The Reactivity of Ditetrelenes Towards Organophosphorus Oxides

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A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in Chemistry
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Abstract

The reactivity of tetramesityldisilene 4 and tetramesityldigermene 5 towards organophosphorus oxides was explored in this thesis. The reaction of dialkyl and diarylphosphine oxides and phosphites with ditetrelenes 4 and 5 resulted in a 1,3-addition to form diorganodisilyl and digermyl phosphinites 27, 28, 31, 32 and disilyl phosphites 35 and 36. The 1,3-addition resulted in a mild two electron reduction of the P(V) centre of the phosphine oxide and phosphite to a P(III) centre in the products, without the use of heat or a catalyst. The reaction of organophosphorus oxides provides another example of a main group oxide that can be activated by ditetrelenes 4 and 5 in addition to nitro and sulfonyl containing compounds, CO and CO₂.

The mechanism for the reaction of diorganophosphorus oxides and phosphites with ditetrelenes 4 and 5 was investigated through deuterium labelling studies and KIE experiments. The mechanism for the formation of disilyl and digermyl phosphinites and phosphites was determined to proceed through a nucleophilic addition. An exchange phenomenon between the OP(pentyl)₂ moiety of 32 and an OPPh₂ group from diphenylphosphine oxide was discovered and the mechanism of this exchange was investigated.

Keywords: Group 14, silicon, germanium, disilene, digermene, organophosphorus oxides, phosphine oxides, phosphites, nucleophilic addition
Summary for Lay Audience

Just as houses can only be utilized after first laying down a stable foundation, understanding the fundamental chemistry of compounds is important for the future development of applications of the chemistry. In this thesis, reactions with compounds containing silicon and germanium are explored. These compounds are of interest because of their ability to easily react with numerous reagents to form new compounds that are not easily synthesized in any other way. The addition of phosphorus oxides to the silicon or germanium species was investigated. The new compounds formed were identified using state-of-the-art analytical techniques and the pathways to these compounds were elucidated using physical inorganic methodology. The chemistry reported is simple to perform and, with the mechanistic insights provided, it is hoped that the chemistry can be utilized in applications such as the organic functionalization of semiconductor surfaces.
Acknowledgements

First and foremost, I’d like to thank my supervisor, Dr. Kim Baines for giving me the opportunity to complete my Masters in her research group. She has provided helpful advice and guidance that allowed me to overcome many obstacles in my research. The time she took to edit and proofread my thesis has enhanced my writing skills and improved my ability to explain concepts clearly in my thesis. It has been pleasure working in her group for the past three years.

I would also like to thank all the members of the Baines group that have helped me throughout my 4491 thesis and my Masters. I would like to give a special thanks to Andrew. He was always there for me in the most stressful times and gave continuous support throughout my time in the lab, especially near the end of my thesis.

I wouldn’t have been able to finish this degree without the support of all the friends that I have made throughout my undergraduate and Masters degrees. Thank you to my friends in the Blacquiere, FLL, Ding and Corrigan groups for always having time to talk about research and for all the pasta lunches on Thursdays. Jonathan, Curtis and Karan would always help me take my mind off all the stress outside of school with all their savage comments that lead to non-stop laughter.

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<th>Abbreviation</th>
<th>Description</th>
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<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>Bu</td>
<td>Butyl</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>d (NMR)</td>
<td>Doublet</td>
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<tr>
<td>$\Delta E_{elast}$</td>
<td>Quasiclassical Electrostatic Interaction Energy</td>
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<tr>
<td>$\Delta E_{int}$</td>
<td>Instantaneous Interaction Energy</td>
</tr>
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<td>Electrospray Ionization</td>
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<td>Energy Partitioning Analysis</td>
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<td>Repulsive Pauli Term</td>
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<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>gHMBC</td>
<td>Gradient Heteronuclear Multiple Bond Correlation</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>KIE</td>
<td>Kinetic Isotope Effect</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>Mes</td>
<td>Mesityl (2,4,6-trimethylphenyl)</td>
</tr>
<tr>
<td>m (IR)</td>
<td>Medium</td>
</tr>
<tr>
<td>m (NMR)</td>
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<td>Definition</td>
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</tr>
<tr>
<td>Tip</td>
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<td>Tetrahydrofuran</td>
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<tr>
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<td>Thin Layer Chromatography</td>
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<tr>
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</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Chapter 1

1 Stable Doubly Bonded Si and Ge Compounds

1.1 Introduction

The chemistry of ditetrelenes, the heavy atom analog of alkenes, has been explored for the last 40 years,¹ and the acquired knowledge is now being utilized in many interesting applications. For example, Scheschkewitz and Manners reported the atom-economic and catalyst free method for synthesis of a σ-π conjugated organosilicon polymer under mild reaction conditions.² Co-monomers tetrasiladiene ¹ and 1,4-diethynylbenzene ² were reacted at room temperature in benzene to form an air stable polymer ³ in 86% yield (Scheme 1). The key reaction in the polymerization takes advantage of the well-known [2+2] cycloaddition of alkynes with disilenes.¹b

![Scheme 1](image)

Tip = 2,4,6-trisopropylphenyl

**Scheme 1.** The synthesis of a mixed inorganic-organic material ³ by copolymerization of ¹ and ².

As a second example, tetramesityldisilene ⁴ and -digermene ⁵ (Mes = mesityl = 2,4,6-trimethylphenyl) have been used as molecular models to understand the chemistry of the Si(100) 2x1 and Ge(100) 2x1 reconstructed surfaces (Figure 1). The elucidation of an unambiguous structure of surface adducts is difficult because surface characterization methods are limited. Such methods include Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunnelling Microscopy (STM)³ which provide information on functional groups, elemental composition and oxidation states, and electronic states, respectively. The use of surface analytical techniques is often complemented by computational studies to ensure the accuracy of the proposed structures of surface adducts. In contrast, the structure of molecular species may be unequivocally determined using characterization techniques such as Nuclear
Figure 1. The structures of a Si/Ge(100) 2x1 surface and tetramesityldisilene and -digermene.

Magnetic Resonance (NMR) Spectroscopy, Mass Spectrometry (MS) and X-ray Crystallography. For this reason, comparisons between the structures derived from reactions of molecular and surface disilenes and digermenes are frequently made. For example, the addition of nitriles to 5 was compared to the reactivity between nitriles and the Ge(100) 2x1 surface. On the basis of theoretical and experimental evidence, the addition of acrylonitrile to the Ge(100) 2x1 surface was proposed to form two types of adducts: ketenimines (a cyclic single-dimer adduct 6a and an interdimer adduct 6b), and a cycloadduct between the surface dimer and the C=C bond of acrylonitrile, digermetane 7 (Scheme 2a). The addition of acrylonitrile to molecular digermene 5, on the other hand, resulted in the formation of 1,2,3-azadigermetine 8 at room temperature (Scheme 2b). The lack of formation of the six-membered cyclic ketenimine 6a in the molecular system suggests that ketenimine 6b is the more likely ketenimine formed on the surface, and not 6a. Furthermore, the surface chemistry suggests that azadigermetine 8 may be the kinetic product, and under equilibrium conditions, a molecular analog of digermetane 7 may be formed.

Scheme 2. The addition of acrylonitrile to (a) the Ge(100) 2x1 surface and (b) tetramesityldigermene 5.
For the continued development of applications using ditetrelene chemistry, it is important to continue to study fundamental chemistry of ditetrelenes. In order to understand the chemistry, the structure, bonding and reactivity of ditetrelenes will be briefly reviewed.

1.2 Structure and Bonding in Ditetrelenes

The increased reactivity of ditetrelenes compared to alkenes, can be understood in terms of the nature of the \( \pi \)-bond between the heavier Group 14 elements, which is significantly weaker than the \( \pi \)-bond in alkenes (estimated \( \pi \)-bond strengths (kcal/mol) for \( \text{H}_2\text{M}=\text{MH}_2 \): \( \text{M} = \text{C}: 65 \), \( \text{M} = \text{Si}: 25 \), \( \text{M} = \text{Ge}: 25 \)).\(^7\) The weak \( \pi \)-bond in non-polar molecules has been studied computationally by Frenking et al. using energy-partitioning analysis (EPA).\(^8\) EPA focuses on the instantaneous interaction energy (\( \Delta E_{\text{int}} \)) of the bond, which is defined as the energy difference between the molecule and its fragments in a specified geometry. The interaction energy can be divided into three terms: the quasiclassical electrostatic interaction energy (\( \Delta E_{\text{elstat}} \)), the repulsive Pauli term (\( \Delta E_{\text{Pauli}} \)) and the orbital interaction energy (\( \Delta E_{\text{orb}} \)). The interaction energies for \( \text{H}_3\text{M}-\text{MH}_3 \) single bonds (\( \text{M} = \text{C} \) to \( \text{Pb} \)) were calculated and shown to decrease down the group, resulting in a weaker \( \sigma \)-bond. While the bonding in ditetrelenes was not investigated, analogous compounds containing multiple bonds between first-row main group elements were analyzed, including diazene (\( \text{HN}=\text{NH} \)). The Pauli repulsion contribution significantly increases from diazene (\( \Delta E_{\text{Pauli}} = 599.4 \) kcal/mol) compared to ethylene (\( \Delta E_{\text{Pauli}} = 281.9 \) kcal/mol), which results in a smaller interaction energy, and therefore, a weaker \( \pi \)-bond. Similar to diazene, ditetrelenes are expected to have a strong Pauli repulsion contribution, explaining the inherently weak \( \pi \)-bond and increased reactivity compared to alkenes.

In contrast to planar alkenes, most ditetrelenes exhibit a \textit{trans}-bent geometry at the silicon and germanium centre and twisting about the \( \text{M}=\text{M} \) bond (Figure 2). The bend angle (\( \theta \)) is the

\[
\begin{align*}
\text{planar} & & \text{trans-bent} & & \text{twist form} \\
\text{M}=\text{M} & & \text{M}=\text{M} & & \text{M}=\text{M}
\end{align*}
\]

\textbf{Figure 2.} Structural deformations of the \( \text{M}=\text{M} \) bond.
angle between the M=M bond axis and the R-M-R plane, whereas, the twist angle (τ) is defined as the dihedral angle between two R-M-R planes (Figure 3).

\[ \theta \]

**trans-bending angle (θ)**

\[ \tau \]

**twisting angle (τ)**

Figure 3. Definition for the trans-bent angle (θ) at M and the twist angle (τ) about the M=M bond.

The trans-bent geometry observed in ditetrelenes can be understood using two molecular orbital (MO) models. The first model rationalizes the formation of the double bond in alkenes as the covalent interaction between singly occupied MOs of two monomeric, ground state triplet carbenes, resulting in a classical planar C=C bond (Figure 4a). The heavy analogues of carbenes (silylenes and germylenes) are ground state singlets. Consequently, the covalent interaction of singlet silylenes and germylenes would result in Pauli repulsion between the doubly occupied n-orbitals (Figure 4b). To form a classical planar M=M bond, a significant amount of energy would be required to overcome the singlet-triplet energy gap (ΔE_{ST}) to promote an electron from n- to p-level. Alternatively, the heavy carbene analogues prefer to interact through two equivalent donor-acceptor interactions to form the non-classical M=M bond, featuring trans-bending at the M centres (Figure 4c).

Figure 4. MO model representing (a) the classical covalent interaction, (b) the non-classical donor-acceptor interaction (M = Si, Ge) and (c) the donor-acceptor double bond.
In an alternative MO model, \textit{trans}-bending in ditetrelenes is rationalized by the mixing of M=M $\pi$- and $\sigma^*$-orbitals, which is possible through bending at the M centres (Figure 5). The $\pi$-$\sigma^*$ interaction is dependant on the $\pi$-$\sigma^*$ energy gap; the mixing of $\pi$-$\sigma^*$ orbitals increases as the energy gap decreases, which results in a larger \textit{trans}-bent angle. In the planar H$_2$M=MH$_2$ (M = C to Pb), the magnitude of the $\pi$-$\sigma^*$ energy separation decreases going down Group 14, thereby increasing $\pi$-$\sigma^*$ mixing and the \textit{trans}-bent angle for the heavier elements. Another factor which influences the degree of \textit{trans}-bending in ditetrelenes is the electronegativity of the substituents on the M=M bond: electronegative substituents (i.e. substituents containing O or N) lead to increased \textit{trans}-bending, while electropositive substituents (i.e. substituents featuring Si) produce smaller bending deformations at the M centres. These trends are evident in the examples given in Table 1.

\textbf{Table 1.} \textit{Trans}-bending angle ($\theta$) and twist angle ($\tau$) of selected disilenes and digermenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\theta$ (deg)</th>
<th>$\tau$ (deg)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mes$_2$Si$\equiv$SiMes$_2$ Mes = 2,4,6-trimethylphenyl</td>
<td>12, 14</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>(Mes$_2$P)$_2$Si$\equiv$Si(PMes$_2$)$_2$</td>
<td>41</td>
<td>46</td>
<td>12</td>
</tr>
<tr>
<td>Mes$_2$Ge$\equiv$GeMes$_2$</td>
<td>33</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>($^i$Pr$_3$Si)$_2$Ge$\equiv$Ge(Si$^i$Pr$_3$)$_2$</td>
<td>16</td>
<td>0</td>
<td>14</td>
</tr>
</tbody>
</table>

1.3 Reactivity of Ditetrelenes

The most common modes of reactivity for ditetrelenes are 1,2-additions and cycloadditions (Scheme 3).$^1$ Typical reagents that react with ditetrelenes via 1,2-addition reaction include polar,
Scheme 3. Common modes of reactivity for ditetrelenes.

