excellent review by Manners details less common inorganic polymers containing boron, silicon, germanium, tin, and phosphorus in the main chain.\textsuperscript{20}

\begin{align*}
\text{39} & : \quad \left[ \begin{array}{c}
R \\
\text{P=N} \\
R \\
\end{array} \right]_n \\
\text{40} & : \quad \left[ \begin{array}{c}
R \\
\text{Si-O} \\
R \\
\end{array} \right]_n \\
\text{41} & : \quad \left[ \begin{array}{c}
R \\
\text{Si} \\
R \\
\end{array} \right]_n
\end{align*}

1.7.1. Polyphosphazenes

The polyphosphazenes are the most varied class of inorganic polymers by a large margin and the most important class of phosphorus polymer as the backbone of the polymer consists of alternating phosphorus(V) and nitrogen atoms. Over 300 different polyphosphazenes are known, covering a wide range of properties. The nature of the side groups determines the properties of the material. The phosphorus substituents can be varied to give polymers that are elastomers or glasses, water-soluble or hydrophobic, bio-inert or bioactive materials, and from electrical insulators to ionic conductors.\textsuperscript{138}

The first molecular phosphazenes \( \text{N}_3\text{P}_3\text{Cl}_6 \) were synthesized in 1834 by Liebig and Wohler,\textsuperscript{139} and Rose\textsuperscript{140} by reacting phosphorus pentachloride with ammonia.
However, the principal contributor of early phosphazene polymer chemistry was H. N. Stokes, who first proposed the cyclic structure of the phosphazene trimer \([\text{PNCl}_2]_3\), and identified cyclic oligomers up to \([\text{PNCl}_2]_7\). Paddock, Trotter and co-workers from UBC published a series of reports on phosphazene crystal structures of larger cyclic oligomers in the 1970’s.\(^{141-144}\) Perhaps Stokes most important achievement was the discovery that thermolysis of chlorophosphazenes led to an insoluble elastomeric material.\(^{145}\) This material became known as “inorganic rubber,” and was later discovered to be highly cross-linked polyphosphazene. In the late 1960’s, Allcock and co-workers reported a synthetic route to linear, soluble polyphosphazene, and are responsible for many advances in this field.\(^{146}\)

Many polyphosphazenes feature glass transition temperatures that are quite low, which indicates that the polymer backbone is flexible. This contrasts with what might be expected for a macromolecule with a formally conjugated backbone, which is rigid in organic polymers. The backbone flexibility is rationalized by postulating that the double bond character between phosphorus and nitrogen is a \((d\pi-p\pi)\) overlap in which empty \(d\)-orbitals on phosphorus overlap with the 2p orbitals on nitrogen. There are several \(d\)-orbitals that could overlap favourably with the 2p orbital with \(\pi\) symmetry as the backbone twists. Thus, the barrier to rotation is expected to be very low, and hence the backbone of the polymer is quite flexible. An “island” model is used to describe the absence of \(\pi\)-conjugation in the polyphosphazene backbone. The \(d\)-orbitals of each phosphorus possess nodes which truncate the \(\pi\)-conjugation, but the backbone is conjugated between the phosphorus atoms.\(^{147}\) Polyphosphazenes are thermally and oxidatively stable, optically transparent from 220 nm to the near IR region, and possess flame retardant properties.\(^{146}\)
As shown in Scheme 16, if the cyclic phosphazene trimer is carefully heated (Scheme 16, route A), an uncross-linked, high molecular weight polyphosphazene results from a ROP reaction. Subsequently, the P-Cl bonds can be replaced by nucleophilic substitution reactions to add any desired side group for the macromolecule (Scheme 16, route D or route E). Polyphosphazene can also be synthesized by condensation reactions of iminophosphines (Scheme 16, route B) or by nitrogen gas elimination of azidophosphines (Scheme 16, route C).

Scheme 16.

There are several examples of poly(heterophosphazene)s in which one of the PR$_2$ moieties has been replaced by CR ($42$, polycarbophosphazene),$^{20,148}$ SR ($43$, polythiophosphazene),$^{149,150}$ S(O)R ($44$, polythionylphosphazene),$^{151}$ and S(O)X ($45$, polythionylphosphazene).$^{152}$ In general, once the cyclic monomer is prepared, it can undergo thermal ROP to afford the corresponding poly(heterophosphazene).
1.7.2. Polysiloxanes

From the perspective of commercial applications, polysiloxanes are perhaps the most important inorganic polymers. There is a wealth of literature describing the synthesis, properties, and applications of these polymers. The strength of the Si-O bonds in the backbone of the macromolecule endow great thermal stability to the material. The difference in atomic radii of the two components, as well as the bond angles lead to some interesting packing effects.

Polysiloxanes have been used as high performance elastomers and fluids, surface modifiers, adhesives, and biomedical materials. The exceptional properties are a direct result of the silicon-oxygen backbone. The polymer backbone, which consists of long silicon-oxygen bonds (1.64 Å compared to 1.54 Å for a C-C bond), lacking substituents on oxygen, and a wide bond angle at oxygen (Si-O-Si ca. 143° compared to C-C-C ca. 109°), has a unique dynamic flexibility. This flexibility leads to materials that retain their elasticity even at very low temperatures. Poly(dimethylsiloxane), perhaps the most common silicone, has a glass transition temperature (Tg) of -123° C. Also, Si-O bonds are stronger than C-C bonds (Si-O: 450 kJ/mol, C-C: 348 kJ/mol) and thus are more resilient towards oxidation and UV radiation. Hydrophobicity and high gas
permeability have led to applications in the medical field, such as contact lenses and artificial skin.\textsuperscript{134}

The area of organosilicon chemistry blossomed when Kipping discovered that organosilicon compounds could be synthesized from SiCl\textsubscript{4} or SiHCl\textsubscript{3} with Grignard reagents. These silanes turned out to be of great importance as they hydrolyzed to form linear and cyclic compounds containing Si-O bonds. These new materials were incorrectly referred to as silicoketones or “silicones” as they were thought to be heavier congeners of ketones, but structural studies revealed the absence of the Si=O bond. However, the misnomer silicone has stuck. Later, the “Rochow process” which converts elemental silicon directly to R\textsubscript{2}SiCl\textsubscript{2} was discovered.\textsuperscript{155-157} Dichlorosilanes can be hydrolyzed to form polysiloxanes directly, however cyclic trimers (46) are also isolated, depending on the reaction conditions (Scheme 17). These trimers can then undergo anionic or cationic initiated ROP to produce the desired polysiloxanes.

\begin{center}
\textbf{Scheme 17.}
\end{center}

\textbf{1.7.3. Polysilanes}

Another type of silicon containing inorganic polymer is the polysilane, more properly termed poly(silylene)s, which feature Si-Si bonds in the main chain.\textsuperscript{158} Though structurally quite similar to organic polymers such as polyethylene, the silicon backbone endows polysilanes with remarkably different properties. The more diffuse orbitals on
silicon (3s and 3p) are large enough that adjacent σ bonds overlap, allowing electron delocalization to take place though the sigma bonds of the polymer backbone (Figure 1.3). The σ-σ* transition observed at 220 nm in Me₃Si-Si-Me₃ is red-shifted as the length of the silicon backbone increases, entirely analogous to lengthening a π-conjugated system. The electron delocalization also leads to a degree of electrical conductivity upon doping. The properties of the polymer depend largely on the silicon pendant groups, as is the case for the phosphorus substituents in phosphazenes. Polysilanes cover a wide range of properties from insoluble, highly crystalline materials, to partially crystalline and flexible solids, to amorphous glasses, and elastomers.

Figure 1.3. a) σ orbitals of polysilane; b) σ orbitals of polyethylene.

Oligomeric poly(diphenylsilanes), including cyclic species (Ph₂Si)ₙ (n = 4 to 6), have been known for 70 years when they were first studied by F. S. Kipping. The first polysilane was prepared in 1949, when dimethyldichlorosilane was heated in an autoclave with sodium metal, affording poly(dimethylsilane) as a highly crystalline,
intractable solid. It was not until the late 1970's that interest in polysilanes picked up again upon the discovery that this polymer could be transformed into β-silicon carbide through heating. An attempt to synthesize cyclic oligosilanes containing methyl and phenyl groups as outlined in Scheme 18, instead lead to a soluble, linear copolymer. Other soluble polysilanes were discovered around the same time. Wurtz coupling of dichlorosilanes with alkali metals is a general route to polysilanes (Scheme 18).

\[
\text{Me}_2\text{SiCl}_2 + \text{PhMeSiCl}_2 \xrightarrow{\text{Na, C}_7\text{H}_8 \text{, 110°C}} \begin{bmatrix} \text{Me} \\ \text{Si} \\ \text{Me} \\ n \end{bmatrix} \begin{bmatrix} \text{Ph} \\ \text{Si} \\ \text{Ph} \\ m \end{bmatrix}
\]

Scheme 18.

Low molecular weight materials have been synthesized by a dehydrogenation route from diorganosilanes catalyzed by dialkyltitano or zirconocenes (Cp₂TiR₂ or Cp₂ZrR₂). A novel ROP synthesis of polysilanes was reported by Matyjaszewski, starting with octaphenylcyclotetrasilane with some of the phenyl groups replaced to make the ring polymerizable (Scheme 19). Also, the asymmetric substituents decrease the crystallinity of the product, allowing the polymer to be soluble in common organic solvents.

\[
\begin{bmatrix} \text{Ph} \\ \text{Me} \\ \text{Me} \\ \text{Ph} \\ \text{Ph} \\ \text{Me} \\ \text{Ph} \\ \text{Me} \\ \text{Ph} \\ \text{Me} \\ \text{Ph} \end{bmatrix} \xrightarrow{R^-} \begin{bmatrix} \text{Me} \\ \text{Si} \\ n \end{bmatrix}
\]

Scheme 19.

Polysilanes were initially dismissed for potential applications since the silicon backbone was thought to be too reactive. Therefore it is quite remarkable that polysilanes are now being sold commercially as precursors for silicon carbide ceramics,

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and being investigated as ultraviolet acting photoresists for microelectronics, and as photoconductors in electrophotography. Polysilanes have also found use as free radical photoinitiators for organic reactions, and show nonlinear optical properties.

1.7.4. Poly(sulphur nitride)

Poly(sulphur nitride) or polythiazyl has a backbone consisting of alternating sulphur and nitrogen atoms. This material was the first electrically conducting polymer, and has attracted interest since reports of its metallic character and superconductivity \( T_c = 0.26 \text{ K} \) appeared in the 1970's. The classical route to polythiazyl is a slow solid-state polymerization (6-8 weeks) of the explosive precursor \( S_2N_2 \) resulting in large crystals of the material. The electronic structure of polythiazyl is an area of active research and a source of much scientific debate.

Poly(thiazylphosphazene)s have been mentioned but little is known of their properties (Scheme 20). These materials could be viewed as hybrids of poly(sulphur nitride) and polyphosphazenes.

\[
\begin{align*}
S_2Cl_2 + \text{MeCN, -20°C} & \rightarrow \\
\text{Cl-P-Cl} & + \\
\text{NSiMe}_3 & \rightarrow \\
\begin{array}{c}
\text{Cl} \\
\text{S=N-P=N-r-} \\
\text{Cl} \\
\text{N(SiMe}_3\text{)_2}
\end{array}
\end{align*}
\]

Scheme 20.

1.7.5. Transition Metal and Main Group Element Containing Macromolecules

Macromolecules containing transition metals in the backbone are of considerable interest due to their interesting properties. Ferrocene has been a popular synthetic group in the preparation of organometallic polymers, as well as heteroatom bridged poly(metallocene)s. Several different main group elements have been used as bridges in [1]ferrocenophanes, which have subsequently been polymerized. Examples are
poly(ferrocenylborane) (48), some macromolecules containing heavier group 14 elements (49), and poly(ferrocenylphosphine) (50).

The synthesis of a polymetallocene containing phosphorus was attempted in 1967. Lewis-acid catalyzed condensation of ferrocene with PhPCl₂, PhP(O)Cl₂, or PhP(S)Cl₂ at elevated temperature (80-170°C) yielded mixtures of oligomeric materials with heteroannular (1,1'-) and homoannular (1,2-, 1,3-) ferrocenylene linkages. Seyferth and co-workers made a breakthrough in 1982 with the synthesis of well-defined oligomers and polymers starting with phosphorus-bridged [1]ferrocenophane monomers (51). Manners and co-workers later reported a thermal ROP forming poly(ferrocenylphosphines) (Scheme 21). A key requirement for ROP is a strained cyclic monomer, which makes the polymerization more thermodynamically favourable.

Scheme 21.

An anionic ROP of the phosphorus-bridged [1]-ferrocenophanes produced poly(ferrocenylphosphines) with controlled molecular weights (Mₘ = 36 000) and narrow polydispersities (PDI = 1.08-1.25). Block copolymers were also prepared, indicating that
the anionic ROP is a living polymerization. The possible \( \pi \)-conjugation of the formally conjugated backbone has not been investigated.

1.8 \( \pi \)-Conjugated Polymers

Polythiazyl, alternatively known as poly(sulfur nitride) or \((SN)_x\) is a polymeric material with a metallic appearance. As mentioned in section 1.7.4, polythiazyl was the first polymer to demonstrate electrical conductivity, and became superconductive at very low temperatures. Although the study of the electronic structure of this polymer remains an active area of research, it is thought that extensive \( \pi \)-conjugation is partially responsible for the metallic-like properties.

Natta and co-workers first produced polyacetylene as a black, air-sensitive, insoluble powder in 1958. In 1974 Shirakawa’s group discovered a method of making polyacetylene films by introducing the acetylene gas to a flask coated with a Ziegler-Natta catalyst. Instead of a black powder, the polyacetylene produced by this method was either a copper or silver coloured film depending on the temperature of the preparation. The difference in colour was rationalized as the polymer having been in the cis or trans orientation for the copper and silver films, respectively. Despite the metallic appearance, the polymer was not conductive.

\[
\begin{align*}
\text{cis-polyacetylene} & \quad \left[ \begin{array}{c}
\cdot \\
\cdot 
\end{array} \right]_n \\
\text{trans-polyacetylene} & \quad \left[ \begin{array}{c}
\cdot \\
\cdot 
\end{array} \right]_n
\end{align*}
\]

In 1975 Heeger and MacDiarmid collaborated to study the properties of the metallic polymer \((SN)_x\). These professors shifted the focus of their research after a meeting with Shirakawa where they learned of polyacetylene. The results of this larger collaboration were detailed in a seminal paper in 1977, in which the authors presented a
nine order of magnitude increase in electrical conductivity of polyacetylene upon
treatment with iodine.\textsuperscript{19} The conductivity of the doped polyacetylene ($10^4 - 10^5$ S cm\textsuperscript{-1}) was comparable with metals (i.e. copper $10^7$ S cm\textsuperscript{-1}). For the discovery of plastics with metal-like conductivity, Heeger, MacDiarmid, and Shirakawa were awarded the Nobel prize in chemistry in 2000.

A $\pi$-conjugated backbone appears to be a requirement for a polymer to be electrically conductive, but not enough in and of itself. What makes the polymer conductive is the presence of charge carriers, which are either extra electrons in the conductance band, or missing electrons known as “holes” in the valence band (Figure 1.4). When an electron jumping from a neighbouring atom fills a hole, that movement creates a new hole on the adjacent atom. This hole propagation leads to long distance charge migration and thus electrical conductivity. The treatment of the polymeric material with a dopant (which was halogen vapour in the work by Shirakawa, Heeger, and MacDiarmid) adds these charge carriers.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Chain length and its effect on the HOMO-LUMO gap.}
\end{figure}

While polyacetylene is the most crystalline conductive polymer, it is easily oxidized by the moisture and oxygen in air. This led to the development of more stable conjugated polymers such as polythiophene and polyaniline.\textsuperscript{18} There are several other examples of organic $\pi$-conjugated macromolecules listed in Chart 1. Of particular
relevance to this thesis is poly(p-phenylenevinylene) (PPV). It was hypothesized that this polymer might provide an excellent framework for an attempt to incorporate phosphaalkenes into the backbone of a conjugated polymer. If it proved feasible to replace the vinyl moiety with a phosphaalkene bond, then it is likely the phenyl groups in the main chain would provide the necessary steric bulk to protect the P=C bonds.

![Chart 1](image)

**Chart 1.**

The electrical conductivity of the conjugated polymers in Chart 1 has led to possible applications as corrosion inhibitors, capacitors, antistatic coatings, electromagnetic shielding of computers, and “smart” windows that control their translucence. More applications were conceived when it was discovered that conjugated polymers have interesting opto-electronic properties. In 1990, while investigating the optical properties of poly(p-phenylene vinylene) or PPV, electroluminescence of this polymer was discovered. Electroluminescence is the emission of light from a material upon an applied voltage. Thus, conjugated polymers are now being used for transistors, light-emitting diodes, lasers, and solar cells.

Due to the wealth of potential applications of \( \pi \)-conjugated polymers, there has been extraordinary interest in these materials by both academic and industrial researchers. Often, due to the rigidity of the backbone of the conjugated macromolecule, direct

*References start on page 50*
analytical characterization and physical study is difficult due to poor solubility. It is common for all polymers to have a length "n" where the properties of the bulk polymer are observed (Figure 1.5).

![Graph showing effects of polymer chain length on properties.](image)

**Figure 1.5.** Effects of polymer chain length on properties.

Thus, electronic, photonic, thermal, and morphological properties of high molecular weight \( \pi \)-conjugated polymers can be extrapolated from soluble, monodisperse oligomers.\(^{193-195}\) For several of these properties, \( \pi \)-conjugated polymers exhibit a convergent limit. For instance, growing \( \pi \)-conjugated oligomer chains will show a red-shift in the absorption maximum as the chain grows longer. This is rationalized as the energy levels of the HOMO and LUMO growing closer together as the number of atomic orbitals increases (Figure 1.4). At some chain length, the absorbance of the oligomer is the same as that of the bulk polymer, and this chain length is called the "effective conjugation length".\(^{196}\) Although the effective conjugation length is a numerical quantity not accessible through physical measurement, it has become a central concept in rationalizing many properties of \( \pi \)-conjugated polymers.\(^{197}\) This limiting of the conjugation length may arise from distortions from planarity of the backbone of the

\*References start on page 50*
molecule, such as rotations about single bonds. The deviation from planarity would lead to less effective π overlap and thus an end of the conjugation pathway.

1.9 Inorganic Element Containing Conjugated Polymers

Hissler, Dyer, and Reau recently comprehensively reviewed the area of π-conjugated molecules containing phosphorus and silicon.\(^{198}\) This seems to be a burgeoning area of research, but only the most relevant examples are discussed.

Phosphorus containing polymers have been used in a wide variety of applications ranging from flame retardant materials,\(^{199,200}\) ionic conducting materials,\(^{201}\) to metal catalyst supports that are easily separable from the reaction product.\(^{202}\)

The incorporation of heteroatoms into the main chain of π-conjugated polymers often results in polymers with properties significantly different from their all carbon analogues. Poly(phenyleneborane) (53),\(^{203,204}\) poly(aniline) (54),\(^{16,205-207}\) and poly(phenylenechalcogens) (55) have been intensely studied.\(^{208-218}\) The heteroatoms can participate in the π-conjugation through overlap of lone pairs with the π system.

\[
\begin{align*}
\text{53} & \quad \text{54} & \quad \text{55} \\
\begin{array}{c}
\text{\includegraphics[width=0.1\textwidth]{borane.png}} \\
\text{\includegraphics[width=0.1\textwidth]{aniline.png}} \\
\text{\includegraphics[width=0.1\textwidth]{chalcogen.png}}
\end{array}
\end{align*}
\]

\(\text{Ch} = \text{O, S, Se}\)

1.9.1. Phosphole Containing Polymers

The incorporation of the phosphole ring into the backbone of a polymer has proven to be synthetically challenging. True poly(phosphole) has not been prepared to date, but several examples of polymers containing phosphole in the main chain of the polymer have been reported. Tilley et al. reported a phosphole containing polymer with an isomeric mixture of connectivities in the backbone (Scheme 22).\(^{219}\) This polymer was

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prepared by assembling the polymer precursor through a non-regioselective zirconocene diyne coupling route, which formed zirconacyclopentadienes (56). The zirconacyclopentadiene moiety can be converted to a phosphole by replacing \( \text{Cp}_2\text{Zr} \) with \( \text{PhP} \) in a reaction with \( \text{PhPCl}_2 \) producing a biphenyl-phosphole polymer (57). After replacement, the backbone consisted of 2,4- and 2,5-connected phosphole rings, with the 2,5-linear connection present in approximately 20%. This polymer was isolated as an air-stable powder soluble in polar organic solvents. Molecular weights of 16,000 (\( M_w \)) were estimated by GPC. The polymer exhibited an UV/Vis absorption maximum at 308 nm.

Scheme 22.

Alternating thiophene rings with other heterocyclopentadiene rings can lead to increased conjugation due to intramolecular charge transfer between neighbouring donor and acceptor moieties.\(^{220,221}\) A 2,5-bis(2-thienyl)phosphole monomer consisting of a phosphole sandwiched between two thiophenes (58) was synthesized by a zirconocene replacement route, isolated by flash chromatography, and fully characterized by Reau and co-workers.\(^{222}\) Model compound 58 can be electrochemically polymerized by anodic oxidation during cyclic voltametry (Scheme 23).\(^{223}\) These polymers are often insoluble,
precluding molecular weight analysis by GPC. Polymer 59 has a UV/Vis spectrum consisting of two broad, overlapping absorbances at 463, and 567 nm.

![Scheme 23.](image)

Reau’s group used derivatives of 58 to produce the first organophosphorus containing OLED (organic light emitting diode). The organic layer was deposited by thermal evaporation under high vacuum. Under these conditions, 58 decomposed, but thioxo-derivative 60, which has a higher decomposition temperature was deposited as a thin film. The photoluminescence spectra of thin films of 60 show a single maximum at 542 nm. OLED devices were constructed that contain 60, and 61. The electroluminescence spectrum of the device closely resembles the photoluminescence spectrum, and the device is a yellow emitter. This suggests similar PLED’s based on phosphorus maybe possible in the future. Some other interesting transition metal-polythiophene hybrid materials where thiophene oligomers are used as a substituent on a phosphine ligand have been reported by Wolf.

![A phosphole containing π-conjugated copolymer was reported by Chujo in 2003.](image) Phenyl and biphenyl spaced diynes containing long chain alkoxy groups for solubilization were coupled with the phosphole monomer using the Heck-Sonogashira
reaction (Scheme 24). Molecular weights (M\textsubscript{w}) of the air-stable, soluble, yellow powders were estimated by GPC to be 9,000, and 14,000 and 15,400 respectively for 63\textsubscript{a}, 63\textsubscript{b}, and 63\textsubscript{c}. The respective UV/Vis absorption maxima are 382, 414, and 410 nm, which show red shifting from a similar 2,5-diphenylphosphole (\(\lambda\text{_{max}} = 354\) nm) identical to 62 except missing the bromines. These polymers fluoresced, and emission maxima were observed at 435, 487, and 490 nm for 63\textsubscript{a-c} respectively.

\[\begin{align*}
\text{Br} & \text{Ph} & \text{Br} \\
62 & + & \text{[Pd] / Cul} \\
\text{Ph} & \text{Ar} \quad n
\end{align*}\]

\[\begin{align*}
63\text{ a-c}
\end{align*}\]

\[\begin{align*}
\text{a:} & \quad \text{b:} & \quad \text{c:} \\
\text{n-C\textsubscript{6}H\textsubscript{13}O} & \quad \text{n-C\textsubscript{12}H\textsubscript{25}O} & \quad \text{n-C\textsubscript{12}H\textsubscript{25}C\textsubscript{12}H\textsubscript{25}O}
\end{align*}\]

Scheme 24.

1.9.2. Other Group 15 Containing Macromolecules

1.9.2.1. Poly(p-phenylene phosphine)

In the recent literature, there have been several examples of formally conjugated polymers containing group 15 elements in the main chain. A phosphorus containing analogue of polyaniline, poly(p-phenylene phosphine) (64) was reported by Lucht and co-workers.\textsuperscript{228} The polymer was prepared by a palladium coupling reaction of 1,4-diiiodobenzene and primary phosphines (Scheme 25).
Scheme 25.

The molecular weight of these soluble polymers was estimated by GPC. The polymer was further characterized by multi-nuclear NMR spectroscopy. Different phosphorus substituents led to different degrees of polymerization as determined by GPC, which varied from 7-14 repeat units.

Table 1.1. Selected characterization data for polymer 64.

<table>
<thead>
<tr>
<th>R</th>
<th>n [a]</th>
<th>(\lambda_{\text{max}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64a: (\text{CH}_2\text{CH(CH}_3)_2)</td>
<td>10</td>
<td>278</td>
</tr>
<tr>
<td>64b: (\text{Ph})</td>
<td>7</td>
<td>291</td>
</tr>
<tr>
<td>64c: (\text{CH}_2\text{CH(CH}_3)_2\text{CH}_2\text{C(CH}_3)_3)</td>
<td>14</td>
<td>276</td>
</tr>
</tbody>
</table>

[a] average number of repeat units determined by GPC versus polystyrene standards.

The electronic structure of these macromolecules was studied by UV/Vis spectroscopy, and the spectra of 64a-c showed \(\lambda_{\text{max}}\) between 276 and 291 nm that have been assigned to the \(\pi-\pi^*\) transition. These small values for \(\lambda_{\text{max}}\) suggest a low amount of \(\pi\)-electron conjugation through the backbone of the polymer. This can be rationalized by observing that the P-atoms in the main chain have a tetrahedral geometry that prevents efficient conjugation of the phosphorus lone pair through the neighbouring aryl groups, unlike N-atoms in polyaniline. The tetrahedral inversion energy for phosphorus (30-35 kcal/mol) is much higher than for nitrogen (5 kcal/mol). Some \(\pi\)-conjugation along the backbone of the polymer is suggested by looking at the \(\lambda_{\text{max}}\) values of triphenylphosphine (\(\lambda_{\text{max}} = 263\) nm) to 1,4-diphenylphosphinobenzene (\(\lambda_{\text{max}} = 275\) nm) and polymer 64b (\(\lambda_{\text{max}} = 291\) nm). A higher molecular weight polymer (\(M_n = 14,400\) by GPC) was subsequently prepared using \(p\)-bromophenyl secondary
Lucht and co-workers followed up this work with a recent report of an alternating copolymer of poly(p-phenylene phosphines)/polyaniline. They reported that conversion of the phosphorus(III) centres to phosphorus(V) phosphine oxides inhibited electronic delocalization through phosphorus, which supported their claims of phosphorus lone pair delocalization.\(^{230}\)

**1.9.2.2. Poly(vinylene arsine)**

A novel poly(vinylene arsine) was synthesized by a free-radical alternating copolymerization of phenylacetylene with cyclooligoarsines. The polymerization (Scheme 26) between pentamethylcyclopentaarsine (65a) or hexaphenylcyclohexaarsine (65b) with phenylacetylene in the presence of a catalytic amount of AIBN (2,2’-azobisisobutyronitrile) in refluxing benzene for 12 hours afforded the corresponding poly(vinylene-arsine)s.\(^{231}\) The cyclooligoarsine backbone is cleaved, either by a radical initiator (or light of the right wavelength in the case of 65a), which generated an elemental arsenic biradical after the other As-As bond was broken homolytically. This atomic biradical added to the acetylenic compound which generated a vinyl radical, that propagated in a similar manner. \(^{1}\)H and \(^{13}\)C NMR spectra support the proposed structure of polymer 66. An integration of the aromatic protons to methyl protons indicates that phenylacetylene/methylarsine ratio was nearly one, which was also supported by elemental analysis.\(^{231}\) Mostly low molecular weight material (\(M_n = 3400-11500\) g/mol) was detected by GPC. A strong absorption in the UV region was observed, and attributed to the \(\pi-\pi^*\) transition of the vinyl group. Another small absorption in the visible region was assigned to the \(n-\pi^*\) transition in the backbone.\(^{232}\) A similar absorption was also noticed in the case of poly(p-phenylene phosphine).\(^{228}\) The poly(vinylene arsine)s also fluoresced, with an emission wavelength maximum at 485 nm. Poly(vinylene-arsine)s with alkyl substituents on the vinyl group have been synthesized in an identical manner to

*References start on page 50*
Chapter One
that outlined in Scheme 26, and reported.\textsuperscript{233} A cross-linked poly(vinylene-arsine) has also been reported.\textsuperscript{234}

\[
\text{cyclo-}(\text{RAs})_m + m \xrightleftharpoons{} \text{Ph} \xrightarrow{\text{AIBN}} \xrightarrow{\text{hv}} \left[ \begin{array}{c} \text{C} = \text{C} \\ \text{Ph} \\ \text{As} \\ \text{R} \\ \text{n} \end{array} \right]
\]

\textbf{Scheme 26.}

1.9.3 PPV Analogues

1.9.3.1. Poly(azomethine)

Poly\textit{(p-phenylenevinylene)} is arguably one of the most studied organic $\pi$-conjugated polymers. There have been a few instances where the one or both of the carbons in the vinylene group have been replaced by another atom. In azomethines, the $\text{C} = \text{C}$ vinyl moiety has been replaced by an imine ($\text{C} = \text{N}$). Poly(azomethine) (67) was first reported in the 1920's.\textsuperscript{235} Poly(azomethine) is usually synthesized by a polycondensation reaction between an aromatic diamine and dialdehyde as outlined in Scheme 27.

\[
\text{H}_2\text{N}-\text{Ar}-\text{NH}_2 + \text{O}-\text{C}\text{Ar}-\text{CO} \xrightarrow{-2n \text{H}_2\text{O}} \left[ \begin{array}{c} \text{N} \\ \text{H} \\ \text{C} \\ \text{Ar} \\ \text{n} \end{array} \right]
\]

\textbf{Scheme 27.}

Poly(azomethine) is isoelectronic with PPV, and belongs to a class of high performance materials that exhibit excellent thermal stability,\textsuperscript{236} good mechanical properties\textsuperscript{237} and environmental resistance. However, due to the conjugated backbone, these polymers also show photoluminescence,\textsuperscript{238} non-linear optical properties,\textsuperscript{239,240} liquid crystallinity, and some magnetic applications.\textsuperscript{241,242} Poly(azomethine)s have also

References start on page 50
been investigated as catalyst supports.\textsuperscript{243} Recently there studies on the crystallinity of poly(azomethine)s and some derivatives were reported.\textsuperscript{244-246}

1.9.3.2. Poly(p-phenylene phosphine imide)

The first poly(p-phenylene phosphine imide) (68) was synthesized by Herring in 1961 as outlined in Scheme 28.\textsuperscript{247} 1,4-bis(diphenylphosphino)benzene was treated with 1,4-diazidobenzene in benzene at room temperature, yielding 68, a red-orange solid.

\begin{align*}
\text{Ph}_2\text{P} - \text{Ph} & \quad \text{benzene, R. T.} \\
\text{N}_3 - \text{Ph} & \quad \text{N}_3 \\
\end{align*}

Scheme 28.

Polymer 68 was also synthesized by Pomerantz and Victor, along with several other derivatives with alkyl instead of aryl spacers in the phosphorus monomer (R = (CH\textsubscript{2})\textsubscript{n} where n = 2, 3, 4, 5 for 69b-e respectively) as outline in Scheme 29.\textsuperscript{248} A molecular weight of approximately 1830 g/mol (M\textsubscript{n}) was determined by end group analysis using \textsuperscript{31}P NMR spectroscopy for 68 prepared by Pomerantz et al. Diffuse reflectance FT-IR spectroscopic analysis of the polymers showed the P=N stretch as a broad absorption at 1303-1311 cm\textsuperscript{-1}. In the spectra of all the polymers, another band was observed at 2117-2125 cm\textsuperscript{-1} which was assigned to azide end groups.

\begin{align*}
\text{N}_3 - \text{Ph} & \quad \text{Ph} - \text{Ph} - \text{P} - \text{R} - \text{P} - \text{Ph} & \quad \text{Ph} - \text{Ph} \\
\text{N}_3 & \quad \text{Ph} & \quad \text{Ph} & \quad \text{Ph} \\
\end{align*}

\text{R = C}_6\text{H}_{14}, (CH\textsubscript{2})\textsubscript{n} \\
n = 2, 3, 4, 5

Scheme 29.

The investigation of these poly(phenylene phosphine imide)s was limited by the low yield synthesis of the 1,4-bis(diphenylphosphino)benzene and poor solubility of the
polymer 68. Recently developed palladium-catalyzed carbon-phosphorus coupling reactions provided a more efficient route to the 1,4-bis(diphenylphosphino)benzene. A 1,4-bis(diphenylphosphino)-2,5-dihexyloxybenzene monomer (70) was similarly produced in 76-88% yield as white crystalline solids. Incorporation of flexible alkoxy side chains often increases the solubility of polymers with rigid backbones. The addition of 70 to p-diazidobenzene in benzene solution resulted in the polymer 71 (Scheme 30).

\[ \begin{align*}
    \text{N}_3-\text{N}_3 + \text{Ph}_2\text{P}-\text{Ph}_2 \rightarrow \begin{array}{c}
    \text{OHex} \\
    \text{HexO}
    \end{array}
    & \rightarrow \begin{array}{c}
    \text{OHex} \\
    \text{Ph} \\
    \text{HexO}
    \end{array}
    \\
    & \rightarrow \begin{array}{c}
    \text{OHex} \\
    \text{Ph} \\
    \text{HexO}
    \end{array}
    \\
    & \rightarrow \begin{array}{c}
    \\
    \text{Ph}
    \end{array}
    \\
    & \rightarrow \begin{array}{c}
    \\
    \text{HexO}
    \end{array}
    \end{align*} \]

Scheme 30.

The polymer 70 proved to be only partially soluble in THF. The THF soluble portion contains oligomers of 3-7 repeat units \((M_n = 2000-4000)\) estimated by GPC. Thermogravimetric analysis (TGA) under \(N_2\) revealed decomposition temperatures around 440° for model compounds 72, 73, and polymer 71. UV/Visible spectra of the soluble oligomers of 71 \((\lambda_{\text{max}} = 355 \text{ nm})\) and model compounds 72 and 73 \((\lambda_{\text{max}} = 353 \text{ nm})\) indicated isolated chromophores with weak electronic communication in the ground state of the polymer and a break in the conjugation at phosphorus. These results are consistent with \(\pi\)-conjugation in the oligomers being limited to P-Ar-P and P-N-Ar-N-P units, as there is a conjugation node at the phosphorus due to the \(d\pi-p\pi\) overlap in the P=N bond, as is the case in polyphosphazenes. The similarities of the electrochemical and optical properties of oligomers 71 and model compound 73 indicate that there is little, if any, extended \(\pi\)-conjugation along the backbone of the molecules.
I expected that an analogue of PPV that contains low-coordinate phosphorus would resemble poly(azomethine)s more than poly($p$-phenylene phosphine imide)s due to the low coordinate phosphorus-carbon analogy.

1.10 Outline of Thesis

Chapter two describes the synthesis and characterization of precursors, molecular model compounds containing phosphaalkenes, and the first polymer to incorporate P=C bonds into the main chain, a poly($p$-phenylenephosphaalkene). In chapter three, investigations concerning incorporating thiophene rings as aromatic spacers in the backbone of the molecules are reported. The effects of switching the steric bulk from the carbon end of the P=C bond to the phosphorus is detailed in chapter four. This simple variation provides stereochemical control over the phosphaalkene bond formation. Chapter five reports initial steps towards synthesizing a poly(arylenephosphaalkene) via a different synthetic route, in an attempt to prepare a more robust material.