σ-bonded compounds such as water and alcohols.\textsuperscript{1d,e,f} Ditetrelenes also react with reagents containing π-bonds, most often in cycloaddition reactions. The most common mode of cycloaddition for ditetrelenes is the [2+2] cycloaddition. Ketones, aldehydes, alkynes and nitriles are typical reagents used in the formation of four-membered heterocyclic rings containing Si-Si/Ge-Ge fragments.\textsuperscript{1b,4,15} For example, the addition of acetonitrile to tetramesityldigermene, 5, resulted in the formation of 1,2,3-azadigermetine 9 (Scheme 4).\textsuperscript{4} The addition of acetonitrile to 5

\[
\text{Mes}_2\text{Ge}=\text{GeMes}_2 + \text{H}_3\text{C} \equiv \text{C} \equiv \text{N} \rightarrow \text{THF} \quad 18 \text{ hr, RT} \quad \text{Mes}_2\text{Ge} \equiv \text{GeMes}_2 \equiv \text{N} \]

Scheme 4. The [2+2] cycloaddition of acetonitrile to tetramesityldigermene 5.

occurs at room temperature, in stark contrast to the [2+2] cycloadditions of alkenes, which are forbidden under thermal conditions. Reactions to form larger heterocyclic rings through [3+2] and [4+2] cycloadditions have been reported; however, these examples are less common. While Diels-Alder reactions are common in alkene chemistry, stable ditetrelenes typically do not undergo [4+2] cycloadditions to form Diels-Alder adducts with conjugated dienes. Diels-Alder reactivity is only known for transient disilenes and digermenes.\textsuperscript{16} However, other examples of [4+2] cycloadditions

6
exist in ditetrelene chemistry. Boudjouk et al. reported the addition of benzil to disilene 4 to yield a six-membered heterocyclic ring 10 (Scheme 5).\textsuperscript{17}

\[
\text{Mes}_2\text{Si}==\text{SiMes}_2 + \overset{\text{O}}{\overset{\text{O}}{\overset{\text{Ph}}{\overset{\text{Ph}}{\text{O}}}}}} \quad \text{THF} \quad 30 \text{ min}, 45 \ ^\circ\text{C} \quad \text{Mes}_2\text{Si}==\text{SiMes}_2
\]

\[10\] (38%)

\textbf{Scheme 5.} The addition of benzil to disilene 4.

While the reactivity of ditetrelenes has focused on reactions with the \(\pi\)-bond, recent research has explored the synthesis of functionalized disilenes.\textsuperscript{1a} These functional disilenes include disilenides, containing a Li substituent, and phosphinodisilenes, containing a \(\text{PR}_2\) substituent bound to the Si centre. By incorporating this functionality into the ditetrelene, reactivity can be explored that focuses on the reaction of the \(\sigma\)-bonded substituents on the ditetrelene instead of the \(\pi\)-bond.

Recently, the focus of reactivity studies in ditetrelene chemistry has shifted towards small molecule activation.\textsuperscript{18} Small molecules such as \(\text{H}_2\), \(\text{NH}_3\) and \(\text{CO}_2\) can be used as synthons for value added chemicals; however, these stable compounds must be activated for further functionalization. The most efficient method to achieve functionalization of these small molecules is through catalytic processes which requires activation of a small molecule (Scheme 6a), and then elimination of the functionalized product (Scheme 6b) with regeneration of the catalyst (Scheme 6c).

\textbf{Scheme 6.} General cycle for the catalytic functionalization of small molecules.
While the activation of small molecules is a new field in ditetrelene chemistry and there have been no reports of catalysis to date, there have been recent reports of small molecule activation. Inoue and co-workers synthesized the (Z)-diiminodisilyldisilene 11, featuring a highly twisted ($\tau = 23^\circ$) and trans-bent ($\theta = 38^\circ, 39^\circ$) geometry about the Si=Si bond, leading to a weaker $\pi$-bond in comparison to other disilenes.\textsuperscript{19} When iminodisilene 11 was allowed to react with NH$_3$ at -78 °C, 1-aminodisilane 12 was formed as the only product in 64% yield (Scheme 7a).\textsuperscript{20} Most notably, 11 was the first multiply bonded silicon compound to activate H$_2$, forming disilane 13 in excellent yield (Scheme 7b).\textsuperscript{19}

![Scheme 7. Activation of (a) NH$_3$ and (b) H$_2$ by iminodisilene 11.](image)

### 1.4 Reactions with Organic Main Group Oxides Including CO$_2$ and CO

Although the reactivity of ditetrelenes has been extensively explored, studies of the addition of organic main group oxides are few. Following the shift in interest towards the activation of small molecules, reactions of CO$_2$ and CO with ditetrelenes have been explored. In addition to NH$_3$ and H$_2$, the reaction of iminodisilene 11 with CO$_2$ selectively formed oxadisilacyclobutanone 14 in 60% yield (Scheme 8).\textsuperscript{20} The activation of NH$_3$, CO$_2$, and H$_2$ by 11 is indicative of the highly

![Scheme 8. The activation of CO$_2$ by 11 to yield oxadisilacyclobutanone 14.](image)
reactive Si=Si bond, which may be attributed to the strongly donating N-heterocyclic imine (N'NBu) substituents which lead to increased trans-bending and twisting at the Si centres. Future investigations by Inoue and co-workers will focus on transferring the CO\(_2\) moiety of 14 to other substrates. Scheschkewitz et al. reported the partial reduction of CO using cyclotrisilene 15.\(^{21}\) Exposure of cyclotrisilene to CO at room temperature resulted in the incorporation of one equivalent of CO per molecule of 15, yielding the tricyclic compound, bis(silene) 16 (Scheme 9). The facile activation of CO by 15 can be explained, in part, by the release of ring strain in the three-membered ring featuring the Si=Si bond.

\[
\text{Tip} = 2,4,6\text{-triisopropylphenyl}
\]

**Scheme 9.** Partial reduction of CO by cyclotrisilene 15.

Ditetrelenes are also known to react with other carbonyl containing compounds. The reaction of ketones and aldehydes with tetramesityldisilene 4, reported by West, undergoes cycloaddition to form 2,3-disilaoxetanes 17a-f (Scheme 10).\(^{22}\) The reactions with the aldehydes and ketones listed in Scheme 10 went to completion within minutes at room temperature, with the exception of the reaction of benzophenone with 4 which was heated to 50 °C for 1 hour to form 17c in 12% yield.

\[
\begin{align*}
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\text{Mes}_2\text{Si} &= \text{SiMes}_2 + \text{R} \text{O} \rightarrow \text{R} \text{O} \rightarrow \\
\end{align*}
\]

**Scheme 10.** The addition of aldehydes and ketones to tetramesityldisilene 4.
Interestingly, disilene 4 was unreactive towards esters including ethyl acetate, methyl benzoate and ethyl p-(dimethylamino)benzoate, even at elevated temperatures over 3 days. Reactivity was observed only with the activated carbonyl in methyl furoate to give the cycloadduct 18, analogous in structure to adducts 17a-f (Scheme 11). The lack of reactivity of esters towards 4 can be accounted for by the less polar C=O bond in esters. Evidently, a moderately strongly polarized π-bond is required for the reaction to proceed.

\[
\text{Mes}_2\text{Si}=\text{SiMes}_2 + \begin{array}{c}
\text{O} \\
\text{OCH}_3
\end{array} \xrightleftharpoons{} \text{Benzene} \xrightarrow{15 \text{ min, } 80 \degree \text{C}} \begin{array}{c}
\text{O} \\
\text{SiMes}_2
\end{array}
\]

18 (83%)

Scheme 11. The addition of methyl furoate to 4.

In contrast to the cycloaddition observed in the reaction of disilene 4 with aldehydes and ketones, the addition of carboxylic acids to digermene 5 resulted in a 1,2-addition that yielded digermyl esters 19a-c (Scheme 12). Carboxylic acids also react rapidly with 5 at room temperature, similar to the conditions for the reactions of aldehydes and ketones with disilene 4.

\[
\text{Mes}_2\text{Ge}=\text{GeMes}_2 + \begin{array}{c}
\text{O} \\
\text{R} \quad \text{OH}
\end{array} \xrightleftharpoons{} \text{THF} \xrightarrow{5 \text{ min, } -70 \degree \text{C}} \begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

19

\(a) R = \text{tBu} (53\%)
\(b) R = \text{Mes} (55\%)
\(c) R = \text{trans-2-phenylcyclopropyl} (55\%)

Scheme 12. The 1,2-addition of carboxylic acids to digermene 5.

The reaction of ditetrelenes and compounds featuring double bonds between oxygen and main group elements other than carbon have also been investigated. Baines et al. reported the addition of nitromethane to tetramesityldisilene 4 and -digermene 5 at room temperature, resulting in the formation of 1,3,2-dioxazolidines, 20 and 21, respectively (Scheme 13). The cycloaddition results in a selective two-electron reduction of the nitrogen in nitromethane. The synthesis of 20 and 21 is facile in comparison to the analogous reactions in alkene chemistry. The generation of a 1,3,2-dioxazolidine ring system by cycloaddition of a nitro group to an alkene only occurs under
Scheme 13. The addition of nitromethane to ditetrelenes 4 and 5.

special circumstances; either photochemically\textsuperscript{24} or thermally, using highly strained alkenes and aromatic nitro compounds.\textsuperscript{25} Since the reduction of nitromethane by ditetrelenes 4 and 5 was a novel, selective two electron reduction and resulted in the formation of new heterocyclic ring systems, Baines and co-workers were interested in exploring the reaction of other organic main group oxides with ditetrelenes. The reactivity of disilene 4 and digermene 5 towards arylsulfonyl chlorides was also explored.\textsuperscript{26} Similar to the reaction with nitromethane, a two electron reduction occurs at the sulfur centre of the sulfonyl chlorides to give arylsulfonates 22, 23 and 24 (Scheme 14). Unlike the reaction with nitromethane, the reduction of the arylsulfonyl chlorides occurs through a 1,3-addition. For both nitroalkanes and the arylsulfonyl chlorides, the reductions are performed under mild conditions, without the use of a catalyst or heat, unlike the analogous reactions with alkenes.\textsuperscript{27}

Scheme 14. The reduction of arylsulfonyl chlorides by ditetrelenes 4 and 5.

1.5 Reactions with Organophosphorus Oxides

The reaction of ditetrelenes with organophosphorus oxides has not been reported in the literature. The only example of the addition of phosphine oxides to a low-valent Group 14 compound was reported by Zhao \textit{et al}.\textsuperscript{28} Diphenylphosphine oxide and other organic phosphorus compounds such as diphenylphosphine, (2-thienyl)\textsubscript{2}PCl, diphenylphosphinic acid and diphenylthiophosphinic acid, were allowed to react with the N-heterocyclic germylene 25, the germanium analogue of a carbene. In the reaction of 25 with diphenylphosphine oxide at elevated
temperatures, the phosphorus centre is reduced from P(V) to P(III) to give 26 (Scheme 15). This one-step process was envisioned as an alternative to the salt metathesis reactions for the formation of oxyphosphorus-substituted germanium (II) complexes.

\[
\begin{align*}
\text{Ar} & = 2,6-iPr_2C_6H_3 \\
\text{Scheme 15.} & \quad \text{The reactivity of diphenylphosphine oxide with germylene 25.}
\end{align*}
\]

In this thesis, the reactivity of tetramesityldisilene 4 and -digermene 5, prototypical examples of a disilene and a digermene, with organophosphorus oxides, namely, phosphine oxides and phosphites (Figure 6) will be examined. The nature of the phosphorus-oxygen bond has been investigated by Natural Bond Order (NBO)/ Natural Resonance Theory (NRT) calculations. The results of these calculations indicate that the phosphinyl moiety in the phosphine oxides and phosphites is a charge-localized dipole with the best Lewis representation of the bonding being P⁺⁻O⁻. However, throughout the thesis, the phosphorus-oxygen bond of the organophosphorus oxides will be represented as a π bond.

\[
\begin{align*}
\text{Phosphine Oxide} & \quad \text{Phosphite} \\
\text{R = alkyl, aryl}
\end{align*}
\]

\[
\begin{align*}
\text{Figure 6.} & \quad \text{Structure of organophosphorus oxides.}
\end{align*}
\]

The reactions of 4 and 5 with diphenylphosphine oxide, diphenyl phosphite and dimethyl phosphite have previously been explored in the group. In all reactions, the formation of a 1,3-adduct was observed, resulting in the reduction of the P(V) centre in the phosphine oxide or phosphite reagent to P(III) in compounds 27, 28, 29 and 30 (Scheme 16). Since compounds 27 and 28 were not sufficiently pure for publication, these reactions will be repeated and the spectroscopic assignments will be reassessed.
In addition to the re-examination of the reactions of 4 and 5 with diphenylphosphine oxide, the scope of the reaction of phosphorus(V) compounds with ditetrelenes 4 and 5, will be expanded upon in this thesis. Specifically, the reaction of 4 and 5 with dipentylphosphine oxide, an alkylphosphine oxide, and the reaction of 4 with diphenyl phosphite and dimethyl phosphite will be explored.