Each chapter is broken up into several sections, starting with a brief introduction. A results section follows in which the synthesis and characterization of required precursors, model compounds, and polymers. A separate discussion section is included which details the significance of the results, followed by a summary of the important results, an experimental section, and the references cited. Chapters two to five each have an appendix (A – D), respectively, at the end of the thesis, in which spectra of starting materials and other relevant data are placed.
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1.11 References


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Chapter Two

Synthesis and Characterization of the First Polymer Containing P=C Bonds in the Main Chain

2.0 Introduction

Approximately twenty years ago, the first stable neutral compounds possessing acyclic (p-p)π bonds involving the heavier p-block elements such as P=C,\(^1\)\(^2\) P=P,\(^3\) Si=C,\(^4\) Si=Si,\(^5\) and P≡C\(^6\) were prepared. Subsequently, the synthesis, structures and reactivity of numerous low coordinate molecules have received extensive study and continue to attract considerable attention.\(^7\)-\(^16\) Despite current interest in the preparation of organic macromolecules possessing π-conjugated backbones,\(^17\)-\(^21\) to our knowledge, the successful incorporation of heavy element multiple bonds into a well-defined π-conjugated polymer had not been achieved before the beginning of this project. The intriguing polymeric metal, (SN)\(_n\), is a superconductor at 0.26 K, however the electronic structure of this solid-state inorganic material is complex and still not entirely understood.\(^22\)

The incorporation of inorganic elements into the polymer backbone is synthetically challenging and often results in materials possessing unique properties.\(^23\)-\(^25\) Therefore, the development of methods to prepare π-conjugated polymers containing heavier main group (p-p)π-bonds is of fundamental interest, and may ultimately lead to materials with novel properties.\(^26\)-\(^34\)

The poly(p-phenylenevinylene)s are a well known, and exciting, class of luminescent organic macromolecules containing C=C bonds and pose many challenges for the synthetic chemist.\(^17\),\(^19\),\(^35\) In contrast, the possible incorporation of other stable multiple bonds, such as the well-established P=C moiety,\(^7\),\(^36\)-\(^40\) into the PPV structure has

References begin on page 94
not been intensely investigated. Polyazomethines, which have been known since the 1920’s, are analogous to PPV except that the vinyl group has been replaced by an imine. As mentioned in section 1.5, the HOMO of an imine group is the nitrogen lone pair, in contrast to the C=C and P=C bonds where the HOMO is the (p-p)π bond.  

\[
\text{Polyazomethine} \quad \leftrightarrow \quad \text{PPV} \quad \leftrightarrow \quad \text{Poly(p-phenylene phosphaalkene)}
\]

In 1976, the very first example of an acyclic, isolable molecule containing a phosphorus(III)-carbon double bond, the phosphorus containing analogue of an alkene, was prepared by Becker using an elegant and versatile route (Scheme 1). In general, compounds containing a P=C bond are known as phosphaalkenes. Becker’s method involved treating a bis(trimethylsilyl)phosphine (A) with a carboxylic acid chloride (B) to form an acylphosphine intermediate (C), which tautomerizes to produce an isomer of phosphaalkene (D). From a preparative standpoint, this method is probably the most convenient and versatile route to phosphaalkenes with minimal steric protection. The rapid and thermodynamically favourable nature of the silatropic migration also makes this reaction attractive when considering a synthetic method of incorporating phosphaalkene bonds into the main chain of a polymer.

\[
\begin{align*}
\text{A} & \quad + \quad \text{B} \quad \rightarrow \quad \text{C} \quad \rightarrow \quad \text{D} \\
\text{SiMe}_3 & \quad \text{Cl} & \quad \text{O} & \quad \text{O} & \quad \text{Me}_3\text{Si} & \quad \text{P} & \quad \text{O} & \quad \text{R} & \quad \text{R'} & \quad \text{R} & \quad \text{R'}
\end{align*}
\]

**Scheme 1.**

Using molecules with similar structures or short-chain oligomers as models for the longer macromolecule is a well-established procedure in polymer chemistry.
Thus, compounds containing a single P=C bond bridging two aryl groups, and two phosphaalkene bonds bridging three aryl groups were prepared. Henceforth, in this thesis, these compounds are referred to as a monophosphaalkene and a bis(phosphaalkene), respectively. Relatively few examples of molecules possessing two or more phosphaalkene moieties bridged by arylene spacers are known (Chart 1).\textsuperscript{56-61} Only one such example (H) was prepared via the Becker route. The other examples (E, F, G, I, and J) required very large (i.e. Mes\textsuperscript{*}), potentially π-conjugation inhibiting substituents. In the present work, three model compounds were synthesized and characterized, along with the target polymer, as is discussed in section 2.1. A large portion of the material presented in this chapter was published in 2002.\textsuperscript{62}

![Chemical structures](image)

*Chart 1.*
2.1 Results

Several of the compounds required to synthesize the phosphaalkene model compounds or polymer have been previously reported. In these cases, references are provided, but often the synthetic route I used was modified from the original. For the sake of completeness, the synthesis of all the precursors are included, though only some are new compounds.

2.1.1. Synthesis of Ph-P(SiMe₃)₂ (74)

As shown in Scheme 1, a key reactant in Becker’s route to phosphaalkenes is a bis(trimethylsilyl)phosphine A (R = alkyl or aryl). Both monofunctional and bifunctional phosphine reagents are needed to synthesize appropriate model compounds and the desired polymer. The synthetic route to bis(trimethylsilyl)phenylphosphine (74) is outlined in Scheme 2. This compound was first reported by Itoh in 1969 as a clear, pyrophoric liquid, although his method is different and the reported yield (56%) is not as high as I was able to obtain (80% after distillation). The silylphosphine product can be purified by distillation under partial vacuum (b.p. 62°C / 0.1 mmHg).

![Scheme 2](image)

**Scheme 2.** Conditions and reagents: i) diethylether, -78°C, 0.6 equiv. LiAlH₄; ii) diethylether, -78°C, 2.1 equiv. of MeLi, 2.1 equiv. of ClSiMe₃.

The $^{31}$P NMR spectrum of 74 shows a single resonance at δ -136 in both proton coupled and decoupled $^{31}$P NMR spectra (Figure A1, Appendix A). The $^1$H NMR spectrum is also straightforward to assign (Figure A2). A multiplet at δ 7.4 is due to the para- and meta-protons of the phenyl ring. A second multiplet at δ 7.2 can be assigned to...
the ortho-phenyl protons. A doublet due to the trimethylsilyl protons is present at δ 0.2, split by $^3J_{PH}$ coupling with the phosphorus nuclei.

2.1.2. Synthesis of 1,4-[P(SiMe$_3$)$_2$]-C$_6$H$_4$ (79)

1,4-Bis(trimethylsilyl)phosphinobenzene (79), the bifunctional equivalent to 74, may be prepared following the synthetic route outlined in Scheme 3. Evleth was the first to report 1,4-bisphosphinobenzene (78) in 1962, and 79 has been mentioned but no experimental details for its preparation were given in a report of a bis(phosphaalkene).

Starting from the 1,4-dibromobenzene (75), the phosphorus moiety is introduced through a Grignard reaction with bis(diethylamino)chlorophosphine (ClP(NEt)$_2$)$_2$. Treatment of the 1,4-bis(diethylamino)phosphinobenzene (76) with dry HCl(g) yields the 1,4-bis(dichlorophosphino)benzene (77). Compound 77 can be reduced with LiAlH$_4$ to give the 1,4-bisphosphinobenzene (78). Once 78 is treated with four equivalents of MeLi, compound 79 is prepared through subsequent addition of ClSiMe$_3$. Full experimental details are given in section 2.5.

**Scheme 3.** Conditions and reagents: i) THF, 2.1 equiv. Mg, reflux for 3-4 hours, 2.1 equiv. ClP(NEt)$_2$)$_2$; ii) CH$_2$Cl$_2$, 0°C, excess dry HCl(g); iii) Et$_2$O, -78°C, 1.1 equiv. LiAlH$_4$; iv) Et$_2$O, -78°C, 4.1 equiv. MeLi, 4.1 equiv. ClSiMe$_3$.

The crude product can be sublimed under reduced pressure to yield analytically pure 79, which is a highly pyrophoric, malodourous, colourless solid. A single resonance is detected in the $^{31}$P NMR spectrum of 79 (Figure A3), which has a chemical shift (δ...
-138) slightly upfield from silylphosphine 74 (δ 136). The presence of two phosphorus atoms in the molecule can be confirmed in the $^1$H NMR spectrum of 79 (Figure A4). Two signals are detected; the first resonance (δ 7.27) is a pseudo-quartet which is in fact a doublet of doublets due to $^3$$J_{PP}$ and $^4$$J_{PH}$ coupling of the phenyl ring protons to the phosphorus nuclei. The second resonance is a doublet (δ 0.22) assigned to the trimethylsilyl protons, and split by $^3$$J_{PH}$ coupling to the nearest phosphorus atom. The product was fully characterized by mass spectrometry ($C_{18}H_{40}P_2Si_4, M^+ = 430$ g/mol), and elemental analysis in addition to multi-nuclear NMR spectroscopy.

2.1.3 Synthesis of Mes-C(O)Cl (82)

The carbon in the phosphaalkene phosphorus(III)-carbon double bond originates from the acid chloride reagent. Previous studies have shown that both bulky alkyl groups and aromatic rings make good carbon substituents to access isolable phosphaalkenes.\textsuperscript{46-48} Beginning with mesityl bromide (80) (Scheme 4), a ring metallation reaction (either a Grignard reaction or treatment with an alkyl lithium reagent) allows the functionalization of the aromatic ring.\textsuperscript{66} The solution of this reactive intermediate was purged with dry CO$_2$, followed by an aqueous acid work-up to afford the mesitylene-2-carboxylic acid (81). Compound 81 was suspended in thionyl chloride (SOCl$_2$), and heated to reflux. The crude mesityl-2-carboxylic acid chloride (82) may be purified by a vacuum distillation (b.p. 110°C / 0.5 mmHg), and was characterized by $^1$H NMR spectroscopy (Figure A5).

Scheme 4. Conditions and reagents: i) THF, 1.1 equiv. Mg, ~3 hours reflux; 0°C, excess dry CO$_2$; HCl (aq). ii) excess SOCl$_2$, 80°C, 12 hours.
2.1.4. Synthesis of 1,4-[C(O)Cl]-C₆Me₄ (86)

Surprisingly, the bulky acid chloride (86) had only previously been reported in a few patents. Our synthetic procedure for a bifunctional, sterically demanding, aromatic acid chloride begins with durene, or 1,2,4,5-tetramethylbenzene (83) (Scheme 5). Durene was brominated to give the 1,4-dibromo-2,3,5,6-tetramethylbenzene product (84). Unlike the facile reaction of mesityl bromide in Scheme 4, the formation of a diGrignard reagent from 84 is not straightforward. Thus, 84 was treated tert-butyl lithium, and subsequently dry CO₂ bubbled through the reaction mixture, followed by an aqueous HCl work-up to afford the 1,4-dicarboxylic acid-2,3,5,6-tetramethylbenzene (85). The 1,4-carboxylic acid chloride-2,3,5,6-tetramethylbenzene (86) was obtained by treating with thionyl chloride. The major impurity, 1-carboxylic acid chloride-2,3,5,6-tetramethylbenzene, can be separated from 86 through fractional sublimation. Compound 86 was characterized by ¹H NMR spectroscopy (Figure A6), ¹³C NMR spectroscopy, and mass spectrometry.

Scheme 5. Conditions and reagents: i) CH₂Cl₂, 0°C, 2 equiv. Br₂; excess KOH (aq). ii) Et₂O, -78°C, 4.1 equiv. 'BuLi, excess dry CO₂; HCl (aq). iii) excess SOCl₂, 80°C, 12 hours.

2.1.5. Synthesis of Monophosphaalkene Ph-P=C(OSiMe₃)-Mes (87)

All three possible model compounds that could be generated from the two monofunctional reagents (74 and 82), and the two bifunctional reagents (79 and 86) were synthesized and fully characterized. The simplest model compound is the monophosphaalkene (87) which was synthesized from mesitylene-2-carboxylic acid chloride (82) and bis(trimethylsilyl)phenylphosphine (74) (Scheme 6). The two clear,

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neat liquids were heated at 50°C for several days. Analysis of reaction mixture by $^{31}\text{P}$ NMR spectroscopy showed only two signals ($\delta$ 149.2, 54%; 134.0, 46%) (Figure 2.1), which can be assigned to the E- and Z-isomers of 87, respectively, by comparison with similar phosphaalkenes in the literature.$^{1,71,72}$ By vacuum distillation, analytically pure 87 was isolated as a pale yellow liquid.

**Scheme 6.** Conditions and reagents: i) neat liquids, 50°C, 2-3 days.

2D-NMR experiments ($^1\text{H},^1\text{H}-\text{COSY}, ^{13}\text{C}, ^1\text{H}-\text{HMQC}, ^{13}\text{C}, ^1\text{H}-\text{HMBC}$) were used to assign the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra (Figure A7). In the $^1\text{H}$ NMR spectrum of 87, the signal for the siloxy group of the Z-isomer is observed upfield of the resonance for the E-
isomer (Figure 2.2). The signals for the ortho and para methyl groups of the mesityl ring are coincident in CDCl₃ for the E-isomer. Interestingly, the resonances of the phenyl ring protons are also coincident for the E-isomer in CDCl₃. In contrast, only the para and meta protons of the phenyl ring are coincident in the Z-isomer, and the signals for the mesitylene ortho and para methyl groups are resolved.

Figure 2.2. ¹H NMR spectrum of monophosphaalkene 87 in CDCl₃.

2.1.6. Synthesis of Bis(phosphaalkene) 1,4-[(Ph-P=CO(OSiMe₃)]₂-C₆Me₄ (88)

Bis(phosphaalkene) 88 was synthesized from a concentrated solution of two equivalents of PhP(SiMe₃)₂ (74) and the 1,4-dicarboxylic acid chloride-2,3,5,6-tetramethylbenzene (86) in a mixture of THF and hexanes (Scheme 7).
Scheme 7. Conditions and reagents: i) THF/hexanes, 85°C, 2-3 days.

After several days of heating and periodic monitoring of the reaction progress by \(^{31}\text{P}\) NMR spectroscopy, the PhP(SiMe\(_3\))\(_2\) was entirely consumed, and analytically pure 88 was isolated as a white powder from a cooled hexanes solution (-35°C). Eight resonances were observed in the \(^{31}\text{P}\) NMR spectrum of 88 (Figure 2.3). These resonances were distributed over the regions expected for E- (44%) and Z-phosphaalkene (56%) isomers. Interestingly, there were two fewer signals detected for OSiMe\(_3\) groups in the \(^1\text{H}\) NMR spectrum (Figure 2.4).

Figure 2.3. \(^{31}\text{P}\) NMR spectrum of bis(phosphaalkene) 88 in CDCl\(_3\).

In the case of the bis(phosphaalkene) 88, only general assignments were made since the presence of several isomers led to broad signals in the 2D-NMR, and hence prevented further specificity. To more accurately assign the different isomers, more
accurate 2D-NMR experiments are required, and in some cases resonances from different isomers exhibit considerable coincidence.

![Diagram of the bis(phosphaalkene) structure](image)

**Figure 2.4.** $^1$H NMR spectrum of bis(phosphaalkene) 88 in CDCl$_3$. * Residual CHCl$_3$

2.1.7. Synthesis of Bis(phosphaalkene) 1,4-[Mes-P=C(OSiMe$_3$)]$_2$-C$_6$H$_4$ (89)

To accurately model the backbone of the target polymer that contains P=C bonds in the main chain, two bis(phosphaalkene)s should be prepared. Each bis(phosphaalkene) is bridged by one of the bifunctional precursors (79 or 86), so the interactions of the P=C bond with that of the aromatic bridge can be investigated. The bis(phosphaalkene) bridged by the tetramethylbenzene aryl group, 88, was discussed above. The complementary bis(phosphaalkene) 89 was synthesized from two equivalents of mesitoyl chloride (82) and 1,4-bis(trimethylsilylphosphino)benzene (79) (Scheme 8). In a manner analogous to the synthesis of 88 above, the progress of the experiment in the heated reaction mixture was monitored by $^{31}$P NMR spectroscopy. When the signal for the silylphosphine 79 disappeared from the $^{31}$P NMR spectrum, the crude product was isolated as a yellow oil. Analytically pure 89 precipitated as a colourless powder from
cold hexanes (-35°C). Four resonances are detected in the $^{31}$P NMR spectrum, and tentative isomer assignments were made (Figure 2.5). There are also only four signals for the OSiMe$_3$ groups in the $^1$H NMR spectrum (Figure 2.6).

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{P} & - \text{P(SiMe}_3\text{)}_2 \\
\text{(Me}_3\text{Si)}_2\text{P} & - \text{P(SiMe}_3\text{)}_2
\end{align*}
\]

Scheme 8. Conditions and reagents: i) THF, 80°C, 2 days.

![Chemical structure](image)

Figure 2.5. $^{31}$P NMR spectrum of bis(phosphaalkene) 89 in CDCl$_3$.

In the $^{31}$P NMR spectrum, the isomers can tentatively be assigned by the chemical shift and relative intensities. I observed that the amount of the $E,Z$- and $Z,Z$- isomers are significantly decreased during precipitation. As was the case for the previous model compound, bis(phosphaalkene) 88, only general $^1$H NMR assignments are made. The protons of the phenyl ring show a distinctive doublet of doublets due to $^3J_{PH}$ and $^4J_{PH}$.
coupling to the two phosphorus nuclei, as is the case for the silylphosphine starting material 79.

Figure 2.6. $^1$H NMR spectrum of bis(phosphaalkene) 89 in CDCl$_3$. * Residual CHCl$_3$.

2.1.8. Synthesis of Polymer [-C$_6$H$_4$-P=C(OSiMe$_3$)-C$_6$Me$_4$-C(OSiMe$_3$)=P-] (90)

The target polymer (90) was synthesized by thermolysis of bifunctional carboxylic acid chloride 86 and silylphosphine 79 as shown in Scheme 9. In a typical experiment, after 24 hours the initially colourless, mobile liquid had become yellow, and highly viscous or even immobile in some cases. Crude poly($p$-phenylene phosphaalkene) (90) was purified by precipitation of the polymer from a concentrated THF solution with cold hexanes (ca. -30°C) and subsequent drying in vacuo.
Scheme 9. Conditions and reagents: i) ground and mixed solids, evacuated and sealed tube, 85°C, ~24 hours (see Table 2.1, page 79).

The brittle yellow solid isolated from the hexanes precipitation was analyzed by $^{31}$P NMR spectroscopy, which revealed broad overlapping signals for the $E$- and $Z$-isomers in 90 and for the polymer end groups (Figure 2.7, page 78). Of note in Figure 2.7, there appears to be a sharp resonance in the $E$-phosphaalkene region which may suggest molecular impurities, however this resonance is 85 Hz wide at half height, so it is quite broad compared to resonances for starting materials and model compounds, and consistent with a polymer. The $^{29}$Si NMR DEPT spectrum of 90 exhibits three signals, at $\delta$ 21, 19, and 1.4. The first two resonances can be assigned to phosphaalkene siloxy groups. The third resonance is a broad multiplet which can be assigned to P(SiMe$_3$)$_2$ polymer end groups. The $^{29}$Si NMR spectrum of 90 exhibited similar chemical shifts ($\delta$ 21.3, 18.2) due to the siloxy groups in the monophosphaalkene. Diagnostic chemical shifts of the P=C carbon were detected in the $^{13}$C NMR spectrum as broad resonances at $\delta$ 212 and 198 (Figure A7). A steady progression can be seen in a stack plot of the $^1$H NMR spectra of monophosphaalkene 87, to bis(phosphaalkene) 88, and polymer 90 (Figure A8). The infrared spectra of films of 90 were remarkably similar to those of 87, 88, and other analogous phosphaalkenes$^{46}$ The thermal stability of 90 was assessed by thermogravimetric analysis (TGA) under dry helium. The polymer 90 was stable to
weight loss up to 190°C, whereupon approximately 40% was lost, followed by an additional 20% at 400°C. Polymer 90 displayed no further change even upon heating to 800°C, as 40% of the mass remained as a black solid. Interestingly, small pinholes in the platinum sample pan were discovered at the end of the TGA run, which may indicate some interaction of the polymer and platinum at high temperature. The electronic structure of these phosphaalkenes was investigated in THF solution (ca. $10^{-5}$ M) using UV/Vis spectroscopy (Figure 2.8, page 80).

![Figure 2.7](image)

Figure 2.7. $^{31}$P NMR spectra of polymer 90 in CDCl$_3$ a) before and b) after precipitation. * Residual bifunctional silylphosphine starting material 79.
Table 2.1. Selected characterization data for model compounds and polymer.

<table>
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<tr>
<th></th>
<th>t_{polym} (h)</th>
<th>$\bar{X}_n^*$</th>
<th>$M_n^*$ (g/mol)</th>
<th>UV/Vis $\lambda_{max}$ (nm)</th>
<th>Z/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td></td>
<td>328</td>
<td>310</td>
<td>314</td>
<td>0.85</td>
</tr>
<tr>
<td>88</td>
<td></td>
<td>550</td>
<td>314</td>
<td>338</td>
<td>1.27</td>
</tr>
<tr>
<td>89</td>
<td></td>
<td>578</td>
<td>332</td>
<td>338</td>
<td>0.13</td>
</tr>
<tr>
<td>90  (trial 1)</td>
<td>21</td>
<td>5</td>
<td>2,900</td>
<td>328</td>
<td>1.12</td>
</tr>
<tr>
<td>90  (trial 2)</td>
<td>27</td>
<td>21</td>
<td>10,500</td>
<td>338</td>
<td>1.14</td>
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<tr>
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<td>34</td>
<td>12</td>
<td>6,300</td>
<td>334</td>
<td>1.05</td>
</tr>
</tbody>
</table>

* $M_n$ and $\bar{X}_n^*$ were estimated using end group analysis.

2.2 Discussion

2.2.1 Model Compounds

For a $\pi$-conjugated system increasing in length, one would expect to see an increase in the wavelength of the maximum absorbance (red-shift) in the UV/Vis spectrum. This is observed when comparing monophosphaalkene 87 to bis(phosphaalkene)s 88 and 89 (Figure 2.8, or Table 2.1). This trend is what one would expect as the conjugation path grows longer from the two aryl groups bridged by the P=C bond in the monophosphaalkene 87 to the three aryl groups bridged by two P=C bonds in the bis(phosphaalkene)s 88 and 89.
Interestingly, there is also a red-shift in $\lambda_{\text{max}}$ between the bis(phosphaalkene) bridged by tetramethylenzene (88) and the phenyl bridged compound 89. The red-shift between the bis(phosphaalkene)s can be rationalized by considering the backbone of the model compounds. As noted previously, bis(phosphaalkene) 88 exhibits eight resonances in its $^{31}$P NMR spectrum, twice the amount expected for a compound with two distinct double bonds. As with any double bond possessing three different substituents, the phosphaalkene may have two isomers. In the Becker type of phosphaalkene the higher priority substituent on the carbon is the oxygen of the OSiMe$_3$ group. As there is only one substituent on the phosphorus, it is automatically the highest priority substituent. For the Becker type phosphaalkene, the $E$-isomer features the two aryl rings in cis positions around the phosphorus-carbon double bond. In contrast, the $Z$-isomer consists of aryl rings in trans positions across the phosphaalkene bond, which is more favourable for

**Figure 2.8.** UV/Vis spectra (ca. $10^{-5}$ M) of model compounds and polymer.

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extended \( \pi \)-conjugation. During the synthesis of Mes-C=P, Regitz and coworkers were able to selectively crystallize the \( E \)-phosphaalkene intermediate from a mixture of isomers, and determined its solid state structure.\(^{52} \) The authors observed that after fifteen minutes, the \( ^{31}P \) NMR spectrum of a crystal of the \( E \)-phosphaalkene shows a mixture of isomers. It has been observed that the \( E \)-isomer exhibits a \( ^{31}P \) NMR chemical shift downfield from the \( Z \)-isomer.\(^{72} \)

Returning to the \( ^{31}P \) NMR spectrum of \( 88 \), one would expect a resonance from the \( E,E \)-isomer, two resonances from the \( E,Z \)-isomer, and another resonance from the \( Z,Z \)-isomer. Bis(phosphaalkene) \( 88 \) is bridged by a \( C_6Me_4 \) aromatic ring, whose methyl groups may hinder rotation of the phosphaalkene moieties about the plane of the \( C_6Me_4 \) ring. As a consequence of restricted rotation, \( \text{syn} \) and \( \text{anti} \)-isomers of the \( E,E-, E,Z- \), and \( Z,Z \)-isomers would be predicted. This is consistent with the observation of eight signals in the \( ^{31}P \) NMR spectrum, as the four signals expected from having a mixture of isomers is doubled by also having \( \text{syn} \) and \( \text{anti} \) isomers.

\[
\text{anti-}Z,Z- \quad 88 \quad \text{syn-}Z,Z- \quad 88
\]

The steric bulk of the \( C_6Me_4 \) spacer which may cause restricted rotation would perturb the planarity of the backbone of the bis(phosphaalkene) \( 88 \). The more planar a compound, the better the \( p \)-orbital overlap of the \( \pi \)-system and the more effective the \( \pi \)-conjugation of the system. The more extensive the \( \pi \)-conjugation becomes, the smaller the HOMO-LUMO energy gap becomes, and thus \( \lambda_{\text{max}} \) is shifted to longer wavelengths. It would appear that there is some \( \pi \)-delocalization through the central aryl group of
bis(phosphaalkene) 88 as the $\lambda_{\text{max}}$ (314 nm) is slightly larger than that of monophosphaalkene 87 (310 nm). If the $\pi$-conjugation did not extend through the central aryl ring, one would expect the $\lambda_{\text{max}}$ of 88 and 87 to be identical.

In contrast to 88, bis(phosphaalkene) 89 whose central bridge consists of a phenyl ring, does not seem to exhibit restricted rotation about the phenyl-C=P bond as there are four resonances are present in the $^{31}\text{P}$ NMR spectrum (Figure 5). One would theorize that this molecule would be more planar about its central bridging aryl ring, leading to more effective $\pi$-conjugation. This more effective conjugation should lead to a red shift in $\lambda_{\text{max}}$ as the HOMO-LUMO gap should shrink with a more conjugated $\pi$-system. In fact, this is what is observed as $\lambda_{\text{max}}$ for bis(phosphaalkene) 89 (332 nm) is larger than that of 88 (314 nm). Jouaiti speculates free rotation about the phenyl ring carbon-phosphaalkene carbon single bond in the bis(phosphaalkene) systems he studied, where the steric bulk resided on the phosphorus substituent ($o$-$E$, $m$-$E$), which parallels the steric arrangement of bis(phosphaalkene) 89.57 His reasoning is that only three signals are observed for the bis(phosphaalkene)s ($EE$ and $EZ$), so that there cannot be rotational isomers present, and thus the system must have free rotation. This is observed for bis(phosphaalkene) 89, but not for bis(phosphaalkene) 88.

In another investigation, Jouaiti and co-workers focused mainly on the ability of these bis(phosphaalkenes) to act as bidentate and terdentate ligands respectively.56-58 During this investigation, Jouaiti compared the electrochemical reduction of the

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corresponding monophosphaalkene Mes*-P=CH-Ph with the bis(phosphaalkene)s. They found that absolute value of the reduction potential of all the bis(phosphaalkene)s are lower than that of the monophosphaalkene, and that order of decreasing potential is meta, ortho, and then para-E.\(^{73}\) The reduction potential could be used as an indication of the HOMO-LUMO gap, in comparison to the monophosphaalkene Mes*-P=CH-Ph, showing that the orientation of the substituents affects the electron delocalization. This result showed that the second phosphaalkene moiety affected the \(\pi\)-system, which is consistent with inclusion into extended \(\pi\)-conjugation.

Yoshifuji et. al. studied the photoisomerization of phenylene bridged phosphaalkenes (p-E, F, and G.) They found that the UV/Vis absorption maximum of a compound containing two or more phosphaalkene moieties is red-shifted from a monophosphaalkene, consistent with weak \(\pi\)-conjugation through the P=C bonds.\(^{59,74}\) These observations mirror the results of the Becker-type phosphaalkenes prepared in this chapter. In all cases, Yoshifuji observed only one isomer, which featured the aryl substituents in \textit{trans} positions across the P=C double bond (E-isomer in this case).

Smith et. al. have prepared several bis(phosphaalkene)s that also support the idea of a less sterically demanding spacer leading to better \(\pi\)-delocalization in phosphaalkenes.\(^{61}\) Bis(phosphaalkene)s I and J have absorption maxima of 349 and 411 nm, respectively. The phenyl spacer of J appears to lead to better \(\pi\)-conjugation, and thus possesses a larger \(\lambda_{\text{max}}\). These results also mirror observations of the phosphaalkenes

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presented in this chapter. The bis(phosphaalkene) 88 has a more sterically demanding central arylene bridge than 89, and exhibits a $\lambda_{\text{max}}$ with a shorter wavelength. Clearly, bulky bridges tend to disrupt extended $\pi$-conjugation.

2.2.2 Poly(p-phenylenephosphaalkene) (90)

Attempts to determine the molecular weight of the poly(p-phenylenephosphaalkene) 90 through GPC measurements were precluded by the air- and moisture sensitivity of the polymer. Similarly, attempts using MALDI-TOF mass spectrometry were inconclusive, likely because the majority of matrices used in this technique are aromatic alcohols which react with the polymer during sample preparation. The molecular weight of the polymer from various trials was determined by end-group analysis which is an absolute method of molecular weight determination. The molecular weights of 90 were estimated by integration of the P(SiMe$_3$)$_2$ and P=C signals in the $^{31}$P NMR spectrum. Spectra recorded with 2 and 30 second relaxation delays resulted in identical integration ratios. A statistical (50:50) mixture of C(0)Cl and P(SiMe$_3$)$_2$ end groups was assumed, and molecular weights estimated by this method match well with elemental analysis, including chlorine analysis.

The UV/Vis spectrum of 90 reveals a broad absorbance ($\lambda_{\text{max}} = 328-338$ nm) and a tail stretching into the visible region. The bathochromic shift observed for poly(p-phenylenephosphaalkene) compared with 87, 88, and 89 suggests some degree of $\pi$-conjugation through the phenylene and P=C units. However, the red-shift for 90 is less
than that for trans-PPV compared with trans-stilbene (ca. 426 nm vs. 294/307 nm),
which can be attributed to conformational nonplanarity of the main chain, caused by the
sterically demanding C₆Me₄ groups in 90. The incorporation of even a few percent of
2,3,5,6-tetramethyl-1,4-phenylene into PPV leads to a blue shift of 20-30 nm in the
absorbance maximum. In addition, the breadth of the absorbance for 90 may be caused,
in part, by the mixture of isomers present (Z/E ≈ 1.1). Comparing cis-stilbene (276 nm)
and trans-stilbene (294/307 nm) illustrates the effect of orientation around the double
bond upon π-delocalization.

There seems to be a fairly good correlation between polymerization time,
estimated molecular weight, and λ_max as seen in Table 2.1. In general, longer reaction
times lead to high molecular weight polymers, which showed UV/Vis absorption maxima
with longer wavelengths. Continuing a polymerization reaction for 48 hours led to a
yellow-orange insoluble gel that swells reversibly in THF. Analysis of the swollen gel by
³¹P NMR spectroscopy showed broad resonances similar to those for the soluble polymer
90. It is possible that this material has become partially cross-linked or is high molecular
weight. A very weak fluorescence was observed for solutions of polymer 90, but it was
not clear whether this emission was due to the polymer or another species present in
solution

Polymer 90 was the first polymer to incorporate P=C bonds into the main chain of
a macromolecule. Shortly after this work was reported, Protasiewicz and coworkers
used a ‘phospha-Wittig’ reaction to synthesize a poly(p-phenylene phosphaalkene) (91).
A 1,4-bis(dichlorophosphino)-2,3,5,6-tetramesitylbenzene which was treated with zinc dust and PMe₃ to generate the phospha-Wittig reagent *in situ*. Subsequent addition of a conjugated dialdehyde afforded polymer 91. Molecular weights of up to 6500 g/mol were estimated by GPC, corresponding to 6 repeat units. The steric protection of the P=C bond provided by the large substituted aryl groups makes the macromolecule reasonably air stable (ca. 1 week in air), but may interfere with extended π-conjugation throughout the backbone of the polymer. In contrast to that observed for our polymer 90, the UV/Vis absorption maximum of model compound bis(phosphaalkene) 92 (λ_{max} = 445 nm) is identical to that of polymer 91, which suggests that the π-conjugation does not extend past the polymer repeat unit. Both the model compound and the polymer exhibit a weak fluorescence. The extreme steric bulk of the tetraaryl substituted arylene bridge may cause enough torsion in the backbone of the macromolecule to preclude extended π-conjugation. In constrast, the poly(p-phenylenephosphaalkene) 90 that I prepared reveals a red-shift in the UV/Vis absorption maxima compared to the model compounds (87, 88, and 89). The λ_{max} of 91 and 92 is significantly red-shifted from polymer 90, though the number of repeat units is approximately the same. This red-shift might be a substitutional effect as the presence of alkoxy substituents has been shown to cause a significant red-shift in PPV. The phospha-Wittig reagent can undergo intermolecular reactions when irradiated to form P=P bonds in the main chain of a conjugated polymer.

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2.3 Summary

In summary, we were able to successfully incorporate P=C bonds into the main chain of a polymer for the first time, using the Becker [1,3]-silatropic migration synthetic route and suitable bifunctional starting materials. Molecular weights of up to 10,500 g/mol or 20 repeat units were obtained, which is fairly standard for step-growth polymerizations, but impressive considering the reactivity of the precursors. In addition, several formally π-conjugated air and moisture sensitive compounds containing P=C bonds were prepared and fully characterized. As expected for a π-conjugated system, the UV/Vis absorptions of 87, 88, and 89 show a trend of increasingly longer wavelength maxima, moving from the monophosphaalkene, to the bis(phosphaalkene) with the sterically bulky central spacer, to the bis(phosphaalkene) with the unhindered central spacer. A moderate degree of π-conjugation throughout the backbone of poly(p-phenylenephosphaalkene) is suggested by comparison with model compounds, as the UV/Vis absorption maximum of 90 is of a slightly longer wavelength, and hence a lower energy. The red-shifts in the UV/Vis absorbances of the bis(phosphaalkene) model compounds compared to monophosphaalkenes have precedence in the literature.66-69, 78, 79 A subsequent preparation of a poly(p-phenylenephosphaalkene) via a different synthetic route did not exhibit signs of π-conjugation that extended beyond the polymer repeat unit.61

2.4 Experimental Section

General Procedures. Unless otherwise stated, these procedures were followed for all compounds prepared in this thesis. 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. \textsuperscript{1}H, \textsuperscript{31}P, \textsuperscript{13}C, \textsuperscript{29}Si NMR spectra were recorded on Bruker Avance 300 MHz or Bruker Avance 400 MHz spectrometers. Chemical shifts are reported relative to residual: CHCl\textsubscript{3} or HC\textsubscript{6}D\textsubscript{5} (\(\delta = 7.24\) and 7.15 for \textsuperscript{1}H); 85\% H\textsubscript{3}PO\textsubscript{4} as an external standard (\(\delta = 0.0\) for \textsuperscript{31}P); CDCl\textsubscript{3} or C\textsubscript{6}D\textsubscript{6} (\(\delta = 77.0\) and 128.0 for \textsuperscript{13}C). \textsuperscript{29}Si NMR spectra were recorded utilizing a DEPT pulse sequence (proton decoupled) with a \(^2\)J\textsubscript{Si-H} coupling constant of 7.0 Hz and referenced externally to SiMe\textsubscript{4} in CDCl\textsubscript{3} (\(\delta 0.0\) for \textsuperscript{29}Si). Infrared spectra were obtained as thin films between NaCl plates using a Bomen MB-series instrument. UV/Vis spectra were recorded on a Unicam UV2 spectrophotometer. Mass Spectra were acquired using Kratos MS 50 instrument. Thermogravimetric analyses of 90 were carried out on a TA Instruments 2000 instrument, heating under dry helium at 10 °C/min from 20 °C to 800 °C. Elemental analyses were performed by Mr. P. Borda in the University of British Columbia Chemistry Department Microanalysis Facility.

**Materials.** Diethyl ether, hexanes, and dichloromethane were dried by passing through activated alumina columns.\textsuperscript{80} Tetrahydrofuran was distilled from sodium/benzophenone immediately prior to use; C\textsubscript{6}D\textsubscript{6} (CIL) was degassed and dried over activated 3 Å molecular sieves; and CDCl\textsubscript{3} (CIL) distilled from P\textsubscript{2}O\textsubscript{5} and degassed. 1,4-dibromobenzene, durene, 2-bromomesitylene, bromine, PCl\textsubscript{3}, Me\textsubscript{3}SiCl, Mg, SOCl\textsubscript{2}, LiAlH\textsubscript{4}, MeLi (1.6 M in ethyl ether), and \textsuperscript{1}BuLi (1.7 M in pentane) were purchased from Aldrich and used as received. Et\textsubscript{2}NH, PhPCl\textsubscript{2} were purchased from Aldrich and distilled prior to use. Mesitylene-2-carboxylic acid chloride,\textsuperscript{66} dibromodurene,\textsuperscript{70} 1,4-diphosphinobenzene,\textsuperscript{64,81} bis(trimethylsilyl)phenylphosphine,\textsuperscript{63} were prepared following the literature procedures.

**2.4.1. Preparation of 1,4-[P(SiMe\textsubscript{3})\textsubscript{2}]-C\textsubscript{6}H\textsubscript{4} (79).** To a stirred solution of 1,4-diphosphinobenzene (1.00 g, 7.04 mmol) in Et\textsubscript{2}O (50 mL) was added MeLi in Et\textsubscript{2}O (18.5...
mL, 1.6 M, 29.6 mmol) at -78° C. The reaction mixture was stirred at -78 °C for ca. 30 min, and the yellow suspension allowed to warm to room temperature and stirred for ca. 1 h. After cooling to -78° C, Me₃SiCl (3.21 g, 29.6 mmol) was added resulting in the immediate formation of a white precipitate (presumably LiCl). After warming to room temperature and removing the solvent in vacuo, the residue was extracted with hexanes (2 x 50 mL) and filtered. The solvent was removed in vacuo leaving a pale yellow crystalline solid. 79 (1.74 g, 60%) was isolated as colorless crystals after vacuum sublimation (100 °C, 0.1 mmHg).

31P NMR (C₆D₆): δ -138.0 (s); 1H NMR (C₆D₆): δ 7.27 (dd, 4H, 3 JₚH = 5.0 Hz, 4 JₚH = 3.5 Hz; C₆H₄), 0.22 (d, 36H, 3 JₚH = 5.0 Hz; Si(C(CH₃)₃)₃); 13C NMR (CDCl₃): δ 136.1 (dd, 2 JₚC = 14.8 Hz, 3 JₚC = 7.2 Hz; o-C₆H₄), 131.3 (d, 1 JₚC = 16.1 Hz; i-C₆H₄), 1.1 (d, 2 JₚC = 12.7 Hz, Si(C(CH₃)₃)); 29Si NMR (C₆D₆): δ 1.9 (d, 1 JₚSi = 24 Hz); MS (EI, 70 eV): m/z (%) 434, 433, 432, 431, 430 (1, 2, 7, 13, 30) [M⁺]; 417, 416, 415 (1, 2, 3) [M⁺-CH₃]; 360, 359, 358, 357 (1, 2, 4, 3) [M⁺-Si(CH₃)₃]; 210, 209, 208, 207 (1, 2, 3, 11) [M⁺-PSi₂(CH₃)₉H]; 75, 74, 73 (3, 8, 100) [SiCH₃]; Elem. Anal.: C₁₈H₄₀P₂Si₄: calcd. C 50.18, H 9.36, found C 49.87, H 9.32.

2.4.2. Preparation of 1,4-[C(O)OH]₂-C₆Me₄ (85). To a stirred solution of 1,4-dibromo-2,3,5,6-tetramethylbenzene (17.62 g, 60.3 mmol) in Et₂O (250 mL) was added 'BuLi (149 mL, 1.7 M, 253 mmol) at -78 °C. After 1.5 h at -78 °C, dry CO₂ was bubbled through the reaction mixture for 30 min. The resulting mixture was extracted with aqueous hydrochloric acid (0.5 M), and the aqueous layer extracted with Et₂O (3 x 175 mL), dried with MgSO₄, and the solvent removed in vacuo affording a colorless powder (11.9 g, 89%).

1H NMR (CD₃C(O)CD₃): δ 11.48 (s, 1H; COOH), 2.16 (s, 6H; CH₃).
2.4.3. Preparation of 1,4-[C(O)Cl]_2-C_6Me_4 (86). 1,4-dicarboxylic acid-2,3,5,6-tetramethylbenzene (11.89 g, 53.5 mmol) was suspended in thionyl chloride (100 mL) and heated to reflux overnight during which time all the solid dissolved forming a brown solution. SOCl\textsubscript{2} was removed \textit{in vacuo}, leaving a pale brown solid. Colorless crystals (12.0 g, 90%) were isolated after vacuum sublimation (50 °C; 0.1 mmHg).

\[ ^1H \text{NMR (CDCl}_3\text{)}: \delta 2.28 \text{ (s, CH}_3\text{); Elem. Anal.: C}_{12}H_{12}Cl_2O_2: \text{calcd. C 55.62, H 4.67, found C 55.44, H 4.75.} \]

2.4.4. Preparation of Ph-P=C(OSiMe}_3\text{-Mes (87).} \text{Bis(trimethylsilyl)phenylphosphine (5.6 g, 22.0 mmol) and mesitylene-2-carboxylic acid chloride (4.0 g, 21.9 mmol) were stirred at 50 °C and over several days quantitative conversion to 87 was observed by } ^{31}\text{P NMR spectroscopy. Pure 87 was isolated as a pale yellow liquid after vacuum distillation (b.p. 110° C; 0.1 mmHg). Yield = 5.4 g, (75%).} \]

\[ ^{31}\text{P NMR (C}_6\text{D}_6\text{):} \delta 149.2 \text{ (s, 54%, E-87), 134.0 (s, 46%, Z-87);} ^{1}\text{H NMR (CDCl}_3\text{):} \]

Isomer 1 (E-87) \[ \delta 7.13 - 7.01 \text{ (m, 5H, o, m, p-Ph), 6.73 (s, 2H, m-Mes), 2.20 (s, 9H, o, p-CH}_3\text{), 0.42 (s, 9H, OSi(CH}_3\text{)_3), Isomer 2 (Z-87) \delta 7.79 (m, 2 H, o-Ph), 7.35 (m, 3H, m, p-Ph), 6.91 (s, 2H, m-Mes), 2.48 (s, 6H, o-CH}_3\text{), 2.32 (s, 3H, p-CH}_3\text{), -0.05 (s, 9H, OSi(CH}_3\text{)_3);} ^{13}\text{C NMR (CDCl}_3\text{):} \]

Isomer 1 (E-87) \[ \delta 197.3 \text{ (d, } ^1\text{J}_\text{PC} = 49 \text{ Hz, C=P), 138.5 (d, } ^1\text{J}_\text{PC} = 39 \text{ Hz, i-Ph), 138.0 (d, } ^2\text{J}_\text{PC} = 9 \text{ Hz, i-Mes), 137.4 (s, p-Mes), 134.2 (d, } ^3\text{J}_\text{PC} = 5 \text{ Hz, o-Mes), 133.0 (d, } ^2\text{J}_\text{PC} = 13 \text{ Hz, o-Ph), 128.0 (s, m-Mes), 127.7 (d, } ^3\text{J}_\text{PC} = 6 \text{ Hz, m-Ph), 127.5 (s, p-Ph), 21.0 (s, p-CH}_3\text{), 19.9 (s, o-CH}_3\text{), 0.3-0.1 (m, OSi(CH}_3\text{)_3), Isomer 2 (Z-87) \delta 210.2 \text{ (d, } ^1\text{J}_\text{PC} = 41 \text{ Hz, C=P), 139.5 (d, } ^1\text{J}_\text{PC} = 44 \text{ Hz, i-Ph), 138.1 (s, p-Mes), 136.8 (d, } ^2\text{J}_\text{PC} = 28 \text{ Hz, i-Mes), 136.5 (d, } ^3\text{J}_\text{PC} = 8 \text{ Hz, o-Mes), 133.3 (d, } ^2\text{J}_\text{PC} = 13 \text{ Hz, o-Ph), 128.4 (s, m-Mes), 128.1 (sh, m-Ph), 127.5 (s, p-Ph), 21.1 (s, p-CH}_3\text{), 20.7 (s, o-CH}_3\text{), 0.3-0.1 (m, OSi(CH}_3\text{)_3);} ^{29}\text{Si NMR (C}_6\text{D}_6\text{):} \delta 21.3 \text{ (s), 18.2 (s); UV/Vis (THF):} \lambda\text{max (e) = 310 nm (6000); IR (neat):} \tilde{\nu} = 2921 \text{ (m), 2853 (m), 1601 (w), 1456 (s), 1377 (m), 1252} \]
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(1s, 1187 (vs), 847 (s) cm⁻¹; MS (EI, 70 eV): m/z (%): 330, 329, 328, (3, 10, 44) [M⁺], 253, 252, 251 (1, 4, 23) [M⁺-C₆H₃], 148, 147 (9, 100) [C₁₀H₁₁O], 74, 73 (5, 72) [C₃H₉Si];

Elem. anal.: C₁₉H₂₅O₃Si: calcd. C 69.48, H 7.67, found C 69.54, H 7.60.

2.4.5. Preparation of 1,4-[Ph-P=C(OSiMe₃)]₂-C₆Me₄ (88). To a mixture of bis(trimethylsilyl)phenylphosphine (74) (0.93 g, 3.7 mmol) and 86 (0.47 g, 1.8 mmol) was added hexanes:tetrahydrofuran (5 mL:2 mL) until dissolved. The reaction solution was stirred at 85°C in a closed vessel for several days and ³¹P NMR spectroscopy showed quantitative formation of 88. The solvent was removed in vacuo giving a pale yellow oil, from which 88 was isolated as a colorless powder from concentrated hexanes solution at -35°C. Yield = 0.42 g (42%).

³¹P NMR (CDCl₃): δ 155.2 (s, 20%), 154.9 (s, 4%), 150.7 (s, 2%), 149.5 (s, 18%), 134.0 (s, 23%), 131.8 (s, 4%), 129.9 (s, 12%), 129.6 (s, 17%); ¹H NMR (CDCl₃): δ 7.8-6.9 (m, 10H, Ph-H), 2.39, 2.38, 2.23, 2.19, 2.11, 2.05, 2.02 (s, 12H, Ar-C); ¹³C NMR (CDCl₃): δ 211.8 (d, ¹JPC = 44 Hz, C=P/Z-88), 198.6 (d, ¹JPC = 49 Hz, C=P/E-88), 140-137 (m, i-Ph and i-Ar), 133 (m, o-Ph), 130.2 (m, o-Ar), 128-127 (m, m-Ph and p-Ph), 18 (m, Ar-CH₃), 0.5 (m, OSi(CH₃)₃); UV/Vis (THF): λₘₐₓ (ε) = 314 nm (28000); IR (neat): ν = 3052 (s), 2956 (vs), 2922 (sh), 1451 (sh), 1432 (s), 1251 (vs), 1192 (vs), 981 (s), 900 (sh), 854 (vs) cm⁻¹; MS (EI, 70 eV): m/z (%): 553, 552, 551, 550 (3, 12, 35, 82) [M⁺], 475, 474, 473 (4, 6, 26) [M⁺-Ph], 443, 442, 441 (2, 3, 7) [M⁺-PHPh], 371, 370, 369 (4, 12, 51) [M⁺-P(Ph)SiMe₃], 74, 73 (9,100) [SiMe₃]; Elem. anal.: C₃₀H₄₀O₂P₂Si₂: calcd. C 65.42, H 7.32, found C 65.32, H 7.47.

2.4.6. Preparation of 1,4-[Mes-P=C(OSiMe₃)]₂-C₆H₄ (89). To a stirred solution of the silylphosphine 79 (300 mg, 0.7 mmol) in THF (3 mL), neat mesitylene-2-carboxylic acid chloride (254 mg, 1.4 mmol) was added. In a Kontes bomb, the reaction mixture was

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heated at 80 °C. The reaction was monitored by $^{31}$P NMR spectroscopy, and silylphosphine 79 was quantitatively consumed after 2 days. The solvent was removed in vacuo and the crude product isolated as a yellow oil. Pure 89 was isolated as a colourless solid from a concentrated hexanes solution cooled to -78°C. Yield = 217 mg, (54%).

$^{31}$P NMR (CDCl$_3$): $\delta$ 149.2 (s, 78%, $E,E$-isomer), 148.3 (s, 10.8%, $E,Z$-isomer), 134.8 (s, 9.2%, $E,Z$-isomer), 132.3 (s, 2.0%, $Z,Z$-isomer); $^1$H NMR (CDCl$_3$): $\delta$ 7.73 (m, $^3$J$_{PH}$ = 7 Hz, 4H, Ph), 7.38 (t, $^3$J$_{HH}$ = 7 Hz, 4 H, o-Ph), 7.00 (t, $^3$J$_{HH}$ = 7 Hz, 4 H, o-Ph), 6.86 (s, 4 H, m-Mes), 6.82 (s, 4 H, m-Mes), 6.69 (s, 4 H, m-Mes), 6.67 (m, 8 H, o-Ph, m-Mes), 2.43 (s, 3 H, p-Mes), 2.37 (s, 6 H, o-Mes), 2.27 (s, 3 H, p-Mes), 2.25 (s, 3 H, p-Mes), 2.22 (s, 3 H, p-Mes), 2.19 (s, 6 H, o-Mes), 2.18 (s, 6 H, o-Mes), 2.04 (s, 6 H, o-Mes), 0.36 (s, 9 H, OSiMe$_3$), 0.31 (s, 9 H, OSiMe$_3$), -0.07 (s, 9 H, OSiMe$_3$), -0.18 (s, 9 H, OSiMe$_3$).

$^{13}$C NMR (CDCl$_3$): $\delta$ 210.4 (d, $^1$J$_{PC}$ = 41 Hz, P=C), 209.7 (d, $^1$J$_{PC}$ = 41 Hz, P=C), 195.5 (d, $^1$J$_{PC}$ = 49 Hz, P=C), 138.8 (d, $^1$J$_{PC}$ = 36.8, i-Ph) 138.2 (m, i-Ph, i-Mes), 137.7 (s, p-Mes), 137.4 (s, p-Mes), 136.8 (s, p-Mes), 136.7 (s, p-Mes), 136.5 (d, $^2$J$_{PC}$ = 8 Hz, i-Mes), 136.4 (d, $^2$J$_{PC}$ = 7 Hz, i-Mes), 134.3 (m, o-Mes), 132.6 (dd, $^3$J$_{PC}$ = 13 Hz, $^3$J$_{PC}$ = 6 Hz, o-Ph), 132.3 (m, i-Ph, o-Ph), 128.4 (m, m-Mes), 128.3 (s, m-Mes), 128.0 (s, m-Mes), 21.1 (m, o, p-CH$_3$ Mes), 20.6 (m, o, p-CH$_3$ Mes), 20.0 (s, o-CH$_3$ Mes), 19.8 (s, o-CH$_3$ Mes), 0.4 (s, OSiMe$_3$), 0.3 (s, OSiMe$_3$), 0.2 (s, OSiMe$_3$), 0.1 (s, OSiMe$_3$); UV/Vis (THF): $\lambda_{\text{max}}$ ($\epsilon$) = 332 nm (39000); MS (EI, 70 eV): m/z (%): 580, 579, 578 (5, 8, 22) [M$^+$], 222, 221 (4, 11) [Mes-COSiMe$_3$], 149, 148, 147 (3, 22, 100) [Mes-CO], 120, 119 (6, 37) [Mes], 74, 73 (4, 36) [SiMe$_3$].

2.4.7. Preparation of [-C$_6$H$_4$P=C(OSiMe$_3$)-C$_6$Me$_4$-C(OSiMe$_3$)=P-] (90). The same procedure was followed for each trial (1-4). All glassware was rinsed with Me$_3$SiCl and flame dried prior to use. Compounds 79 (0.601 g, 2.32 mmol) and 86 (1.00 g, 2.32 mmol) were intimately mixed as finely ground powders, and flame sealed in vacuo in a thick
walled Pyrex tube. The sample was placed in a pre-heated (85 °C) oven whereupon the solids melted forming a colorless free flowing liquid. After 6-8 h, the reaction mixture showed an increase in viscosity and was yellow. The reaction was monitored until the liquid was almost immobile (ca. 24 h), and the yellow/orange material was removed from the oven. The tube was broken, Me₂SiCl was removed in vacuo, and the residue dissolved in a minimum amount of THF (ca. 3 mL). The viscous solution was evenly distributed over the walls of the flask, and cold hexanes (ca. -30° C) was added rapidly to precipitate the polymer as a yellow solid. The hexanes soluble fraction was removed and the polymer 90 remained as a bright yellow glassy solid after drying in vacuo. Yield = 0.384 b, (35%).

³¹P NMR (CDCl₃; 121.5 MHz): δ=152 (br m; E-90), 132 (br m; Z-90), -137 (br; P(SiMe₃)₂ end groups) (See Table 2.1 for Z/E ratio, and degree polymerization for each trial). All integrations for end group analyses are reported for a relaxation delay of 2.0 s; however, spectra were obtained using 20 s and 30 s delays, and identical integrations were observed. ²⁹Si NMR (CDCl₃, 79.5 MHz): δ=21.7 (br m), 18.4 (br m), 1.4 (br m, end groups); ¹H NMR (CDCl₃, 400.1 MHz): δ=7.8-6.6 (br m; C₆H₄), 2.5-2.1 (br m; C₆(CH₃)₄), 0.5 -0.5 (br m; Si(CH₃)₃); ¹³C NMR (CDCl₃, 100.6 MHz): δ=211.9 (br; Z-C=P), 197.9 (br; E-C=P), 142.0 (br; i-C₆Me₄), 139.1 (br; i-C₆H₄), 132.4, 130.2 (br; o-C₆H₄, o-C₆Me₄), 18.6, 17.5 (br s; C₆(CH₃)₄), 0.7, 0.2 (br s; OSi(CH₃)₃); UV/Vis (see Table 2.1); IR (film): ν=2955 (m), 2921 (m), 2849 (m), 1252 (vs), 1187 (s), 846 (vs) cm⁻¹; Elem. Anal. [C₂₄H₃₄O₂P₂Si₂]ₙ+[C₂₆H₄₃O₂P₂Si₃Cl]: trial 1 calcd. (n = 5) C 59.80, H 7.32, found C 59.89, H 7.26, trial 3 calcd. (n = 12) C 60.43, H 7.28, Cl 0.57, found C 60.27, H 7.39, Cl 0.62, trial 4 calcd. (n = 12) C 60.43, H 7.28, Cl 0.57, found C 59.64, H 7.39, Cl 1.10.
2.5 References


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Chapter Three

Polythiophene -Poly(p-phenylenephosphaalkene) Hybrids

3.0 Introduction

Having been able to successfully incorporate phosphaalkene bonds into the main chain of a polymer as shown in chapter two,\(^1\) I sought to investigate the generality of this synthetic method. One of the reasons that the Becker phosphaalkene synthetic route was selected was that this method is quite versatile, and phosphaalkenes with a variety of alkyl and aryl groups have been isolated and characterized.\(^2\sim4\) It would seem that there is no limit to the number of phosphaalkenes accessible by this method, provided there is enough steric protection of the P=C bond to prevent dimerization to the 1,2- or 1,3-diphosphetane.\(^5\sim6\) Another reason that the Becker route was selected is that this method is quite tolerant to substituents of only modest steric bulk, as phosphaalkenes with only a methyl group\(^2\) or chlorine atom\(^7\) as phosphine substituents are known. Other phosphaalkene routes seem to require much larger protective groups.\(^4\) It is likely that bulky substituents would limit the efficiency of \(\pi\)-conjugation.

Clearly, one of the first avenues to be investigated was varying the aromatic spacer between the P=C functionality. A survey of well-known organic conjugated polymers shows that a variety of aromatic groups may be incorporated into these macromolecules. Polyacetylene, poly\((p\)-phenylene\)), polypyrrole, polyaniline, and polythiophene are perhaps the most well studied polymers along with poly\((p\)-phenylenevinylene\)).\(^8\)

\[
\begin{align*}
\text{Polyacetylene} & \quad [\text{H}]_n \\
\text{Poly}(p\text{-phenylene}) & \quad [\text{C}_6\text{H}_4]_n \\
\text{Poly}(p\text{-phenylenevinylene}) & \quad [\text{C}_6\text{H}_4\text{C}_2\text{H}_4]_n
\end{align*}
\]

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Of these aromatic systems, I thought that thiophene would be the most straightforward to utilize as an aromatic spacer for inclusion into a poly(arylene phosphaalkene). The thiophene ring, unlike that of benzene, can be directly metallated with alkyl lithium reagents for easy addition of functional groups. Thiophene has recently found utility as part of extended $\pi$-conjugated systems containing heavier main group elements such as phosphorus. Materials containing thiophene and phosphole heterocycles have been used in light-emitting diodes. A survey of the literature brought several interesting compounds to our attention. Poly(2,5-thienylenevinylene)s are a class of conjugated polymers, first synthesized by Kossmehl in 1969 in a powder form. Several years after this development, Murata et al. reported a synthetic route via a soluble precursor, which was then converted to the conjugated form via an acid catalyzed reaction. The insertion of the vinyl linkage into the backbone lowers the band gap by 0.3 eV for poly(thienylenevinylene) compared to the parent polythiophene. By varying the ratio of thiophene to vinyl groups, materials with properties intermediate to those of polythiophene and poly(2,5-thienylenevinylene) can be prepared. Similar to PPV in chapter two, the poly(2,5-thienylenevinylene) could be used as a framework for incorporating P=C bonds into the main chain of a conjugated polymer. It is likely that thiophene cannot be used as the sole aromatic spacer, as it will not provide the necessary kinetic stabilization for the phosphaalkene bond.
The second compound of interest was phosphaalkene $K$, studied by Jouaiti *et al.*

To our knowledge, this was the first phosphaalkene reported that contains a thiophene substituent.\(^{18}\) A furan derivative was also synthesized and characterized crystallographically.\(^{18}\) Subsequently, Protasiewicz and coworkers reported the incorporation of thiophene as an aromatic spacer in poly(arylenephosphaalkene) ($L$), which was insoluble, and therefore received minimal characterization.\(^{19}\)

![Diagram of $K$ and $L$](image)

When contemplating using thiophene as an aromatic spacer, one can see by comparison with polymer $90$ from chapter two, there are two possible aromatic rings which could be substituted. The phenyl group bridging the two phosphorus atoms could be replaced by thiophene to give an analogous poly(thiénylenephénylenephosphaalkene) ($93$). Alternatively, the tetramethylbenzene aromatic spacer of $90$ could also be replaced with thiophene, however this would require a bulky phosphine monomer to provide the necessary steric bulk for the $P=C$ bonds. In this chapter, the synthesis and characterization of $93$, and three molecular model compounds are described. A monophosphaalkene in which thiophene is a substituent of the carbon of the $P=C$ bond, much like that of $K$, is also discussed.

![Diagram of $90$ and $93$](image)

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The synthesis of the model compounds with thiophene as a substituent at phosphorus were first prepared by Cecily Ma in the course of her undergraduate thesis project. Due to time constraints however, these materials were not fully characterized, and thus were synthesized again. Similarly, Justin Kingsley first prepared model compounds with thiophene as a substituent at carbon during an undergraduate NSERC summer research project. It was necessary to repeat these syntheses to obtain full characterization of the model compounds.

3.1 Results

By analogy with the preparation of 90 via a Becker route in chapter two, to prepare polymer 93, one would require 2,5-bis(trimethylsilyl)phosphinothiophene and the 1,4-di(carboxylic acid chloride)-2,3,5,6-tetramethylbenzene (86). The preparation of the 86 was described in chapter two. When this work was started, the 2,5-bis(trimethylsilyl)phosphinothiophene was not known. Very recently, Schmidbaur et al. reported a synthetic route to 2,5-phosphinothiophene that essentially mirrors the method used to synthesize the 2- and 2,5-bis(trimethylsilyl)phosphinothiophene. The route we followed was adapted from the one reported for 1,4-phosphinobenzene, as outlined in chapter two. The 2-bis(trimethylsilyl)phosphinothiophene is required to synthesize model compounds. The preparation of oligomers as model compounds for conjugated polymers has proven to be a viable comparison. To probe the effects of using thiophene as a carbon substituent instead of a phosphorus substituent, thiophene carboxylic acid chlorides were also prepared, for use in model compounds, and eventually a polymer.

3.1.1 Synthesis of 2-[P(SiMe₃)₂]-Tp (98)

A solution of thiophene (94) is directly metallated with nBuLi, which generates a 2-lithiothiophene species, as shown in Scheme 1. The lithiate is subsequently treated
with ClP(NEt₂)₂. A ³¹P NMR spectrum of the product exhibits a signal at δ 89.1, which was consistent with the desired 2-bis(diethylamino)phosphinothiophene (95). A solution of 95 is treated with anhydrous HCl gas to afford 2-dichlorophosphinothiophene (96). A ³¹P NMR spectrum of compound 96 exhibits a single resonance at δ 146. The volatile 2-phosphinothiophene (97) is synthesized by reducing a solution of 96 with LiAlH₄. The ³¹P NMR spectrum of 97 (Figure B1, Appendix B) reveals a triplet at δ -150.7 (³JₚH = 207 Hz), as expected for a primary phosphine. 2-Bis(trimethylsilyl)phosphinothiophene (98) was prepared by treating a solution of 97 with MeLi, and subsequent addition of chlorotrimethylsilane (Me₃SiCl). Compound 98 was obtained as a colourless, pyrophoric liquid by vacuum distillation (b.p. ca. 150° C / 6 mmHg). Phosphine 98 exhibits a single resonance at δ -156.7 in its ³¹P NMR spectrum (Figure B2). The ¹H NMR spectrum of 98 (Figure B3) reveals four signals; three aromatic protons from the thiophene ring (δ 7.0-7.3), and a doublet from the protons of the trimethylsilyl group at δ 0.26 (³JₚH = 5.3 Hz). Compound 98 was also characterized by ¹³C NMR spectroscopy and mass spectrometry.

![Scheme 1](image)

**Scheme 1.** Conditions and reagents: i) THF, nBuLi, ClP(NEt₂)₂; ii) CH₂Cl₂, 0° C, excess HCl (g); iii) Et₂O, -78° C, 0.6 equiv. LiAlH₄; iv) Et₂O, 0° C, 2 equiv. MeLi, 2 equiv. Me₃SiCl.

### 3.1.2 Synthesis of 2,5-[P(SiMe₃)₂]-Tp (102)

The thiophene ring was doubly lithiated in the 2- and 5- positions by treating a solution of thiophene with two equivalents of "BuLi, and N,N'-tetramethylethlenediamine (TMEDA) (Scheme 2). The metallated thiophene ring was
then treated with ClP(NEt₂)₂ to afford 2,5-bis(diethylamino)phosphinothiophene (99).

The ³¹P NMR spectrum of 99 in C₆D₆ (the aminophosphine compounds react with chloroform) reveals a singlet at δ 89.4. A solution of 99 is purged with anhydrous HCl gas to form 2,5-bis(dichlorophosphine)thiophene (100). Compound 100 shows a singlet at δ 142.7 in its ³¹P NMR spectrum. An solution of 100 was reduced with LiAlH₄ to produce 2,5-bisphosphinothiophene (101). The crude product was vacuum distilled (b.p. 40° C / 0.6 mmHg) to give pure 101, as a malodorous colourless liquid. Analysis of 101 by ³¹P NMR spectroscopy revealed a triplet at δ -150.8 (³¹JₚH = 209 Hz) (Figure B4).

2,5-bis(trimethylsilyl)phosphinothiophene (102) was produced by treating a solution of 101 with MeLi, and subsequently adding chlorotrimethylsilane. After purification by vacuum distillation (b.p. 120° C / 0.6 mmHg), the ³¹P NMR spectrum of 102 in CDCl₃ (Figure B5) exhibited a single resonance at δ -154.8. Analysis of 102 by ¹H NMR spectroscopy showed two signals, a doublet of doublets at δ 6.94 (³¹JₚH = 5.2 Hz, ³¹JₚH = 3.6 Hz) and a large doublet at δ 0.21 (³¹JₚH = 5.3 Hz) shown in Figure B6.

Scheme 2. Conditions and reagents: i) hexanes, -78° C, 2 equiv. "BuLi, 2 equiv. TMEDA; 2 equiv. ClP(NEt₂)₂. ii) CH₂Cl₂, -78° C, excess dry HCl(g). iii) Et₂O, -78° C, 1.1 equiv. LiAlH₄. iv) Et₂O, -78° C, 4 equiv. MeLi; 4 equiv. Me₃SiCl.

3.1.3 Synthesis of 2-[C(O)Cl]₂-Tp (104)

In an early report of the synthesis of compound 104, the authors reacted α-thienylmagnesium iodide with gaseous carbon dioxide to give the thiophene-2-carboxylic
However, in this preparation, a solution of thiophene is treated with one equivalent of \(^{n}\text{BuLi}\), and the resulting solution was purged with dry CO\(_2\) for approximately two hours, affording a white suspension (Scheme 3) of carboxylic acid 103. The product was analyzed by \(^1\text{H NMR spectroscopy}\), and four resonances are detected. A very broad signal at \(\delta\) 10.9 is assigned to the carboxylic acid proton. The three other resonances are in the aromatic region, and are due to the three thiophene ring protons.

\[
\begin{align*}
94 & \rightarrow 103 \rightarrow 104 \\
\text{Scheme 3. Conditions and reagents: i) Et}_2\text{O, } -78^\circ \text{C, } ^{n}\text{BuLi; excess dry CO}_2, \text{HCl (aq).} \\
& \text{ii) neat SOCl}_2, 12 \text{ hours, } 85^\circ \text{C.}
\end{align*}
\]

The 2-(carboxylic acid chloride)thiophene (104), or thienoyl chloride, was first prepared from the corresponding carboxylic acid via a reaction with thionyl chloride (SOCl\(_2\)) by Jones and Hurd in 1921.\(^{28}\) Early reports used PCl\(_5\) as a chlorinating agent, however SOCl\(_2\) was used in this preparation. A Schlenk flask is charged with 103, and an excess of SOCl\(_2\). Unreacted SOCl\(_2\) was removed in vacuo, affording crude 104 as a pale brown liquid. The product was purified by vacuum distillation (b.p. 31° C / 1 mmHg), and isolated as a colourless liquid in 86% yield. Compound 104 was characterized by \(^1\text{H NMR}\) (Figure B7) and \(^{13}\text{C NMR spectroscopy}\) (Figure B8). The \(^1\text{H NMR spectrum of 104 revealed three signals in the aromatic region due to the thiophene ring protons. The }^{13}\text{C NMR spectrum of 104 exhibited five resonances, four of which can be assigned to the thiophene ring carbons, and the downfield fifth signal to the carbonyl carbon of the acid chloride group.}
3.1.4 Synthesis of 2,5-[C(O)Cl]₂-Tp (106)

A synthesis of the 2,5-bis(carboxylic acid)thiophene was reported in 1984, starting from the 2,5-dibromothiophene.²⁹ In this altered synthesis, a solution of thiophene is treated with "BuLi, and TMEDA, and an excess of dry CO₂ (Scheme 4). Crude dicarboxylic acid 105 is isolated as a pale yellow powder. In the ¹H NMR spectrum of 105 only one signal is detected, for the 3,4-thiophene ring protons. The ¹³C NMR spectrum consists of three signals (δ 162.5, 140.4, 134.2) that are assigned to the carbonyl, the 2- and 5-thiophene, and the 3- and 4-thiophene ring carbons, respectively.

Scheme 4. Conditions and reagents: i) hexanes, -78°C, 2 TMEDA, 2 "BuLi; 100°C, 30 min.; -78°C, dry CO₂. ii) SOCl₂, 14 hours, 85°C.

To our knowledge, the first report of the synthesis of the 2,5-di(carboxylic acid chloride)thiophene prepared from the corresponding carboxylic acid with thionyl chloride was in 1984.³⁰ Here, a Schlenk flask was charged with 105, and SOCl₂ was added to form a suspension. The reaction mixture was heated to reflux for 12-14 hours until a homogeneous solution formed before removing unreacted thionyl chloride in vacuo. A white crystalline solid was obtained as the precipitate from a concentrated hexanes solution cooled to -78°C. The ¹H NMR spectrum of 106 (Figure B9) exhibits a single resonance, as expected for the symmetrically substituted thiophene -2,5-di(carboxylic acid chloride). The ¹³C NMR spectrum of 106 supports the proposed structure as three signals are detected (Figure B10). The singlet at δ 159.7 is assigned to the carbonyl carbons, and the signal at δ 145.4 is assigned to the 2- and 5-thiophene carbons due to its

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lower intensity. The remaining signal at δ 136.4 has a much higher intensity, and is likely due to the 3- and 4-thiophene ring carbons.

3.1.5. Synthesis of Monophosphaalkene Tp-P=C(OSiMe₃)-Mes (107)

One equivalent of 2-bis(trimethylsilyl)phosphinothiophene 98 and mesitoyl chloride 82 were dissolved in a minimal amount of THF (Scheme 5). After three days, an aliquot of the reaction mixture was removed and examined by ³¹P NMR spectroscopy. Two new signals were observed at δ 129.2 and 110.1, along with the resonance for 98, indicating that the reaction was not complete. The reaction was heated to 50° C, and another aliquot taken after a further 7 days. At this point, the ³¹P NMR spectrum showed only a trace of 98, and two isomers of monophosphaalkene 107. The solvent was removed in vacuo, and crude 107 was isolated as a viscous yellow fluid. The crude product was purified by vacuum distillation (b.p. 125° C / 0.1 mmHg). Two signals at δ 128.8 and 109.1 in the ³¹P NMR spectrum of pure 107 are assigned to the E- and Z-isomer, respectively (Figure 3.1).³, ³¹ The Z-isomer is the major product, making up 76% of the total phosphaalkene product. Figures 3.2 and 3.3 show the ¹H and ¹³C NMR spectra respectively, and confirm the presence of two isomers of monophosphaalkene 107. The parent ion of monophosphaalkene 107, along with several molecular fragments are detected via EI mass spectrometry. A UV/Vis spectrum of a THF solution of 107 (~10⁻⁵ M) shows an absorption maximum at 328 nm.

Scheme 5. Conditions and reagents: i) THF, 50° C, 10 days.
Figure 3.1. $^{31}\text{P}$ NMR spectrum of monophosphaalkene 107 in CDCl$_3$.

Assignments of the $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra were made with the aid of 2D-NMR experiments such as $^1\text{H}$, $^1\text{H}$-COSY, $^{13}\text{C}$-$^1\text{H}$ HMQC, and $^{13}\text{C}$-$^1\text{H}$ HMBC. In the $^1\text{H}$ NMR spectrum (Figure 3.2), the protons of the ortho and para methyl groups of the mesityl ring of the Z-isomer exhibit two different signals ($\delta$ 2.42 and 2.26, respectively), while the corresponding signals are coincident at $\delta$ 2.31 for the E-isomer. All other resonances are resolved for both isomers.
Figure 3.2. $^1$H NMR spectrum of monophosphaalkene 107 in CDCl$_3$.