\[
\text{Mes}_2M=\text{MMes}_2 + \begin{array}{c}
\text{O} \\
\text{P}
\end{array} \xrightarrow{\text{Benzene or THF}} \begin{array}{c}
\text{Mes}_2M=\text{MMes}_2 \\
\text{P} \\
\text{O} \\
\text{H}
\end{array}
\]

\[R \quad \text{H} \quad \text{R}
\]

\[4 \ M = \text{Si} \]
\[5 \ M = \text{Ge} \]

\(27: M = \text{Si}, R = \text{Ph} (63\%, \text{ crude})\)
\(28: M = \text{Ge}, R = \text{Ph} (72\%, \text{ crude})\)
\(29: M = \text{Ge}, R = \text{OCH}_3 (52\%)\)
\(30: M = \text{Ge}, R = \text{OPh} (68\%)\)

**Scheme 16.** The addition of phosphine oxides and phosphites to 4 and 5.
1.6 References


Chapter 2

2 Synthesis and Characterization of Disilyl and Digermyl Phosphinates and Phosphites

2.1 The Addition of Organophosphorus Oxides to Ditetrelenes

The reactivity of dialkyl and diarylphosphine oxides and phosphites towards ditetrelenes 4 and 5 is reported. The addition of phosphine oxides to a yellow solution of 4 or 5 at room temperature in benzene resulted in the formation of disilyl and digermyl phosphinates 27, 28, 31 or 32 (Scheme 17). The reactions occurred rapidly under mild conditions as evidenced by the rapid fading (5 min) of the yellow colour of the solutions to light yellow. The isolation of 27 and 28 was achieved by recrystallization of the crude oil from hexanes to yield white solids in 56% and 54% yield, respectively. By repeating the synthesis of 27 and recollecting the spectroscopic data, the assignment of the chemical shifts for the mesityl moieties could be corrected. For 28, the $^{13}$C chemical shifts for the mesityl $i$- and $p$-carbons were reassigned, and a spectrum with better resolution was obtained which enabled the correct assignment of the broad peaks originally reported in the $^{13}$C{$^1$H} NMR spectrum of 28. Since, the purification of 31 and 32 was difficult due to the sensitivity of the compounds to air and moisture, characterization of the products was performed on the crude reaction mixtures.

\[
\begin{align*}
\text{Mes}_2M=MMes_2 & \quad + \quad O^+ \quad \rightarrow \quad \text{Mes}_2M=MMes_2 \\
4 \quad M = \text{Si} & \quad 5 \quad M = \text{Ge} & \quad \text{Benzene} & \quad 5 \text{ min, RT} & \quad \text{Disilyl / Digermyl Phosphinite} \\
\end{align*}
\]

\[
\begin{align*}
27: M = \text{Si, R = Ph (56\%)} \\
28: M = \text{Ge, R = Ph (54\%)} \\
31: M = \text{Si, R = penty1 (61\%, crude)} \\
32: M = \text{Ge, R = penty1 (94\%, crude)}
\end{align*}
\]

Scheme 17. The addition of diphenyl- and dipentylphosphine oxide to 4 and 5.

The reaction of diethylphosphine oxide with 4 was also examined. The addition of diethylphosphine oxide (95%, Alfa Aesar) to a solution of 4 resulted in a colour change of the solution from bright yellow to pale yellow after 10 minutes. The solvent was evaporated, resulting in a pale yellow oil which was recrystallized from hexanes to yield an off-white solid which
contained two products, 33 and 34 in a ratio of 1:10, respectively (Scheme 18). The electrospray ionization (ESI) mass spectrum of the recrystallized solid contains a base peak at m/z 677.3 which is consistent with C_{40}H_{55}O_2PSi_2Na (34 plus Na\(^+\)), corresponding to a 1:1 adduct between diethylphosphine oxide and disilene 4 plus an oxygen. A less intense signal was also observed at m/z 639.4 which is consistent with the molecular formula C_{40}H_{56}OPSi_2 (33 plus H\(^+\)). The \(^{31}\)P\{\(^{1}\)H\} NMR spectrum of the solid revealed a signal at 135.4 ppm which is characteristic of a P(III) centre, and therefore, was assigned to 33. However, it is in minor amounts compared to the signal at 47.5 ppm, which is indicative of a P(V) centre and was assigned to 34. An attempt was made to separate compounds 33 and 34 by preparative TLC; however, only 34 was isolated as a clear, colourless oil. The oil was recrystallized from benzene to give 34 as clear, colourless crystals. The structure of 34 was determined using X-ray crystallography (Figure 7). All bond lengths and angles in the structure of 34 are within expected ranges.\(^1\)

\[
\begin{align*}
\text{Mes}_2\text{Si} & \equiv \text{SiMes}_2 \\
4 & + \quad \begin{array}{c}
O
\\
\text{Et}
\end{array} \\
& \quad \begin{array}{c}
\text{H}
\\
\text{Et}
\end{array} \\
\text{Benzene} & \quad \begin{array}{c}
18 \text{ h, RT}
\\
\end{array} \\
\rightarrow & \quad \begin{array}{c}
\text{Mes}_2\text{Si} \equiv \text{SiMes}_2 \\
\text{O}
\\
\text{Et}
\end{array} \\
& \quad \begin{array}{c}
\text{H}
\\
\text{Et}
\end{array} \\
& \quad \begin{array}{c}
\text{O}
\\
\text{Et}
\end{array}
\end{align*}
\]

\textbf{Scheme 18.} The addition of 95\% diethylphosphine oxide to 4.
Figure 7. Displacement ellipsoid plot of 34. Ellipsoids are at the 50% probability level and hydrogen atoms are omitted for clarity except the hydrogen on Si2. Selected bond lengths (Å) and angles (deg): Si1-O1 = 1.6830(17), Si1-Si2 = 2.3742(10), P1-O1 = 1.5802(17), P1-O2 = 1.4711(18), O1-Si1-Si2 = 105.63(7), Si1-Si2-H2 = 100.6(10), P1-O1-Si1 = 150.79(12).

The formation of 34 was surprising given that the reaction was performed under inert conditions. The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy which revealed that 34 is formed during the early stages of the reaction (Figure 8). Analysis of the reagent by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed that the reagent was primarily diethylphosphinic acid (Et$_2$P(O)OH) with only minor amounts of diethylphosphine oxide present (95: 5 ratio). Evidently, compound 34 is formed by reaction of disilene 4 with diethylphosphinic acid and 33 is formed by reaction of 4 with diethylphosphine oxide. Compound 33 is susceptible to oxidation, as the intensity of the signal at 135.4 ppm decreases over time, while the intensity of the signal at 47.5 ppm increases.
Figure 8. The reaction of 4 with diethylphosphinic acid monitored by $^{31}\text{P}[^1\text{H}]$ NMR spectroscopy (C$_6$D$_6$, 162 MHz).

Diethylphosphine oxide was synthesized by the reaction of diethyl phosphite with excess ethylmagnesium bromide in diethyl ether at room temperature (Scheme 19). The phosphine oxide was isolated as a white solid after recrystallization of the crude oil from hexanes. Multiple attempts were made to react 4 with diethylphosphine oxide, however, the phosphine oxide was only soluble in water and slightly soluble in chloroform. These solvents could not be used for the reaction of diethylphosphine oxide with 4 since both water and chloroform readily react with 4. Since the

Scheme 19. The synthesis of diethylphosphine oxide.
reaction of diethylphosphine oxide with 4 proved to be problematic, the study of the reaction of
diethylphosphine oxide with 4 was discontinued.

Similar to the addition of diphenyl- and dipentylphosphine oxide to ditetrelenes 4 and 5, one equivalent of dimethyl or diphenyl phosphite was added to a yellow solution of disilene 4 dissolved in benzene to yield disilyl phosphites 35 and 36, respectively (Scheme 20). Unlike the phosphine oxides which reacted within 5 minutes, the reaction of the ditetrelenes with the phosphites took 18 hours to go to completion. The purification of 35 involved recrystallization of the crude oil from hexanes to yield clear, colourless crystals. In the reaction of diphenyl phosphite with 4, excess phosphite was separated by preparative thin layer chromatography (TLC) and 36 was isolated as a white solid by recrystallization from hexanes in 46% yield.

\[ \text{Mes}_2\text{Si} \equiv \text{SiMes}_2 + \text{RO} \begin{array}{c} \text{P} \\text{H} \end{array} \text{OR} \xrightarrow{\text{Benzene}} 18 \text{ h, RT} \text{Mes}_2\text{Si} \equiv \text{SiMes}_2 \begin{array}{c} \text{RO} \\text{P} \\text{H} \end{array} \text{OR} \]

**Disilyl Phosphite**

35: R = OCH\(_3\) (44%)
36: R = OPh (46%)

**Scheme 20.** The addition of dimethyl and diphenyl phosphite to 4.

### 2.2 Characterization of Disilyl and Digermyl Phosphinites and Phosphites

The compounds synthesized from the reaction of diorganophosphine oxides and phosphites with ditetrelenes 4 and 5 were characterized by NMR spectroscopy, high resolution mass spectrometry, infrared (IR) spectroscopy, and when appropriate, X-ray crystallography. The exact mass for each compound, as determined by ESI-MS in positive ion mode, was consistent with the formation of a 1:1 adduct between the diorganophosphine oxide or phosphite and disilene 4 or digermene 5, plus Na\(^+\) or H\(^+\).

NMR spectroscopy was extremely useful in the characterization of the disilyl and digermyl phosphinites and phosphites as the compounds contained multiple NMR active nuclei including \(^1\text{H}, \text{}^{13}\text{C}, \text{}^{31}\text{P}, \text{ and } ^{29}\text{Si}\) (for the derivatives formed from the reactions with tetramesityldisilene 4). The most diagnostic nucleus for assessing the outcome of the reactions was \(^{31}\text{P}\).
Diorganophosphites with a P(III) centre, resonate downfield in comparison to compounds with P(V) centres as exemplified by the $^{31}$P chemical shifts of trimethyl phosphite (P(OCH$_3$)$_3$) and trimethyl phosphate (O=P(OCH$_3$)$_3$) which resonate at 142.0 ppm and 3.7 ppm, respectively.$^5$ The same trend is seen in the reaction of phosphine oxides and phosphites with ditetrelenes 4 or 5. The phosphine oxides and phosphite reagents containing a P(V) centre resonate below 40 ppm, whereas the disilyl and digermyl phosphinite and phosphite derivatives formed, containing a P(III) centre, resonate at chemical shifts significantly shifted downfield (above 100 ppm) compared to the starting phosphorus reagent (Table 2).

Table 2. $^{31}$P chemical shifts of P(V) reagents, disilyl/ digermyl phosphinites and phosphites.

<table>
<thead>
<tr>
<th>R</th>
<th>$^{31}$P Chemical Shift (ppm)$^a$</th>
<th>$^{31}$P Chemical Shift (ppm)$^a$</th>
<th>$^{31}$P Chemical Shift (ppm)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{Mes}_2\text{M}$$-\text{MMes}_2$</td>
<td></td>
</tr>
<tr>
<td>R = Ph</td>
<td>16.9</td>
<td>$\text{M} = \text{Si}, \text{R} = \text{Ph}$ (27)</td>
<td>107.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{M} = \text{Ge}, \text{R} = \text{Ph}$ (28)</td>
<td>104.5</td>
</tr>
<tr>
<td>R = pentyl</td>
<td>29.7</td>
<td>$\text{M} = \text{Si}, \text{R} = \text{pentyl}$ (31)</td>
<td>130.6$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{M} = \text{Ge}, \text{R} = \text{pentyl}$ (32)</td>
<td>129.0</td>
</tr>
<tr>
<td>R = OCH$_3$</td>
<td>9.8</td>
<td>$\text{M} = \text{Si}, \text{R} = \text{OCH}_3$ (35)</td>
<td>132.8</td>
</tr>
<tr>
<td>R = OPh</td>
<td>-0.4</td>
<td>$\text{M} = \text{Si}, \text{R} = \text{OPh}$ (36)</td>
<td>133.3</td>
</tr>
</tbody>
</table>

$^a$ Measured in C$_6$D$_6$.

$^b$ Tentatively assigned.

For the reactions with tetramesityldisilene 4, $^1$H-$^{29}$Si gHMBC (gradient heteronuclear multiple bond correlation) spectroscopy also provided valuable structural information. In HMBC spectroscopy, correlations are seen between heteronuclei and hydrogens which are 1 to 3 bonds away, which gives insight into the connectivity of the molecule. Two signals were consistently observed in the disilyl phosphinite and phosphite derivatives synthesized with $^{29}$Si chemical shifts of approximately -55 and -5 ppm and coupling constants of ~ 180 Hz and 15 Hz, respectively (Table 3). For example, the $^1$H NMR spectrum of 35 revealed a signal at 5.67 ppm, which integrated to 1H and was assigned to the Si-H moiety. In the $^1$H-$^{29}$Si gHMBC spectrum of disilyl phosphite 35, each signal in the $^{29}$Si dimension correlates to the signal at 5.67 ppm in
Table 3. The $^{29}$Si chemical shifts and coupling constants of disilyl phosphinites and phosphites.