As was the case for the $^1$H NMR spectrum, the $^{13}$C NMR spectrum (Figure 3.3) of 107 shows resolved signals at $\delta$ 20.6 and 19.6 for the mesitylene ortho and para methyl carbons of the Z-isomer, respectively. The resonances due to the mesityl methyl group carbons of the E-isomer appear to be almost coincident, the signal for the para carbon being present as a shoulder on the signal for the ortho carbons. The signal for the OSiMe$_3$ group of the Z-isomer is downfield from that of the E-isomer in the $^1$H NMR spectrum, but the reverse is true for the $^{13}$C NMR spectrum. Of particular note in the $^{13}$C NMR spectrum are the doublets at $\delta$ 207.5 and 192.7 which may be assigned to the P=C carbon of the E- and Z-isomers, respectively.
Figure 3.3. $^{13}$C NMR spectrum of monophosphaalkene 107 in CDCl$_3$.

3.1.6. Synthesis of Monophosphaalkene Mes-P=C(OSiMe$_3$)-Tp (109)

Under an inert atmosphere, bis(trimethylsilyl)mesitylphosphine 108 and 2-(carboxylic acid chloride)thiophene 104, both colourless liquids at room temperature,
were weighed out and dissolved in THF (Scheme 6). The reaction was stirred at room
temperature for one day, over which time the reaction mixture turned yellow. An aliquot
from the reaction mixture analyzed by $^{31}$P NMR spectroscopy showed that the
silylphosphine starting material 108 had been completely consumed, and converted to a
phosphaalkene. Crude monophosphaalkene 109 was isolated as a viscous yellow liquid
by removing the solvent in vacuo. The product was purified by vacuum distillation (b.p.
$110^\circ$ C, 0.6 mmHg). The monophosphaalkene 109 was characterized by UV/Vis
spectroscopy, and the absorption maximum of a THF solution of 109 was 357 nm. EI
mass spectrometry was also used to characterize 109, and the parent ion was detected at
334 g/mol. Compound 109 was examined by using $^{31}$P NMR spectroscopy, and two
resonances were observed at $\delta$ 134.8 (41%) and 134.3 (59%) (Figure 3.4). These signals
are assigned to the $E$- and $Z$-isomer of 109, respectively. Interestingly, the isomeric
distribution was considerably different before the distillation ($E/Z$: 64%/36%) (Figure
3.5). Presumably, the heat during the distillation caused isomerization, and the more
thermodynamically stable $Z$-isomer was favoured. The change in signal ratio is not a
solvent effect as the $Z/E$ ratio has changed from the reaction aliquot (Figure 3.5) to the
distilled product (Figure 3.4). Different solvent environments can effect the signal of a
proton nucleus in an $^1$H NMR experiment.\(^3\)

\[
\begin{align*}
\text{Scheme 6.} \quad \text{Conditions and reagents: i) THF, room temperature, 1 day.}
\end{align*}
\]
Figure 3.4. $^{31}$P NMR spectrum of monophosphaalkene 109 after distillation, in CDCl$_3$.

Figure 3.5. $^{31}$P NMR spectrum of monophosphaalkene 109 before distillation, in THF.

$^1$H NMR and $^{13}$C NMR spectra are also consistent with the presence of two isomers of 109. In the $^1$H NMR spectrum, all the signals are resolved (Figure 3.6). The proton resonance of the siloxy group of the Z-isomer is upfield from the corresponding signal from the E-isomer. The signals for the ortho and para mesityl methyl groups of the E-isomer are sandwiched between those of the Z-isomer. The meta mesityl proton of the Z-isomer is also upfield from the meta mesityl proton of the E-isomer. This trend is mostly reversed for the aromatic thiophene protons in which the Z-isomer resonances are downfield from those of the E-isomer, and all the thiophene ring protons come downfield.

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from the mesityl protons. Two of the thiophene ring protons resonate upfield of the mesityl meta protons in the E-isomer.

![Diagram of E-109 and Z-109](image)

**Figure 3.6.** $^1$H NMR spectrum of monophosphaalkene 109 in CDCl$_3$.

In the $^{13}$C NMR spectrum of 109, most of the signals are resolved (Figure 3.7). The two most important resonances are doublets at $\delta$ 191.6 ($^1J_{PC} = 43$ Hz) and 188.4 ($^1J_{PC} = 54$ Hz) which can be assigned to the P=C carbon of the $E$- and Z-isomer, respectively. A singlet is observed for the siloxy group of the Z-isomer ($\delta$ -0.33), which comes slightly upfield from the doublet observed for the siloxy group carbons of the $E$-isomer ($\delta$ 0.15, $^4J_{PC} = 5$ Hz). The signals for the ipso mesityl carbons overlap for both isomers, as well as a few of the thiophene ring carbons. For many of the resonances, there is only a slight shift between the corresponding carbon signals of each isomer (i.e. l vs. n, c vs. s, u vs. e).

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3.1.7. Synthesis of Bis(phosphaalkene) 2,5-[Mes-C(OSiMe₃)=P]₂-Tp (110)

To a THF solution of bis(trimethylsilyl)phosphinothiophene 102 was added a solution of mesitoxy chloride 82 in THF (Scheme 7). The reaction mixture was stirred at room temperature for several days. An aliquot from the reaction mixture was removed and analyzed by ³¹P NMR spectroscopy. Several signals were observed. Specifically, a resonance at δ -155 ppm can be attributed to unreacted silylphosphine 102, while several sharp resonances observed in the region from δ 130 to 109 suggesting the formation of P=C bonds. In an effort to enhance the progress of the reaction, the mixture was heated to 80° C. However, it took an additional eight days before 102 was completely consumed. Crude 110 was isolated as a viscous yellow liquid in 92% yield. Pure 110 was obtained as a colourless solid by a recrystallization from a hexanes solution cooled to -78° C. UV/Vis spectroscopy was performed upon a THF solution of 110, revealing a λ_max of 347 nm. The parent ion of bis(phosphaalkene) 110 is detected at 584 g/mol by EI mass spectrometry. The ³¹P NMR spectrum of 110 in CDCl₃ reveals four major signals
in the phosphaalkene region (Figure 3.8). The resonances at δ 129.0 (18%) and 110.2 (40%) were assigned to the E,E- and Z,Z-isomer, respectively. The signals at δ 127.8 (21%) and 109.6 (21%) can be assigned to the E,Z- isomer of 110. The two minor resonances indicated with an asterisk in the inset of Figure 3.8 could be the result of an impurity, such as a species in which one of the phosphaalkene moieties has undergone a protonolysis reaction.

Scheme 7. Conditions and reagents: i) THF, 2-3 days, room temperature; 8 days, 80° C.

Figure 3.8. $^{31}$P NMR spectrum of bis(phosphaalkene) 110 in CDCl$_3$. * Not assigned.

Analysis of 110 by $^1$H NMR spectroscopy revealed several resonances for each distinct set of signals due to different groups (Figure 3.9). There are four resonances for...
SiMe₃ protons, five resonances for mesityl methyl protons (both ortho and para), three distinct resonances for meta-mesityl protons, and three resonances that can be attributed to the 3,4-thiophene aromatic protons.

![Chemical structure](image)

**Figure 3.9.** ¹H NMR spectrum of bis(phosphaalkene) 110 in CDCl₃.

The presence of multiple isomers of 110 resulted in complex ¹H and ¹³C NMR spectra. Although detailed assignments were not made, the spectra were consistent with the assignment of 110. Signals were observed in the expected regions for the ¹³C NMR spectrum of bis(phosphaalkene) 110 (Figure 3.10). Signals from δ 0.7-1.7 can be attributed to siloxy groups, and signals from δ 19-21 are due to the mesityl methyl groups. There are many signals in the aromatic region due to mesityl and thiophene ring carbons. Most importantly, there are doublets at δ 208.4 and 194.3 that can be assigned to the P=C carbon of the E- and Z-isomer, respectively.

*References begin on page 143*
3.1.8. Attempted Synthesis of Bis(phosphaalkene) 2,5-[Mes-P=C(OSiMe$_3$)]$_2$-Tp (111)

In a nitrogen-filled glovebox, one equivalent of 2,5-bis(carboxylic acid chloride)thiophene 106 and two equivalents of bis(trimethylsilyl)mesitylphosphine 108 were weighed out and dissolved in a minimal amount of THF (Scheme 8). The resulting solution was heated to 80° C, and periodically an aliquot was removed from the reaction mixture for analysis by $^{31}$P NMR spectroscopy. When all of the silylphosphine starting material 108 had been consumed after two days, the crude bis(phosphaalkene) was isolated. Unfortunately, unlike many of other reactions reported herein, this reaction does not proceed cleanly as can be seen by the $^{31}$P NMR spectrum (Figure 3.11). In this spectrum there are many unidentified peaks, but a notable signal is a triplet at -145 ppm, which is likely some of the silylphosphine starting material 108, which has been hydrolyzed to the primary phosphine. Attempts at purification via recrystallization have not been successful to date.

**Figure 3.10.** $^{13}$C NMR spectrum of bis(phosphaalkene) 110 in CDCl$_3$. 
Scheme 8. Conditions and reagents: i) THF, 80°C, ca. 2 days.

Figure 3.11. $^{31}$P NMR spectrum of a mixture of 108 and 106 in an attempt to prepare 111 in THF.

3.1.9. Synthesis of Polymer \([-\text{Tp-P=}(\text{OSiMe}_3)\text{-C}_6\text{Me}_4\text{-C}(\text{OSiMe}_3)=\text{P-}]\) (93)

Polymer 93 was synthesized by thermolysis of the two bifunctional starting materials, 86 and 102 (Scheme 9). As silylphosphine 102 is a liquid at room temperature, 86 was added to the thick-walled Pyrex tube first, and 102 added second to try and wash all material to the bottom of the tube. Crude polymer 93 was dissolved in a minimal amount of THF, and precipitated with cold hexanes. The precipitated polymer 93 was dissolved in CDCl$_3$ and characterized by multi-nuclear NMR spectroscopy (Figure 3.12-3.14), and UV/Vis spectroscopy. A dilute (ca. 10$^{-5}$ M) THF solution of 93 shows an
absorption maximum at 379 nm. Broad resonances centred at δ 126 and 107 in the $^{31}$P NMR spectrum are consistent with the formation of P=C bonds as expected for polymer 93. An estimate of the molecular weight of the polymer can be made by end group analysis. An integration of the $^{31}$P NMR signals for the silylphosphine polymer endgroups of the precipitated polymer versus the phosphaalkene signals gives a degree of polymerization of eight repeat units, corresponding to a molecular weight of approximately 4,100 g/mol.

Scheme 9. Conditions and reagents: i) neat, 90° C, 24 hours.

Figure 3.12. $^{31}$P NMR spectrum of polymer 93 in CDCl$_3$. *-HP-C(O)- hydrolysis product.
The only aromatic protons present in the system are those of the thiophene ring. Thus, the signals in the $^1$H NMR spectrum of 93 in the aryl region must be assigned to these protons (Figure 3.13). Similarly, the broad resonance in the alkyl region of the spectrum were attributed to the methyl groups of the tetramethylbenzene ring. There are two broad resonances in the siloxy region, centred at approximately δ 0.3 and 0.0. These signals can be assigned to the $E$- and $Z$-phosphaalkene isomers, respectively. An integration of the proton resonances is consistent with the structure proposed for 93.

![Figure 3.13. $^1$H NMR spectrum of polymer 93 in CDCl$_3$. * Residual CHCl$_3$.](image)

The $^{13}$C NMR spectrum of 93 is consistent with a polymeric species containing P=C bonds in the main chain of the macromolecule (Figure 3.14). Small, broad resonances are detected at δ 210 and 195, which are diagnostic signals for the carbon of the P=C bond of the $E$- and $Z$-isomer, by comparison with polymer 90. The broad resonance stretching from δ 145-127 can be assigned to the tetramethylbenzene and thiophene ring protons. The signals at δ 20-15 are attributed to the methyl groups of the tetramethylbenzene ring, and from δ 2 to -4 were assigned to polymer siloxy groups. Of
note, a resonance is detected at δ 171 ppm, which may be due to the carbonyl groups of unreacted 1,4-bis(carboxylic acid chloride)-2,3,5,6-tetramethylbenzene not removed during precipitation. However, it is also possible this resonance is a result of carboxylic acid chloride polymer end groups.

![Figure 3.14. $^{13}$C NMR spectrum of polymer 93 in CDCl$_3$. * Solvent peak CDCl$_3$; † C=O from residual starting material 86 or polymer C(O)Cl endgroup.](image)

3.2 Discussion

3.2.1 Phosphaalkenes with a Thiophene Substituent at Phosphorus

There have been few molecules reported that contain both a phosphaalkene moiety and a thiophene substituent. Thus, the compounds most relevant for comparison to those reported here are those discussed in chapter two. The chemistry of the compounds in which thiophene is a phosphorus substituent (107, 110, 93) parallel that of the compounds in which benzene is the phosphorus substituent (87, 89, 90) as discussed in chapter two. The $^{31}$P NMR spectra corresponding to each pair of molecules are quite similar. The monophosphaalkenes 87 and 107 show two signals in the $^{31}$P NMR spectrum due to the E- and Z-isomer. Bis(phosphaalkene)s 80 and 110 show four
resonances due to three isomers \((E,E-, E,Z-, \text{and } Z,Z-)\). Polymers 90 and 93 each show broad resonances in the phosphaalkene region due to a mixture of isomers, with a small signal near that of the silylphosphine starting material that indicates the presence of – P(SiMe3)2 end groups.

The main difference between the benzene-bridged molecules and the thiophene-bridged molecules is that the preparation of the thiophene phosphaalkene compounds takes longer. At approximately the same temperature, the reaction to form monophosphaalkene 87 is complete in two days, but it takes ten days to form 107. Similarly, bis(phosphaalkene) 89 can be prepared in two days, but 110 requires eight days. For all of these model compounds, the P=C carbon substituent mesityl ring provides steric protection for the carboxylic acid chloride moiety during intermolecular approach, and later the carbonyl group in the acylphosphine intermediate (Scheme 10, 112a and 112b). This steric bulk may interfere with the [1,3]-siloxy migration that forms the P=C bond. The difference in reactivity of the corresponding model compounds can

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be rationalized by the smaller thiophene phosphorus substituent of 107 and 110 exerting less steric pressure on the phosphorus trimethylsilyl groups during formation of the phosphaalkene than the phenyl group of 87 and 89. Contrast this with the 24 hours at room temperature formation of monophosphaalkene 109, prepared from a bulky silylphosphine and thiophene-2-carboxylic acid chloride. Alternatively, the slower reaction rate of formation of 107 may be rationalized by a decrease in basicity of the silylphosphine 98 due to an inductive effect of the thiophene substituent.

Scheme 10.

The UV/Vis absorption of monophosphaalkene 107 is red-shifted from the absorption of 87 by 18 nm (Table 3.1 and Figure 3.15). Continuing this trend, the $\lambda_{\text{max}}$ of the bis(phosphaalkene) 110 is red-shifted by 33 nm compared to bis(phosphaalkene) 89. The poly($p$-phenylenephosphaalkene) 90 shows a maximum absorbance at 338 nm, which is 41 nm shorter than the $\lambda_{\text{max}}$ for poly(thienylenephenylene-phosphaalkene) 93. This suggests a greater degree of $\pi$-conjugation in the thiophene compounds. This may be rationalized by considering that the Z/E ratio is much higher for 107, 110, and 93 compared to 87, 89, and 90 which may contribute to the observed red-shift in $\lambda_{\text{max}}$. A
comparison of the UV/Vis absorbance maxima of cis- and trans-stilbene (276 versus 294/307 nm) \(^{33}\) shows that the trans-isomer has more extensive \(\pi\)-conjugation due to its more planar structure.\(^{34-39}\) The cis-stilbene does not possess \(\pi\)-conjugation to the same extent, mostly due to the non-planarity of the backbone of the system caused by the neighbouring phenyl rings.\(^{40-43}\) A similar comparison of poly(\(p\)-phenylene) and PPV show that the twisted backbone of poly(\(p\)-phenylene) leads to an absorbance maximum of 390 nm, while the more planar chain of PPV exhibits a \(\lambda_{\text{max}}\) of 500 nm.\(^{44}\) From this data, one might conclude that molecules with the aryl groups in \(\text{trans}\) positions across a double bond will exhibit better \(\pi\)-conjugation than those in \(\text{cis}\) positions. In the Becker type phosphaalkenes, the \(Z\)-isomer features the aryl groups in a \(\text{trans}\) orientation.

The smaller steric presence of the thiophene ring compared to the benzene ring could be invoked to rationalize the red-shifts seen in the UV/Vis absorption maxima of 107, 110, and 93 compared to 87, 89, and 90. Thiophene’s smaller ring may allow for a more planar arrangement of the backbone of the molecule, and consequently better \(\pi\)-conjugation with the P=C bond. It is likely that there is a larger angle between the plane of the mesityl ring and the P=C bond that reduces but does not preclude extended \(\pi\)-conjugation. Unfortunately, crystals suitable for X-ray crystallography could not be grown to confirm this supposition, but comparison of the furan derivative of monophosphaalkene \(\mathbf{K}\) would support this theory.\(^{18}\)

\[
\begin{array}{c}
\text{S} \\
\text{H} \quad \text{'Bu} \\
\text{C} \\
\text{P} \\
\text{'Bu} \\
\text{'Bu} \\
\text{mesitylene ring as a phosphorus substituent. In the furan derivative the P=C bond was}
\end{array}
\]

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determined to be 1.673(2) Å in length, which is slightly shorter than average. The dihedral angle between the phosphaalkene plane and the Mes* ring was 85.6°, which makes these two planes almost perpendicular. In contrast, the angle between the phosphaalkene plane and the furan ring was only 2°. EPR studies of K showed the electron of the radical anion was delocalized over the furan ring and the phosphaalkene bond. No UV/Vis studies of either the furan or thiophene containing phosphaalkenes were reported. This solid state structure suggests that the angle between the plane of the P=C bond and the thiophene substituent is likely to be small, and the angle between the P=C bond and the mesityl ring to be large. This larger angle would make \( \pi \)-conjugation through the mesityl ring less efficient than through the almost co-planar thiophene ring. The EPR data of K also supports this idea, and the charge was spread over the furan ring and the P=C bond, but not the Mes* group.

Table 3.1. Selected phosphaalkene characterization data.

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<th>Entry</th>
<th>Compound</th>
<th>polymer</th>
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<th>( M_n^* ) (g/mol)</th>
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</table>

* \( M_n \) and \( X_n^* \) were estimated using end group analysis.

Now we will compare the trend of \( \lambda_{max} \) within the series 107, 110, and 93. The UV/Vis data for these compounds would seem to indicate some degree of extended \( \pi \)-conjugation through the P=C bonds as the absorption for bis(phosphaalkene) 110 is red-shifted from that of monophosphaalkene 107 by nearly 20 nm. Polymer 93 has a \( \lambda_{max} \) red-shifted beyond that of 110 by a further 32 nm, mirroring the trend by the phenylene spaced monophosphaalkene 87, bis(phosphaalkene) 89, and polymer 90. Also of interest,
all the thiophene compounds show a secondary, smaller absorbance around 270 nm, which may be due to the thiophene ring. A comparison with some other compounds where thiophene has a phosphorus substituent, diphenylphosphino-2-thiophene, and bis(diphenylphosphino)-2,5-thiophene show absorbances at 265 and 300 nm, respectively. The incorporation of thiophene as an aromatic spacer leads to a red-shift in $\lambda_{\text{max}}$ when compared to a phenyl analogue as the maximum absorbance of 1,4-diphenylphosphinobenzene is at 275 nm.

If the P=C units are part of the $\pi$-conjugation pathway, one would expect $\lambda_{\text{max}}$ of the compounds to increase in wavelength as the length of the chain increases. This is, in fact, what is observed (Table 3.1). This observation suggests a degree of $\pi$-conjugation through the phosphaalkene bonds in the main chain of the formally conjugated polymer 93. It would be interesting to see if a higher molecular weight macromolecule 93 would show an even longer wavelength absorbance. Unfortunately, since the silylphosphine is liquid and carboxylic acid chloride reagent is solid, it was extremely difficult to match the stoichiometries exactly as required to synthesize a high molecular weight condensation polymer. This difficulty is the major contributor to polymer 93 being of significantly lower molecular weight than 90 (Table 3.1).
3.2.2 Phosphaalkenes With a Thiophene Substituent at Carbon

Remarkably, the preparation of phosphaalkenes with thiophene at carbon is considerably more challenging than those with thiophene at phosphorus. Whereas the compounds with thiophene at phosphorus possess a strong resemblance to the phosphaalkenes discussed in chapter two, the phosphaalkenes with thiophene at carbon seem to be qualitatively different. For example, the $^{31}\text{P}$ NMR spectra of 87 and 107 both reveal two distinct signals for E- and Z-isomers, which were separated by 15 and 19 ppm, respectively. In contrast, the two isomers of 109 are separated by only 0.5 ppm. Also, lending credence to the idea that the steric bulk of the phosphorus substituent versus the carbon substituent affects the reaction rate, the reaction to produce 109 takes less than a day, versus two and ten days for 87 and 107, respectively. During purification by distillation, an appreciable difference in the isomer ratio appeared. The $Z/E$ ratio changed from less than one before distillation, to 1.43 after (Figure 5 and Figure 6). It has been previously noted that during the formation of Becker type phosphaalkenes, the $E$-isomer
is observed first, followed by the formation of the Z-isomer. This can be rationalized by looking at the rotational isomers of the acylphosphine intermediate (113a and 113b, Scheme 11) formed during the preparation of 109. It is clear that the intramolecular [1,3]siloxy migration must occur from 113a, thus leading to a kinetic preference for the E-isomer (path A, Scheme 11). However, the Z-isomer of 109 features the two aromatic rings in trans positions about the P=C bond, so that it is likely that the Z-isomer is slightly thermodynamically favoured. There would seem to be a preference for the trans orientation since after the distillation, there is a prevalence of the Z-isomer. Presumably, the E-isomer is formed first, and the Z-isomer is formed later, likely via tautomerization (path B, Scheme 11), or less likely through a direct migration (path C, Scheme 10).

However, the possibility that the siloxy migration may proceed through an intermolecular mechanism has not been investigated to our knowledge.

Scheme 11.

Thiophene substitution at carbon appears to lead to some interesting electronic effects as evinced by the UV/Vis spectrum of 109 (Figure 15). This monophosphaalkene
has a $\lambda_{\text{max}}$ significantly red-shifted from that of monophosphaalkenes 107 and 87 (by 29 and 47 nm, respectively). Only polymer 93 shows an absorbance with a longer wavelength. One could rationalize this observation by noting that the sterically unhindered substituent now resides on the carbon of the P=C bond, so that the thiophene and P=C have a better orientation for good $\pi$-overlap than the bulky mesityl phosphorus substituent. It could also be that the 2p orbital of the carbon from the P=C bond forms a much better overlap with the $\pi$-system of the thiophene ring than the 3p orbital of the phosphorus in the P=C bond as is the case for 107.

The synthesis of bis(phosphaalkene) 111 did not proceed as cleanly as one might have expected from the other reactions discussed in this chapter. Despite great care taken in obtaining dry solvent, and flame-drying glassware, each attempted synthesis of 111 yielded a variety of products that included phosphaalkenes. Also present were hydrolyzed starting materials as well as peaks tentatively assigned to acylphosphines (114) that resulted from the apparent hydrolysis of the siloxy group followed by a tautomerization (Scheme 12). The difficulty in preparing 111 is hypothesized to stem from two sources. It possible that despite recrystallization, there is still a proton source present in the 2,5-bis(carboxylic acid chloride)thiophene 106, possibly hydrogen chloride as well as some carboxylic acid. This could perhaps be circumvented by the addition of a non-protic base into the reaction mixture such as DBU (1,5-diazabicyclo[5.4.0]undec-5-ene). The second possible difficulty may be linked to the first in that switching the steric bulk from the phosphaalkene carbon to the phosphorus opens up a greater access to the siloxy group, which is sensitive towards protonolysis. However, on the plus side, this leads to better $\pi$-delocalization, as proven by comparing $\lambda_{\text{max}}$ for 107 and 109 which are 328 versus 357 nm, respectively.
3.3 Summary

The model compounds 107 and 110 for the polymer 93 were prepared and fully characterized. The chemistry of these compounds parallels that discussed in chapter two quite closely. These compounds exhibit better π-conjugation than the corresponding phenylene molecules (87, 89, and 90) as evinced by red-shifted UV/Vis absorptions. The expected trend of increasing wavelength of the UV/Vis absorbance maxima for increasing chain length (monophosphaalkene 107, bis(phosphaalkene) 110, to polymer 93) was observed. The bifunctional starting materials were of different states of matter, which made matching the stoichiometries difficult, and subsequently lead to the molecular weight of 93 being significantly lower than that estimated for polymer 90 (10,500 g/mol versus 4,100 g/mol).

A complementary system in which the aromatic spacer of the carboxylic acid chloride reagent was replaced by thiophene was also investigated. Monophosphaalkene 109 was successfully synthesized and fully characterized by multi-nuclear NMR spectroscopy, EI-mass spectrometry, and UV/Vis spectroscopy. The synthesis of bis(phosphaalkene) 111 was attempted. The compound was prepared, but could not be isolated in pure form. Switching the steric bulk from the carbon substituent to the phosphorus substituent seems to lead to a more hydrolytically sensitive, but better
conjugated system. Monophosphaalkene 109 has a $\lambda_{\text{max}} = 357$ nm, which was only surpassed by polymer 93.

### 3.4 Experimental Section

Elemental analyses of several compounds were attempted by Minaz Lakha, but did not match theoretical results despite being clean by $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy.

**Materials.** 2-bromomesitylene, PCl$_3$, Me$_3$SiCl, Mg, SOCl$_2$, LiAlH$_4$, MeLi (1.6 M in ethyl ether), and t-BuLi (1.7 M in pentane) were purchased from Aldrich and used as received. Et$_2$NH, thiophene were purchased from Aldrich and distilled prior to use. Bis(trimethylsilyl)mesitylphosphine$^{46}$ was prepared following the literature procedure.

#### 3.4.1. Preparation of 2-[P(NEt$_2$)$_2$]-Tp (95).

95 was prepared according to a modification of a literature procedures.$^{21}$ One equivalent of 1.6 M butyl lithium (53 mL, 85.0 mmol) in hexane was added dropwise to thiophene (7.10 g, 84.8 mmol) in THF (ca. 60 mL) at -78° C. The solution was stirred at room temperature under nitrogen for about 30 minutes. To the resultant pale yellow solution was added dropwise one equivalent of bis(diethylamino)chlorophosphine (17.7 g, 0.0838 mol) in hexane at -78° C. The solvent was removed in vacuo, followed by the addition of hexane (ca. 100 mL). The mixture was filtered through a glass frit to remove insoluble lithium salts, and the hexanes were removed in vacuo, affording a yellowish orange liquid. Crude yield: 20.8 g (97%).

$^{31}$P NMR (C$_6$D$_6$, 121.5 MHz, 300K): $\delta$ 89.1 ppm; $^1$H NMR (C$_6$D$_6$, 300 MHz, 300K): $\delta$ 7.3-7.0 (m, 3H, Tp-H), 3.2-3.0 (m, 8H, $^3$J$_{HH} = 6.9$, N(CH$_2$-)), 1.0 ppm (m, 12H, $^3$J$_{HH} = 6.9$ Hz, -CH$_3$); $^{13}$C NMR (C$_6$D$_6$, 75 MHz, 300K): $\delta$ 145.6-129.5 ppm (s, Tp), 42.8 (d, $^3$J$_{PC} = 17.7$ Hz, -CH$_2$), 14.85 (s, CH$_3$); MS (EI, 70eV): $m/z$ (%): 258, 259, 260 (2, 4, 24) [M$^+$].

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3.4.2. Preparation of 2-[PCl$_2$]-Tp (96). Crude 95 (20.8 g, 80.4 mmol) was dissolved in 90 mL of CH$_2$Cl$_2$ and cooled to -78° C. HCl(g) was generated in a separate Schlenk flask by treating sodium chloride (ca. 70 g) dropwise with concentrated sulfuric acid (ca. 150 mL) via an additional funnel. The flask and the drying tube were flushed with HCl gas for few minutes before purging HCl gas through the reaction mixture. When HCl gas was added to the solution, a white precipitate formed and the orange solution became yellowish. The reaction progress was monitored by $^{31}$P NMR spectroscopy. Upon complete conversion, the solvent was removed in vacuo. A hexanes extraction (ca. 150 mL) was passed through a filter frit, and the solvent was removed in vacuo, resulting in an amber liquid. Compound 96 was purified by a vacuum distillation (b.p. 39° C; 5 mmHg). Crude yield: 12.2 g (82 %); after distillation: 7.0 g (47 %).

$^{31}$P NMR (CDCl$_3$, 121.5 MHz, 300K): $\delta$ 145.7 ppm; $^1$H NMR (CDCl$_3$, 300 MHz, 300K): $\delta$ 7.8-7.1 ppm (m, 3H, Tp-#); $^{13}$C NMR (CDCl$_3$, 75 MHz, 300K): $\delta$ 142.7 (d, $^1$J$_{CP}$ = 72.6 Hz, i-Tp-P), 136.3-127.7 ppm (s, Tp); MS (EI, 70eV): \textit{m/z} (%): 190, 189, 188, 187, 186, 185, 184 (0.4, 0.5, 6, 2, 31, 3, 46) [M$^+$], 153, 152, 151, 150, 149 (2, 2, 38, 6, 100) [M$^+$-Cl].

3.4.3. Preparation of 2-[PH$_2$]-Tp (97). To a stirred suspension of LiAlH$_4$ (1.34 g, 35.6 mmol) in diethyl ether (ca. 100 mL) at -78° C was added a solution of 96 (6.52 g, 35.3 mol) in diethyl ether (ca. 100 mL). An aliquot of the reaction mixture was analyzed by $^{31}$P NMR spectroscopy, and confirmed that the reduction was immediately complete. Degassed, distilled water (ca. 200 mL) was slowly added to the reaction mixture at 0° C to quench the aluminum hydrides. The organic layer was then transferred by cannula into another Schlenk flask, and the aqueous layer was washed with more diethyl ether (ca. 80
mL). The washings were combined with the organic layer, which was then filtered through magnesium sulphate to remove residual water. Solvent was removed in vacuo yielding a volatile, clear liquid. Pure 97 was obtained by distillation under partial vacuum (b.p. 30° C in partial vacuum). Crude yield: 2.67 g (65%); after distillation: 0.86 g (21%).

$^{31}$P NMR (CDCl$_3$, 121.5 MHz, 300K): $\delta$ -150.7 (t, $^1$J$_{PH}$ = 207 Hz, -PH$_2$); $^1$H NMR (CDCl$_3$, 300MHz, 300K): $\delta$ 7.5-7.0 (m, 3H, Tp-//), 4.1 (d, 2H, $^1$J$_{PH}$ = 207 Hz; -PH$_2$); $^{13}$C NMR (CDCl$_3$, 75 MHz, 300K): $\delta$ 137.7 (d, $^1$J$_{CP}$ = 28 Hz, i-Tp-P), 132-124 (s, Tp). MS (EI, 70eV): m/z (%): 118, 117, 116 (5, 8, 100) [M$^+$], 115 (84) [M$^+$-H], 114 (24) [M$^+$-2H], 85, 84, 83 (2, 8, 11) [Ar$^+$].

3.4.4. Preparation of 2-[P(SiMe$_3$)$_2$]-Tp (98). To a stirred solution of 2-phosphinothiophene 97 (0.708g, 6.1 mmol) in diethyl ether (ca. 80 mL) at -78° C was added a solution of 1.5 M methylithium (8.54 mL, 13.0 mmol) in diethyl ether, resulting in a pale yellow solution. After stirring for 1 hour at -78° C, two equivalents of chlorotrimethylsilane (1.55 mL, 13.0 mmol) was added to the solution, resulting in a white precipitate. The solvent was removed in vacuo, and a hexanes extraction (ca. 150 mL) was filtered to separate the lithium salts. The solvent was then removed in vacuo, yielding a pale yellow liquid. Pure 98 was obtained by vacuum distillation (b.p. ca. 150° C, 6 mmHg). Crude yield: 1.21 g (78%); after distillation: 0.94 g (59%).

$^{31}$P NMR (CDCl$_3$, 121.5 MHz, 300K): $\delta$ -156.7; $^1$H NMR (CDCl$_3$, 300MHz, 300K): $\delta$ 7.3-7.0 (m, 3H, Tp-//), 0.26 (d, 18H, $^3$J$_{PH}$ = 5.3 Hz, -Si(CH$_3$)$_3$); $^{13}$C NMR (CDCl$_3$, 75 MHz, 300K): $\delta$ 130.6 (d, $^1$J$_{CP}$ = 49.6 Hz, i-Tp-P), 137.3 (d, $^2$J$_{PH}$ = 24 Hz, 2-Tp), 129.7 (d, $^3$J$_{PH}$ = 8.7 Hz, 3-Tp), 127.6 (d, $^3$J$_{PH}$ = 7.6 Hz, 4-Tp), 0.9 (s, Si(CH$_3$)$_3$); MS (EI, 70eV): m/z (%): 264, 263, 262, 261, 260 (0.3, 1, 4, 7, 30) [M$^+$], 249, 247, 246, 245 (0.2, 1, 2, 6) [M$^+$-
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3.4.5. Preparation of 2,5-[P(NEt₂)₂]-Tp (99). Freshly distilled thiophene (7.09g, 8.4 mmol) was dissolved with 60 mL of hexanes, followed by the addition of two equivalents of TMEDA (22.5 mL, 17.0 mmol). The mixture was cooled to -78° C, and two equivalents of 1.6 M butyllithium in hexane (104 mL, 17.0 mmol) were added slowly to the solution. After warming to room temperature, the reaction mixture was heated to reflux at 100° C for 30 minutes, resulting in a pale yellow suspension. Two equivalents of bis(diethylamino)chlorophosphine (35.2 g, 16.7 mmol) in hexane (ca. 50 mL) was added dropwise to the reaction mixture at -78° C. The magnesium salts were filtered, and the solvent was removed in vacuo, affording pale yellowish crystals of 99. Crude yield: 35.5 g (98 %) after recrystallization in hexane at -78° C: 32.6 g (91 %).

³¹P NMR (C₆D₆, 121.5 MHz, 300K): δ 89.4 ppm; ¹H NMR (C₆D₆, 300 MHz, 300K): δ 7.2 (m, 2H, Tp-H), 3.2 (m, 16H, ³Jₜₜ = 6.99Hz, N(CH₂-)), 1.1 (m, 24H, ³Jₜₜ = 7.0 Hz, -CH₃); ¹³C NMR (C₆D₆, 75 MHz, 300K): δ 149.8 (d, ²Jₙₜ = 5.96 Hz, Tp), 132.6 (d, ¹Jₙₜ = 14.9 Hz, Tp-P), 42.9 (d, ³Jₙₜ = 17.7 Hz, N(CH₂-)), 14.9 (s, -CH₃); MS (EI, 70eV): m/z (%): 435, 434, 433, 432 (0.5, 2, 8, 30) [M⁺], 363, 362, 361, 360 (1, 6, 21, 100) [M⁺-N(CH₂CH₃)₂], 289, 288 (6, 14) [M⁺-2 N(CH₂CH₃)₂], 259, 258, 257 (3, 2, 13) [M⁺-P(N(CH₂CH₃)₂)], 105, 104(2, 43) [M⁺-PN(CH₂CH₃)₂], 72, 73 (15, 3) [-NCH₂CH₃]

3.4.6. Preparation of 2,5-[PCl₂]-Tp (100). A stirred solution of 99 (32.6 g, 0.0755 mol) in CH₂Cl₂ (90 mL) was cooled to -78° C. HCl(g) was generated in a separate Schlenk flask by treating sodium chloride (ca. 70g) dropwise with sulfuric acid (ca. 150 mL) via an additional funnel. The flask and drying tube were flushed with HCl gas for few minutes before purging HCl gas through the reaction mixture. The reaction progress was monitored by ³¹P NMR spectroscopy. Upon complete conversion, the solvent was
removed in vacuo. A hexanes extraction (ca. 150 mL) was filtered through a glass frit to
remove the lithium salt, followed by the removal of solvent in vacuo, resulting in an
orange-yellow solid. Crude yield: 18.3 g (85 %).

\[^{31}\text{P} \text{NMR (CDCl}_3\text{, 121.5 MHz, 300K): } \delta\text{ 142.7; } ^{1}\text{H NMR (CDCl}_3\text{, 300MHz, 300K): } \delta\text{ 7.6 (m, 2H, Ar-}\text{-H}; } ^{13}\text{C NMR (CDCl}_3\text{, 75.48MHz, 300K): } \delta\text{ 152.1 (d, } ^{1}\text{J}_{CP}\text{ = 77.7 Hz, 2,5-Tp); 136.5-134.2 (m, 3,4-Tp); MS (EI, 70eV): } m/z\text{ (%): 292, 291, 290, 289, 288, 287, 286, 285, 284 (1, 0.6, 7, 2, 27, 3, 48, 3, 44) [M\text{'+}], 256, 255, 254, 253, 252, 251, 250, 249 (0.3, 5, 2, 35, 5, 100, 6, 99) [M\text{'+}-Cl], 220, 218, 217, 216, 215, 214 (0.4, 2, 1, 8, 1, 14) [M\text{'+}- 2Cl], 189, 188, 187, 186, 185, 184, 183 (0.4, 0.4, 4, 1, 17, 2, 28) [M\text{'+}-PCl}_2\text{], 152, 151, 150, 149, 148 (0.4, 2, 4, 2, 9) [M\text{'+}-PCl}_2\text{.-Cl], 116, 115, 114, 113 (0.6, 3, 3, 44) [M\text{'+}- PCl}_2\text{.-2Cl]. 84, 83, 82 (1, 1, 19) [Ar\text{+}].

3.4.7. Preparation of 2,5-[PH2]2-Tp (101). A stirred solution of 100 (6.95 g, 24.3 mol)
in diethyl ether (100 mL) was mixed with two equivalents of LiAlH4 (2.06 g, 54.4 mmol)
in diethyl ether (ca. 100 mL) at -78° C. An aliquot of the reaction mixture was studied by
using \[^{31}\text{P} \text{NMR spectroscopy to confirm the completion of the reaction. Degassed,}
distilled water (ca. 200 mL) was slowly added to the reaction mixture at 0° C to quench
unreacted aluminum hydrides. The organic layer was cannulated to another Schlenk
flask, and the aqueous layer was washed with more diethyl ether (ca. 80 mL). The
washings were combined, then filtered through magnesium sulphate to remove residual
water. Solvent was removed in vacuo, yielding a clear liquid. Pure 101 was obtained by
partial vacuum distillation (b.p. 40° C; 0.6 mmHg). Crude yield: 2.12 g (59 %); after
distillation: 1.44 g (40 %).

\[^{31}\text{P} \text{NMR (CDCl}_3\text{, 121.5 MHz, 300K): } \delta\text{ -150.8 (t, } ^{1}\text{J}_{PH}\text{ = 209 Hz, -PH}_2\text{); } ^{1}\text{H NMR (CDCl}_3\text{, 300 MHz, 300K): } \delta\text{ 7.1 (m, 2H, 3,4-Tp-}\text{-H}, 4.05 (d, 4H, } ^{1}\text{J}_{PH}\text{= 207 Hz; -PH}_2\text{); } ^{13}\text{C NMR (CDCl}_3\text{, 75 MHz, 300K): } \delta\text{138.4 (d, } ^{1}\text{J}_{CP}\text{ = 29 Hz, 2,5-Tp), 131.6 (dd, } ^{2}\text{J}_{CP}\text{ = 25 Hz,}

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3.4.8. Preparation of 2,5-[P(SiMe$_3$)$_2$]$_2$-Tp (102). To a stirred solution of 101 (1.32g, 8.9 mmol) in diethyl ether (ca. 80 mL) at -78° C was slowly added 4.2 equivalents of 1.5 M methyllithium (25 mL, 37.4 mmol). The reaction was allowed to stir for one hour at -78° C, resulting in a bright yellow solution. Chlorotrimethylsilane (4.53 mL, 0.0357 mol) was then added to the reaction mixture at -78° C and allowed to stir for another hour while warming to room temperature, yielding a white suspension. The solvent was removed in vacuo. And a hexanes extraction (ca. 100 mL) was added to the mixture and filtered. The hexanes was removed in vacuo, affording an orange liquid. Pure 102 was obtained by vacuum distillation (b.p. ca. 160° C, 6 mmHg). Yield: 0.66g (16.9%).

$^3$J$_{CP}$ = 9 Hz, 3,4-Tp; MS (EI, 70eV): $m/z$ (%):150, 149, 148 (1, 1, 32) [M$^+$], 118, 117, 116, 115 (0.4, 5, 7, 100) [M$^+$-PH$_2$],

3.4.9. Preparation of 2-[C(O)OH]-thiophene (103). To a stirred solution of thiophene (20.00 g, 238 mmol) in diethyl ether (250 mL) at -78° C was added dropwise a 1.6 M hexanes solution of n-BuLi (156.25 mL, 250 mmol). The reaction mixture was allowed to warm to room temperature, and left stirring for 30 minutes. The reaction was cooled to -78° C again, and dry CO$_2$ was purged through solution for ca. 2 hours. The reaction was left to warm to room temperature again, and washed with aqueous HCl (0.2 M). The ether layer was washed twice with HCl (aq), and the water layer was washed three times.

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(ca. 150 mL each). The ether layer was dried over magnesium sulphate, and the solvent evaporated, yielding crude 103 as a beige powder. Yield: 25.36 g (72.8%).

\[ \text{H NMR ((CD}_3\text{)}_2\text{CO, 300 MHz, 300 K): } \delta 10.9 \text{ (br s, 1H, COOH), 7.78 (m, 2H, J} _{HH} = 3.8 \text{ Hz, 3J} _{HH} = 5.0 \text{ Hz, 4J} _{HH} = 1.0 \text{ Hz, 3-, 5-Tp-H)}, 7.18 \text{ (dd, 1H, 3J} _{HH} = 3.8 \text{ Hz, 3J} _{HH} = 5.0 \text{ Hz, 4-Tp-H)}; \]

\[ \text{C NMR ((CD}_3\text{)}_2\text{CO, 75 MHz, 300 K): } \delta 163.1 \text{ (s, COOH), 135.1 (s, 2-Tp), 134.3 (s, 3-Tp), 133.7 (s, 4-Tp), 128.8 (s, 5-Tp).} \]

3.4.10. Preparation of 2-[C(0)Cl]-Tp (104). Thiophene-2-carboxylic acid (13.0 g, 101 mmol) was measured into a Schlenk flask. Under nitrogen, a condenser was fitted to the Schlenk flask, and an excess of freshly distilled thionyl chloride (SOCl\(_2\)) (50 mL) was added via a syringe, forming a suspension. The reaction mixture was heated at reflux for 12 hours, and became a dark brown solution. Unreacted thionyl chloride was removed in vacuo, affording a brown liquid. The product distills as a clear liquid under vacuum (b.p. 31° C, 1 mmHg). Yield: 12.85 g (86%).

\[ \text{H NMR (CD}_2\text{Cl}_2, 300 MHz, 300 K): } \delta 7.96 \text{ (dd, 1H, J} _{HH} = 2.6 \text{ Hz, 4J} _{HH} = 1.3 \text{ Hz, 5-Tp-H)}, 7.87 \text{ (dd, 1H, J} _{HH} = 3.7 \text{ Hz, 4J} _{HH} = 1.3 \text{ Hz, 3-Tp-H)}, 7.20 \text{ (dd, 1H, J} _{HH} = 2.6 \text{ Hz, 3J} _{HH} = 3.7 \text{ Hz, 4-Tp-H)}; \]

\[ \text{C NMR (CD}_2\text{Cl}_2, 75 MHz, 300 K): } \delta 159.8 \text{ (s, COCl), 138.5 (s, 3-Tp), 138.4 (s, 4-Tp), 137.3 (s, 2-Tp), 129.1 (s, 5-Tp).} \]

3.4.11. Preparation of 2,5-[C(O)OH]-Tp (105). To a stirred solution of thiophene (16.8 g, 200 mmol) in hexanes at -78° C was added dropwise a hexanes solution of 1.6 M \(^{9}\text{BuLi (256 mL, 410 mmol). The reaction mixture was allowed to warm to room temperature, the flask fitted with a condenser, and heated at reflux at 100° C for 30 minutes. The reaction was cooled to -78° C before purging with dry CO}_2\) for ca. 2 hours, resulting in a white suspension. The suspension was washed with HCl (aq) (0.5 M) and the aqueous layer removed in a separatory funnel. Three aliquots of diethyl ether (150 mL) were used to extract the product from the water layer. The ether was dried over

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magnesium sulphate, and solvent removed under reduced pressure, affording crude 105 as a pale yellow powder. Yield: 24.6 g (71.5%).

$^1$H NMR ((CD$_3$)$_2$CO, 300 MHz, 300 K): δ 7.78 (s, 2H, 3-, 4-Tp-H); $^{13}$C NMR ((CD$_3$)$_2$CO, 75 MHz, 300 K): δ 162.5 (s, COOH), 140.4 (s, 2-, 5-Tp), 134.2 (s, 3-, 4-Tp).

3.4.12. Preparation of 2,5-[C(O)Cl]$_2$-Tp (106). A flask was charged with 105 (12.0 g, 69.7 mmol), and fitted with a condenser. 60 mL of freshly distilled thionyl chloride was added with a syringe, affording a pink suspension. The reaction mixture was heated to reflux for 12-14 hours. Unreacted thionyl chloride was removed in vacuo, yielding a pale brown solid. Pure 106 was obtained by a hexanes recrystallization, affording a white, crystalline solid. Yield: 6.58 g (45%).

$^1$H NMR (CDCl$_3$, 300 MHz, 300 K): δ 7.93 (s, 2H, 3-, 4-Tp-H); $^{13}$C NMR (CDCl$_3$, 75 MHz, 300 K): δ 159.7 (s, COCl), 145.4 (s, 2-, 5-Tp), 136.4 (s, 3-, 4-Tp).

3.4.13. Preparation of Monophosphaalkene Tp-P=C(OSiMe$_3$)-Mes (107). All glassware was rinsed with Me$_3$SiCl and flame dried prior to use. Silylphosphine 98 (0.894 g, 3.44 mmol) and mesitylene-2-acid chloride 82 (0.632g, 3.46 mmol) were stirred at 50° C in THF (ca. 3 mL) and over 10 days quantitative conversion to 107 was observed by $^{31}$P NMR spectroscopy. Pure 107 was isolated as yellow liquid after vacuum distillation (b.p. 125° C; 0.1 mmHg). Crude yield: 0.74 g (64%); After distillation yield: 0.17 g (14.5%).

$^{31}$P NMR (CDCl$_3$, 121.5 MHz, 300K): Isomer $E$-107: δ 128.8 (s, 24 %); Isomer Z-107: δ 109.1 (s, 76 %); $^1$H NMR (CDCl$_3$, 400.1 MHz, 300K): Isomer $E$-107: δ 7.26 (d, 1H, $^3$J$_{HH}$ = 5.0 Hz, 5-Tp), 7.10, (dd, 1H, $^3$J$_{PC}$ = 8.5 Hz, $^3$J$_{HH}$ = 3.5 Hz, 3-Tp), 6.93 (dd, 1H, $^3$J$_{HH}$ = 4.2 Hz, 4-Tp), 6.88 (s, 2H, $m$-Mes), 2.31, (s, 9H, $o,p$-Mes-CH$_3$), 0.4 (s, 9H, OSi(CH$_3$)$_3$); Isomer Z-107: δ 7.57 (d, 1H, $^3$J$_{HH}$ = 4.5 Hz, 5-Tp), 7.47 (dd, 1H, $^3$J$_{PC}$ = 8.9 Hz, $^3$J$_{HH}$ = 3.5 Hz, 3-Tp), 7.15 (dd, 1H, $^3$J$_{HH}$ = 4.2 Hz, 4-Tp), 6.90 (s, 2H, $m$-Mes), 2.42 (s, 6H, $o$-Mes-.
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$CH_3$, 2.26 (s, 3H, p-Mes-CH$_3$), 0.11 (s, 9H, -OSi(CH$_3$)$_3$); $^{13}$C NMR (CDCl$_3$, 100.6 MHz, 300K): Isomer E-107: $\delta$ 207.5 (d, $^1$J$_{PC} = 34.8$ Hz, C=P), 138.5 (d, $^3$J$_{PC} = 9.46$ Hz, o-Mes), 137.9 (d, $^3$J$_{PC} = 9.3$ Hz, p-Mes), 137.9 (d, $^1$J$_{PC} = 60.7$ Hz, 2-Tp), 134.9 (d, $^2$J$_{PC} = 26.3$ Hz, 3-Tp), 130.58 (s, 5-Tp), 128.61 (s, m-Mes), 126.9 (d, $^3$J$_{PC} = 11$ Hz, 4-Tp), 21.2 (s, p-CH$_3$), 21.1 (s, o-CH$_3$), 0.8 (s, OSi(CH$_3$)$_3$); Isomer Z-107: $\delta$ 192.7 (d, $^1$J$_{PC} = 40.5$ Hz, C=P), 139.4 (d, $^1$J$_{PC} = 67.4$ Hz, 2-Tp), 137.15 (d, $^3$J$_{PC} = 4.1$ Hz, o-Mes), 135.96 (d, $^2$J$_{PC} = 29.5$ Hz, i-Mes), 134.92 (d, $^5$J$_{PC} = 5.3$ Hz, p-Mes), 134.54 (d, $^2$J$_{PC} = 30.2$ Hz, 3-Tp), 129.76 (d, $^3$J$_{PC} = 4.3$ Hz, 5-Tp), 128.41 (s, m-Mes), 126.63 (d, $^3$J$_{PC} = 11$ Hz, 4-Tp), 20.6 (s, p-CH$_3$), 19.6 (s, o-CH$_3$), -0.2 (d, $^4$J$_{PC} = 2$ Hz, OSiMe$_3$); UV/Vis: $\lambda_{\text{max}}$ ($\epsilon$) = 328 nm (6700); MS (EI, 70eV): m/z (%): 337, 336, 335, 334 (1, 5, 12, 45) [M$^+$], 148, 147 (11, 100) [Mes-CO], 120, 119 (3, 21) [Mes], 74, 73 (3, 39) [Si(CH$_3$)$_3$].

3.4.14. Preparation of Monophosphaalkene Mes-P=C(OSiMe$_3$)-Tp (109). Thiophene-2-carboxylic acid chloride 104 (3.25 g, 22.2 mmol) and bis(trimethylsilyl)mesitylphosphine 108 (6.61 g, 22.3 mmol) were weighed out in a glovebox, and transferred to a small Schlenk bomb using minimal solvent (ca. 3 mL). After 24 hours at room temperature, the reaction mixture had turned orange. The progress of the reaction was monitored at this time using $^{31}$P NMR spectroscopy, and silylphosphine 108 was totally converted to monophosphaalkene 109. The solvent was removed in vacuo, affording an orange liquid. The product was purified by a vacuum distillation (b.p. ca. 120° C, 1 mmHg). Yield: 5.8 g (76%).

$^{31}$P NMR (CDCl$_3$, 121.5 MHz, 300 K): Isomer E-109: $\delta$ 134.8 (s, 41%); Isomer Z-109: $\delta$ 134.3 (s, 59%); $^1$H NMR (CDCl$_3$, 300 MHz, 300 K): Isomer E-109: $\delta$ 7.1 (m, 1H, 5-Tp), 6.9 (s, 2H, m-Mes), 6.6 (m, 1H, 3-Tp), 6.4 (m, 1H, 4-Tp), 2.40 (s, 6H, o-Mes-CH$_3$), 2.36 (s, 3H, p-Mes-CH$_3$), 0.48 (s, 9H, OSi(CH$_3$)$_3$); Isomer Z-109: $\delta$ 7.4 (m, 1H, 5-Tp), 7.2 (s, 1H, 3-Tp), 6.9 (m, 1H, 4-Tp), 6.8 (s, 2H, m-Mes), 2.47 (s, 6H, o-Mes-CH$_3$), 2.31 (s, 3H,

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\[
p\text{-Mes-CH}_3\), -0.09 (9H, OSi(CH\_3\_3)); \textsuperscript{13}C NMR (CDCl\_3, 75 MHz, 300K): Isomer \textit{E}-109: \\
\delta 191.6 (d, J_{PC} = 43 Hz, P=C), 145.1 (d, J_{PC} = 18 Hz, 2-Tp), 141.4 (d, J_{PC} = 6 Hz, o-Mes), 138.7 (s, p-Mes), 132.6 (d, J_{PC} = 39 Hz, i-Mes), 128.9 (s, m-Mes), 127.2 (d, J_{PC} = 16 Hz, 3-Tp), 127.1 (s, 5-Tp), 126.2 (d, J_{PC} = 10 Hz, 4-Tp), 21.0 (s, p-Mes-CH\_3), 20.9 (s, o-Mes-CH\_3), 0.15 (d, J_{PC} = 5 Hz, OSi(CH\_3\_3)); Isomer \textit{Z}-109: \delta 188.4 (d, J_{PC} = 54 Hz, P=C), 147.3 (d, J_{PC} = 34 Hz, 2-Tp), 141.9 (d, J_{PC} = 7 Hz, o-Mes), 138.0 (s, o-Mes), 132.5 (d, J_{PC} = 37 Hz, i-Mes), 128.1 (s, m-Mes), 127.1 (s, 5-Tp), 125.5 (d, J_{PC} = 12 Hz, 4-Tp), 123.7 (d, J_{PC} = 21 Hz, 3-Tp), 22.3 (s, p-Mes-CH\_3), 22.2 (s, o-Mes-CH\_3), -0.33 (s, OSi(CH\_3\_3)); UV/Vis: \lambda_{max} (\varepsilon) = 357 nm (7600); MS (EI, 70 eV): 337, 336, 335, 334 (2, 10, 25, 90) [M\textsuperscript{+}], 304, 303, 302, 301 (1, 6, 24, 97) [M\textsuperscript{+} - HS], 246, 245, 244 (1, 4, 12) [M\textsuperscript{+} - HOSi(CH\_3\_3)], 73 (100) [Si(CH\_3\_3)].
\]

3.4.15. Preparation of Mes-C(OSiMe\_3)=P-Tp-P=C(OSiMe\_3)-Mes (110). All glassware was rinsed with Me\_3SiCl and flame dried prior to use. Under inert atmosphere, two equivalents of mesitylene-2-carboxylic acid chloride \textit{82} (0.36g, 1.97 mmol) was mixed with 2,5-bis(trimethylsilyl)phosphinothiophene \textit{102} (0.42g, 0.962 mmol) in THF (ca. 20 mL). The reaction was allowed to stir for 8 days at 80° C under nitrogen. The solvent was removed in vacuo. The product was purified by a hexanes recrystallization. Crude yield: 0.514g (96.8%); after recrystallization from hexane at -78° C: 0.041g (7.3%).

\textsuperscript{31}P NMR (CDCl\_3, 121.5 MHz, 300K): \delta 129.0 (s, 18\%, \textit{E},\textit{E}-110), 127.8 (s, 21\%, E,Z-110), 110.2 (s, 40\%, Z,Z-110) 109.6 (s, 21\% E,Z-110). \textsuperscript{1}H NMR (CDCl\_3, 300 MHz, 300K): \delta 7.4 (d, 2H, J_{PH} = 7.2 Hz, Z,Z-110, 3-, 4-Tp), 7.2 (d, 2H, J_{PH} = 3.0 Hz, E,E-110/Z,Z-110, 3-, 4-Tp), 7.1 (d, 2H, J_{PC} = 3.3 Hz, E,E-110/E,Z-110, 3-, 4-Tp), 6.9-6.8 (s, 4H, m-Mes), 2.3 -2.0 (s, 18H, o-, p-Mes-CH\_3), 0.35, (s, 18H, OSi(CH\_3\_3). E,Z-110) 0.29 (s, 18H, OSi(CH\_3\_3). E,E-110), 0.06, (s, 18H, OSi(CH\_3\_3). Z,Z-110), -0.01 (s, 18H,

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OSi(CH₃)₃, E,E-110; ¹³C NMR (CDCl₃, 75.48MHz, 300K): δ 208.4 (d, ¹JCP = 37 Hz; C=P, E,E-110), 194.3 (d, ¹JCP= 35Hz; C=P, Z,Z-110), 143.5-128.4 (Tp, Mes), 20.6-19.6 (s, o-, p-Mes-CH₃), 1.7- -0.2 (s, OSi(CH₃)₃); UV/Vis: λmax (ε) = 347 nm (4900); MS (EI, 70eV): m/z (%): 588, 567, 586, 584 (2, 4, 13, 24, 54) [M⁺], 514, 513, 512 (2, 5, 9) [M⁺-Si(CH₃)₃], 148, 147 (32, 100) [Mes-CO], 120, 119 (5, 32) [Mes], 74, 73 (1, 11) [Si(CH₃)₃].

3.4.16. Attempted preparation of Mes-P=C(OSiMe₃)-Tp-C(OSiMe₃)=P-Mes (111).

All glassware was rinsed with Me₃SiCl and flame dried prior to use. Under inert atmosphere, one equivalent of 2,5-bis(carboxylic acid chloride)thiophene 106 (2.45 g, 11.7 mmol) and two equivalents of bis(trimethylsilyl)mesitylphosphine 108 (7.00 g, 23.6 mmol) were weighed into small beakers, and dissolved in minimal THF (ca. 5 mL) total. Once dissolved, the resulting solutions were transferred into a Kontes bomb sealable with a Teflon stopcock. After 2 days heating at 80° C, silylphosphine 108 is totally consumed. The solvent is removed in vacuo, and crude 111 is isolated as an orange liquid. Crude yield 4.62 g, (70%). A dark red powder was isolated from a concentrated hexanes solution of 111 cooled to -78° C.

³¹P NMR (THF, 121.5 MHz, 300K): δ 145-136 (P=C isomers), 42.5 (s, HP-COH).

3.4.17. Preparation of Polymer [-Tp-P=C(OSiMe₃)-C₆Me₄-C(OSiMe₃)=P-] (93).

Under an inert atmosphere one equivalent of carboxylic acid chloride 86 (0.500 g, 193 mmol) was transferred into a thick-walled Pyrex tube. Silylphosphine 102 (0.843 g, 193 mmol), which is a liquid at room temperature, was pipetted into the beaker used to weigh out 86, then transferred to the Pyrex tube, where the two reagents form distinct layers. The tube was evacuated and sealed, then set into an oven pre-heated to 90° C. After 10 minutes, the reaction mixture has become a transparent yellow fluid. After 24 hours in the oven, the reaction mixture has become a viscous orange fluid. The tube is cracked

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and evacuated to remove ClSiMe₃, which is the condensation molecule. The orange fluid
becomes a brittle yellow/orange solid during evacuation, and the crude 93 is isolated as
such. The crude polymer is dissolved in a minimal amount of THF, and coated onto the
inside of a 500 mL flame-dried Schlenk flask. 20 mL of cold hexanes (ca. -78° C) is
transferred by cannula into the flask to wash the crude polymer, and quickly transferred
by cannula out again. The precipitated polymer was weighed by difference, and
transferred into a small vial. Yield: 0.326 g, (39%).

³¹P NMR (CDCl₃, 121.5 MHz, 300K): δ 132-121 (br s, 40%, E-P=C), 111-106 (br s, 
59%, Z-P=C), -46 (br s, 1%, HP-C(O)), -152 (br s, 1%, -P(SiMe₃)₂); ³¹H NMR (CDCl₃,
300 MHz, 300K): δ 7.4 (br s, m-Mes), 7.2 (br s, Tp-H), 7.1 (br s, Tp-H), 6.7 (br s, Tp-H),
6.5 (br s, Tp-H), 2.4 (br s, o-, p-Mes-CH₃), 0.3 (br s, E-OSiMe₃), -0.1 (br s, Z-OSiMe₃);
¹³C NMR (CDCl₃, 75.48MHz, 300K) : δ 210 (br s, E-P=C), 196 (br s, Z-P=C), 145-127 
(br s, Mes, Tp ring carbons), 20-15 (br s, o-, p-Mes-CH₃), 2- -4 (br s, OSiMe₃); UV/Vis:
λ_max (ε) = 379 nm (10,200).
3.5 References


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   **1997**, *529*, 143.


   257.


   *49*, 5250.


   193.


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Chapter Four
All Trans-Poly($P$-Phenylene phosphaalkene)

4.0 Introduction

As noted at the end of the previous chapter, switching the steric bulk from the carbon substituent (107) to the phosphorus substituent (109) of the $P=C$ bond resulted in a change in the chemistry of the phosphaalkenes discussed. These differences are summarized below, and helped to shape the direction of this project. The compounds without a sterically demanding substituent on the carbon of the phosphaalkene bond appear to be more sensitive towards protonolysis reactions. This might be rationalized by the fact that the siloxy group, arguably the part of the molecule most reactive with protons, has less steric protection. In contrast, a solution of a phosphaalkene with all carbon substituents (115) can be washed with degassed water without a reaction. Monophosphaalkene 115, originally reported in 1978,\(^1\) is prepared via a condensation route. These types of phosphaalkenes are discussed in more detail in chapter five.

Interestingly, the Becker-type phosphaalkene 109 showed a significantly larger $Z/E$ ratio compared to 107, which suggests that a bulky phosphorus substituent makes the formation of the $Z$-isomer more favourable. This interesting observation is worth further investigation. Yoshifuji et al. prepared a Becker-type phosphaalkene (116) with a bulky

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substituent at the phosphorus atom of the P=C bond which was present in only one isomer. The authors were able to grow crystals suitable for examination by X-ray crystallography and confirmed that it was the Z-isomer.²

The first poly(p-phenylenephosphaalkene) (90) featured phosphaalkene bonds in the main chain of the polymer that were a mixture of the E- and Z-isomers as is discussed in chapter two. Similarly, poly(thienylenephenylenephosphaalkene) (93) also contains both isomers in the backbone of the macromolecule. Protasiewicz has published a couple of examples of macromolecules containing P=C and P=P bonds in the main chain, an example of which is shown (117).³⁻⁵ Interestingly, in this case only the E-isomer formed which features the aryl groups in trans positions about the P=E (E = C, P) bond.

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In this chapter the effect of switching the sterically demanding substituent from the carbon to the phosphorus of the P=C bond are examined. A sterically demanding substituent at phosphorus leads to the selective formation of the Z-phosphaalkene isomer. The presence of a single isomer allows the monophosphaalkene and bis(phosphaalkene) model compounds to be crystallized, and confirms the formation of the Z-isomer. We can use these solid state structures to rationalize our UV/Vis spectroscopic observations. It should be recognized that these solid state structures may not be representative of the structure of the model compounds in solution in which the UV/Vis spectroscopy was performed. As well, the observed orientations in the solid state structure may be an effect of crystal packing forces, and not solely an effect of steric and electronic interactions.

Stilbene is the model compound often used for comparison to PPV. The phenyl rings of cis stilbene are twisted significantly, with a dihedral angle of $43^\circ \pm 3.2^\circ$ from a gas phase electron diffraction experiment.\textsuperscript{6} This out-of-plane twisting is due to steric interference between the phenyl rings. An X-ray crystal structure of 1,2-diphenylcyclopentene, an analogue of cis-stilbene, showed similar dihedral angles of $43.8^\circ$ and $-47.5^\circ$ in the solid state.\textsuperscript{7} Several theoretical studies of cis-stilbene have shown a dihedral angle between the plane of the phenyl rings and the vinyl moiety of 30-40°.\textsuperscript{8-12}

The structure of trans-stilbene was first reported in 1937.\textsuperscript{13} This structure was re-investigated several times and has been shown to be almost planar featuring a dihedral angle between $3 - 7^\circ$.\textsuperscript{14-17} Recall that the $\lambda_{\text{max}}$ of trans-stilbene is red-shifted from that of cis-stilbene by some 30 nm.\textsuperscript{18} From this comparison it is clear that the more planar $\pi$-system corresponds the aromatic groups in trans positions about the double bond. The

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less distorted system possesses more effective $\pi$-conjugation as evinced by the smaller HOMO-LUMO energy gap of trans-stilbene. For organic $\pi$-conjugated systems, the more extensive the $\pi$-conjugation, the smaller the HOMO-LUMO gap becomes, and the longer the wavelength of $\lambda_{\text{max}}$ observed for this system. For these systems, $\lambda_{\text{max}}$ is often used as an indication of the degree of $\pi$-conjugation.\textsuperscript{19}

Several well known organic polymers exhibit extended $\pi$-conjugation despite non-planar backbones. The ortho protons of the phenyl groups of poly($p$-phenylene) have enough steric interaction to cause a 26° angle between the planes of neighbouring rings.\textsuperscript{20,21} The backbone of PPV is not planar either.\textsuperscript{22} Neutron diffraction of films of PPV with deuterated phenyl rings show the rings are twisted about the vinyl linkages by $\pm 7^\circ$ at room temperature, and up to $11^\circ$ at elevated (616 K) temperatures.\textsuperscript{23} An X-ray diffraction study of PPV found the dihedral angle ranges from 8 – 16°, with the best fit at $10^\circ \pm 3^\circ$. This study also found a trend of increasing dihedral angle with an increased temperature.\textsuperscript{22} A similar study on a tetramer of PPV (five phenyl rings, four vinyl linkages) revealed nearly identical structure.\textsuperscript{24} There is a wealth of literature outlining theoretical studies of the electronic properties and backbone planarity of this important $\pi$-conjugated polymer\textsuperscript{25-29} These observations illustrate that despite a certain amount of non-planarity in the polymer backbone, these materials exhibit properties consistent with extensive $\pi$-conjugation. A compound does not have to be perfectly planar to possess $\pi$-conjugation, although it is clear that the more planar system exhibit more efficient $\pi$-conjugation.
4.1 Results

4.1.1. Synthesis of 1,4-[P(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}-C\textsubscript{6}Me\textsubscript{4} (121)

In order to fully test the hypothesis that placing the necessary steric bulk on the substituent at phosphorus leads to selective Z-isomer formation, a suitable sterically demanding bifunctional phosphine monomer was required. Thankfully, we did not need to synthesize both the carboxylic acid chloride monomer as well as the bifunctional silylphosphine. In the case of the carboxylic acid chloride reagents, both benzoyl chloride and terephthaloyl chloride are inexpensive materials readily available through commercial sources. The preparation of a bifunctional silylphosphine monomer with a substituted-benzene spacer proved to be much more difficult than expected. The selected synthetic route, after several trials, is outlined in Scheme 1. Starting with the 1,4-dibromotetramethylbenzene (84), which was treated with tert-butyl lithium and subsequently bis(diethylamino)chlorophosphine to afford the 1,4-bis(diethylamino)phosphino-2,3,5,6-tetramethylbenzene (118). The aminophosphine 118 was treated with an excess of dry hydrogen chloride gas, which produces the 1,4-dichlorophosphino-2,3,5,6-tetramethylbenzene (119). The chlorophosphine 119 was reduced with LiAlH\textsubscript{4} to the 1,4-phosphino-2,3,5,6-tetramethylbenzene (120). The bifunctional 1,4-bis(trimethylsilyl)phosphino-2,3,5,6-tetramethylbenzene (121) was produced by treating 120 with MeLi, and subsequent addition of chlorotrimethylsilane. Pure 121 was isolated via vacuum sublimation (ca 100-110° C / 1 mmHg) as a white, colourless powder. A \textsuperscript{31}P NMR spectrum of 121 shows a single resonance at δ -153.7 (Figure C1, Appendix C). Two resonances are present in the \textsuperscript{1}H NMR spectrum of 121, a singlet at δ 2.56 and doublet at δ 0.20 (\textsuperscript{3}J\textsubscript{PH} = 5.8 Hz) that are assigned to the benzene and
silyl methyl groups respectively (Figure C2). The parent ion of compound 121 was detected by EI mass spectrometry.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \quad \xrightarrow{\text{i}} \quad (\text{Et}_2\text{N})_2\text{P} \quad \xrightarrow{\text{ii}} \quad \text{Cl}_2\text{P} \quad \xrightarrow{\text{iii}} \quad (\text{Me}_3\text{Si})_2\text{P} \\
84 & \quad 118 & \quad 119 & \quad 121 & \quad 120
\end{align*}
\]

**Scheme 1.** Conditions and reagents: i) THF, -78°C, 4 equiv. 'BuLi; 2 equiv. CIP(NEt)\_2. ii) CH\_2\_2, 0°C, excess dry HCl(g). iii) Et\_2O, -78°C, 1.1 equiv. LiAlH\_4. iv) Et\_2O, -78°C, 4 equiv. MeLi; 4 equiv. ClSiMe\_3.

The preparation of the bifunctional silylphosphine 121 was difficult and time consuming. The installation of the two phosphorus atoms onto the aromatic ring proved to be the point of the synthesis that caused problems. In many cases, despite great care being taken to ensure dry solvents and glassware, the crude product was a mixture of the mono- (118b, 119b) and disubstituted product (118, 119), as shown in Scheme 2. The presence of the monosubstituted products was confirmed via a \(^1\text{H}\) NMR spectrum (Figure C3). In a straightforward reaction, 84 is treated with four equivalents of 'BuLi to give the dilithiated benzene ring. This reaction works quite well, as we have previously used this methodology to prepare the 1,4-di(carboxylic acid)-2,3,5,6-tetramethylbenzene 85 as discussed in chapter two. It is likely that during the reaction of the dilithiated tetramethylbenzene ring with CIP(NEt)\_2 (122), ammonium salt (123), which are a by-product of the reaction to form 122 (Scheme 3), are a source of protons causing the

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protonolysis leading to the monosubstituted product \(118b\). It has proven impossible to completely separate \(123\) from \(122\), even after repeated hexanes extractions and distillations. The salt dissociates, sublimes, then reassociates in the distilled product.

Cooling the distillate causes the ammonium salt to dissolve into \(122\). In the preparation of the 1,4-bis(trimethylsilyl)phosphinobenzene \(79\), the phosphorus atoms are introduced in a similar manner, using phosphine \(122\) and a Grignard reaction as discussed in chapter two. This reaction proceeds smoothly, and the 1,4-bis(diethylamino)phosphinobenzene product is crystalline when isolated. Perhaps, this is a consequence of the diGrignard reagent being less hydrolytically sensitive then the diliithio reagent, and hence less susceptible to protonolysis by the ammonium salt. Attempts to prepare the 2,3,5,6-tetramethylbenzene diGrignard reagent were unsuccessful. Eventually a procedure to isolate pure \(12\) was worked out. It is necessary to carry out a very careful fractional vacuum sublimation of \(119\) and \(119b\), slowly subliming \(119b\). Following the reduction by \(\text{LiAlH}_4\), a subsequent recrystallization from \(\text{Et}_2\text{O}\) resulted in pure \(120\), from which it was relatively simple to prepare \(121\).

\[
\begin{align*}
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
 & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
\text{84} & \quad \text{84} & \quad \text{84} & \quad \text{84} \\
\text{(Et}_2\text{N})_2\text{P} & \quad \text{P} & \quad \text{P(NEt}_2\text{)}_2 & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
& \quad \text{P} & \quad \text{P(NEt}_2\text{)}_2 & \quad \text{P} & \quad \text{P(NEt}_2\text{)}_2 & \quad \text{P} & \quad \text{P(NEt}_2\text{)}_2 \\
\text{118} & \quad \text{118} & \quad \text{118} & \quad \text{118} \\
\text{119} & \quad \text{119} & \quad \text{119} & \quad \text{119} \\
\text{119b} & \quad \text{119b} & \quad \text{119b} & \quad \text{119b} \\
\text{199b} & \quad \text{199b} & \quad \text{199b} & \quad \text{199b} \\
\end{align*}
\]

**Scheme 2.** Conditions and reagents: i) THF, -78° C, 4 equiv. \(^t\text{BuLi}; 2\) equiv. ClPNET\(_2\). ii) \(\text{CH}_2\text{Cl}_2\), 0° C, excess dry HCl(g).