<table>
<thead>
<tr>
<th></th>
<th>$^{29}$Si chemical shifts of $\text{Si}_A$ (ppm)</th>
<th>$^2J_{\text{Si-H}}$ coupling constant (Hz)</th>
<th>$^{29}$Si chemical shifts of $\text{Si}_B$ (ppm)</th>
<th>$^1J_{\text{Si-H}}$ coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{R} = \text{Ph}$ (27)</td>
<td>-1.8</td>
<td>15</td>
<td>-56.4</td>
<td>175</td>
</tr>
<tr>
<td>$\text{R} = \text{pentyl}$ (31)</td>
<td>-5.6</td>
<td>13</td>
<td>-54.8</td>
<td>177</td>
</tr>
<tr>
<td>$\text{R} = \text{OCH}_3$ (35)</td>
<td>-7.3</td>
<td>13</td>
<td>-55.3</td>
<td>180</td>
</tr>
<tr>
<td>$\text{R} = \text{OPh}$ (36)</td>
<td>-5.9</td>
<td>15</td>
<td>-55.7</td>
<td>179</td>
</tr>
</tbody>
</table>

The $^1$H dimension. The signal at -55.3 ppm correlates through a $J$ coupling of 180 Hz and this, was assigned to an Si-H moiety on the basis of the magnitude of the $J$ and the chemical shift. The signal at -7.3 ppm correlates through a $J$ coupling of 13 Hz and thus, was assigned to $\text{Si}_A$ (Figure 9).

Figure 9. The $^1$H-$^{29}$Si gHMBC spectrum of 35 showing the correlations to the signal at 5.67 ppm in the $^1$H dimension.
The structures of 27 and 35 (Figure 10) were identified unambiguously through single crystal X-ray diffraction. The phosphorus centre of 35 exhibits trigonal pyramidal geometry; the displacement of the phosphorus atom from the plane of the attached atoms is 0.764 Å. The geometry at the phosphorus centre is indicative of the P(III) oxidation state. All bond lengths and angles in 35 are within expected ranges. For example, the Si2-H2 (1.39 Å), Si1-O1 (1.67 Å), Si1-Si2 (2.38 Å) and P1-O1 (1.60 Å) bond lengths in 35 are within the ranges of 1.39-1.45, 1.64-1.71, 2.35-2.40 and 1.59-1.66 Å, respectively, for related compounds. In some crystal samples of disilyl phosphite 35, a disorder was observed in the molecular structure where a hydroxyl group was bound to Si2, 5% of the time, instead of a hydrogen, as a result of oxidation of the Si-H centre.

![Figure 10](image.png)

**Figure 10.** Displacement ellipsoid plot of 35. Ellipsoids are at the 50% probability level and hydrogen atoms are omitted for clarity except the hydrogen on Si2. Selected bond lengths (Å) and angles (deg): Si1-O1 = 1.6685(11), Si1-Si2 = 2.3806(7), P1-O1 = 1.6043(11), O1-Si1-Si2 = 108.52(4), Si1-Si2-H2 = 100.0(7), P1-O1-Si1 = 141.92(7).

Infrared spectroscopy is also useful in this chemistry. The appearance of the characteristic signals for Si-H (or Ge-H) groups and the disappearance of the signals characteristic of the P=O moiety of the phosphine oxides and phosphites are particularly diagnostic. For example, the IR spectrum of 36 (Figure 11) shows a medium intensity signal at 2129 cm\(^{-1}\), which is characteristic of an Si-H stretching vibration (typically 2250 – 2100 cm\(^{-1}\)). Additionally, the absence of strong
signals in the regions 2425 – 2325 cm\(^{-1}\) and 1350 – 1300 cm\(^{-1}\), corresponding to phosphorus ester P-H stretching and aromatic P=O stretching, respectively, indicates the lack of a O=P(V)-H moiety in the compound. Instead, a strong signal at 851 cm\(^{-1}\) is observed and can be assigned to the P(III)-O stretching of the P(III)-(OPh)\(_2\) functional group, which are typically found in the range of 875 – 830 cm\(^{-1}\).\(^8\)

![IR spectrum of compound 36.](image)

### Figure 11. IR spectrum of compound 36.

#### 2.3 Reactivity of Disilyl and Digermyl Phosphinites and Phosphites

The disilyl and digermyl adducts 31, 32, 35, and 36 were prone to oxidation of the M-H bond, hydrolysis at the P-OR bond or oxidation of the P(III) centre. The reactions were typically accelerated by chromatography, except for the oxidation of the Si-H bond of disilyl phosphite 35. The dialkyldisilyl and digermyl phosphinites were particularly prone to oxidation of the P(III) centre and hydrolysis of the P-O moiety bound to the M centre.

Attempted purification of 31 by preparative TLC resulted in the isolation of two compounds, 37 and 38. Compound 37 is a result of the oxidation of the P(III) centre in 31 and compound 38 is proposed to form through hydrolysis of the P-O moiety bound to the Si centre. (Scheme 21a). Compound 39 was the only compound isolated from the attempted purification of 32 by preparative TLC and is proposed to form by hydrolysis of the P-O moiety bound to the Ge centre, similar to the formation 38 (Scheme 21b).
The secondary reactivity observed for (a) disilyl phosphinite 31 and (b) digermyl phosphinite 32.

Dimethylidisilyl phosphite 35 was also susceptible to oxidation of the Si-H bond to form compound 40 (Scheme 22). The presence of 40 was observed in the molecular structure obtained from single-crystal X-ray diffraction, and in the ESI mass spectrum at \( m/z \) 681.3 of samples of 35.

Attempts to separate 35 and 40 by preparative TLC resulted in the isolation of compound 41 in 6% isolated yield (Scheme 23). The ESI mass spectrum of 41, revealed a base peak at \( m/z \) 651.3 corresponding to the molecular formula \( \text{C}_{37}\text{H}_{49}\text{O}_{3}\text{PSi}_{2} \) plus \( \text{Na}^{+} \), which is consistent with a 1:1 adduct between 35 and water, and the loss of methanol. Consistent with the loss of \( \text{CH}_3\text{O} \), in the \( ^1\text{H} \) NMR spectrum of 41, the doublet assigned to the methoxy group at 3.24 ppm integrates to

![Scheme 21](image)  
**Scheme 21.** The secondary reactivity observed for (a) disilyl phosphinite 31 and (b) digermyl phosphinite 32.

![Scheme 22](image)  
**Scheme 22.** The oxidation of the Si-H moiety of 35.

![Scheme 23](image)  
**Scheme 23.** The formation of 41 following preparative TLC.
3H relative to the signal at 5.66 ppm which was assigned to the Si-H moiety. An additional doublet appears at 6.80 ppm. The coupling constant of the doublet is 690 Hz, which is typical of a one-bond hydrogen-phosphorus(V) coupling, and therefore, is assigned to the hydrogen directly bonded to the P(V) centre.\(^9\) In the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 41, a signal is observed at -5.2 ppm which is shifted upfield compared to the chemical shift of the signal for disilyl phosphite 35 at 132.8 ppm, consistent with a P(V) centre. These data are consistent with the structure proposed for 41.

The formation of compound 41 was proposed to occur through the hydrolysis of the P-\(\text{OCH}_3\) bond in 35, followed by tautomerization. Indeed, 41 could be formed independently by hydrolysis to give a white solid consisting of 41 in an 82% yield as determined by \(^{31}\text{P}\) NMR spectroscopy (Scheme 24).

\[
\begin{align*}
\text{Mes}_2\text{Si}-\text{SiMes}_2 \\
\text{H}_3\text{COPOH} \\
\text{OCH}_3
\end{align*}
\xrightarrow{\text{H}_2\text{O} \quad 18 \text{ h}, \text{RT}}
\begin{align*}
\text{Mes}_2\text{Si}-\text{SiMes}_2 \\
\text{POH} \\
\text{H}_3\text{CO}
\end{align*}
\]

\[41\] (82%, NMR Yield)

**Scheme 24.** The direct hydrolysis of dimethyldisilyl phosphite 35.

Preparative TLC of a sample of 35 also resulted in the formation of 41, indicating the hydrolysis was accelerated by chromatography. The hydrolysis of trialkyl phosphites to give dialkyl phosphites is well known; the mechanism for the hydrolysis of P(OMe)\(_3\) has been studied by Alam et al. and the results are consistent with the observations reported herein (Scheme 25).\(^{10}\)

\[
\text{(MeO)}_3\text{P} + 2 \text{H}_2\text{O} \rightarrow \text{MeO} \underset{\text{H}}{\text{P}} \underset{\text{MeO}}{\text{O}} \text{Me} \underset{\text{H}}{\text{O}} \text{H} \rightarrow \text{MeO} \underset{\text{MeOH}}{\text{P}} \underset{\text{H}}{\text{O}} \text{H}
\]

**Scheme 25.** The hydrolysis of trimethyl phosphite with \(^{17}\text{O}\)-labelled water.\(^{10}\)

Diphenyldisilyl phosphite 36 is not as susceptible to hydrolysis or oxidation in comparison to the dialkyldisilyl phosphite since 36 was successfully isolated from the TLC plate as a white solid, although minor contaminants were observed. On the basis of ESI mass spectrometry and \(^{31}\text{P}\) NMR...
spectroscopy the contaminants were identified as triphenyl phosphite (P(OPh)₃) and compounds 42, 43, and 44; the ratio of 36 relative to the contaminants was 100: 12: 1: 1: 1, respectively (Figure 12). Compound 42 is proposed to form through the hydrolysis of the P-OPh bond in 36, followed by tautomerization, similar to the formation of 41. The formation of 43 can be explained by the oxidation of the P(III) centre, and 44 is a result of the oxidation of both the P(III) centre and the Si-H moiety.

![Figure 12. Compounds isolated from the preparative TLC plate.](image)

The diaryldisilyl and digermyl phosphinites 27 and 28 showed no signs of further chemistry. Upon exposure to air, 27 and 28 were stable, and no oxidation or hydrolysis was observed by NMR spectroscopy. The diaryl phosphinites and phosphites were more stable in comparison to the dialkyl derivatives. This observation is in line with the computational studies performed on the stability of dialkyl and diarylphosphines by Higham et al. In order for a phosphine to be oxidized, it must go through a cationic radical intermediate [R₂HP⁺]. The authors report that [Ph₂HP⁺] is more stable due to the steric bulk and conjugation provided by the aryl groups in comparison to the dialkyl derivative [Et₂HP⁺]. As a result, the P(III) centre of diethylphosphine is more susceptible to oxidation compared to diphenylphosphine.

2.4 Discussion

The reactivity of ditetrelenes 4 and 5 towards compounds containing P=O bonds, resulted in the formation of 1,3-adducts 27, 28, 31, 32, 35 and 36 under mild conditions (Scheme 26). In each case, the reaction resulted in the formation of an M-O and M-H bond, and the breaking of a P-H bond to reduce the P(V) centre in the phosphine oxides and phosphites to P(III) in the adducts.
The addition of organophosphorus oxides to 4 and 5.

Reductions of phosphine oxides to form phosphines are often achieved using alumino hydride or chlorosilane reagents such as LiAlH₄ or HSiCl₃ at elevated temperatures. The use of hydrosilanes as alternatives to alumino hydrides and chlorosilane reagents has also been explored in the reduction of phosphine oxides, although this method requires a catalyst to activate the Si-H bond. While these methods have been extensively investigated with tertiary phosphine oxides (O=PR₃), the reduction of secondary phosphine oxides (O=PHR₂) has been explored to a lesser extent. Blanchet et al. recently reported the reduction of tertiary and secondary phosphine oxides using bis(2-chlorophenyl)borinic acid as a precatalyst and phenylsilane as the hydride source. The reduction of diphenylphosphine oxide by the borinic acid precatalyst to form diphenylphosphine was conducted at 80 °C (Scheme 27). In contrast, the reduction of diphenyl- and dipentylphosphine oxide by disilene 4 and digermene 5 yields phosphinite (R₂P(OR’)) derivatives 27, 28, 31 and 32, and not dialkyl- or diarylphosphines. While the formal oxidation number for P is (III) in both types of products, the chemical state of P in the phosphinite derivatives is intermediate between that of phosphine oxides and phosphines.

The reduction of diorganophosphine oxides and phosphites by disilene 4 is reminiscent of the reaction of diorganophosphine oxides and phosphites with chlorosilanes at elevated temperatures.

Scheme 26. The addition of organophosphorus oxides to 4 and 5.

Scheme 27. Reduction of diphenylphosphine oxide by a borinic acid precatalyst.
in the presence of an amine which also gives silyl phosphinite and phosphite derivatives 46 and 47, respectively (Scheme 28). However, in the reactivity with disilene 4, the Lewis acid and Lewis base are contained within the same molecule, and the reaction can be performed under neutral conditions and at room temperature.

Scheme 28. Reaction of diorganophosphine oxides and phosphites with chlorosilanes in the presence of amines.

The synthesis of germyl phosphinite 48 has previously been reported to occur through the reduction of dibutylphosphine oxide by potassium to form the salt derivative (R₂POK). A salt metathesis reaction occurs when the salt is added to Bu₃GeCl to yield germyl phosphinite 48 (Scheme 29a). Similarly, diethylgermyl phosphite 49 is synthesized from the reaction of a phosphite salt with a chlorogermane at 70 °C (Scheme 29b).

Scheme 29. The synthesis of (a) germyl phosphinite 48 and (b) germyl phosphite 49 through a salt metathesis reaction.

In the salt metathesis method, the P(V) centre of dibutylphosphine oxide and diethyl phosphite is already reduced to a P(III) centre in the salt derivative. In this case, the germane is only involved in a substitution reaction. In contrast, the formation of the digermyl phosphinites and phosphites
by the reaction between phosphine oxides or phosphites with digermene 5 is a result of the Ge centre being directly involved in the reduction of the P(V) centre of the phosphorus oxides.