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Scheme 3. Conditions and reagents: i) CH₂Cl₂, -78°C, 4 equiv. HNEt₂.

4.1.2 Synthesis of the Monophosphaalkene Mes-P=C(OSiMe₃)-Ph (125)

Surprisingly, the simple monophosphaalkene 125 (Scheme 4) had not been reported previously, despite the ready availability of the starting materials. It was therefore prepared conveniently from the reaction of bis(trimethylsilyl)mesitylphosphine (108) and benzoyl chloride (124) in THF solution. Remarkably, $^{31}$P NMR spectroscopic analysis of the reaction mixture revealed only a single resonance in the phosphaalkene region (δ 141.5). This was unexpected as monophosphaalkene 109 has two isomers. This data suggested that, unlike the monophosphaalkenes discussed in previous chapters that were a mixture of $E$ and $Z$-isomers, one isomer of 125 was formed selectively. On the basis of the known chemistry of tert-butyl and Mes* substituents, we speculated that this was the $Z$-isomer.² $^{30}$ Monophosphaalkene 125 was crystalline since it was a single isomer and yellow crystals suitable for X-ray crystallography were obtained from a concentrated hexanes solution stored at -35°C. Compound 125 was fully characterized by multinuclear NMR, mass spectrometry, UV/Vis spectroscopy, and X-ray crystallography. Model compound 125 has an UV/Vis absorption maximum at 324 nm in an approximately 10⁻⁵ M THF solution.

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Scheme 4. Conditions and reagents: i) THF, room temperature, 1 day.

Interestingly, monitoring the reaction by $^{31}$P NMR spectroscopy showed that phosphaalkene 125 formed quantitatively after only one day at 25° C (Figure 4.1). This is in stark contrast to the preparation of the monophosphaalkenes where the sterically demanding substituent resides on the carbon of the phosphaalkene bond described in chapters two and three. These monophosphaalkenes required several days at elevated temperatures (50-80° C) for the reaction to proceed to completion. There is a notable parallel to monophosphaalkene 109 discussed in the last chapter that was the product of the reaction of bulky phosphine 108 and thiophene-2-carboxylic acid chloride. Model compound 109 also formed in a day at room temperature. Presumably, the difference in formation rates between the model compounds where the bulky substituent resides on the phosphorus or carbon of the P=C bond is a consequence of the more facile approach of 108 to the corresponding carboxylic acid chloride. The ortho-methyl groups of the mesityl ring might also provide some steric pressure on the trimethylsilyl groups, to make the condensation and [1,3]siloxy migration more favourable.
Figure 4.1. $^{31}$P NMR spectrum of monophosphaalkene 125 in CDCl₃.

The $^1$H NMR spectrum of 125 shows only six resonances, one fewer than expected for this compound. The signals for the meta and para protons of the phenyl group are coincident. All the other signals are fully resolved as can be seen in Figure 4.2. The resonance due to the trimethylsilyl group is at δ -0.20, which is consistent with the signals assigned to the Z-isomer of monophosphaalkenes discussed in previous chapters.

Figure 4.2. $^1$H NMR spectrum of monophosphaalkene 125 in CDCl₃. * Residual CHCl₃, hexanes.
For all of the model compounds discussed in this chapter, $^1$H and $^{13}$C NMR assignments were made with the assistance of $^1$H-$^1$H COSY, $^1$H-$^{13}$C HMQC, and $^1$H-$^{13}$C HMBC 2D-NMR experiments. In the $^{13}$C NMR spectrum of 125, most of the signals are completely resolved (Figure 4.3). The only incidences of concidence are those of the ipso-phenyl (h) and ortho-mesityl (d) at δ 142.1, and the meta-mesityl (c) and para-phenyl carbons (k) at δ 128.2. The signal due to the carbon of the P=C bond (g) is observed as a distinctive doublet at δ 197.3 ($^1$J$_{PC}$ = 56 Hz). The ipso-mesityl carbon signal is a doublet at δ 133.2 ($^1$J$_{PC}$ = 37 Hz). The resonances marked with asterisks in the alkyl region of the $^1$H and $^{13}$C NMR spectra are due to molecules of the recrystallization solvent (hexanes) trapped in the crystals of 125.

![Figure 4.3. $^{13}$C NMR spectrum of monophosphaalkene 125 in CDCl$_3$. * Solvent CDCl$_3$.](image)
4.1.3 Synthesis of the Bis(phosphaalkene) 1,4-[Mes-P=C(OSiMe$_3$)]$_2$C$_6$H$_4$ (127)

A bis(phosphaalkene) closely structurally related to monophosphaalkene 125 was synthesized by treating 108 with half an equivalent of terephthaloyl chloride (126) (Scheme 5). Upon addition of 108 to the stirred solution of 126, the previously colourless solution immediately turned yellow. Over a few hours the solution became darker, and the colour changed to orange. When the progress of the reaction was checked after five hours using $^{31}$P NMR spectroscopy, the reaction was already complete (Figure 4.4). Phosphine 108 had been consumed to quantitatively produce bis(phosphaalkene) 127. This new compound was highly crystalline, as during the process of isolating the crude product, crystals of 127 started forming on the wall of the Schlenk flask. The saturated solution was left to sit at room temperature overnight, and yellow crystals precipitated that could be readily separated from the dark orange supernatant solution. These crystals proved suitable for X-ray crystallography and a solid state structure was obtained which confirmed it as the Z,Z-isomer. Bis(phosphaalkene) 127 was characterized by multinuclear NMR spectroscopy, and UV/Vis spectroscopy. The UV/Vis spectrum of bis(phosphaalkene) 127 reveals an absorption maximum of 388 nm.

Scheme 5. Conditions and reagents: i) THF, room temperature, 5 hours.
Only one signal is present in the $^{31}\text{P}$ NMR spectrum of bis(phosphaalkene) 127, $\delta$ 146.3 ppm, which can be attributed to the Z,Z-isomer (Figure 4.4). The single resonance indicates that the two phosphorus atoms are magnetically equivalent in solution, as one might expect from a symmetric molecule such as 127. The $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra are consistent with the Z,Z-isomer bis(phosphaalkene) assignment.

![Figure 4.4. $^{31}\text{P}$ NMR spectrum of bis(phosphaalkene) 127 in CDCl$_3$.](image)

There are only five resonances present in the $^1\text{H}$ NMR spectrum of 127 (Figure 4.5). The signal for the siloxy group is at $\delta$ -0.19, which is almost identical to that of 125 ($\delta$ -0.20). In the alkyl region there are two resonances present in a 2:1 ratio at $\delta$ 2.40 and 2.27. These signals were assigned to the ortho and para methyl groups of mesitylene, respectively. These shifts are almost identical to the corresponding signals for 125, which are $\delta$ 2.41 and 2.27. Two resonances, each integrating to four protons, are observed in the aromatic region of the spectrum at $\delta$ 7.75 and 6.87, which are due to the ortho-phenyl central bridging aromatic ring protons, and the meta-mesityl protons.
Again, highlighting the similarities between bis(phosphaalkene) 127 and monophosphaalkene 125, the signal of the ortho-phenyl protons of 125 comes at δ 7.81, and the meta-mesityl protons at δ 6.87.

![Figure 4.5. 1H NMR spectrum of bis(phosphaalkene) 127 in CDCl₃. * Residual CHCl₃](image)

The 13C NMR spectrum of 127 (Figure 4.6) is not as simple as the 1H NMR spectrum. As was the case for the 1H NMR spectra, the 13C NMR spectra of 127 and 125 are quite similar. The resonance of the carbon atom of the P=C bond is present as a doublet at δ 196.4 (1J_PC = 60 Hz). The ipso-mesityl ring carbon signal of 127 is a doublet at δ 133.1 (1J_PC = 41 Hz), which is only slightly shifted from that of 125 (δ 133.2, 1J_PC = 37 Hz). Of note, the one bond coupling constant is slightly larger for 127 than for 125 (1J_PC = 41 versus 37 Hz). The ortho-mesityl ring carbon shift for 127 is a doublet (δ 142.1, 2J_PC = 3 Hz) with a slightly smaller coupling constant than the corresponding carbon of 125 (δ 142.1, 2J_PC = 7 Hz). The signal of the ipso-carbon of the phenyl ring of 127 is a doublet at δ 142.8 (2J_PC = 34 Hz), which is similar to 125 (δ 142.1, 2J_PC = 28 Hz). In contrast to 125 where both signals are doublets (2J_PC = 9 Hz), the resonances for the
ortho-methyl mesityl groups (δ 22.2) and meta-mesityl ring carbons (δ 128.3) are singlets for 127. The ortho-phenyl ring carbon signal is a doublet of doublets present at δ 124.4 as these carbons are coupled to two phosphorus nuclei ($^3J_{PC} = 18$ Hz, $^4J_{PC} = 17$ Hz).

**Figure 4.6.** $^{13}$C NMR spectrum of bis(phosphaalkene) 127 in CDCl$_3$. * Solvent CDCl$_3$.

### 4.1.4 Synthesis of the Bis(phosphaalkene) 1,4-[Ph-C(OSiMe$_3$)=P]$_2$-C$_6$M$_4$ (128)

The bis(phosphaalkene) complementary to 127 was prepared by adding a concentrated THF solution of benzoyl chloride (124) to a stirred solution of 1,4-bis(trimethylsilylphosphino)-2,3,5,6-tetramethylbenzene (121) (Scheme 6). The bifunctional silylphosphine starting material was quantitatively consumed over several days at room temperature as monitored by $^{31}$P NMR spectroscopy (Figure 4.7). When the reaction was completed, the THF was removed, and crude 128 was isolated as a yellow
oil. The crude product was redissolved in THF, and crystals of 128 suitable for X-ray crystallography were obtained by slow solvent evaporation. Bis(phosphaalkene) 128 was fully characterized by multinuclear NMR, mass spectrometry, UV/Vis spectroscopy, and X-ray crystallography. The UV/Vis spectrum of 128 shows a maximum absorption at 337 nm.

Scheme 6. Conditions and reagents: i) THF, room temperature, 3 days.

Unlike the $^{31}$P NMR spectra of 125 and 127, there are traces of isomers other than the Z,Z-isomer present for 128 (Figure 4.7). Only phosphaalkene resonances are observed, and the major signal at $\delta$ 150.2 was assigned to the Z,Z-isomer with confidence due to the solid state structure obtained. A trace amount of the E,E- and E,Z-isomers appear to be present, though not in enough quantity to interfere with the crystallization of the Z,Z-isomer. Alternatively, these signals may arise due to the presence of rotational isomers (syn and anti). The major signal is slightly downfield from monophosphaalkene 125 ($\delta$ 141.5) and bis(phosphaalkene) 127 ($\delta$ 146.3). It is also possible that E/Z isomerization occurs in solution under a suitable light source.
Additional support for our conclusion that there are trace amounts of isomers other than the $Z, Z$-isomer present, can also be seen in the $^1$H NMR spectrum of 128 (Figure 4.8). Small resonances in the siloxy and aryl region can be attributed to these minor products. In particular, the signal at $\delta$ 0.38 can be assigned to an $E$-isomer siloxy group by comparison to the phosphaalkenes in chapters two and three. The resonance of the siloxy group of an $E$-isomer is always downfield from zero ppm, and the signal for the $Z$-isomer is upfield from zero ppm. Due to the coincidence of the para- and meta-phenyl protons resonances at $\delta$ 7.32, a resonance that integrates to six protons, there are only four signals present in the $^1$H NMR spectrum of 128. The high symmetry of the molecule in solution is indicated by the simplicity of the spectrum. The broad singlet at $\delta$ 7.80 is due to the ortho-phenyl protons. The signal of the four equivalent methyl groups of the tetramethylbenzene spacer is present as a singlet at $\delta$ 2.42. A resonance at $\delta$ -0.24 can be attributed to the trimethylsiloxy group protons.
Figure 4.8. $^1$H NMR spectrum of bis(phosphaalkene) 128 in CDCl$_3$. * Residual CHCl$_3$

The $^{31}$P NMR shift of bis(phosphaalkene) 128 (δ 150.2) is downfield from 125 (δ 141.5) and 127 (δ 146.3). Conversely, the signal for the carbon of the P=C bond, a doublet at δ 195.9 ($^1$J$_{PC} = 55$ Hz) in the $^{13}$C NMR spectrum (Figure 4.9), is observed upfield to those of 125 and 127 by comparison, as can be seen in Table 4.1. The ipso-phenyl ring carbon signal is a doublet at δ 142.1 ($^2$J$_{PC} = 28$ Hz). The resonance of the ipso-tetramethylbenzene ring carbon is a doublet (δ 139.5, $^1$J$_{PC} = 22$ Hz). This coupling constant is roughly half of that for the ipso carbon of the phosphorus substituent of 125 and 127. The resonance assigned to the ortho-tetramethylbenzene ring carbons comes at δ 137.6 ($^2$J$_{PC} = 6$ Hz). The tetramethylbenzene methyl groups have a chemical shift of δ 19.9 ($^3$J$_{PC} = 10$ Hz). The signal assigned to the ortho-phenyl ring carbons is at δ 124.8 ($^3$J$_{PC} = 20$ Hz), and has a coupling constant quite similar to 125 and 127 for the same carbon. The resonance of the meta-phenyl ring carbons is at δ 129.1 with a $^4$J$_{PC}$ of 5 Hz, the same as is found for 125. The para-phenyl (δ 128.1), and trimethylsiloxy (δ -0.1) carbon signals are both singlets.
Figure 4.9. $^{13}$C NMR spectrum of bis(phosphaalkene) 128 in CDCl$_3$. * Solvent peak CDCl$_3$.

Table 4.1. Selected $^{13}$C NMR chemical shifts and $J_{PC}$ coupling constants.

<table>
<thead>
<tr>
<th></th>
<th>17</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$, (Hz)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P=C ($^1$J$_{PC}$)</td>
<td>197.3 (56)</td>
<td>196.4 (60)</td>
<td>195.9 (55)</td>
</tr>
<tr>
<td>Ipso-Mesityl ($^1$J$_{PC}$)</td>
<td>133.2 (37)</td>
<td>133.1 (41)</td>
<td>139.5 (22)</td>
</tr>
<tr>
<td>Ipso-Phenyl ($^2$J$_{PC}$)</td>
<td>142.1 (28)</td>
<td>142.8 (34)</td>
<td>142.1 (28)</td>
</tr>
<tr>
<td>Ortho-Mesityl ($^2$J$_{PC}$)</td>
<td>142.1 (7)</td>
<td>142.1 (3)</td>
<td>137.6 (6)</td>
</tr>
<tr>
<td>Ortho-Methyl Mes ($^3$J$_{PC}$)</td>
<td>22.2 (9)</td>
<td>22.2 (0)</td>
<td>19.9 (10)</td>
</tr>
<tr>
<td>Meta-Mesityl ($^2$J$_{PC}$)</td>
<td>128.2 (9)</td>
<td>128.3 (0)</td>
<td>-</td>
</tr>
<tr>
<td>Ortho-Phenyl ($^3$J$_{PC}$)</td>
<td>124.8 (19)</td>
<td>124.4 (18)</td>
<td>124.8 (20)</td>
</tr>
<tr>
<td>Meta-Phenyl ($^3$J$_{PC}$)</td>
<td>129.3 (5)</td>
<td>-</td>
<td>129.1 (5)</td>
</tr>
</tbody>
</table>
4.1.5 Synthesis of the Polymer [-C₆Me₄-P=C(OSiMe₃)₃-C₆H₄-C(OSiMe₃)=P-] (129)

The synthesis of the corresponding all trans-isomer poly(p-phenylene-Z-phosphaalkene) (129) was attempted using a condensation polymerization (route A, Scheme 7). The bifunctional monomers 121 and 126 were intimately mixed and transferred into a thick walled Pyrex tube. The polymerization solidified into a bright orange glass after just four hours, unlike polymers 90 or 93, which required twenty-four hours of heating to become immobile. This faster formation rate is consistent with observations made on the model compounds that featured the bulky substituent at phosphorus. The brittle solid proved to be almost entirely insoluble in common organic solvents, which unfortunately precluded solution characterization. This is not unusual as there are many examples of stereo-regular, unsubstituted organic π-conjugated polymers that are crystalline and insoluble (e.g. PPV, PT, PA). The product was characterized by multinuclear CP-MAS NMR spectroscopy, and thermogravimetric analysis.

Scheme 7. Conditions and reagents: A) neat, 85°C, 2 hours. B) CDCl₃, room temperature, 14 hours.

³¹P CP-MAS NMR was used to characterize the orange polymer 129 (Figure 4.10). The major signal was detected at δ 153, which is attributed to the phosphorus in a P=C bond. This is likely due to the Z-isomer as the resonances for the model

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compounds, all of which are Z or Z,Z-isomers, are approximately δ 150. Signals at δ -147 and -155 ppm can be assigned to polymer end groups and residual 121, respectively. An unexpected signal is observed at δ 30. Its possible that this signal can be attributed to either a bis(acyl)phosphine or a 1,2- or 1,3-diphosphetane caused by two phosphaalkenes undergoing a [2+2] cycloaddition. Either moiety may be cross-linking polymer chains, leading to an insoluble material. Following the synthesis of a bis(acyl)phosphine model compound (130) which will be discussed later, we tentatively assign this signal as a bis(acyl)phosphine. There are several peaks marked with asterisks in the $^{31}$P CP-MAS NMR spectrum (Figure 4.10). These peaks are spinning side bands, derived from the main signal at δ 153. Running two spectra at different spin rates will identify spinning side bands, since the distance between the main signal and the spinning side band is exactly equal to the spin rate in Hertz. Thus, the real signals do not move, and the spinning side bands shift upon changing the spin rate.

![Diagram](image)

**Figure 4.10.** $^{31}$P CP-MAS NMR spectrum ($R_0 = 15$ kHz) of polymer 129. * Spinning side bands.
\(^{13}\)C CP MAS NMR (cross polarization magic angle spinning) spectroscopy was also used to characterize 129 (Figure 4.11). There is a diagnostic signal present at \(\delta 194\) which can assigned to \(\text{P}=\text{C}\) carbons. A broad singlet was detected at \(\delta 140\), which can attributed to the \textit{ipso} carbons of the phenyl and tetramethylbenzene rings, along with the \textit{ortho} carbons of the tetramethylbenzene by comparison with the model compounds. Another broad single resonance is present at \(\delta 126\) due to the \textit{ortho} phenyl ring carbons. The relatively sharp resonance present at \(\delta 21\) is due to the methyl carbons of the tetramethylbenzene aromatic group. The small, sharp resonance at \(\delta 3.4\) is possibly due to residual, unreacted starting material 121, or to P(SiMe\(_3\))\(_2\) polymer end groups. The larger, broad resonance can be assigned to siloxy group carbons.

![Figure 4.11. ^{13}\)C CP-MAS NMR spectrum (R\(_{0} = 15\)kHz) of polymer 129.](image)

4.1.6. Synthesis of the Bis(acyl)phosphine Mes-P-[C(O)-Ph]\(_2\) (130)

In the \(^{31}\)P CP-MAS NMR spectrum of 129, there is an unexpected signal present at \(\delta 30\). This resonance is attributed to a moiety thought to be causing cross-linking between polymer chains. There are two possible ways that poly(\(\rho\)-phenylene phosphaalkene) chains could cross-link. In the first instance, the P=\(\text{C}\) bond
could form, and subsequently cyclodimerize with another P=C bond from a neighbouring chain to form a 1,2- or 1,3-diphosphetane. Becker-type phosphaalkenes without sufficient bulk have been known to spontaneously dimerize caused by heat or light.\textsuperscript{31-48}

It seems unlikely that the cross-linking moiety is a diphosphetane as the monophosphaalkenes prepared throughout the course of this work seem to be reasonably thermally stable, as shown by the vacuum distillation of these compounds at 110-120\degree C. Heating 125 in a Schlenk bomb in a silicone oil bath at 160\degree C for a week causes sublimation even at atmospheric pressure, and a miniscule amount of decomposition is observed in the $^{31}$P NMR spectrum of an aliquot of the reaction mixture. Therefore, it is unlikely that polymer 129 is forming diphosphetanes under the reaction conditions (temperature $= 80$\degree C) given the similar steric environments.

The second possibility is that a bis(acyl)phosphine is formed when the acylphosphine intermediate reacts with a second equivalent of terephthaloyl chloride 126 before the [1,3]siloxy migration to form the phosphaalkene bond has taken place. To obtain support for the hypothesis that the unexpected signal in the $^{31}$P MAS NMR spectrum of polymer 129 was due to a bis(acyl)phosphine, two experiments were performed. The first was the preparation of bis(phenylacyl)mesitylphosphine (130) (Scheme 8). To a solution of benzoyl chloride 124 in THF heated to reflux was added dropwise a solution of 108 in THF. Several products were observed in the reaction mixture by $^{31}$P NMR spectroscopy, of which one minor component was monophosphaalkene 125. Compound 130 was purified by recrystallization from a concentrated hexanes solution stored at -35\degree C. Model compound 130 exhibits a signal at

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δ 24.9 in the $^{31}$P NMR spectrum (Figure 4.12). The multinuclear NMR solution characterization is consistent with the proposed structure of 130.

Scheme 8. Conditions and reagents: i) THF, reflux.

Figure 4.12. $^{31}$P NMR spectrum of bis(acyl)phosphine 130 in CDCl$_3$.

The acyl carbons have a $^{13}$C NMR signal at δ 209.5 ($^1J_{PC} = 34.9$ Hz) (Figure 4.13). The ipso-mesityl ring carbon resonance is a doublet at δ 145.2 ($^1J_{PC} = 15$ Hz), and the ipso-phenyl ring carbon signal is a doublet at δ 140.2 ($^2J_{PC} = 37$ Hz). The singlet at δ 131.4 can be attributed to the ortho-mesityl ring carbons, and the doublet at δ 128.3 ($^3J_{PC} = 6$ Hz) is assigned to the ortho-phenyl carbons. The para-phenyl ring carbon signal is
observed at δ 133.3 as a singlet, and similarly a singlet at δ 123.8 is attributed to the
para-mesityl ring carbon. A doublet detected at δ 129.8 (\(^3J_{PC} = 6\) Hz) is assigned to the
meta-mesityl ring carbons. The meta-phenyl ring carbons resonance is present as a
singlet at δ 128.4. The signal of the ortho-methyl mesityl group carbons can be detected
as a doublet at δ 23.4 (\(^3J_{PC} = 13.5\) Hz), and the para-methyl mesityl carbon resonance is
observed at δ 21.2 as a singlet. A comparison of the NMR spectral data of 130 to a
structurally similar bis(acyl)phosphine, \((\text{Ph-C(O)-})_2\text{P-FeCp}\), prepared by Weber and
Bungardt shows clear parallels. Weber \textit{et al.} observed a single resonance at δ 21.6 in the
\(^{31}\text{P}\) NMR spectrum, and the acyl carbon signals are detected as a singlet at δ 222 in the
\(^{13}\text{C}\) NMR spectrum.\(^{49}\)

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{figure4.13}
\caption{\(^{13}\text{C}\) NMR spectrum of bis(acyl)phosphine 130 in CDCl\(_3\). * Solvent CDCl\(_3\).}
\end{figure}

4.1.7. Solution Synthesis of \(\text{[-C}_6\text{Me}_4\text{-P=C(OSiMe}_3\text{-C}_6\text{H}_4\text{-C(OSiMe}_3\text{-P-]} (129)\)

The second experiment performed to determine whether or not the unexpected
resonance at δ 30 ppm in the \(^{31}\text{P}\) MAS NMR spectrum of 129 is due to an
bis(acyl)phosphine was an attempted solution synthesis of the target polymer on an NMR scale (route B, Scheme 7, page 165). It was speculated that if the melt in the neat polymerization was poorly mixed, this might lead to the presumed chain branching. In solution, this should not be a problem, and thus the bis(acyl)phosphine should not be observed. While monitoring the formation of 129 in solution by $^{31}$P NMR spectroscopy, several signals were observed in the phosphaalkene region, as well as the silylphosphine. Initially, the majority of the phosphaalkene resonances were observed around $\delta$ 175, significantly downfield from model compounds 125, 127, and 128 (whose chemical shifts are ca. $\delta$ 150). These resonances can be assigned to the E-isomer of the P=C bond. As discussed in the previous chapter, the formation of the E-isomer is kinetically favoured. As the polymer chains grew, however, the majority of the signal due to phosphaalkenes was detected as the Z-isomer as seen in Figure 4.14. Only trace signals were observed at $\delta$ 30, supporting the supposition that this signal is indeed due to a cross-linking bis(acyl)moiety. Unfortunately, a signal at $\delta$ -42, which can be attributed to phosphaalkene protonolysis was detected. This is not surprising, as when the first poly($p$-phenylene phosphaalkene) 90 was being prepared, extensive protonolysis was encountered when the condensation molecule, ClSiMe$_3$, was not removed prior to attempting to precipitate the polymer. It is believed that any residual amount of water in the solvent reacts with the ClSiMe$_3$ to produce HCl, which then adds across the P=C double bond. Interestingly, after several hours, the growing polymer chain precipitates out of solution as an orange/brown solid. The precipitated polymer will not redissolve. Polymers 90 and 93 are quite soluble in THF, and partially soluble in hexanes. Similar problems with insolubility are known for rigid, stereo-regular organic $\pi$-conjugated
polymers such as PPV.\textsuperscript{19} A THF extraction of solid 129 prepared from solution was analyzed by UV/Vis spectroscopy. The maximum absorbance was detected at 394 nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_14.png}
\caption{$^{31}$P NMR spectra of 129 in THF. Spectra collected after 15 min, 1 h, 2 h, 4 h, 6 h, and 8 h. * hydrolysis product.}
\end{figure}

4.2 Discussion

4.2.1. X-ray Crystal Structure of Monophosphaalkene 125

Monophosphaalkene 125 was crystallized from a concentrated hexanes solution stored at -35° C (Figure 4.15). Having the more sterically demanding substituent on the phosphorus leads to stereoselectivity for the Z-isomer. The P=C bond is 1.708Å, which is quite close to standard for a phosphorus(III)-carbon double bond.\textsuperscript{51} The sum of angles around the sp² hybridized carbon of the phosphaalkene is 359.8°. The dihedral angle ($\phi_P$) between the sterically bulky mesityl ring phosphorus substituent and the P=C plane is 65.6°, which was calculated using WinGX software.\textsuperscript{52} This is significantly larger than

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the 27.8° dihedral angle ($\phi_C$) between the P=C plane and the carbon substituent phenyl ring. Selected crystallographic data for 125, 127, and 128 is displayed in Table 4.2.

![Molecular structure of 125](image)

**Figure 4.15.** Molecular structure of 125 (50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)-C(1) = 1.7081(12), P(1)-C(11) = 1.8397(13), C(1)-C(2) = 1.4871(17), C(1)-O(1) = 1.3712(14), O(1)-Si(1) = 1.6842(9); C(1)-P(1)-C(11) = 104.20(6), P(1)-C(1)-O(1) = 125.23(9), C(2)-C(1)-O(1) = 114.46(10), C(2)-C(1)-P(1) = 120.08(9), C(2)-C(1)-P(1)-C(11) = 178.12(10).

**Table 4.2.** Comparison of key data from the X-ray analysis of 125, 127, and 128.

<table>
<thead>
<tr>
<th>Compound</th>
<th>P=C Bond (Å)</th>
<th>$\phi_P^b$</th>
<th>$\phi_C^c$</th>
<th>CP=CC Torsion Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>1.7081(12)</td>
<td>65.6</td>
<td>27.8</td>
<td>178.1(1)</td>
</tr>
<tr>
<td>127$^b$</td>
<td>1.700(2)</td>
<td>62.18</td>
<td>16.5</td>
<td>179.1</td>
</tr>
<tr>
<td></td>
<td>1.696(2)</td>
<td>66.67</td>
<td>26.55</td>
<td>-176.2</td>
</tr>
<tr>
<td>128</td>
<td>1.7014(19)</td>
<td>59.88(8)</td>
<td>25.54(9)</td>
<td>179.9</td>
</tr>
</tbody>
</table>

a) The P=C units are unique in 127; (b) this is the angle between the planes defined by the P-substituted aromatic ring (possessing steric bulk) and the plane containing the P=C bond; (c) this is the angle between the planes defined by the C-substituted aromatic ring and the plane containing the P=C bond.

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An interesting correlation appears when examining the phosphorus-carbon coupling constants. It is clear that the mesityl ring is not as strongly coupled to the phosphorus atom as the phosphaalkene carbon. The ipso-mesityl carbon one bond phosphorus-carbon coupling constant is 37 Hz, whereas the coupling constant for the carbon of the P=C bond is 56 Hz. Extending this comparison to two bonds, the ipso-phenyl carbon (δ 142.1, $^2J_{PC} = 28$ Hz) would be compared with the ortho-mesityl carbons (δ 142.1, $^2J_{PC} = 7$ Hz). There is a significant difference between the two coupling constants. A comparison of three bond phosphorus-carbon coupling constants also continues this trend. The ortho-methyl groups of the mesityl ring (δ = 22.2, $^3J_{PC} = 9$ Hz) and the meta-mesityl ring carbon (δ = 128.2, $^3J_{PC} = 9$ Hz) both show smaller coupling constants than the ortho-phenyl carbon (δ = 124.8, $^3J_{PC} = 28$ Hz). The meta-phenyl ring carbon (δ = 129.3, $^4J_{PC} = 5.4$ Hz) shows four bond phosphorus-carbon coupling while the para-mesityl ring carbon is a singlet (δ 138.2). The phenyl group, which is the ring with the smaller dihedral angle with the plane of the P=C bond shows higher $J_{PC}$ constants. It is possible that these larger coupling constants may be due to better electronic communication with the carbon atoms of the phenyl ring caused by more efficient π-conjugation. This phenomenon requires further study.

A survey of the Cambridge crystallographic database (CCD) shows eighteen reported structures of Becker-type phosphaalkenes. Of these compounds, six feature carbon substituents on the phosphorus and carbon of the P=C bond, and thus are comparable to the model compounds prepared in this chapter. Two of these structures are monophosphaalkenes (116 and 132), and four containing two phosphaalkene moieties, 131, 133, 134, and 135. The average P=C bond length of

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these compounds is 1.69 Å, which is slightly shorter than the distances for 125, 127, and 128. The average torsion angle about the C-P=C-C bond is 5.9° as reported in the CCD, which is larger than for 125, 127, and 128 which is 1.7°.

4.2.2. X-ray Crystal Structure of Bis(phosphaalkene) 127

In bis(phosphaalkene) 127, the central phenylene spacer bridges the carbons of the phosphaalkene moieties. The solid state structure determined by X-ray crystallography does not possess a centre of inversion (Figure 4.16), though 127 is quite symmetrical in solution as shown by the relatively simple NMR spectra. The two P=C bonds are very similar in length (1.700 Å versus 1.696 Å). The sum of angles around the sp² hybridized carbon of the P=C bond are also very similar, and close to 360° (359.3° versus 359.7°). The planes defined by the phosphaalkene bonds are almost coplanar with the central aryl ring (ϕC). The dihedral angles are 16.5° and 26.6° respectively, which are smaller than dihedral angles between the phosphaalkene plane and the bulkier mesityl plane (ϕP), which are 62.1° and 66.7°. Presumably, there is some π-conjugation through
the mesityl aryl ring, but not to the same extent as that through the central phenylene bridge.

Figure 4.16. Molecular structure of 127 (50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)-C(10) = 1.700(2), P(2)-C(20) = 1.696(2), P(1)-C(1) = 1.826(2), P(2)-C(24) = 1.831(2), C(10)-C(14) = 1.479(3), C(20)-C(17) = 1.481(3), C(10)-O(1) = 1.369(2), C(20)-O(2) = 1.368(2), O(1)-Si(1) = 1.6743(15), O(2)-Si(2) = 1.6788(16); C(10)-P(1)-C(1) = 106.31(9), C(20)-P(2)-C(24) = 104.19(9), O(1)-C(10)-C(14) = 114.61(16), O(1)-C(10)-P(1) = 135.79(15), C(14)-C(10)-P(1) = 119.48(14), O(2)-C(20)-C(17) = 114.23(17), O(2)-C(20)-P(2) = 125.18(14), C(17)-C(20)-P(2) = 120.33(14), C(10)-O(1)-Si(1) = 130.36(13), C(20)-O(2)-Si(2) = 127.03(13), C(1)-P(1)-C(10)-C(14) = 179.09(16), C(17)-C(20)-P(2)-C(24) = -176.24(17).

Observing the coupling constants between the phosphorus and the carbon atoms of the aryl rings, one notes that barring the ipso-carbon of the mesityl ring ($^1J_{CP} = 41$ Hz), the coupling constants are larger in the central ring. The ortho carbons of the central phenyl ring have three and four bond coupling constants ($^3J_{CP} = 18.2$ Hz, $^4J_{CP} = 17.0$ Hz) which are larger than the two bond coupling constant for the ortho carbons of the mesityl ring ($^2J_{CP} = 3.3$ Hz). As for monophosphaalkene 125, the larger coupling constants are observed in the ring with the smaller dihedral angle with the plane of the P=C group.

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This is also the ring in which one would expect better $\pi$-conjugation with the phosphaalkene bond.

### 4.2.3. X-ray Crystal Structure of Bis(phosphaalkene) 128

Considering what is observed in the solid state structures of monophosphaalkene 125 and bis(phosphaalkene) 127, one would expect that bis(phosphaalkene) 128 would exhibit a large dihedral angle between the sterically demanding central $\text{C}_6\text{Me}_4$ bridge and the plane of the $\text{P}=$C bond. One would also expect a smaller dihedral angle with the capping phenyl ring to the $\text{P}=$C plane than for the $\text{P}=$C to the central plane (Figure 4.17). Indeed, this is the case as the angles are 59.9° and 25.5°, respectively. The magnitude of the $^{31}\text{P}^{13}\text{C}$ coupling constants may provide insight into the relative amount of $\pi$-conjugation through the rings. The coupling constant for the ipso ($^2J_{\text{CP}} = 28.4 \text{ Hz}$) and ortho phenyl carbons ($^3J_{\text{CP}} = 19.5 \text{ Hz}$) are larger than the corresponding coupling constants for the ipso ($^1J_{\text{CP}} = 21.9 \text{ Hz}$) and ortho carbons ($^2J_{\text{CP}} = 5.9 \text{ Hz}$) of the tetramethylbenzene ring. Experimental crystallographic collection data is detailed in Table C1 in Appendix C.
Figure 4.17. Molecular structure of 128 (50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)-C(7) = 1.7014(19), P(1)-C(13) = 1.8432(19), C(1)-C(7) = 1.487(2), C(7)-O(1) = 1.361(2), O(1)-Si(1) = 1.6695(14); C(7)-P(1)-C(13) = 102.94(9), P(1)-C(7)-O(1) = 124.22(14), P(1)-C(7)-C(1) = 121.05(14), O(1)-C(7)-C(1) = 114.48(16), C(7)-O(1)-Si(1) = 129.94(13), C(1)-C(7)-P(1)-C(13) = 179.93(15).

There are two reported structures of bis(phosphaalkene)s in which the central phenyl group bridges between phosphorus atoms. In 1995, Knoch and Appel prepared a phenylene spaced Becker-type bis(phosphaalkene) 135 that possessed terteriary-butyl substituents at the carbons of the P=C bonds.\textsuperscript{67} The angle between the central phenyl ring plane and that of the phosphaalkene bond is 56.9°. This angle is significantly larger than the corresponding angles between the phosphaalkene plane and the unhindered aryl group in 125, 127, and 128 (Table 4.2). The bulky tert-butyl carbon substituents are a likely source of steric strain causing this large dihedral angle.
In 2000, Protasiewicz's group synthesized a 2,3,5,6-tetraarylbenzene spaced bis(phosphaalkene) 136 through a "phospha-Wittig" reaction. The torsion (dihedral) angle between the phosphaalkene plane and that of the tetraaryl substituted central spacer ($\phi_p$) was reported as 71° (69.8°), and 22° (21.8°) (numbers in parentheses calculated with the CCD browser) between the P=C plane and that of the phenyl substituent on the carbon of the phosphaalkene. Surprisingly, this dihedral angle ($\phi_p$) is only slightly larger than those observed for 125, 127, and 128 (average 63.6°). The steric bulk of the methyl groups are enough to cause a 60° twisting in the backbone of these phosphaalkenes. The sterically demanding tetraaryl substituted arylene bridge only causes a slightly larger $\phi_p$ dihedral angle, perhaps because the aryl groups twist and project past the P=C moiety. As well, these phosphaalkenes possess a very small substituent so that there is little steric interaction on one side of the P=C bond.

The solid state structures of 125, 127, and 128 show some similarities. In all cases, a large dihedral angle (> 60°) is found between the methyl substituted ring and the plane of the P=C bond. A much smaller dihedral angle is found between the unhindered ring and the plane of the P=C bond (< 30°). The rings with the smaller dihedral angle exhibit better $\pi$-conjugation with the P=C bond, as one might intuitively expect.

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4.2.4. UV/Vis Spectroscopic Data

UV/Vis spectroscopy of a THF solution of 125 revealed a broad absorbance with $\lambda_{\text{max}}$ at 324 nm (Figure 4.18, page 181). The absorbance maximum value is red-shifted by 14 nm from monophosphaalkene 87, which is a conformational isomer. The $\lambda_{\text{max}}$ of 125 is also red-shifted 10 nm from that of bis(phosphaalkene) 88. This may be partially due to the selective formation of the Z-isomer. The effect on absorption of a single isomer versus that of a mixture has not been investigated. Using $\lambda_{\text{max}}$ as an indication of the HOMO-LUMO gap, one could argue that 125 exhibits better $\pi$-conjugation. The $\lambda_{\text{max}}$ of 125 is blue-shifted by 4 nm from the maximum absorbance of bis(phosphaalkene) 110. Model compound 110 features thiophene as an aromatic bridge between phosphorus atoms, whose smaller ring size and different electronic nature appears to lead to better $\pi$-conjugation. Monophosphaalkene 109, which is analogous in structure to 125 as the phosphorus substituent is more sterically demanding than the carbon substituent, has an absorbance maximum of 357 nm, which is the longest wavelength of all the monophosphaalkenes (87, 107, 109, and 125). From the UV/Vis data, thiophene bridges lead to better $\pi$-conjugation than phenylene. Also, only having only one isomer present, preferentially the Z-isomer, leads to more efficient $\pi$-conjugation.
Table 4.3. $\lambda_{\text{max}}$ values for Becker-type phosphaalkenes prepared in this thesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Z/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td>310</td>
<td>0.85</td>
</tr>
<tr>
<td>88</td>
<td>314</td>
<td>1.27</td>
</tr>
<tr>
<td>89</td>
<td>332</td>
<td>0.13</td>
</tr>
<tr>
<td>Polymer 90</td>
<td>338</td>
<td>1.14</td>
</tr>
<tr>
<td>107</td>
<td>328</td>
<td>3.17</td>
</tr>
<tr>
<td>109</td>
<td>357</td>
<td>1.43</td>
</tr>
<tr>
<td>110</td>
<td>347</td>
<td>1.56</td>
</tr>
<tr>
<td>Polymer 93</td>
<td>379</td>
<td>1.51</td>
</tr>
<tr>
<td>125</td>
<td>324</td>
<td>-</td>
</tr>
<tr>
<td>127</td>
<td>388</td>
<td>-</td>
</tr>
<tr>
<td>128</td>
<td>337</td>
<td>-</td>
</tr>
<tr>
<td>Polymer 129</td>
<td>394</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.18. UV/Vis Spectra of model compounds and polymer in THF (ca. $10^{-5}$ M).
The UV/Vis spectrum of a THF solution of bis(phosphaalkene) 127 exhibited an absorbance maximum of 388 nm. The small dihedral angles between the central phenylene bridge and the planes of the P=C allows effective \( \pi \)-conjugation from one phosphaalkene moiety to the other. Having the \( \pi \)-system of the central aromatic spacer interact with the phosphaalkene \( \pi \)-bond through the carbon seems to lead to better \( \pi \)-conjugation as seen by comparing 127 with bis(phosphaalkene) 89. The UV/Vis absorption maximum of 89 is 332 nm, which is blue-shifted by 56 nm in comparison to 127. Presumably the more diffuse 3p orbital of the phosphorus atom does not overlap as well with the \( \pi \)-system of the central aromatic spacer. Similarly, the P=C \( \pi \) bond is approximately 65% the strength of C=C bond.\(^70\) Following the same trend starting with monophosphaalkene 125 and 109, a comparison of bis(phosphaalkene)s 89 and 110, shows that 110 has a more effective \( \pi \)-conjugation as evinced by the larger \( \lambda_{\text{max}} \) of 347 nm. In bis(phosphaalkene) 127, there is likely some \( \pi \)-conjugation through the capping mesityl aryl rings, but not to the same extent as that through the central bridging phenylene spacer due to the larger dihedral angles (\( \phi_p = 64.4^\circ \) average).

Bis(phosphaalkene) 127 has the UV/Vis maximum absorption of the longest wavelength out of all the model compounds prepared. Only polymer 129 has a \( \lambda_{\text{max}} \) with a longer wavelength (394 nm).

The UV/Vis absorption maximum of bis(phosphaalkene) 128 is 337 nm, red-shifted by 13 nm from monophosphaalkene 125. In general, a red shifted absorption maximum indicates a longer conjugation pathway, or more efficient \( \pi \)-conjugation if the two systems being compared are the same size. Thus, a red-shift in \( \lambda_{\text{max}} \) between 125 and 128 indicates some \( \pi \)-conjugation through the central tetramethylbenzene spacer despite

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that large dihedral angle ($\phi_p = 59.9^\circ$). If there were no communication of the $\pi$ systems on each side of the tetramethylbenzene spacer the $\lambda_{\text{max}}$ for 128 and 125 would be the same. This suggests that the poly(arylene-$Z$-phosphaalkene) should show extended $\pi$-conjugation through the P=C bonds in the backbone of the macromolecule. The $\lambda_{\text{max}}$ of bis(phosphaalkene) 128 compared to bis(phosphaalkene) 127 is blue-shifted by 51 nm. This data can be rationalized by observing the large dihedral angles between the central bridge of bis(phosphaalkene) 128 ($59.9^\circ$) compared to bis(phosphaalkene) 127 ($21.5^\circ$ average). This suggests that the larger dihedral angle of 128 does not conduct $\pi$-conjugation as well as the more planar phenyl bridge of 127. Bis(phosphaalkene) 88 is more structurally similar to 128, as both share a central tetramethylbenzene bridge, and capping phenyl groups. The $\lambda_{\text{max}}$ of 88 is 314 nm, which is blue shifted from that of 128 by 23 nm. This comparison suggests that the majority of the $\pi$-conjugation is taking place through the P=C bonds and the capping phenyl rings, and not through the central bridge, although we have already seen that some communication does span the tetramethylbenzene ring. This seems intuitive as the dihedral angle ($\phi_p = 59.9^\circ$) between the plane of the phenyl ring and the P=C bond is much smaller than between the P=C bond and the tetramethylbenzene bridge ($\phi_C = 25.5^\circ$). The observed increase in $\lambda_{\text{max}}$ of 128 compared to 88 is likely caused by the capping phenyl $\pi$-system having a better interaction the with 2p orbital of the carbon of the P=C bond in 128 than the 3p orbital of the phosphorus atom of the P=C bond in 88.

The UV/Vis spectrum of polymer 129 synthesized in solution shows an absorbance maximum of 394 nm. This absorbance maximum has the longest wavelength of any of the Becker-type phosphaalkene materials prepared to date. The red-shift in the
absorbance maximum compared to model compounds indicates that there are compounds in solution with longer conjugation pathways than the model compounds. A molar absorptivity could not be determined for this experiment as not all of the material weighed out dissolved into solution. Note that the UV/Vis spectroscopy of 129 was performed on a THF extraction of a poorly soluble polymer. This suggests that the species in solution are not the longest chains of polymer, but likely the shortest. This rationalizes the relatively small shift in \( \lambda_{\text{max}} \) between bis(phosphaalkene) 127 and polymer 129. A \( \lambda_{\text{max}} \) of even longer wavelength would likely be observed if a solid-state UV/Vis spectrum was acquired. However, the only apparatus available could not be sealed, and thus the air and moisture sensitivity of the polymer precluded this measurement.

4.3 Summary

Using precursors for which the substituent at phosphorus is more sterically demanding than the substituent at carbon leads to selective formation of the Z-isomer of the phosphaalkene bond. This is fortunate, as the Z-isomer features the aryl groups in \textit{trans} positions across the phosphorus(III)-carbon double bond. Model compounds 125, 127, and 128 were synthesized and characterized. As these phosphaalkenes consist of only one isomer, it was possible to grow crystals suitable for X-ray crystallography, and determine solid state structures of these compounds. These compounds with only the Z-isomer show UV/Vis absorbance maxima that are red shifted from the corresponding mono- (87) and bis(phosphaalkene)s (88, 89) with the steric bulk on the carbon of the P=C bond discussed in chapter two.

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An attempted synthesis of the poly(arylene-Z-phosphaalkene) 129 by a previously published method led to an orange, partially cross-linked material. $^{31}$P and $^{13}$C CP MAS solid state NMR showed this material to contain P=C bonds. Synthesizing the same polymer in solution leads to a linear chain that precipitates after a few hours. The growing polymer’s insolubility precluded most solution characterization, but a THF extraction of the polymer gave a UV/Vis absorption maximum that is red shifted from that of the model compounds. This shift in the absorbance maximum to a lower energy indicates that there are soluble molecules in the extraction that have a more extensive $\pi$-conjugated system than that of the model compounds. Monitoring the formation of 129 in solution by $^{31}$P NMR spectroscopy, it appears that the $E$-isomer of the P=C bond is initially formed, but subsequently converted to the $Z$-isomer.
4.4 Experimental Section

General Procedures. X-ray crystallography performed by Dr. Brian Patrick in the Departmental Crystallography Lab. A Bruker X8 Apex and a Rigaku/ADSC CCD diffractometer were used to collect refraction data. Elemental analysis of several compounds were performed by Minaz Lakha, but did not match theoretical values despite the samples being pure by $^1$H, $^{31}$P, and $^{13}$C NMR spectroscopy.

Materials. 1,2,4,5-tetramethylbenzene (durene), 2-bromomesitylene, bromine, PCl$_3$, Me$_3$SiCl, Mg, SOCl$_2$, LiAlH$_4$, MeLi (1.6 M in ethyl ether), and tBuLi (1.7 M in pentane) were purchased from Aldrich and used as received. PhCOCl, Et$_2$NH, PhPCl$_2$ were purchased from Aldrich and distilled prior to use. 1,4-C$_6$H$_4$(COCl)$_2$, MesCOCl, PhCOCl, Et$_2$NH, PhPCl$_2$ were prepared following the literature procedures.

4.4.1 Preparation of 1,4-[P(NEt$_2$)$_2$]$_2$-C$_6$Me$_4$ (118). To a stirred solution of 1,4-dibromotetramethylbenzene (9.98 g, 34.2 mmol) in THF (350 mL) was added drop wise tBuLi (83 mL, 1.7 M, 140 mmol) at $-78^\circ$ C. The reaction mixture was allowed to warm to ambient temperature and stirred for four hours. The peach colored lithiate suspension was recooled to $-78^\circ$ C and was added drop wise to a stirred solution of chlorobis(diethylamino)phosphine (15.8 g, 75.2 mmol) in Et$_2$O (100 mL) at $-78^\circ$ C. Subsequently, the reaction mixture was allowed to warm slowly to room temperature (1 hour). The solvent was removed in vacuo, the product was extracted into hexanes (2 x 350 mL) and filtered, and the hexanes was removed in vacuo affording a viscous yellow fluid. Yield = 14.1 g (85%).
31P NMR (C\textsubscript{6}D\textsubscript{6}): δ 111.5 (s); \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}): δ 3.2 (q, \textsuperscript{3}J\textsubscript{HH} = 7 Hz, 16H, N-CH\textsubscript{2}CH\textsubscript{3}), 1.2 (s, 12H, Ar-CH\textsubscript{3}), 1.0 (t, \textsuperscript{3}J\textsubscript{HH} = 7 Hz, 24H, N-CH\textsubscript{2}CH\textsubscript{3}).

4.4.2 Preparation of 1,4-1,4-\textsubscript{2}PCl\textsubscript{2}-C\textsubscript{6}Me\textsubscript{4} (119). A stirred solution at 0° C of 1,4-bis(diethylaminophosphino)-2,3,5,6-tetramethylbenzene (14.1 g, 29.2 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (100 mL) was slowly purged with anhydrous HCl. After approximately 30 min of purging, 119 (δ 164) was formed quantitatively as determined from 31P NMR spectroscopy. The solvent was removed in vacuo, the product extracted with hexanes (2 x 350 mL) and filtered, and the hexanes was removed in vacuo. Vacuum sublimation (50 °C, 0.1 mmHg) afforded 119 as a white solid. Yield = 4.1 g (43 %).

31P NMR (CDCl\textsubscript{3}): δ 163.7 (s); \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 2.67 (s, o-CH\textsubscript{3}).

4.4.3 Preparation of 1,4-1,4-\textsubscript{2}PH\textsubscript{2}-C\textsubscript{6}Me\textsubscript{4} (120). To a cooled (-78 °C) suspension of LiAlH\textsubscript{4} (0.6 g, 15.8 mmol) in Et\textsubscript{2}O (100 mL) was added drop wise 1,4-bis(dichlorophosphino)-2,3,5,6-tetramethylbenzene (1.69 g, 5.0 mmol) in Et\textsubscript{2}O (200 mL). After the addition was complete, the reaction was warmed to room temperature. \textsuperscript{31}P NMR spectroscopy of an aliquot removed from the reaction mixture confirmed that 120 had been formed quantitatively. Degassed water (ca 200 mL) was added to quench excess LiAlH\textsubscript{4} (CAUTION: extreme care should be taken when adding the first few mL of water since the quenching is highly exothermic and H\textsubscript{2} is evolved). The Et\textsubscript{2}O layer was separated and the aqueous layer was extracted with a further 150 mL of Et\textsubscript{2}O. The organic layers were combined, filtered, dried with MgSO\textsubscript{4}, and the ether was removed in vacuo. Vacuum sublimation (30 °C, 0.1 mm Hg) of the product afforded 120 as a colorless solid. Yield: 0.80 g (80 %).
$^{31}$P NMR (CDCl$_3$): δ $-145.4$ (t, $^1$J$_{PH} = 207$ Hz); $^1$H NMR (CDCl$_3$): δ 3.70 (d, $^1$J$_{PH} = 207$
Hz, -PH$_2$), 2.33 (s, o-CH$_3$).

**4.4.4 Preparation of 1,4-1,4-[P(SiMe$_3$)$_2$]-C$_6$Me$_4$ (121).** To a cooled (−78 °C) solution of 1,4-phosphino-2,3,5,6-tetramethylbenzene (1.2 g, 6.1 mmol) in Et$_2$O (150 mL) was added drop wise MeLi (17.0 mL, 1.5 M, 25.5 mmol). The reaction was allowed to warm to room temperature where it was stirred for 2 h. Subsequently, the solution was cooled to −78°C and Me$_3$SiCl (3.2 mL, 2.5 mmol) was added drop wise. Analysis of an aliquot removed from the reaction mixture by $^{31}$P NMR spectroscopy revealed that 121 was formed quantitatively. The solvent was removed in vacuo, the product was extracted into hexanes (2 x 150 mL) and filtered, and the hexanes was removed in vacuo. Vacuum sublimation (ca. 100−110 °C using a heat gun, 1 mmHg) afforded colorless crystals of 121. Yield = 2.1 g (71 %).

$^{31}$P NMR (CDCl$_3$): δ $-153.7$ (s); $^1$H NMR (CDCl$_3$): δ 2.56 (s, 12H, o-CH$_3$), 0.20 (d, 36H, $^3$J$_{PH} = 5.8$ Hz, Si(CH$_3$)$_3$), $^{13}$C NMR (CDCl$_3$): δ 140.4 (dd, $^2$J$_{PC} = 4$ Hz, $^3$J$_{PC} = 3$ Hz, o-tmb), 131.4 (d, $^1$J$_{PC} = 11$ Hz, i-tmb), 24.9 (d, $^3$J$_{PC} = 13$ Hz, tmb-CH$_3$), 2.1 (d, $^2$J$_{PC} = 12$
Hz, Si(CH$_3$)$_3$); MS (EI, 70 eV): 490, 489, 488, 487, 486, (1, 4, 15, 30, 66) [M$^+$], 473,
472, 471, (2, 5, 8) [M$^+$ − CH$_3$], 416, 415, 414, 413, (2, 7, 15, 22) [M$^+$ − SiMe$_3$], 310, 309,
308, (2, 2, 7) [M$^+$ − P(SiMe$_3$)$_2$], 75, 74, 73, (4, 8, 100) [SiMe$_3^+$].

**4.4.5 Preparation of Monophosphaalkene Z-Mes-P=C(OSiMe$_3$)-Ph (125).** To a solution of bis(trimethylsilyl)mesitylphosphine (6.07 g, 204 mmol) in THF (20 mL) was added drop wise PhCOCl (2.87 g, 204 mmol) in THF (5 mL). After a day at room temperature 125 was formed quantitatively as suggested by $^{31}$P NMR spectroscopy and the solvent was removed in vacuo. Recrystallization from a minimal amount of hexanes

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at -35° C afforded crystals of 125 suitable for X-ray crystallography. Yield = 2.7 g (40 %).

$^{31}$P NMR (CDCl$_3$): δ 141.5 (s); $^1$H NMR (CDCl$_3$): δ 7.81 (m, 2H, o-Ph), 7.30 (m, 3H, m, p-Ph), 6.87 (s, 2H, m-Mes), 2.41 (s, 6H, o-CH$_3$), 2.27 (s, 3H, p-CH$_3$), -0.20 (s, 9H, Si(CH$_3$)$_3$), $^{13}$C NMR (CDCl$_3$): δ 197.3 (d, $^1$J$_{PC}$ = 56 Hz, P=O), 142.1 (d, $^2$J$_{PC}$ = 28 Hz, i-Ph; d, $^2$J$_{CP}$ = 7 Hz, o-Mes), 138.2 (s, p-Mes), 133.2 (d, $^1$J$_{CP}$ = 37 Hz, i-Mes), 129.3 (d, $^4$J$_{CP}$ = 5.4 Hz, m-Ph), 128.2 (d, $^3$J$_{CP}$ = 9 Hz, m-Mes, p-Ph), 124.8 (d, $^3$J$_{CP}$ = 19 Hz, o-Ph), 22.2 (d, $^3$J$_{CP}$ = 9 Hz, o-CH$_3$ Mes), 22.1 (s, p-Mes), -0.1 (s, Si(CH$_3$)$_3$); UV/Vis: $\lambda_{\text{max}}$(ε) = 324 nm (14000); MS (EI, 70 eV): 330, 329, 328, (7, 26, 100) [M$^+$], 314, 313, (2, 8) [M$^+$ - CH$_3$], 252, 251, (3, 12) [M$^+$ - Ph], 240, 239, 238, (2, 14, 48) [M$^+$ - HOSiMe$_3$], 79, 78, 77, (2, 4, 29) [Ph$^+$], 74, 73, (5, 59) [SiMe$_3^+$].

4.4.6 Preparation of Bis(acyl) phosphine Mes-P(-C(0)-Ph)$_2$ (130). To a solution of PhCOCl (3.01 g, 21.4 mmol) in THF (10 mL) heated to reflux was added drop wise bis(trimethylsilyl)mesitylphosphine (3.17 g, 10.7 mmol) in THF (5 mL). The reaction mixture was heated to reflux for 1 h and, subsequently, the solvent was removed in vacuo. Recrystallization from hexanes at -35 °C afforded crystals of 130. Yield = 2.7 g (70 %).

$^{31}$P NMR (CDCl$_3$): δ 24.9 (s); $^1$H NMR (CDCl$_3$): δ 7.8 (dt, $^3$J$_{HH}$ = 8 Hz, $^3$J$_{HH}$ = 1 Hz, m-Ph), 7.5 (tt, $^3$J$_{HH}$ = 7 Hz, $^4$J$_{HH}$ = 1 Hz, p-Ph), 7.4 (td, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 1 Hz, o-Ph), 6.8 (d, $^4$J$_{PH}$ = 3 Hz, m-Mes), 2.4 (s, o-CH$_3$ Mes), 2.2 (s, p-CH$_3$ Mes); $^{13}$C NMR (CDCl$_3$): δ 209.5 (d, $^1$J$_{PC}$ = 35 Hz, P-C=O), 145.2 (d, $^1$J$_{PC}$ = 15 Hz, i-Mes), 141.5 (s, o-Mes), 140.2 (d, $^2$J$_{PC}$ = 37 Hz, i-Ph), 133.3 (s, p-Ph), 129.8 (d, $^3$J$_{PC}$ = 6 Hz, m-Mes), 128.4 (s, m-Ph), 128.3 (d, $^3$J$_{PC}$ = 6 Hz, o-Ph), 123.8 (s, p-Mes), 23.4 (d, $^3$J$_{PC}$ = 13.5 Hz, o-CH$_3$ Mes), 21.2
4.4.7 Preparation of Bis(phosphaalkene) $Z,Z-1,4-[\text{Mes-P=C(OSiMe}_3)]_2-C_6H_4$ (127).

To a solution of bis(trimethylsilyl)mesitylphosphine (1.07 g, 3.6 mmol) in THF (10 mL) was added drop wise 1,4-(Cl(0)C)$_2$C$_6$H$_4$ (366 mg, 1.8 mmol) in THF (20 mL). After ca. 5 h at room temperature 127 was formed quantitatively as suggested by $^{31}$P NMR spectroscopy. The solvent was removed slowly in vacuo until the solution was saturated and crystals began to form (ca. half the initial volume). Yellow crystals of 127 suitable for X-ray crystallography were isolated upon standing (ca. 18 h, 25 °C). Yield = 1.48 g (71%).

$^{31}$P (CDCl$_3$): $\delta$ 146.3 (s); $^1$H NMR (CDCl$_3$): $\delta$ 7.75 (s, o-Ph), 6.87 (s, m-Mes), 2.40 (o-CH$_3$ Mes), 2.27 (s, p-CH$_3$ Mes), −0.19 (s, Si(CH$_3$)$_3$); $^{13}$C NMR (CDCl$_3$): $\delta$ 196.4 (d, $^1$J$_{CP}$ = 60 Hz, P=C), 142.8 (d, $^2$J$_{CP}$ = 34 Hz, i-Ph), 142.1 (m, $^2$J$_{CP}$ = 3 Hz, o-Mes), 138.3 (s, p-Mes), 133.1 (d, $^1$J$_{CP}$ = 41 Hz, i-Mes), 128.3 (s, m-Mes), 124.4 (dd, $^3$J$_{CP}$ = 18 Hz, $^4$J$_{CP}$ = 17 Hz, o-Ph), 22.2 (s, o-CH$_3$ Mes), 21.1 (s, p-CH$_3$ Mes), −0.1 ppm (s, Si(CH$_3$)$_3$); UV/Vis (THF): $\lambda_{\text{max}}(\epsilon) = 388$ nm (6400).

4.4.8 Preparation of Bis(phosphaalkene) $Z,Z-1,4-[\text{Ph-(OSiMe}_3]C=P]_2-C_6Me_4$ (128).

To a solution of 121 (300 mg, 0.6 mmol) in THF (3 mL) was added drop wise PhCOCl (173 mg, 1.2 mmol) in THF (1 mL). After several days at room temperature 128 was formed quantitatively as suggested by $^{31}$P NMR spectroscopy and the solvent was removed in vacuo. Crystals of 128 suitable for X-ray crystallography were obtained by slow solvent evaporation from a THF solution. Yield = 0.21 g (62%).
Chapter Four

$^{31}$P{${}^1$H} NMR (CDCl$_3$): $\delta$ 150.2 (s); $^1$H NMR (CDCl$_3$): $\delta$ 7.80 (br s, o-Ph), 7.32 (br s, p-Ph), 7.31 (br s, m-Ph), 2.42 (s, o-CH$_3$tmb), -0.24 (s, Si(CH$_3$)$_3$); $^{13}$C{${}^1$H} NMR (CDCl$_3$):

$\delta$ 195.9 (d, $^1$J$_{CP}$ = 55 Hz), 142.1 (d, $^2$J$_{CP}$ = 28 Hz, i-Ph), 139.5 (d, $^1$J$_{CP}$ = 22 Hz, i-tmb), 137.6 (d, $^2$J$_{CP}$ = 6 Hz, o-tmb), 129.1 (d, $^4$J$_{CP}$ = 5 Hz, m-Ph), 128.1 (s, p-Ph), 124.8 (d, $^3$J$_{CP}$ = 20 Hz, o-Ph), 19.9 (d, $^3$J$_{CP}$ = 10 Hz, o-CH$_3$tmb), -0.1 ppm (s, Si(CH$_3$)$_3$). UV/Vis

(THF): $\lambda_{\text{max}}(\epsilon) = 337 \text{ nm (28000)}$; MS (EI, 70 eV): 553, 552, 551, 550, (1, 4, 11, 25) [M$^+$], 478, 477, (2, 5) [M$^+$ - SiMe$_3$], 463, 463, 361, (1, 3, 8) [M$^+$ - OSiMe$_3$], 179, 178, (2, 12) [Ph-C(OSiMe$_3$)$_2$ $^+$], 106, 105, (8, 100) [Ph-CO$^+$], 78, 77, (3, 43) [Ph$^+$], 74, 73, (5, 68) [SiMe$_3^+$].

4.4.9 Preparation of Polymer [-C$_6$Me$_4$P=C(OSiMe$_3$)-C$_6$H$_4$-(OSiMe$_3$)C=P-] (129).

Silylphosphine 121 (1.10 g, 2.26 mmol) and terephthaloyl chloride (459 mg, 2.26 mmol) were intimately mixed as finely ground powders, and flame sealed in vacuo in a thick walled Pyrex tube. The sample was placed in a pre-heated oven (85° C) whereupon the solids melted forming a colorless free flowing liquid. The clear fluid quickly became yellow, then orange. After two hours, the reaction mixture had become a dark orange solid. The sealed tube was evacuated to remove the condensation molecule, chlorotrimethylsilane. The polymer proved to be totally insoluble in polar, aprotic solvents. The polymer is a hard, brittle solid, which was broken into pieces in order to remove the polymer from the polymerization tube. The isolated yield was 0.95 g (88%).

$^{31}$P MAS NMR (Rotation =15 kHz): $\delta$ 153 (br s, P=C), 30.0 (br s, P(C=O)$_2$), -147 (br s, polymer P(SiMe$_3$)$_2$ end groups), -155 ppm (br s, P(SiMe$_3$)$_2$ starting material); $^{13}$C CP MAS NMR (Ro = 15 kHz): $\delta$ 194 (s, P=C), 140 (br s, i-Ph, i-tmb, o-tmb), 126 (br s, o-Ph), 21 (br s, tmb-CH$_3$), 3.4 (br s, OSiMe$_3$), 2.3 (br s, OSiMe$_3$), 0.5 (br s, SiMe$_3$).

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4.4.10 Solution Preparation of Polymer [-C₆Me₄-P=C(OSiMe₃)-C₆H₄-(OSiMe₃)C=P-] (129). To a stirred solution of 121 (100 mg, 0.2 mmol) dissolved in THF (0.75 mL) was added drop wise terephthaloyl chloride (42 mg, 0.2 mmol) in THF (0.75 mL). The reaction progress was followed by $^{31}$P NMR and after approximately 6 hours an orange solid precipitated from solution. The solvent was removed in vacuo leaving a yellow film, and an orange, insoluble solid.

$^{31}$P{¹H} NMR (THF) $\delta$ 180-170 (br s, $E$-P=C), 155-145 (br s, $Z$-P=C), 30 (s, P(-C=O-Ph)$_2$), -43 (s, PH-C=O), -153 (s, P(SiMe$_3$)$_2$ end groups), -155 (s, P(SiMe$_3$)$_2$ residual starting material); UV/Vis (THF): $\lambda_{max}(\varepsilon) = 394$ nm (unknown).

References start on page 193
4.5 References


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Chapter Five
Towards Air and Moisture Stable Poly(p-phenylenephosphaalkene)s

5.0 Introduction

Many of the difficulties in characterizing the materials presented in this thesis up to this point stem from the sensitivity of the compounds towards air and moisture. This sensitivity is likely not due to the strength of the P=C bond, which is calculated to be approximately 2/3 the strength of the C=C bond (45 versus 65 kcal/mol), but due to the presence of the trimethylsiloxy group (Scheme 1). The phosphaalkene (137), or more accurately the siloxy group of the phosphaalkene, reacts with water, or an alcohol. The siloxy group is eliminated, and abstracts a group from the three-coordinate oxygen intermediate (138). This newly formed alcohol (139) tautomerizes to an acyl phosphine (140).

![Scheme 1.](image)

Initially, one of the reasons we chose the Becker synthetic route was that the production of the siloxy group is thermodynamically quite favourable due to the

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formation of the silicon-oxygen bond, ensuring the reaction proceeds quantitatively.\(^7\) As we must use a step-growth polymerization to synthesize macromolecules containing P=C bonds in the main polymer chain, the reaction must be efficient to form a macromolecule of appreciable weight as shown by the Carother’s equation (Equation 1). Recall that \(p\), the degree of reaction, is a normalized measure of reaction progress. The equation governing the relationship between \(p\) and \(\bar{X}_n\) becomes more complex if the stoichiometries of the two monomers are not matched exactly (i.e. when the monomer molar ratio, \(r \neq 1\)) (Equation 2).

\[
\bar{X}_n = \frac{1}{(1 - p)} \quad (1)
\]

\[
\bar{X}_n = \frac{1 + r}{(1 + r - 2rp)} \quad (2)
\]

However, the Becker route is not the only synthetic method for preparing phosphaalkenes.\(^7,8\) Two years after Becker reported the first isolable, acyclic compound containing a localized P=C bond in 1976,\(^9\) Bickelhaupt and coworkers presented a phosphaalkene consisting of three aryl substituents (Scheme 2).\(^10\) Starting with dichloromesitylphosphine (141), subsequent treatment with diphenylmethyllithium affords chlorophosphine 142. The \(P\)-mesityldiphenylmethylenephosphine (115) was prepared via a base induced 1,2-elimination outlined in Scheme 2.

Scheme 2. Conditions and reagents: i) THF, -20°C, 1 equiv. LiCH(C\(_6\)H\(_5\))\(_2\). ii) THF, 22°C, 1 equiv. DBU.

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A few years after this report, Becker et al. prepared 115 through a novel, arguably more convenient synthetic method. Starting with bis(trimethylsilyl)mesitylphosphine (108) and benzophenone (143), Becker used a base catalyzed condensation reaction to prepare phosphaalkene 115 (Scheme 3). One of the products of the condensation, hexamethyldisiloxane (144) is easily separated due to its low boiling point. In the Gates lab, this reaction has been used with great success to prepare a variety of phosphaalkenes, as well as synthesizing 115 on multigram scales in only a few hours. During purification, a solution of crude 115 can be extracted with degassed H₂O to remove the base catalyst (NaOH or KOH). A similar addition of an alcohol to a solution of a Becker-type phosphaalkene results in the formation of an acylphosphine as outlined in Scheme 1. Phosphaalkenes with all carbon substituents are significantly more robust than Becker-type phosphaalkenes. Perhaps, with suitable bifunctional starting materials, and the correct conditions, a poly(p-phenylene phosphaalkene) could be prepared with phosphaalkenes lacking the hydrolytically sensitive siloxy group. In this chapter, some preliminary results towards this goal, namely the synthesis and characterization of a bis(phosphaalkene) are presented.

Scheme 3.
5.1 Results

5.1.1. Synthesis of the Bis(phosphaalkene) 1,4-[Ph₂C=P]₂-C₆Me₄ (145)

In the same paper that detailed the first synthesis of 115, Bickelhaupt and coworkers also reported the attempted synthesis of the phosphaalkenes with phenyl, and ortho-Me-phenyl phosphorus substituents. In the latter two cases, these phosphaalkenes were not isolable, and a "polymeric material" resulted. The phrase "polymeric material" is occasionally used in heavier main group element multiple bond chemistry to describe the result of failed attempts to prepare the desired low coordinate compound.

Interestingly, while 2-methylphenyl does not appear to have enough steric bulk to prevent subsequent reaction of the P=C bond, the 2,6-dimethylphenyl group does. This would seem to indicate that conjugation with the aromatic rings is not enough to stabilize these systems, and that steric protection is also required.

As the monophosphaalkene 115 was already known, we turned our attention to the synthesis of a bis(phosphaalkene). To our knowledge, a bis(phosphaalkene) has never been prepared via this synthetic route. Thankfully, a suitable sterically demanding, bifunctional silylphosphine (121) had previously been synthesized for work discussed in chapter four. Compound 121 and two equivalents of 143 were dissolved in a minimal amount of THF, and a catalytic amount of solid KOH was introduced into the reaction mixture (Scheme 4). The reaction mixture was heated to 80°C, and the reaction progress was monitored by ³¹P NMR spectroscopy. Near quantitative formation of bis(phosphaalkene) 145 was observed over 3-4 days. Crystals of 145 suitable for X-ray crystallography were grown by slow solvent evaporation of the reaction mixture.
Bis(phosphaalkene) 145 was further characterized by multinuclear NMR spectroscopy, UV/Vis spectroscopy, and mass spectrometry.

Scheme 4. Conditions and reagents: i) THF, 22° C, cat. KOH, 3 days; 80° C, 2 days.

Unlike the Becker-type bis(phosphaalkene)s discussed in chapter four, the $^{31}$P NMR spectrum of 145 has more than one resonance (Figure 5.1). There are two resonances detected, of approximately equal intensity. Although $E$ and $Z$-isomers are not possible as the phosphaalkene carbon substituents being identical, this could possibly be due to syn and anti isomers. The two phenyl substituents at carbon may have restricted rotation about the plane of the tetramethylbenzene spacer. Similar observations were made in chapter two where the $^{31}$P NMR spectrum of a bis(phosphaalkene) spaced by a tetramethylphenyl ring revealed twice the number of resonances expected for $EE$, $EZ$, and $ZZ$ isomers.

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The $^{1}$H NMR spectrum of 145 also reveals that the molecule is not symmetric in solution on the NMR timescale as there are two signals for the methyl groups of the central tetramethylphenyl ring (Figure 5.2). Other than these two singlets, there is a series of five multiplets in the aromatic region due to the twenty protons of the four phenyl rings.

The $^{13}$C NMR spectrum of 145 also indicates a lack of symmetry in solution (Figure 5.3). Significantly, there is a pair of doublets in the phosphaalkene carbon region.
at δ 193.2 (1J_{PC} = 42 Hz) and δ 192.3 (1J_{PC} = 43 Hz). This would seem to indicate that the phosphaalkene carbon centres are magnetically inequivalent. A multiplet at δ 144.5 can be assigned to the ipso carbon of the phenyl rings. Several doublets at δ 142.6 (1J_{PC} = 43.2 Hz) and a doublet of doublets at δ 137.5 (2J_{PC} = 8.2 Hz, 3J_{PC} = 7.5 Hz) can be assigned to the ipso and ortho carbons of the tetramethylphenyl central ring, respectively. The resonances detected at δ 21 can be assigned to the methyl groups of the tetramethylphenyl ring. The signals may be split due to three bond phosphorus-carbon coupling, but may also be reflecting the lack of molecular symmetry in solution.

Figure 5.3. 13C NMR spectrum of bis(phosphaalkene) 145 in CDCl₃. ~ Solvent peak CDCl₃, offscale.