The reaction of diorganophosphine oxides and phosphites with ditetrelenes is in stark contrast to that with alkenes. The reaction of diorganophosphine oxides and phosphites with alkenes leads to cleavage of the P-H bond and the formation of a C-P bond and requires the use of heat with or without a transition metal catalyst. For example, the addition of diphenylphosphine oxide to 1-decene yields the anti-Markovnikov adduct 50 at 80 °C (Scheme 30a). In another example, the hydrophosphorylation of alkenes with dialkyl phosphites is catalyzed by Mn(OAc)₂ at high temperatures (ranging from 90 to 110 °C) to yield dialkyl phosphonates 51 (Scheme 30b). In both examples, the reaction of the organophosphorus oxide with the alkene involves addition of the P-H across the C=C bond.

Scheme 30. (a) Anti-Markovnikov addition of diphenylphosphine oxide to 1-decene. (b) Hydrophosphorylation of an alkene with dialkyl phosphites.

In contrast, ditetrelenes react readily with phosphine oxides and phosphites without the use of heat or a catalyst. Instead of the formation of a C-P bond, the stronger and more thermodynamically favoured M-O (M = Si, Ge) bond is formed. The phosphorus centre in the reaction of phosphine oxides and phosphites with ditetrelenes is reduced from P(V) to P(III). In the reaction with alkenes, the oxidation state of the phosphorus centre remains the same.

Since ditetrelenes 4 and 5 successfully activated organophosphorus oxides, it is also interesting to compare the reactivity of phosphine oxides and phosphites with transition metals, particularly those used to facilitate the addition to alkenes. In the Ni-catalyzed hydrophosphinylation of 1-octene with a primary phosphite, ethyl phosphinate (EtOP(O)H₂), the
anti-Markovnikov adduct 52 was formed in 96% yield as determined by $^{31}$P NMR spectroscopy (Scheme 31).

\[
\text{C}_8\text{H}_{13} + \text{EtO} - \text{P} \longrightarrow \text{H}, \quad \text{Cl}_2\text{Ni(dppe) (5 mol\%)} \quad \text{Toluene} \quad 24 \text{ h, RT} \quad \text{H}_3\text{C} - \text{C} - \text{EtO} - \text{P} \longrightarrow \text{H} \quad 52 \quad (96\% \text{ NMR yield})
\]

\[
dppe = \text{Ph}_2\text{P} \longrightarrow \text{PPh}_2
\]

**Scheme 31.** The Ni-catalyzed hydrophosphinylation of 1-octene.

The mechanism proposed by the authors (Scheme 32) involves the coordination of the ethyl phosphinate tautomer to the Ni(0) centre, to generate intermediate species I. Following the complexation of Ni(0) to the phosphinate tautomer, intermediate I can add to the alkene. Subsequent reductive elimination would regenerate the Ni catalyst and yield the functionalized product 52.

\[
\text{EtO} - \text{P} \longrightarrow \text{H} \quad \text{EtO} - \text{P} \longrightarrow \text{OH} \quad \text{EtO} - \text{P} \longrightarrow \text{OH} \quad \text{EtO} - \text{P} \longrightarrow \text{NiLn} \quad \text{EtO} - \text{P} \longrightarrow \text{NiLn} \quad \text{H}_2\text{C} \rightarrow \text{CR}_2
\]

**Scheme 32.** Proposed mechanism for the hydrophosphinylation of 1-octene.

The enantioselective hydrophosphinylation of diene 53 with diphenylphosphine oxide is facilitated by a Pd-based catalyst and diphenylphosphinic acid as a co-catalyst to yield the Markovnikov adduct 54 in 86% yield (Scheme 33). The authors proposed the mechanism depicted in Scheme 34 based on literature precedence and experimental observations. The Pd(0)
precatalyst undergoes ligand substitution with the Josiphos ligand (L3) to form chiral species I. Subsequent oxidative addition of co-catalyst (diphenylphosphinic acid), yields the Pd-H species II. Addition of the 1,3-diene results in coordination of the Pd to the less hindered alkene to form species III. Species III undergoes hydropalladation to generate the Pd-π-allyl intermediate IV, which is subjected to ligand exchange upon addition of diphenylphosphine oxide. As a result of the substitution of diphenylphosphinic acid with Ph₂P(O)H, a Pd-P(V) intermediate V is formed and the co-catalyst is regenerated. Reductive elimination results in the formation of the functionalized product VI and regeneration of chiral species I.

Scheme 33. The Pd-catalyzed hydrophosphinylation of 54.

In the Pd-catalyzed hydrophosphinylation of 1,3-dienes, the alkene is activated before addition of the phosphine oxide; whereas, in the Ni-catalyzed hydrophosphinylation of terminal alkenes with primary phosphites, the phosphite is activated first, then addition to the alkene occurs.
While the mechanism for the transition metal catalyzed hydrophosphinylation of alkenes differs between reactions with phosphine oxides and phosphites, a similarity is seen where the phosphorus reagent binds to the transition metal through the P atom. In contrast, for the reactions of phosphine oxides and phosphites with ditetrelenes, the phosphine oxide or phosphite is attached to the metal centre through the oxygen. The reactivity observed between phosphine oxides and phosphites with 4 and 5 is evidently governed by the strong M-O bond that is formed from addition of the P⁺-O⁻ bond of the organophosphorus oxide to the M=M bond. This imparts unique reactivity to the reactions of ditetrelenes with phosphine oxides and phosphites which can be utilized in further chemistry.

2.5 Summary

The reaction of phosphine oxides and phosphites with disilene 4 and digermene 5 resulted in a mild two electron reduction of the P centre, to yield diorganodisilyl and digermyl phosphinites and phosphites (Figure 13). The formation of diorganodisilyl phosphinites and phosphites by 4 provides an alternative synthetic route to the traditional reduction of phosphine oxides and phosphites by chlorosilanes in the presence of amines at elevated temperatures, under neutral conditions at room temperature. For the previous synthesis of a diorganogermyl phosphinite, the phosphine oxide was reduced by potassium to form a salt of the phosphine oxide, followed by a salt metathesis reaction with a chlorogermaine. The new synthesis of diorganodigermyl phosphinites with 5 shows the reduction of the P(V) centre of the phosphine oxide directly by the Ge centre.

The formation of an M-O bond in the disilyl and digermyl phosphinites and phosphites is in contrast to alkene chemistry, which adds the P-H moiety of the phosphine oxide or phosphite across the C=C bond to form a C-P bond. Furthermore, alkenes require heat and/or a catalyst to
facilitate the addition of phosphine oxides and phosphites. The reactions of organophosphorus oxides with ditetrelenes 4 and 5 are performed under mild conditions, without the use of a catalyst. Therefore, ditetrelenes 4 and 5 are capable of activating organophosphorus oxides. However, the reactivity of phosphine oxides and phosphites with ditetrelenes differs from the reactivity with transition metals. Transition metals react directly with the P centre, often through a P-OH containing species, whereas ditetrelenes react with the oxygen of the P^+O^- moiety. The reaction of organophosphorus oxides with 4 and 5 provides another example of the activation of organic main group oxides by ditetrelenes, in addition to the activation of nitromethane, arylsulfonyl chlorides, CO$_2$ and CO$_2$.

While all reactions lead to the formation of a 1,3-adduct containing a P(III) centre, secondary reactions of certain adducts were observed. Upon exposure to air and moisture, three classes of secondary reactions were observed: i) hydrolysis of the P-OR bond, ii) oxidation of the M-H bond and iii) oxidation of the P(III) centre. The dipentyldisilyl and digermyl phosphinites were the most susceptible to secondary reactions, while the diphenyldisilyl and digermyl phosphinites were the most stable. This trend can be rationalized by the steric bulk of the aryl derivatives providing increased stability of the P(III) center.

The importance of the purity of commercially available reagents is exemplified in the attempted addition of diethylphosphine oxide to 4. The 95% reagent that was purchased was made up of diethylphosphinic acid, and only about 5% diethylphosphine oxide. The addition of diethylphosphinic acid to 4 resulted in the formation of 34, containing a P(V) centre.

2.6 Experimental

2.6.1 General Experimental Details

All reactions were carried out using flame dried apparatus under an inert atmosphere of argon using general Schlenk techniques or in an MBraun glovebox under an atmosphere of nitrogen, unless otherwise stated. All anhydrous solvents were collected from an Innovative Technology solvent purification system and dried over 4 Å molecular sieves. All reagents were purchased from Millipore Sigma or Alfa Aesar. Disilene 4 was prepared by photolysis of Mes$_2$Si(Si(CH$_3$)$_3$)$_2$ in hexanes in a quartz tube with Ushio G8T5 Mercury UV-C lamps (254 nm)
and cooled to -45 °C using a Thermo Scientific Neslab ULT 80 bath circulator. DiGERmene 5 was prepared through a similar procedure as 4, by the photolysis of (Mes$_2$Ge)$_3$ in THF at 350 nm. NMR spectra were acquired using a Varian INOVA I600 FT-NMR spectrometer or a Bruker AvIII HD 400 spectrometer. The $^1$H and $^{13}$C chemical shifts (δ) are listed in ppm against residual C$_6$D$_5$H (7.15 ppm) and C$_6$D$_6$ (128 ppm) relative to tetramethylsilane, respectively. The chemical shifts for the $^{31}$P{$^1$H} NMR spectrum were referenced externally to 85% H$_3$PO$_4$. The $^{29}$Si chemical shifts were obtained from the $^{29}$Si dimension of the $^1$H-$^{29}$Si gHMBC spectrum relative to tetramethylsilane. Electrospray ionization time of flight mass spectrometry was performed using the Bruker microOTOF 11 instrument in positive ion mode. Infrared spectra were collected through Attenuated Total Reflectance (ATR)-IR spectroscopy on a solid sample using the Perkin Elmer Spectrum Two IR Spectrometer. Reaction mixtures were purified outside of the glovebox using preparative thin-layer chromatography on 20 x 20 cm plastic TLC plates consisting of silica gel coated with a fluorescent indicator and purchased from Millipore Sigma.

2.6.2 Addition of Diphenylphosphine Oxide to Tetramesityldisilene 4

\[
\text{Mes}_2\text{Si} - \text{SiMes}_2
\]

Diphenylphosphine oxide (19 mg, 0.10 mmol) was added to a yellow solution, consisting of tetramesityldisilene 4 (52 mg, 0.10 mmol) dissolved in benzene (4 mL), at room temperature; the colour of the solution immediately changed to pale yellow. The benzene was evaporated giving a colourless oil which was redissolved in a minimal amount of hexanes. The flask was placed in the freezer (-20 °C) for 24 hours. A white precipitate formed and the solid was isolated by decantation (37 mg, 56 %). mp: 186 – 190 °C; ATR-FTIR (solid, cm$^{-1}$) 2919 (m), 2132 (m, Si-H), 1602 (m), 1435 (m), 940 (s), 842 (m), 795 (m), 696 (s); $^1$H NMR (C$_6$D$_6$, 600 MHz) δ 7.57 – 7.52 (m, 4H, Ph$_m$-H), 7.06 – 6.98 (m, 6H, Ph$_o$ and p-H), 6.67 (s, 4H, Mes m-H), 6.63 (s, 4H, Mes m-H), 5.66 (s, 1H, Si-H), [2.32 (s, Mes o-CH$_3$), 2.31 (s, Mes o-CH$_3$) all together 24H], 2.07 (br s, 12H, Mes p-CH$_3$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 151 MHz) δ 145.41 (Mes o-C), 144.19 (Mes o-C), 143.94 (d, J = 24 Hz, Ph i-C), 139.19 (Mes p-C), 138.56 (Mes p-C), 135.06 (Mes i-C), 131.73 (d, J = 25 Hz, Ph o-CH), 131.49 (Mes i-C), 129.71 (Mes m-CH), 129.22 (Ph p-CH), 128.86 (Mes m-CH), 128.1 (Ph m-CH)$^a$, 25.14 (Mes o-CH$_3$), 25.12 (Mes o-CH$_3$), 25.06 (br s, Mes o-CH$_3$), 21.05 (Mes p-CH$_3$), 20.99 (Mes p-CH$_3$); $^{29}$Si (C$_6$D$_6$)

$^a$ Chemical shift extracted from $^{13}$C{$^1$H} gHMBC spectrum.
\[ \delta -1.8 \text{ (Si-O), -56.4 (Si-H); } ^{31}\text{P}\{^1\text{H}\} \text{ (C}_6\text{D}_6, 243 \text{ MHz) } \delta 107.2; \text{ ESI-MS for [C}_{48}\text{H}_{55}\text{Si}_2\text{OP} + \text{H}^+] \text{ calcd: 735.3607, found: 735.3604.} \]

2.6.3 Addition of Diphenylphosphine Oxide to Tetramesityldigermene 5

Diphenylphosphine oxide (28 g, 0.14 mmol) was added to a yellow solution of tetramesityldigermene 5 (85 mg, 0.14 mmol) dissolved in benzene (5 mL), at room temperature. The colour of the solution changed to light yellow after 5 minutes. The benzene was evaporated to give a light yellow oil. The oil was dissolved in a minimal amount of hexanes and stored in the freezer (-20 °C) for 24 hours. A white precipitate formed and the solid was isolated by decantation (72 mg, 54 % contaminated with 9% Ph$_2$P(O)H). mp: 196 – 200 °C; FTIR (thin film, cm$^{-1}$) 2918 (m), 2024 (m, Ge-H), 1601 (m), 1556 (m), 1436 (s), 1290 (w), 1186 (s), 1122 (m), 1026 (m), 953 (m), 846 (s), 737 (s), 693 (s); $^1\text{H NMR (C}_6\text{D}_6, 600 \text{ MHz) } \delta 7.65 – 7.63 \text{ (m, 4H, Ph}_o\text{-H), 7.09 – 7.06 \text{ (m, 4H, Ph}_m\text{-H), 7.01 – 6.99 \text{ (m, 2H, Ph}_p\text{-H), 6.68 \text{ (s, 4H, Mes}_m\text{-H), 6.63 \text{ (s, 4H, Mes}_m\text{-H), 5.98 \text{ (s, 1H, Ge-H), [2.332 (s, Mes}_o\text{-CH}_3\text{), 2.327 (s, Mes}_o\text{-CH}_3\text{) all together 24H], [2.07 (s, Mes}_p\text{-CH}_3\text{), 2.06 (s, Mes}_p\text{-CH}_3\text{) all together 12H)]; } ^{13}\text{C}\{^1\text{H}\} \text{ NMR (C}_6\text{D}_6, 151 \text{ MHz) } \delta 147.06 \text{ (d, } J = 25 \text{ Hz, Ph}_i\text{-C})^b, 144.02 \text{ (Mes}_o\text{-C), 143.18 \text{ (Mes}_o\text{-C), 139.07 \text{ (Mes}_p\text{-C), 138.43 \text{ (d, } J = 2.2 \text{ Hz, Mes}_i\text{-C), 138.31 \text{ (Mes}_p\text{-C), 135.01 \text{ (Mes}_i\text{-C), 130.90 \text{ (d, } J = 24 \text{ Hz, Ph}_o\text{-CH})}^a, 129.67 \text{ (Mes}_m\text{-CH), 128.96 \text{ (Mes}_m\text{-CH), 128.63 \text{ (Ph}_p\text{-CH), 128.29 \text{ (Ph}_m\text{-CH), 25.22 \text{ (d, } J = 2.6 \text{ Hz, Mes}_o\text{-CH}_3\text{), 24.59 \text{ (d, } J = 1.8 \text{ Hz, Mes}_o\text{-CH}_3\text{), 20.95 \text{ (Mes}_p\text{-CH}_3\text{); } ^{31}\text{P}\{^1\text{H}\} \text{ NMR (C}_6\text{D}_6, 243 \text{ MHz) } \delta 104.8; \text{ ESI-MS for [C}_{48}\text{H}_{55}\text{OP}^{70}\text{Ge}_2 + \text{Na}^+] \text{ calcd: 841.2373, found: 841.2398.}} \]

2.6.4 Addition of Dipentylphosphine Oxide to Tetramesityldisilene 4

Dipentylphosphine oxide (15 mg, 0.079 mmol) was added to a yellow solution of tetramesityldisilene (42 mg, 0.079 mmol) dissolved in C$_6$D$_6$ (4 mL). The colour of the solution faded to light yellow after 1 minute of stirring at room temperature. The C$_6$D$_6$ was removed under vacuum, yielding 31 as a light yellow oil (35 mg, 61%), which was contaminated with compound 40, formed from the oxidation of the Si-H bond (16%)$^c$ and dipentylphosphine (20%)$^d$. Attempts

$^b$ Similar magnitude for $J$ found in PhCH$_2$P(Ph)$_2$.$^{26}$
$^c$ Tentatively assigned by $^{31}$P chemical shift.
$^d$ Assigned on the basis of $^{31}$P chemical shift reported in the literature.$^{27}$
at purification by preparative TLC (silica gel; 30: 70 DCM to hexanes) resulted in the isolation of 37 and Mes$_2$HSiSiOHMes$_2$. Since purification of 31 was difficult, the characterization of the compound was performed on the crude reaction mixture.

**31**: $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 6.75 (s, 4H, Mes $m$-H), 6.66 (s, 4H, Mes $m$-H), 5.64 (s, 1H, Si-H), 2.46 (br s, Mes $o$-CH$_3$), 2.38 (s, 12H, Mes $o$-CH$_3$), 2.11 (s, 6H, Mes $p$-CH$_3$), 2.09 (br s, Mes $p$-CH$_3$), 1.73 – 1.56 (m, P-$CH_2$), 1.44 – 1.31 (m, P-$CH_2$CH$_2$), 1.30 – 1.20 (m, $CH_2$CH$_2$CH$_3$), 0.88 (t, $J = 7.0$ Hz, 6H, CH$_3$); $^{13}$C($^1$H) NMR (C$_6$D$_6$, 151 MHz) $\delta$ 145.47 (Mes $o$-C), 144.09 (Mes $o$-C), 139.10 (Mes $m$-C), 138.64 (Mes $m$-C), 135.58 (Mes $i$-C), 131.71 (Mes $i$-C), 129.73 (Mes $m$-CH), 128.98 (Mes $m$-CH), 35.58 (d, $J = 25$ Hz, P-$CH_2$), 34.06 (d, $J = 12$ Hz, $CH_2$CH$_2$CH$_3$), 25.22 (br, Mes $o$-CH$_3$), 24.29 (d, $J = 15$ Hz, P-$CH_2$CH$_2$), 22.84 ($CH_2$CH$_3$), 21.14 (Mes $p$-CH$_3$), 21.04 (Mes $p$-CH$_3$), 14.27 (CH$_3$); $^{29}$Si (C$_6$D$_6$) $\delta$ -5.2 (Si-O), -55.8 (Si-H); $^{31}$P($^1$H) (C$_6$D$_6$, 162 MHz) $\delta$ 130.6. Satisfactory ESI-MS high resolution data could not be obtained likely due to a contaminant with the same $m/z$ as 31.

**37**: $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 6.73 (s, 4H, Mes $m$-H), 6.66 (s, 4H, Mes $m$-H), 5.66 (d, $J = 1.8$ Hz) 1H, Si-H), 2.42, 2.41 [(br s and s, 24 H all together, Mes $o$-CH$_3$)], 2.10 (s, 6H, Mes $p$-CH$_3$), 2.06 (s, 6H, Mes $p$-CH$_3$), 1.61 – 1.49 (m, P-$CH_2$CH$_2$)$^6$, 1.42 – 1.26 (m, P-$CH_2$CH$_2$)$^6$, 1.22 – 1.07 (m, $CH_2$CH$_2$CH$_3$)$^6$, 0.84 (t, $J = 6.9$ Hz, 6H, CH$_3$); $^{29}$Si (C$_6$D$_6$) $\delta$ -5.2 (Si-O), -55.6 (Si-H); $^{31}$P($^1$H) (C$_6$D$_6$, 162 MHz) $\delta$ 44.7; ESI-MS for [C$_{46}$H$_{67}$Si$_2$O$_2$P + Na$^+$] calcd: 761.4315, found: 761.4326.

### 2.6.5 Addition of Dipentylphosphine Oxide to Tetramesityldigermene 5

Dipentylphosphine oxide (31 mg, 0.16 mmol) was added to a yellow solution of tetramesityldigermene (0.10 g, 0.16 mmol) dissolved in benzene (3 mL), and the reaction was allowed to stir at room temperature. The colour of the solution changed to light yellow after 5 min. The benzene was evaporated under vacuum, yielding 32 as a light yellow oil (0.12 g, 94%), likely contaminated by the compound formed upon oxidation of the P(III) centre (5%). Attempts to purify 32 by preparative TLC or micropipette...

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$^6$ Tentatively assigned on the basis of chemical shifts.
columns under inert conditions resulted in hydrolysis of the Ge centre with the P(III) moiety to give Mes$_2$HGeGeOHMes$_2$. Since purification was difficult, 32 was characterized from the crude reaction mixture. $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 6.75 (s, 4H, Mes m-H), 6.67 (s, 4H, Mes m-H), 5.93 (s, 1H, Ge-H), 2.47 (s, 12H, Mes o-CH$_3$), 2.41 (s, 12H, Mes o-CH$_3$), 2.10 (s, 6H, Mes p-CH$_3$), 2.07 (s, 6H, Mes p-CH$_3$), 1.63 (t, $J = 7.9$ Hz, 4H, P-CH$_2$), 1.47 – 1.37 (m, P-CH$_2 $CH$_2$) $^f$, 1.34 – 1.23 (m, CH$_2 $CH$_2$CH$_3$) $^i$, 0.88 (t, $J = 7.1$ Hz, 6H, CH$_3$); $^{13}$C($^1$H) NMR (C$_6$D$_6$, 151 MHz) $\delta$ 144.17 (Mes o-C), 143.11 (Mes o-C), 138.99 (Mes p-C), 138.81 (Mes i-C), 138.32 (Mes p-C), 135.19 (Mes i-C), 129.67 (Mes m-CH), 129.04 (Mes m-CH), 36.31 (d, $J = 25$ Hz, P-CH$_2$), 34.29 (d, $J = 10$ Hz, CH$_2 $CH$_2$CH$_3$), 25.30 (Mes o-CH$_3$), 24.62 (d, $J = 5.6$ Hz, Mes o-CH$_3$), 24.22 (d, $J = 16$ Hz, P-CH$_2 CH_2$), 22.94 (CH$_2$CH$_3$), 21.05 (Mes p-CH$_3$), 21.00 (Mes p-CH$_3$), 14.33 (CH$_3$); $^{31}$P($^1$H) NMR (C$_6$D$_6$, 162 MHz) $\delta$ 129.0; ESI-MS for [C$_{46}$H$_{67}$OP$^{70}$Ge$_2$ + Na$^+$] calcd: 829.3312, found: 829.3306.

2.6.6 Addition of Dimethyl Phosphite to Tetramesityldisilene 4

Dimethyl phosphite (0.011 mL, 0.12 mmol) was added to a yellow solution of tetramesityldisilene 4 (66 mg, 0.12 mmol) dissolved in benzene (5 mL) and the solution was allowed to stir at room temperature. After 18 hours, the colour of the solution changed from yellow to pale yellow. The benzene was evaporated under vacuum to give a pale yellow oil which was re-dissolved in a minimal amount of hexanes. The vial was stored in the freezer (-20 ºC) for 7 days. Clear, colourless crystals of 35 and 40 (36 mg, 19:1) were isolated.

35: mp: 168 – 172 ºC; ATR-FTIR (solid, cm$^{-1}$) 2916 (m), 2147 (m, Si-H), 1603 (m), 1445 (m), 1011 (s), 940 (m), 847 (s), 733 (s); $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 6.73 (s, 4H, Mes m-H), 6.67 (s, 4H, Mes m-H), 5.67 (s, 1H, Si-H), 3.20 (d, 6H, OCH$_3$, $J = 11$ Hz), 2.46 (br s, 12H, Mes o-CH$_3$), 2.37 (s, 12H, Mes o-CH$_3$), 2.10 (s, 6H, Mes p-CH$_3$), 2.06 (s, 6H, Mes p-CH$_3$); $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz) $\delta$ 145.56 (Mes o-C), 144.31 (Mes o-C), 139.26 (Mes p-C), 138.74 (Mes p-C), 134.32 (Mes i-C), 131.20 (Mes i-C), 129.73 (Mes m-CH), 128.97 (Mes m-CH), 48.34 (d, OCH$_3$, $J = 4.9$ Hz), 24.80 (br, Mes o-CH$_3$), 24.53 (d, Mes, o-CH$_3$, $J = 3.3$ Hz), 21.08 (Mes p-CH$_3$), 21.00 (Mes, p-CH$_3$); $^{31}$P($^1$H) NMR (C$_6$D$_6$, 162 MHz) $\delta$ 132.8; $^{29}$Si (C$_6$D$_6$) $\delta$ -55.3 (Si-H), -7.3 (Si-OP(OCH$_3$)$_2$); ESI-MS for [C$_{38}$H$_{51}$O$_3$PSi$_2$ + Na$^+$] calcd: 665.3012, found: 665.3006.

$^i$ Chemical shifts extracted from $^{13}$C-$^1$H gHSQC spectrum.
The reaction was repeated and the crude yellow oil was dissolved in a minimal amount of dichloromethane (DCM) and purified by preparative TLC. The mixture was separated into two bands using an 80:20 DCM to hexanes solvent ratio. Compound 41 (4.5 mg, 6%) was isolated as a pale yellow oil from the band closest to the baseline and is contaminated with a compound tentatively identified as (Mes$_2$SiH)$_2$O (10%).

(Mes$_2$SiH)$_2$O was isolated cleanly from the second band in the TLC plate, directly above 41, and was tentatively assigned by $^1$H NMR spectroscopy and mass spectrometry. $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 6.80 (d, 1H, P-H, $J = 690$ Hz), 6.71 (s, 4H, Mes m-H), 6.63 (s, 2H, Mes m-H), 6.62 (s, 2H, Mes m-H), 5.66 (d, 1H, Si-H, $J = 1.8$ Hz), 3.23 (d, 3H, OCH$_3$, $J = 12$ Hz), [2.42, 2.41, 2.40 (each br s, total 12H, Mes o-CH$_3$)], 2.32 (s, 12H, Mes o-CH$_3$), 2.09 (s, 3H, Mes p-CH$_3$), 2.08 (s, 3H, Mes p-CH$_3$), 2.04 (s, 6H, p-CH$_3$); $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz) $\delta$ 145.51 (Mes o-C), 144.44 (Mes o-C), 139.88 (Mes p-C), 139.87 (Mes p-C), 139.12 (Mes p-C), 139.10 (Mes p-C), 132.39 (Mes i-C), 132.32 (Mes i-C), 130.14 (Mes i-C), 130.06 (Mes i-C), 129.87 (Mes m-CH), 129.12 (Mes m-CH), 129.11 (Mes m-CH), 51.48 (d, OCH$_3$, $J = 4.6$ Hz), 24.51 (br, Mes o-CH$_3$), 24.17 (Mes, o-CH$_3$), 21.06 (Mes p-CH$_3$), 20.98 (Mes p-CH$_3$), 20.97 (Mes p-CH$_3$); $^{31}$P NMR (C$_6$D$_6$, 162 MHz) $\delta$ -5.2 (dqd, $^1J = 696$ Hz, $^2J = 12$ Hz, $^4J = 1.8$ Hz); $^{29}$Si (C$_6$D$_6$) $\delta$ -56.0 (Si-H), -3.2 (Si-OP(O)OCH$_3$); ESI-MS for [C$_{37}$H$_{40}$O$_3$Si$_2$ + Na$^+$] calcd: 651.2856, found: 651.2852.