The electronic structure of 145 was investigated by UV/Vis spectroscopy (Figure 5.4). A THF solution (ca. 10⁻⁵ M) was examined, and two broad absorptions were observed. The higher energy absorbance was detected at 245 nm, as a shoulder on a larger absorption. The absorption maximum of the second peak is 331 nm. Of the two transitions possible for the P=C bond, namely the n-π* and the π-π*, it is likely that this

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absorbance may be attributed to a $\pi-\pi^*$ transition.\(^\text{15}\) The $n-\pi^*$ transitions is formally a spin (parity) forbidden transition, and rarely observed in the UV/Vis absorption spectra of phosphaalkenes.\(^\text{2,7}\) Klebach et al. attributed the higher energy absorbance to the $n-\pi^*$ transition, as this absorption was missing for a complex of monophosphaalkene 115 coordinated to a metal centre.\(^\text{10}\)

![UV/Vis spectrum of 145](image)

**Figure 5.4.** UV/Vis spectrum of 145 (ca. $10^{-5}$ M) in THF.

5.1.2. Attempted Synthesis of the Bis(phosphaalkene) $1,4$-[Mes-P=C(Ph)]$_2$-C$_6$H$_4$ (147)

Having successfully prepared bis(phosphaalkene) 145, we attempted the synthesis of a bis(phosphaalkene) where the central aromatic spacer bridged the phosphaalkene carbon atoms (Scheme 5). We chose 1,4-dibenzoylbenzene (146) as the bifunctional reagent, and bis(trimethylsilyl)mesitylphosphine (108) as the bulky phosphorus
compound. In the first attempt at synthesizing 147, a similar base catalyzed condensation synthetic route was employed as was utilized to prepare 145. After several hours, a reaction aliquot examined by $^{31}$P NMR spectroscopy suggested that a small amount of phosphaalkene had formed, but a larger amount of unidentified products had also formed (Figure 5.5). After several days of stirring at room temperature, the reaction had hardly progressed as monitored by $^{31}$P NMR spectroscopy. Additional KOH was added to the reaction mixture in an attempt to drive the reaction to completion. After the reaction had proceeded for one week, the reaction mixture was transferred into a Kontes bomb and heated to 100°C for 24 hours. Little change in the progress of the reaction was observed (Figure 5.5, spectrum f).

Scheme 5. Conditions and reagents: i) THF, 22°C, cat. KOH, 1 week.
While monitoring the reaction by $^{31}$P NMR spectroscopy, it was noted that several of the signals appeared to exhibit phosphorus-phosphorus coupling. An aliquot from the reaction mixture was examined by a two dimensional $^{31}$P-$^{31}$P COSY NMR experiment.
(Figure 5.6). Several off-diagonal resonances were detected. A pair of coincident doublets at $\delta$ -24 ($J_{PP} = 180$ Hz) are coupled with a resonance in the series of unresolved signals centred at $\delta$ -102. A doublet situated at $\delta$ -108 ($J_{PP} = 184$ Hz) is coupled to a triplet observed at $\delta$ -143 ($J_{PP} = 184$ Hz). The magnitude of the coupling constants are consistent with two bond $^{31}$P-$^{31}$P coupling. To account for the coupling pattern, a molecule with three phosphorus atoms in which two of the atoms are magnetically similar, and coupled to the third could be proposed. These species were not isolated nor characterized beyond detection in the $^{31}$P NMR spectrum of a reaction mixture aliquot.

Figure 5.6. $^{31}$P-$^{31}$P COSY NMR spectrum in THF of an aliquot of the reaction mixture to produce 147.
An alternate synthetic route to bis(phosphaalkene) 147 was investigated (Scheme 6). In the well-known “phospha-Peterson” reaction, a bulky aryl silylphosphide is reacted with an aldehyde or ketone precursor to produce a phosphaalkene.\(^8\) The research groups of Jouaiti and Yoshifuji used this method to successfully prepare several mono- and bis(phosphaalkene)s.\(^{16-21}\) Thus, bis(trimethylsilyl)mesityl phosphine 108 was treated with one equivalent of butyllithium to form the lithiumphosphide (148) \textit{in situ}. To the solution of this reactive species was subsequently added half an equivalent of diketone 146. An aliquot was removed from the reaction mixture and examined by \(^{31}\text{P}\) NMR spectroscopy (Figure 5.7). No signals in the phosphaalkene region were detected. The reaction mixture was transferred to a Kontes bomb, and heated to 100°C for 24 hours. Unfortunately, little to no change was noted in the \(^{31}\text{P}\) NMR spectrum of the reaction mixture.

Scheme 6. Conditions and reagents: i) THF, 22°C, 1 equiv. \(^6\text{BuLi}\), 12 hours. ii) THF, -78°C, 0.5 equiv. 1,4-dibenzoylbenzene (146).
Figure 5.7. $^{31}$P NMR spectrum in THF of attempt to prepare 147 in THF via Scheme 6.

It is interesting to compare $^{31}$P NMR spectra of the reaction mixtures in the two attempts to prepare 147 via Scheme 5 and Scheme 6. A stack plot of the two $^{31}$P NMR spectra is shown in Figure 5.8 and reveals that the different synthetic routes seem to produce many of the same species or by-products. In both spectra a singlet is detected at $\delta$ -43, a doublet at $\delta$ -110, a triplet at $\delta$ -145, and a set of singlets with a similar ratio at $\delta$ -160 and $\delta$ -162. The top spectrum, the reaction mixture via the "phospha-Peterson" route, has a large singlet at -190 ppm, which can be assigned to the trimethylsilylmesityllithiumphosphide 148. There are also some minor resonances at $\delta$ 83 and $\delta$ -70 that are observed solely in this reaction.
Figure 5.8. $^{31}$P NMR spectra in THF of attempts to prepare bis(phosphaalkene) 147 via: (a) Scheme 5, (b) Scheme 6.

5.2 Discussion

As mentioned in chapter four, there are only two previous reports of a phenylene spaced bis(phosphaalkene) in which the central phenyl ring bridges the phosphorus atoms. Bis(phosphaalkene) 136 was prepared via a phospha-Wittig route by Protasiewicz and coworkers in 2000. The reported dihedral angles between the planes of the central phenylene ring and the P=C unit ($\Phi_P$), and between the P=C unit and the outer phenyl rings ($\Phi_C$) are 71° and 22°, respectively. The P=C bond distance was found to be 1.676(5) Å. The Cambridge Crystal Database was used to obtain the dihedral angles and reported angles of 69.9° and 21.8°, respectively. The reported P=C bond length was 1.68 Å. The Becker-type bis(phosphaalkene) 135 with tert-butyl substituents was reported by Appel and coworkers in 1995. Similarly, the Cambridge Crystal Database was used to obtain the angle between the central phenyl ring and the P=C planes ($\Phi_P$) to be 56.9°, and the P=C bond length to be 1.68 Å.
Of the three crystal structures presented in chapter four, compounds 125, 127, and 128, the average angle between the P-aryl plane and the P=C plane (\(\Phi_p\)) is 63.6° and the average angle between the P=C plane and the C-aryl plane (\(\Phi_C\)) is 24.1° (Table 5.1, page 217). \(\Phi_p\) for 145 is 63.5°, \(\Phi_{C1}\) and \(\Phi_{C2}\) are 72.9° and 45.9°, respectively (Figure 5.9). The two phenyl ring substituents would seem to be more sterically congested than the flexible siloxy group and the phenyl ring substituents of 125, 127, and 128 discussed in chapter four, as the larger \(\Phi_C\)'s of 145 indicate that a larger dihedral angle is required for each of the phenyl rings.
Figure 5.9. X-ray crystal structure of 145 (50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)-C(1) = 1.6926(14), P(1)-C(16) = 1.8374(13), C(1)-C(2) = 1.4915(17), C(1)-C(8) = 1.4844(18), C(8)-C(1)-C(2) = 116.25(11), C(8)-C(1)-P(1) = 128.09, C(2)-C(1)-P(1) = 115.66(9), C(1)-P(1)-C(16) = 107.04(6), C(8)-C(1)-P(1)-C(16) = -0.75(14), C(2)-C(1)-P(1)-C(16) = 179.67(10), C(17)-C(16)-P(1)-C(1) = 118.73(11), C(15)-C(16)-P(1)-C(1) = -65.59(13).

A comparison of Φ’s with reported crystal structures of triaryl substituted monophosphaalkenes reveals that the values for 145 are similar (Table 5.1). One can note a significantly larger Φ_P for compounds 153 and 154, which feature Mes* as the phosphorus substituent, as might be expected for this more sterically demanding substituent. Also of interest are the small Φ_C’s of 154 due to the fused ring system of the fluorenyl group.
Table 5.1. Dihedral angles between aryl and P=C planes in 145 and selected phosphaalkenes. \(^a\) defined as the angle between the planes defined by C(15)-C(15)* and P(1)-C(1)-C(8)-C(2) in the case of 145. \(^b\) defined as the angle between the planes defined by C(2)-C(7) and P(1)-C(1)-C(8)-C(2) in the case of 145. \(^c\) defined as the angle between the planes defined by C(8)-C(13) and P(1)-C(1)-C(8)-C(2) in the case of 145.

| Compound | \(\Phi_P\) (deg.)
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>145</td>
<td>63.5</td>
<td>72.9</td>
<td>45.9</td>
</tr>
<tr>
<td>136</td>
<td>69.9</td>
<td>21.8</td>
<td>-</td>
</tr>
<tr>
<td>135</td>
<td>56.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>115</td>
<td>71.4</td>
<td>36.6</td>
<td>42.6</td>
</tr>
<tr>
<td>115</td>
<td>71.6</td>
<td>22.6</td>
<td>56.7</td>
</tr>
<tr>
<td>149</td>
<td>69.3</td>
<td>47.3</td>
<td>66.8</td>
</tr>
<tr>
<td>150</td>
<td>77.8</td>
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</tr>
<tr>
<td>151</td>
<td>63.7</td>
<td>46.4</td>
<td>34.9</td>
</tr>
<tr>
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<td>37.6</td>
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</tr>
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<td>79.5</td>
<td>34.8</td>
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</tr>
<tr>
<td>154</td>
<td>86.2</td>
<td>2.7</td>
<td>3.6</td>
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</tbody>
</table>

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A comparison of the backbones of the Becker-type phosphaalkenes 125, 127, and 128 with the tri-aryl substituted bis(phosphaalkene) 145 reveals an interesting similarity. The $\Phi_P$ for the bis(phosphaalkene) 145 is approximately equal to that of the Becker-type phosphaalkenes, which might be expected as the phosphorus substituent is the bulky tetramethylphenyl or mesityl ring in all compounds. However, $\Phi_C$ for the Becker-type phosphaalkenes 125, 127, and 128 averages 24.1°, which is substantially smaller than either of the $\Phi_C$'s for 145, which are 72.9° and 45.9° (Table 1). The UV/Vis absorption maxima of 125, 127, and 128 are 324, 388, and 337 nm, respectively. The bis(phosphaalkene) 128 is structurally the most similar to 145. The smaller dihedral angle between the P=C plane and the capping phenyl group of 128 appears to lead to better $\pi$-conjugation than in 145 as the $\lambda_{\text{max}}$ of 128 is red-shifted by 6 nm compared to 145. Some $\pi$-conjugation though the central tetramethylphenyl spacer is indicated though a comparison with the UV/Vis absorption maximum of 115, which is 324 nm.\(^{10}\) This absorption is blue-shifted by 7 nm from the $\lambda_{\text{max}}$ of 145.

Based on these results one can conclude that a phosphaalkene with three aryl substituents may exhibit less extensive $\pi$-conjugation due to twisting of the carbon aryl substituents caused by steric interference between the two aromatic groups. However, although the triaryl substituted phosphaalkenes are certainly more robust than the Becker-type phosphaalkenes, the phospha-Peterson reaction does not seem to be as efficient in preparing bis(phosphaalkene)s. It would be interesting to compare the electronic properties of the corresponding polymer 155 to that of the poly($p$-arylene-Z-phosphaalkene) discussed in chapter four. From a comparison of the model compounds (145 vs. 128), one might predict that polymer 155 would exhibit a UV/Vis absorption

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maximum with shorter wavelength than the poly(\(\rho\)-arylene-Z-phosphaalkene) 129, as the
dihedral angles between the P=C and phenyl ring planes are larger, leading to less
efficient \(\pi\)-conjugation. This effect might be offset by the fact that longer chains of 155
could be present in solution than the insoluble polymer 129. However, 155 would likely
be much more robust, and perhaps more soluble.

\[
\begin{align*}
\text{155}
\end{align*}
\]

Smith and Protasiewicz reported a study on the effect of the incorporation of low
coordinate phosphorus into conjugated oligomers.\textsuperscript{31} During this investigation, the
authors prepared a variety of oligomers (156 – 164, Chart 1)\textsuperscript{31} with P=C and P=P bonds
in the backbone of the molecule, and compared them to PPV oligomers (OPPV) of
corresponding length (Table 5.2).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{C=C} & \text{\(\lambda_{\text{max}}\) (nm)} & \text{Ref.} & \text{P=C} & \text{\(\lambda_{\text{max}}\) (nm)} & \text{P=P} & \text{\(\lambda_{\text{max}}\) (nm)} \\
\hline
\text{OPPV-1} & 317 & & 156 & 334 & 161 & 372 \\
\text{OPPV-2 (x = 1)} & 354 & 32 & 156 & 341 & 162 & 398 \\
\text{} & & & 157 & 349 & 158 & 411 \\
\text{} & & & 159 & 411 & & \\
\text{OPPV-3 (x = 2)} & 384 & 33 & & 163 & 407 \\
\text{OPPV-4 (x = 3)} & 385 & 33 & 160 & 417 & 164 & 422 \\
\hline
\end{tabular}
\caption{UV/Vis maxima absorptions of PPV oligomers and selected compounds.}
\end{table}

\textit{References begin on page 221}
Chart 1.
As a general trend, increasing the phosphorus content of the conjugated backbone, from the all carbon examples (OPPV-1 – OPPV-4), to those containing P=C bonds (156 – 160), to those containing P=P bonds (161 – 164) leads to a significant red-shift in the observed UV/Vis absorption maxima.\textsuperscript{31} The incorporation of low coordinate phosphorus centres into the conjugation pathway appears to lead to a smaller HOMO-LUMO gap despite the significant twisting in the backbone of these systems. In part, this may be due to the weaker (p-p\textupsilon\textupsilon) bond between low coordinate phosphorus. Also of note in these systems, the molar absorptivity, which increases uniformly with oligomer length in organic systems, does not follow this trend in the phosphorus containing analogues.\textsuperscript{31} Smith et al. postulated this observation might also be caused by steric factors.

This work illustrates that the inclusion of low coordinate phosphorus into conjugated systems has some interesting effects. Clearly, investigation of this field of conjugated molecules and polymer incorporating heavier main group element multiple bonds has just begun. However, if more robust compounds could be synthesized, it is not impossible that such materials might find some utility in technology. Recall from the introduction, that polysilanes, a polymer whose main chain consists of sensitive silicon-silicon bonds have become commercially important.\textsuperscript{34}

5.3 Summary

A bis(phosphaalkene) containing solely aromatic substituents was synthesized and fully characterized. Crystals suitable for X-ray crystallography were grown, and a solid state structure of bis(phosphaalkene) 145 was obtained. Comparison with the crystal structures discussed in chapter four (125, 127, and 128) show similar $\Phi_p$ angles, but
significantly larger $\Phi_C$ angles for 145. The increase in carbon aromatic substituent steric bulk apparently leads to less effective $\pi$-conjugation as evinced by a slightly blue-shifted $\lambda_{\text{max}}$ when compared to bis(phosphaalkene) 128 (331 vs. 337 nm, respectively). A preliminary attempt to synthesize a bis(phosphaalkene) from a diketone resulted in evidence of phosphaalkene formation but the compound could not be isolated.

5.4 Experimental Section

General Procedures. X-ray crystallography performed by Dr. Brian Patrick in the Departmental Crystallography Lab. A Bruker X8 Apex diffractometer were used to collect refraction data.

Materials. 1,4-dibenzoylbenzene, 1,2,4,5-tetramethylbenzene (durene), 2-bromomesitylene, bromine, PCl$_3$, Me$_3$SiCl, Mg, LiAlH$_4$, MeLi (1.6 M in ethyl ether), and tBuLi (1.7 M in pentane) were purchased from Aldrich and used as received. Et$_2$NH were purchased from Aldrich and distilled prior to use. 1,4-C$_6$Me$_4$Br$_2$ (dibromodurene),$^{35}$ and MesP(SiMe$_3$)$_2$$^{36}$ were prepared following the literature procedures.

5.4.1. Synthesis of the bis(phosphaalkene) 1,4-[Ph$_2$C=P]$_2$-C$_6$Me$_4$ (145). To a stirred solution of 1,4-bis(trimethylsilyl)phosphino-2,3,5,6-tetramethylbenzene (121) (300 mg, 0.61 mmol) in THF was added dropwise a solution of benzophenone (143) (225 mg, 1.23 mmol) in THF. A catalytic amount of solid KOH (2 mg, 4.2 x $10^{-5}$ mol) was added and the reaction left to stir at room temperature. Aliquots of the reaction mixture were periodically removed and studied by $^{31}$P NMR spectroscopy. The reaction was only partially complete after three days, so more KOH was added. The reaction was then heated to 80°C for two days. The silylphosphine 121 was completely consumed at this
time, and bis(phosphaalkene) 145 had been produced quantitatively. Crystals suitable for X-ray crystallography were grown by slow solvent evaporation of the reaction mixture at room temperature. The product was isolated as yellow crystals. Yield = 171 mg (56%).

$^3\text{P NMR (CDCl}_3): \delta$ 239.6 (s, P=C), 239.1 (s, P=C0, 238.6 (s, P=C), 237.8 (s, P=C); $^1\text{H NMR (CDCl}_3): \delta$ 7.52 (br s, Ph), 7.31 (m, Ph), 7.22 (m, Ph), 7.07 (m, Ph), 6.83 (m, Ph), 2.20 (s, o-Me-tmb), 2.14 (s, o-Me-tmb); $^{13}\text{C NMR (CDCl}_3): \delta$ 193.2 (d, $^1\text{J}_{PC} = 42.4$ Hz, P=C), 192.3 (d, $^1\text{J}_{PC} = 43$ Hz), 145.9 (d, $^2\text{J}_{PC} = 24.6$ Hz), 144.5 (m, i-Ph), 142.6 (d, $^2\text{J}_{PC} = 43.2$ Hz, i-tmb), 142.5 (s, p-Ph), 137.5 (dd, $^2\text{J}_{PC} = 8.2$ Hz, $^2\text{J}_{PC} = 7.5$ Hz, o-tmb), 130-127 (br s, o-, m-Ph), 21.4 (s, o-Me-tmb), 21.2 (s, o-Me-tmb); UV/Vis (THF): $\lambda_{max}$ ($\varepsilon$) = 331 nm (1.37 x 10$^4$); MS (EI, 70 eV): m/z (%): 528, 527, 526 (5.5, 28.4, 71) [M$^+$], 450, 449 (3, 7) [M$^+$ - Ph], 361, 360 (4, 15) [M$^+$ - CPh$_2$], 330, 329 (26, 7) [M$^+$ - PCPh$_2$], 167, 166 (14, 100) [CPh$_2^+$].
5.5 References


12. Tsang, C.-W.; Rohrick, C. A.; Saini, T. S.; Patrick, B. O.; Gates, D. P.

   *Organometallics* 2002, 21, 1008.

13. Tsang, C.-W.; Rohrick, C. A.; Saini, T. S.; Patrick, B. O.; Gates, D. P.

   *Organometallics* 2004, 23, 5913.


References begin on page 221


Chapter Six

Summary and Future Work

6.0 Summary

The main hypothesis of this work was that alternating an aromatic bridge with phosphaalkene moieties would allow the preparation of formally π-conjugated polymers which incorporated P=C bonds into the backbone of the molecule. It has been noted that low coordinate phosphorus has the ability to mimic the chemistry of carbon in unsaturated systems, though the phosphaalkene moieties are generally more reactive.\textsuperscript{1-4} It was expected that the incorporation of low coordinate phosphorus into the main chain of a formally conjugated macromolecule would lead to a material which exhibited signs of extended π-conjugation. A survey of the literature on phosphaalkene synthesis indicated that Becker's elegant [1,3]-silatropic migration is perhaps the most versatile and efficient method of generating the phosphorus-carbon double bond.\textsuperscript{2} Thus, with the objective in mind, and a synthetic route selected, I set out to prepare a phosphorus containing analogue of poly(p-phenylenevinylene), in which the vinylene group is replaced by an isolobal phosphaalkene moiety.

It is often true that polymers are more difficult to characterize than molecular compounds. Taking this piece of conventional wisdom into account, as well as noting that oligomers are often used as models for π-conjugated macromolecules,\textsuperscript{5-7} I first decided to prepare molecular compounds as models for the poly(p-phenylenephosphaalkene). Once the appropriate carboxylic acid chloride and bis(trimethylsilyl)arylphosphine starting materials had been synthesized, I prepared and fully characterized a monophosphaalkene (87), and two bis(phosphaalkene) (88 and 89) model compounds for the poly(p-phenylenephosphaalkene) (90). Multi-nuclear NMR
spectroscopy, IR and UV/Vis spectroscopy, mass spectrometry, and elemental analysis were used to characterize these compounds.

As the length of the conjugation path increased, the observed maximum absorbance in the UV/Vis spectrum shifted to longer wavelengths, or lower energy. Indeed, a red-shift is observed in the $\lambda_{\text{max}}$ of 88 compared to 87, and this trend continues when comparing 89 to 88, and polymer 90 to bis(phosphaalkene) 89. These observations support extended $\pi$-conjugation in 90.

Having successfully prepared 90, the first polymer incorporating heavier main group element multiple bonds in the main chain, I wanted to continue our investigation of this new class of $\pi$-conjugated macromolecule. Perhaps an obvious perturbation to investigate was the effect of incorporating different aromatic groups into the polymer. I chose to try to incorporate thiophene, and set out to prepare suitable 2- and 2,5-bis(carboxylic acid chloride)thiophene and 2- and 2,5-bis(trimethylsilyl)phosphinothiophene precursors. With these materials in hand, I were able to successfully prepare several model compounds. Monophosphaalkenes 107 and 109 are conformational isomers, with the thiophene and mesityl groups on different ends of the P=C bond. Similarly, bis(phosphaalkene)s 110 and 111 both feature thiophene as the central aromatic spacer, bridging the phosphorus atoms of the P=C bonds in 110 and
the carbon atoms of the P=C bonds in 111. Compounds 107 and 110 are model compounds for polymer 93. All thiophene containing compounds were fully characterized, with the exception of 111. Despite several attempts, compound 111 could not be isolated in a pure form.

Qualitatively, in terms of preparation and characterization, phosphaalkenes 107, 110, and polymer 93 are quite similar to 87, 89, and polymer 90. Each of the thiophene containing compounds 107, 110, and 93 exhibit a significant red-shift when compared to 87, 89, and 90. This may be due, in part, to a higher Z/E ratio. These compounds also exhibit the trend one would expect for a π-conjugated system growing in length. The UV/Vis maximum absorption of polymer 93 has a longer wavelength than 110, which has a longer wavelength than 107. Monophosphaalkene 109 turned out to be significantly different from 107 in terms of its properties. Of note, the UV/Vis absorption of 109 was red-shifted compared with 107, but also in comparison to bis(phosphaalkene) 110. It
would seem that the incorporation of thiophene into the backbone of 93 leads to more efficient π-conjugation than in polymer 90.

A comparison of the UV/Vis absorptions of 107 and 109 suggests another avenue of inquiry into the poly(p-phenyleneosphaalkene) system. Switching the location of steric bulk from a substituent at carbon to the substituent at phosphorus leads to more effective π-conjugation as suggested by an increase in $\lambda_{\text{max}}$. The synthesis of a suitable bulky, bifunctional silylphosphine precursor proved to be arduous. After much effort, the synthesis of pure 1,4-bis(trimethylsilylphosphino-2,3,5,6-tetramethylbenzene was eventually achieved. The preparation of the model compounds provided an interesting result, in that one isomer was produced almost exclusively. Crystals suitable for X-ray diffraction were grown of the highly desirable trans isomer of monophosphaalkene 125, and the bis(phosphaalkene)s 127 and 128. Following a thermolysis procedure similar to that used to synthesize 90 and 93, produced an insoluble, brittle, orange solid 129. Solid state CP-MAS NMR spectroscopy was used to characterize this material. An attempted solution synthesis of 129 monitored by $^{31}$P NMR spectroscopy resulted in the polymer precipitating after several hours. It appears that the E-isomer forms initially, but is later converted to the Z-isomer. Organic π-conjugated polymers with a regular stereochemistry such as PPV are usually crystalline, and insoluble.

![Chemical Structures]

References begin on page 235
The UV/Vis maximum absorptions of 125, 127, 128, and 129 are red-shifted from compounds 87 – 90. However, the absorbance of monophosphaalkene 125 is blue-shifted compared to monophosphaalkenes 107 and 109. Interestingly, the $\lambda_{\text{max}}$ of bis(phosphaalkene) 127 is the second longest wavelength, longer than that observed for polymer 93. A THF extraction of the insoluble polymer 129 exhibited the absorbance with the longest wavelength of any compound in this thesis.

These compounds that contain steric bulk on the phosphorus substituent seem to be even more sensitive to protonolysis (e.g. bis(phosphaalkene) 111 could not be purified). There are numerous other synthetic routes to compounds possessing a P=C bond other than the [1,3]-silatropic migration. A base catalyzed condensation reaction between a bis(trimethylsilyl)phosphine and a ketone produces a phosphaalkene with three carbon substituents. Using this synthetic route, a bis(phosphaalkene) (145) was synthesized. Crystals suitable for X-ray crystallography were grown.

Bis(phosphaalkene) 145 was characterized by multi-nuclear NMR spectroscopy, mass spectrometry, and UV/Vis spectroscopy. A comparison of the UV/Vis maximum absorptions of 145 and bis(phosphaalkene) 128 reveal that the $\lambda_{\text{max}}$ of 145 is slightly blue-shifted. This can be rationalized by comparing the dihedral angles between the capping phenyl groups and the plane of the P=C bond. The dihedral angle of 145 is significantly larger than for 128. Preliminary attempts to prepare bis(phosphaalkene) 147

References begin on page 235
have not been successful thus far. It could be that AlCl₃ might prove to be a better catalyst than KOH or NaOH.

![145](image1.png) ![147](image2.png)

In conclusion, the first examples of poly(p-phenylenephosphaalkene)s have been prepared, and their properties are consistent with a degree of π-conjugation through the backbone. The Becker [1,3] silatropic phosphaalkene synthetic route proved amenable to an extension into polymer science.

### 6.1 Future Work

#### 6.1.1. Theoretical Calculations

As this project has yielded a versatile synthetic route to a new class of formally π-conjugated polymers, there is clearly much work yet to be done. The next aspect of this work that I think should be undertaken are theoretical calculations using a density functional theory (B3LYP) approach. It would be of interest to compare the relative energies of the $E$- and $Z$-isomer, especially for phosphaalkenes $125, 127-129$, in which the $Z$-isomer is selectively formed. It would also be attractive to compare substitutional isomers such as $107$ and $109$, or $87$ and $125$, and to observe the effects of twisting in the backbone of the molecule on the orbitals involved in π-conjugation. Also of interest are the shapes of the HOMO and LUMO.

References begin on page 235
6.1.2. Poly(p-phenylenephosphaalkene)s Prepared Via [1,3] Silatropy Route

Although these compounds are quite sensitive, there are several experiments with the Becker type polymers that might prove to be quite exciting. Monophosphaalkene 165 cannot be isolated, as it dimerizes readily to form a diphosphetane. The thermodynamic stabilization of the \( \pi \)-conjugation is not enough to make this compound isolable. However, what if the corresponding poly(p-phenylenephosphaalkene) (166) was synthesized? Surely, the polymer stability should benefit by additional \( \pi \)-conjugation. Also, due to the lack of steric bulk, the phenyl rings of the polymer backbone should be more planar, increasing the effectiveness of the \( \pi \)-conjugation. Conversely, if the polymer did not prove to be isolable, the product might form rings linked by diphosphetane moieties formed via an intramolecular reaction, which would also be quite interesting.

As mentioned very briefly in chapter two, only very weak fluorescence was observed for polymer 90, and it was not clear whether this emission was due to the polymer or another species present in solution. It is possible that the siloxy group quenches emission. It would be appealing to prepare a polymer (167) with an aromatic spacer that is fluorescent, such as a terthiophene unit, as outlined in Scheme 1.
Scheme 1.

There are several other poly(p-phenylenephosphaalkene)s that are worth pursuing. In an attempt to solubilize the all trans polymer 129, a 1,4-di(carboxylic acid chloride)-2,5-bishexyloxybenzene was prepared, and yielded polymer 168. This polymer was only prepared on the scale of an NMR reaction, but seemed to give a mixture of E- and Z-isomers. Keeping in mind what was observed during the solution preparation of polymer 129, perhaps the Z/E isomer ratio would change as the reaction progressed. In any case, it would be interesting to examine the effects of the hexyloxy groups on the UV/Vis absorption spectrum. In PPV, the addition of hexyloxy groups produces a significant red-shift in the UV/Vis spectrum, and also has beneficial effects on luminescent properties.⁹

A thermolysis procedure similar to that used to first synthesize polymer 129 was followed in an attempt to prepare polymer 169. The reaction seemed to proceed more
quickly however, as the dark orange material became immobile after only one hour in the oven. I would expect the properties of this polymer to have a similar relationship to the properties of 129 as polymer 93 had with the original polymer 90. That is to say, the UV/Vis absorption maximum of 169 is likely red-shifted compared to that of 129, and I would expect the NMR to be qualitatively similar. When the material suspected to be 169 was prepared, I did not have access to solid state NMR, so this solid was never characterized.

It seemed that the hexyloxy groups have enough steric presence to negate the stereochemical selectivity seen in polymer 129 and the related model compounds. It is possible that the hexyloxy group might be large enough to provide steric protection for the P=C bond, and hence polymer 170 might be isolable. Unfortunately, time constraints have prevented me from completing this synthesis. The bifunctional phosphine monomer required to synthesize this polymer is still being prepared, and is at the 1,4-bis(dichlorophosphine)-2,5-bis(hexyloxy)benzene stage.
6.1.3. Low Coordinate Phosphorus In Conjugated Materials

Phosphaalkynes are compounds that contain a phosphorus(III)-carbon triple bond. With a lone pair, and two accessible π-bonds, phosphaalkynes have a rich coordination chemistry. In 1986, the research groups of Nixon and Binger independently reported the first examples of phosphaalkyne cyclodimerization at cobalt, rhodium, and iridium centres. If a bis(phosphaalkyne) could be prepared, it might cyclodimerize at a metal centre resulting in a conjugated polymer with a coordinated metal centre in each repeat unit as shown in Scheme 2.

![Scheme 2](image)

Another interesting polymer that would be extremely exciting to synthesize is a polyacetylene analogue (173, Scheme 3). A lithiumphosphide could react with phosgene to produce a phosphaalkene intermediate with a chlorine and trimethylsilyl substituents. This intermediate could then undergo a condensation polymerization to afford 173.

![Scheme 3](image)

References begin on page 235.
Phosphabenzene, also known as phosphinine is a six-membered aromatic ring. Phosphinines have found use as \( \eta^1 \) and arene ligands,\(^{13-15} \) so it might be intriguing to prepare a poly(phosphinine) (174). Poly(p-phenylene) is a blue-emitting conjugated polymer, despite the significant twist angle in the backbone of the molecule. A poly(phosphinine) might be a material that could coordinate metals to the conjugated backbone of the polymer.

![Phosphinine diagram](image)

6.2 Closing Remarks

The area of research contained in the thesis, the incorporation of low coordinate phosphorus into \( \pi \)-conjugated polymers, has proven to be challenging and fascinating. Future applications may or may not develop from this project, but it is undeniable that a substantial amount of interesting, fundamental chemistry is still to be explored.
6.3 References


Appendix A

Figure A1. $^{31}$P NMR spectrum of phosphine 74 in CDCl$_3$.

Figure A2. $^1$H NMR spectrum of phosphine 74 in CDCl$_3$. 
Figure A3. $^{31}$P NMR spectrum of phosphine 79 in C₆D₆.

Figure A4. $^1$H NMR spectrum of phosphine 79 in C₆D₆.
Figure A5. $^1$H NMR spectrum of 82 in CDCl$_3$.

Figure A6. $^1$H NMR spectrum of 86 in CDCl$_3$. * Residual CHCl$_3$. 
Figure A7. Stack plot of $^{13}$C NMR spectra in CDCl$_3$ of a) 87, b) 88, and c) 90.

* Solvent CDCl$_3$. 
Figure A8. Stack plot of $^1$H NMR spectra in CDCl$_3$ of a) 87, b) 88, and c) 90. * Residual CHCl$_3$. 
Appendix B

Figure B1. $^{31}$P NMR spectrum of phosphine 97 in CDCl$_3$.

Figure B2. $^{31}$P NMR spectrum of phosphine 98 in CDCl$_3$. 
Figure B3. $^1$H NMR spectrum of phosphine 98 in CDCl$_3$.

Figure B4. $^{31}$P NMR spectrum of phosphine 101 in CDCl$_3$. 
**Figure B5.** $^{31}$P NMR spectrum of phosphine 102 in CDCl$_3$.

**Figure B6.** $^1$H NMR spectrum of phosphine 102 in CDCl$_3$.
**Figure B7.** $^1$H NMR spectrum of thienoyl chloride 104 in CD$_2$Cl$_2$.

**Figure B8.** $^{13}$C NMR spectrum of 104 in CD$_2$Cl$_2$. *Solvent peak CD$_2$Cl$_2$
Figure B9. $^1$H NMR spectrum of 106 in CDCl$_3$.

Figure B10. $^{13}$C NMR spectrum of 106 in CDCl$_3$. * Solvent peak CDCl$_3$. 

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Appendix C

Figure C1. $^{31}$P NMR spectrum of phosphine 121 in CDCl$_3$.

Figure C2. $^1$H NMR spectrum of phosphine 121 in CDCl$_3$. * Residual CHCl$_3$. 
Figure C3. $^1$H NMR spectrum of phosphines 119 and 119b in CDCl$_3$. * Residual CHCl$_3$. 
Table C1. Crystal Data and Structural Refinement Details for 125, 127, and 128.

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(a) R1 = Σ ||Fo| - |Fc|| / |Fo|, (b) wR2 = [ Σ (w(Fo² - Fc²)²) / Σ w(Fo²)² ]¹/²
Appendix D

Table D1. Crystal Data and Structural Refinement Details for 145.

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<td>θ max (deg)</td>
<td>28.6</td>
</tr>
<tr>
<td>limiting indices</td>
<td>-10 &lt; h &lt; 10</td>
</tr>
<tr>
<td></td>
<td>-21 &lt; k &lt; 21</td>
</tr>
<tr>
<td></td>
<td>-19 &lt; l &lt; 19</td>
</tr>
<tr>
<td>reflns collected</td>
<td>20589</td>
</tr>
<tr>
<td>unique reflns (Rint)</td>
<td>3462</td>
</tr>
<tr>
<td>R$_{int}$</td>
<td>0.034</td>
</tr>
<tr>
<td>absorption correction</td>
<td>SADABS</td>
</tr>
<tr>
<td>max and min transmission</td>
<td>0.986 and 0.853</td>
</tr>
<tr>
<td>refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Reflection/Params</td>
<td>3462/174</td>
</tr>
<tr>
<td>R1 [I &gt; 2σ(I)]$^a$</td>
<td>0.051</td>
</tr>
<tr>
<td>wR2 [all data]$^b$</td>
<td>0.112</td>
</tr>
<tr>
<td>GOF</td>
<td>1.06</td>
</tr>
<tr>
<td>largest diff peak and hole (e Å$^{-3}$)</td>
<td>0.30 and -0.18</td>
</tr>
</tbody>
</table>

(a) $R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$, (b) $wR2 = [\Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$