2.6.7 Direct Hydrolysis of 35

Degassed water (4 mL, 0.17 mmol) was added to the yellow solid 35 (58 mg, 0.090 mmol), and the reaction stirred at room temperature. The colour of the solid changed from yellow to white after 18 hours. The water was removed under vacuum to yield a white solid consisting of a mixture of 35 and 41 (57 mg, 1:5).
2.6.8 Addition of Diphenyl Phosphite to Tetramesityldisilene 4

Diphenyl phosphite (0.023 mL, 0.12 mmol) was added to a yellow solution of tetramesityldisilene 4 (66 mg, 0.12 mmol) dissolved in benzene (5 mL), and the reaction was allowed to stir at room temperature. The colour of the solution changed to light yellow after 18 hours. The benzene was removed under vacuum, yielding a light yellow oil. The oil was redissolved in a minimal amount of DCM and purified by preparative TLC (silica gel; 20:80 DCM to hexanes) Compound 36 was extracted as a colourless oil from the band of silica closest to the baseline. The oil was redissolved in a minimal amount of hexanes and stored in the freezer for 7 days (-8 °C). A white solid consisting of 36 (42 mg, 46%) with contaminants including P(OPh)₃, 42, 43 and 44 present in a 100: 12: 1: 1 ratio relative to 36, was isolated.

mp: decomposes at 60 °C; ATR-FTIR (solid, cm⁻¹) 2919 (m), 2129 (m, Si-H), 1594 (m), 1489 (m), 1200 (m), 995 (m), 851 (s), 763 (m), 690 (m); ¹H NMR (C₆D₆, 600 MHz) δ 6.94 – 6.98 (m, 4H, Phₗ-CH), 6.88 – 6.91 (m, 4H, Ph₋CH), 6.78 – 6.82 (m, 2H, Phₚ-CH), 6.70 (s, 4H, Mes₋CH), 6.64 (s, 4H, Mes₋CH), 5.72 (s, 1H, Si-H), 2.50 (br s, 12H, Mes₋CH₃), 2.40 (s, 12H, Mes₋CH₃), 2.08 (s, 6H, Mes₋CH₃), 2.06 (s, 6H, Mes₋CH₃); ¹³C{¹H} NMR (C₆D₆, 151 MHz) δ 152.85 (d, Ph₋C, J = 8.1 Hz), 145.64 (Mes₋C), 144.33 (Mes₋C), 139.47 (Mes₋C), 138.86 (Mes₋C), 133.90 (Mes₋C), 130.74 (Mes₋C), 129.86 (Mes₋CH), 129.72 (Ph₋CH), 129.03 (Mes₋CH), 123.61 (Ph₋CH), 120.85 (d, Ph₋CH, J = 9.0 Hz), 24.83 (br, Mes₋CH₃), 24.63 (d, Mes₋CH₃, J = 3.6 Hz), 21.08 (Mes₋CH₃), 20.99 (Mes₋CH₃); ²⁹Si (C₆D₆) δ -55.7 (Si-H), -5.9 (Si-OP(OPh)₂); ³¹P{¹H} NMR (C₆D₆, 243 Hz) δ 133.3; ESI-MS for [C₄₈H₅₅O₃PSi₂ + Na⁺] calcd: 789.3325, found: 789.3328.

2.6.9 Addition of Diethylphosphinic Acid to Tetramesityldisilene 4

Diethylphosphinic acid (15 mg, 0.12 mmol) was added to a yellow solution of 4 (66 mg, 0.12 mmol) dissolved in benzene (5 mL) and the solution was allowed to stir at room temperature. After 10 minutes, the colour of the solution changed to pale yellow. The benzene was evaporated under vacuum, yielding a light yellow oil which was redissolved in a minimal amount of hexanes. The vial was stored in the freezer (-20 °C) for 24 hours, yielding a mixture of 33 and 34 as an off-

⁸ P(OPh)₃ is a contaminant in diphenyl phosphite and was characterized by ¹H, ³¹P{¹H}, ¹³C{¹H} NMR spectroscopy.⁹

³¹ Compounds 42, 43, and 44 are tentatively assigned by ³¹P{¹H} and ³¹P NMR spectroscopy and ESI-MS.
white solid. The solid was dissolved in a minimal amount of DCM and the compounds were separated by preparative TLC (silica gel; 50:50 DCM to hexanes). Compound 34 (3.8 mg, 39%) was isolated as a clear, colourless oil from the silica and recrystallized in a minimal amount of benzene to yield clear, colourless crystals. In a separate band, Mes₂HSi(OH)Mes₂ (4.2 mg, 43%) was isolated.  

Mes₂Si—SiMes₂  
33: ²¹H and ²⁹Si chemical shifts are not listed because the signals for the product overlapped with those assigned to 34 in the NMR spectra of the mixture, and thus, were not easily distinguished. ³¹P{¹H} NMR (C₆D₆, 162 MHz) δ 135.4; ESI-MS for [C₄₀H₅₅OPSi₂ + H⁺] calcd: 639.3607, found: 639.3612.  

Mes₂Si—SiMes₂  
34: ¹H NMR (C₆D₆, 400 MHz) δ 6.71 (s, 4H, Mes m-CH), 6.63 (s, 4H, Mes m-CH), 5.64 (d, 1H, Si-H, J = 1.9 Hz), 2.38, (s, 12H, Mes o-CH₃), 2.37 (br s, 12H, Mes o-CH₃), 2.10 (s, 6H, Mes p-CH₃), 2.04 (s, 6H, Mes p-CH₃), 1.39 – 1.54 (m, 4H, CH₂CH₃), 0.96 (dt, 6H, CH₂CH₃, J = 7.6 Hz, 18 Hz); ¹³C{¹H} NMR (C₆D₆, 101 MHz) δ 145.21 (Mes o-C), 144.49 (Mes o-C), 139.71 (Mes p-C), 138.92 (Mes p-C), 133.59 (Mes i-C), 130.99 (Mes i-C), 129.84 (Mes m-CH), 128.97 (Mes m-CH), 24.80 (Mes o-CH₃), 23.36 (d, CH₂CH₃, J = 94 Hz), 21.07 (Mes p-CH₃), 20.97 (Mes p-CH₃), 7.04 (d, CH₂CH₃, J = 5.0 Hz); ³¹P{¹H} NMR (C₆D₆, 162 MHz) δ 47.6; ²⁹Si (C₆D₆) δ -55 (Si-H), -5 (Si-OP(CH₂CH₃)₂); ESI-MS for [C₄₀H₅₅O₂PSi₂ + Na⁺] calcd: 677.3376, found: 677.3402.
2.7 References


Chapter 3

Mechanistic Studies and Competition Experiments

3.1 Introduction

In this chapter, the mechanism for the addition of organophosphorus oxides to ditetrelenes 4 and 5 will be discussed. Five plausible mechanisms can be envisioned for the reaction (Scheme 35). Stepwise electrophilic addition, which is common in alkene chemistry, would involve abstraction of a proton from the secondary phosphine oxide or phosphite, followed by addition of the conjugate base to the disilyl or digermyl cation to give disilyl and digermyl phosphinites or phosphites (Scheme 35a). Another option is a concerted addition where the abstraction of the proton from the organophosphorus oxide and nucleophilic addition of the oxygen in the phosphine oxide or phosphite towards the M centre occurs in one step (Scheme 35b). A stepwise nucleophilic addition mechanism should also be considered. In this pathway, the nucleophilic addition of the oxygen in the phosphine oxide or phosphite towards the M centre generates a disilyl or digermyl anion which undergoes intramolecular proton abstraction to form the disilyl or digermyl phosphinites and phosphites (Scheme 35c). An intermolecular proton abstraction between the disilyl or digermyl anion and another molecule of phosphine oxide or phosphite is also plausible following nucleophilic addition of the oxygen from the organophosphorus oxide (Scheme 35d). The last mechanism involves the addition of the phosphine oxide or phosphite tautomer (R₂P-OH) to 4 and 5 (Scheme 35e). The alcoholic oxygen attacks the M centre to generate the disilyl or digermyl anion intermediate, which undergoes intramolecular or intermolecular proton abstraction to form the product.

On the basis of previous mechanistic studies on the addition of water, alcohols and HCl to disilenes,¹² the electrophilic addition mechanism was eliminated since phosphine oxides and phosphites are weak acids and ditetrelenes 4 and 5 are weak bases. The mechanism which involves addition through the organophosphorus oxide tautomer (R₂P-OH) was also eliminated since the oxygen of the P⁺-O⁻ bond in the organophosphorus oxide is expected to be more nucleophilic than the hydroxyl oxygen of the tautomer and higher in concentration compared to the tautomer.

To distinguish between the concerted or stepwise nucleophilic addition mechanisms, deuterium labelling and kinetic isotope effect experiments were performed. In addition,
competition experiments between dialkyl and diarylphosphine oxides were investigated to determine which derivative reacts more readily with digermene 5.

Scheme 35. Plausible reaction mechanisms for the addition of organophosphorus oxides to 4 and 5.
3.2 Deuterium Labelling Experiment

The addition of organophosphorus oxides to 4 or 5 is proposed to proceed through either a concerted or a stepwise nucleophilic addition mechanism. In both, the P-H bond is broken and a M-H bond is formed. To determine if the hydrogen of the phosphine oxide or phosphite is transferred to the ditetrelene, deuterated diphenylphosphine oxide was added to digermene 5. Diphenylphosphine oxide-\textit{d}\textsubscript{1} was synthesized by stirring diphenylphosphine oxide in excess MeOH-\textit{d}\textsubscript{4} at 30 °C for 18 hours (Scheme 36).\textsuperscript{3}

![Scheme 36. The synthesis of diphenylphosphine oxide-\textit{d}\textsubscript{1}.

One equivalent of diphenylphosphine oxide-\textit{d}\textsubscript{1} was added to a yellow solution of 5 dissolved in benzene and the reaction was allowed to stir at room temperature (Scheme 37). After 5 minutes, the colour of the solution faded from yellow to light yellow. Evaporation of benzene yielded a light yellow oil which was recrystallized from hexanes to give 55 as a white solid in 61% yield. The \textsuperscript{1}H chemical shifts of 55 matched the chemical shifts observed in the \textsuperscript{1}H NMR spectrum of the protonated analogue 28 within experimental error (± 0.01 ppm). A signal at 5.98 ppm in the \textsuperscript{1}H NMR spectrum of 55 was observed and was assigned as the Ge-H from residual amounts of 28. Since the signal at 5.98 ppm integrated to 0.08 relative to the signals assigned to the mesityl protons of 55, 92% of 55 was deuterated in both the crude and recrystallized product. The level of deuterium incorporation in the phosphine oxide reagent and 55 are within experimental error. In the \textsuperscript{2}H NMR spectrum of 55, only one signal appeared at 5.99 ppm, which was assigned to the
Ge-D moiety. The isolation of 55 confirms that the hydrogen attached to the P of the phosphine oxide is transferred exclusively to a Ge of the former digermene 5, during the reaction.

3.3 Kinetic Isotope Effect

Kinetic isotope effect (KIE) experiments are a useful experimental technique to gain an understanding of which bonds are broken, formed or rehybridized in the rate determining step (rds) of a reaction. The KIE is a measurement of the change in the rate of the reaction when an atom is replaced with its isotope, the most common exchange being H/D. KIEs are expressed as a ratio of the rate constants of the reaction for the protonated and the deuterated analogues (KIE = \( k_H/k_D \)). If the value for \( k_H/k_D >> 1 \), then a primary isotope effect is observed meaning the labelled atom is transferred in the rate determining step of the reaction. The maximum \( k_H/k_D \) value for a primary isotope effect is 6.5 – 7 at 298 K.\(^4\) In contrast, if the labelled atom is not transferred in the rds, a secondary isotope effect where \( k_H/k_D \approx 1 \) (normally 1.1–1.2, estimated theoretical maximum is 1.4) is observed.\(^5\)

Diphenylphosphine oxide, and its deuterated analog were combined in a 1:1 ratio (0.05 M stock solution in \( \text{C}_6\text{D}_6 \) for each reagent). The phosphine oxide mixture was added to a 0.06 M solution of 5 dissolved in \( \text{C}_6\text{D}_6 \). The reaction was monitored by following the disappearance of the \(^{31}\text{P} \) chemical shifts for the deuterated and protonated phosphine oxide over time, since 28 and 55 have indistinguishable \(^{31}\text{P} \) chemical shifts.

Figure 14 shows the graph of the absolute integrals of the deuterated and non-deuterated phosphine oxides versus time. Even though the protonated phosphine oxide was present in a slightly higher concentration, both reagents are consumed at similar rates. After 20 minutes, the plot for both reagents plateaus, indicating the reaction has gone to completion. The KIE for the reaction was calculated according to Equation (1) which expresses the KIE ratio as the change in concentration over time of the protonated species over the deuterated species. To account for the higher concentration of the protonated phosphine oxide, the integrals at each time point for the protonated and deuterated species were subtracted from the integrals at \( t_0 \).

\[
\text{KIE} = \frac{k_H}{k_D} = \frac{\Delta[H]}{\Delta[D]} \approx \frac{\text{Int}_H(t_0) - \text{Int}_H(t)}{\text{Int}_D(t_0) - \text{Int}_D(t)}
\]  

(1)
From the integrals, the average $k_H/k_D$ value over all time points was calculated to be 1.3, which is indicative of a secondary isotope effect. This result provides evidence against a concerted mechanism since the P-H/P-D bond is not broken in the rds. Therefore, the 1,3-addition of diorganophosphine oxides and phosphites to 4 and 5 is proposed to proceed through a stepwise nucleophilic addition mechanism, with the nucleophilic attack of the oxygen atom in the $P^+\cdot O^-$ bond at the M centre as the rds. However, the KIE results cannot distinguish whether the subsequent step involves an intramolecular or intermolecular abstraction of the hydrogen.

![Graph](image)

**Figure 14.** Consumption of protonated and deuterated diphenylphosphine oxide in the reaction with digermene 5.

The addition of ethanol to disilene 56 to regioselectively form ethoxydisilane 57 was also proposed to take place by nucleophilic addition on the basis of KIE experiments (Scheme 38). When ethanol-$d_1$ was allowed to react with 56, no significant isotope effect was observed, which suggests a concerted addition is not the rds.

![Scheme 38](image)

**Scheme 38.** The addition of ethanol to transient disilene 56.
The mechanism of the addition of phenol derivatives to disilene 4 was investigated by Apeloig et al. through KIE experiments. The authors observed a trend where electron-donating substituents on the phenol, resulted in $k_H/k_D$ values close to 1. For example, the addition of deuterated 4-methoxyphenol to 4 had a $k_H/k_D$ value of 0.71, which is consistent with the rate determining step involving nucleophilic attack of the alcoholic oxygen to the Si centre (Scheme 39a). In contrast, the addition of phenols containing electron-withdrawing substituents resulted in primary KIEs. The addition of deuterated 4-(trifluoromethyl)phenol to 4 resulted in a large KIE value of 5.27, indicating a primary KIE. The primary KIE strongly supports an electrophilic addition where the phenolic H or D is transferred to 4 in the rds which is rationalized by the increased acidity of the phenolic H (Scheme 39b).

Scheme 39. The (a) nucleophilic addition and (b) electrophilic addition of phenols to disilene 4.

Since diphenylphosphine oxide is a weak acid (pK$_a$ is approximately 25), an electrophilic addition to digermene 5 is not likely. The KIE results for the addition of diphenylphosphine oxide to 5 are consistent with the results from the addition of electron-donating substituted phenols to disilene 4, which takes place through a stepwise nucleophilic addition. In both reactions, the nucleophilic addition by an oxygen atom to the M centre is involved in the rate determining step of the reaction.
3.4 Relative Rate Studies and Exchange Reactivity on the Addition of Phosphine Oxides to Tetramesityldigermene 5

A competition experiment between dipentyl- and diphenylphosphine oxide was performed to determine the relative rates of reaction between the dialkyl and diarylphosphine oxide with digermene 5. A 1:1 mixture of dipentylphosphine oxide and diphenylphosphine oxide was added to a yellow solution of 5 dissolved in C\textsubscript{6}D\textsubscript{6}. The colour of the solution faded to light yellow within 5 minutes after adding the phosphine oxide mixture. The reaction was monitored by \textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy (Figure 15), which revealed the appearance of two new signals within 5 minutes at 104.5 and 129.0 ppm, assigned to 28 and 32, respectively. At the 5 minute time point, 28 and 32 are present in a 3:1 relative ratio, indicating that diphenylphosphine oxide reacts with 5 more readily compared to dipentylphosphine oxide. The \textsuperscript{1}H NMR spectrum of the reaction after 20 minutes confirms the reaction has gone to completion which was indicated by the disappearance of the signals for digermene 5 in the \textsuperscript{1}H NMR spectrum of the reaction mixture. Interestingly, the relative ratio of 28 to 32 changes over time, which is noticeable at the 24 hour time point where the relative ratio of products is 7:1. The change in the relative ratio of products is not due to oxidation of 32 since no new signals appeared in the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum. The increase of 28 and decrease of 32 over time suggests that the OP(pentyl)\textsubscript{2} group can be exchanged for a OPPh\textsubscript{2} group.

The faster rate for the addition of diphenylphosphine oxide to digermene 5 compared to the addition of dipentylphosphine oxide suggests the oxygen of the aryl substituted phosphine oxide is more nucleophilic than the alkyl substituted phosphine oxide. These conclusions were made based on the assumption that diphenyldigermyl phosphinite 28 is the kinetic product. However, it is possible that dipentyldigermyl phosphinite 32 could be the kinetic product and the exchange with the OPPh\textsubscript{2} group likely occurs because 28 is the thermodynamic product. The early stages of the reaction should be monitored to determine which phosphinite is the kinetic product.
To probe the exchange between the OP(pentyl)$_2$ moiety and the OPPh$_2$ group, excess diphenylphosphine oxide was added to a crude sample of dipentyldigermyl phosphinite 32, and the reaction was monitored by $^{31}$P{$^1$H} NMR spectroscopy using OPEt$_3$ ($^{31}$P chemical shift = 46.1 ppm) as an internal standard inside a sealed capillary tube (Figure 16). Within the first 10 minutes of the reaction, the appearance of a signal at 104.7 ppm was observed and assigned to diphenyldigermyl phosphinite 28. The appearance of another signal at 29.2 ppm is indicative of the regeneration of dipentylphosphine oxide, which is in line with the disappearance of the signal at 128.9 ppm, assigned to dipentyldigermyl phosphinite 32. The reaction occurs quite rapidly under mild conditions, as evident at the 1 hour time point, where the signal for 32 has almost disappeared. The reverse reaction, where excess dipentylphosphine oxide was added to dipentyldigermyl phosphinite 28, was also monitored by $^{31}$P{$^1$H} NMR spectroscopy; however, appearance of a signal at 128.9 ppm was not observed after 24 hours, indicating no reaction occurred.
Figure 16. $^{31}$P{H} NMR (C$_6$D$_6$, 162 MHz) spectra of the addition of diphenyl phosphine oxide to dipentylgermyldigermaphosphinite 32.

The exchange phenomenon was also explored with the disilene derivatives. The addition of excess diphenyl phosphite to dimethylidisilyl phosphite 35 (Scheme 40a) was monitored by $^{31}$P{H} NMR spectroscopy. After 18 hours at room temperature, no change in the $^{31}$P{H} NMR spectrum was observed. Since no reaction was observed, the mixture was heated at 50 ºC for an additional 18 hours, however, no change was observed in the $^{31}$P{H} NMR spectrum. The reaction of 35 with excess diphenylphosphine oxide (Scheme 40b) was also tested, however after 22 hours, no change was observed in the $^{31}$P{H} NMR spectrum. On the basis of the results from these two experiments, the exchange of the OP(OCH$_3$)$_2$ group in 35 for another OPR$_2$ group is not possible under the reaction conditions examined.
The addition of (a) diphenyl phosphite and (b) diphenylphosphine oxide to 35.

Scheme 40. The addition of (a) diphenyl phosphite and (b) diphenylphosphine oxide to 35.

Scheme 41. The addition of diphenylphosphine oxide-d$_1$ to 32.

Within 10 minutes, the appearance of signals at 104.7 and 29.2 ppm are observed, which were assigned to diphenyldigermyl phosphinite 28 and dipentylphosphine oxide, respectively. At the 30 minute time point, it is clear that the deuterium label is incorporated in the dipentylphosphine oxide that is formed based on the appearance of a triplet at 28.4 ppm, which is isotopically shifted from the protonated analog (Figure 17b). The integration of the signal for 28 stopped increasing after 15 hours, indicating diphenyldigermyl phosphinite 28 was no longer being formed. In the $^2$H$\{^1$H$\}$ NMR spectrum, two doublets were observed at 7.80 ppm ($J = 73$ Hz) and 6.60 ppm ($J = 70$ Hz) and are assigned to diphenylphosphine oxide-d$_1$ and dipentylphosphine oxide-d$_1$, respectively. The observed coupling constants are within 3 Hz of the calculated coupling constants for Ph$_2$P(O)D (72 Hz) and pentyl$_2$P(O)D (67 Hz). A third doublet at 7.33 ppm ($J = 22$ Hz) was also observed, however the identity of this compound is unknown, although the magnitude of the coupling
constant suggests a 2 to 3 bond D-P coupling. The absence of a signal at 5.98 ppm indicates the deuterium label was not being incorporated into 28.

![Figure 17. $^{31}$P{¹H} NMR (C₆D₆, 162 MHz) spectra of the addition of diphenylphosphine oxide-$d_{1}$ to 32. (a) Shows all signals present in the spectra. (b) Expansion shows the zoomed region containing the signals for protonated and deuterated dipentylphosphine oxide.](image)

Five mechanisms can be envisioned for the reaction of diphenylphosphine oxide-$d_{1}$ with 32 (Scheme 42). In the first mechanism, an intramolecular abstraction of the Ge-H proton results in the regeneration of digermene 5, followed by the stepwise addition of diphenylphosphine oxide to form deuterated diphenylidigermyl phosphinite 28. Mechanisms (b) and (c) involve the intermolecular abstraction of the Ge-H proton by diphenylphosphine oxide. In mechanism (b), 5
is regenerated and adds to diphenylphosphine oxide by stepwise nucleophilic addition; while in mechanism (c), a digermyl anion adds to diphenylphosphine oxide. The remaining mechanisms, (d) and (e), are substitution pathways. In mechanism (d), an $S_N1$ type mechanism is shown where dissociation of the $\text{OP(pentyl)}_2$ group forms a digermyl cation intermediate, which forms 28 by nucleophilic addition to the Ge cation. A direct substitution mechanism is depicted in mechanism (e) where nucleophilic attack of diphenylphosphine oxide and dissociation of the $\text{OP(pentyl)}_2$ moiety occurs in the same step. In mechanisms (b), (c), (d) and (e), the deuterium label is incorporated on the regenerated dipentylphosphine oxide and not diphenyl digermyl phosphinite 28. On the basis of the results from the deuterium labelling experiment where diphenylphosphine oxide-$d_1$ was added to 5, mechanism (a) can be eliminated, since there was no signal for the Ge-D moiety of 28 in the $^2\text{H}[^1\text{H}]$ NMR spectrum. Since deuterium is incorporated in dipentylphosphine oxide instead of 28, mechanisms (b), (c), (d), and (e) are all plausible, although the mechanism cannot be distinguished with the results obtained. If the Ge-H of 32 is retained, then the reaction likely proceeds through substitution mechanisms (d) or (e). However, if the Ge-H of 32 is broken, then the reaction likely proceeds through either mechanism (b) or (c). Digermyl cations are not readily formed, so the reaction proceeding through mechanism (d) is not likely. Since no deuterium is incorporated into the Ge-H position of 28, the direct substitution, mechanism (e), is proposed to be the most plausible mechanism since some deuterium incorporation into the Ge-H moiety is expected to occur in mechanisms (b) and (c).
Scheme 42. Proposed reaction mechanisms for the addition of diphenylphosphine oxide-\(d_1\) to 32.
3.5 Summary

The reaction mechanism for the addition of organophosphorus oxides to ditetrelenes 4 and 5 was investigated. The addition of diphenylphosphine oxide-d$_1$ to 5, confirmed the breaking of the P-H bond and formation of the Ge-H bond to yield compound 28. Furthermore, the reaction was confirmed to proceed through a stepwise nucleophilic addition and not a concerted reaction pathway by a KIE experiment. The $k_{\text{H}}/k_{\text{D}}$ value of 1.3 obtained from the KIE experiment indicates a secondary isotope effect, suggesting the breaking of the P-D bond or formation of the Ge-D bond is not involved in the rate determining step, thereby, providing evidence which supports a nucleophilic addition mechanism. However, the KIE experiments could not distinguish between an intramolecular or intermolecular proton abstraction in the second step of the mechanism (Scheme 43).

![Scheme 43. Plausible mechanisms for the nucleophilic addition of diphenylphosphine oxide to 5.](image)

A competition experiment between diphenyl- and dipentylphosphine oxide was also explored to determine which reagent reacted with digermene 5 more readily. Since 28 was formed in larger amounts, it can be concluded that diphenylphosphine oxide reacts more rapidly with 5.

Interestingly, the relative ratio of products changed after 24 hours to favour the formation of 28, giving evidence that the OP(pentyl)$_2$ group can be exchanged with a OPPh$_2$ group. The
exchange phenomenon of the reaction was confirmed by adding excess diphenyl phosphine oxide to dipentylgermyl phosphinite 32 (Scheme 44).  

\[
\text{Mes}_2\text{Ge} = \text{GeMes}_2 + \text{Ph} \quad \text{P} \quad \text{H} + \text{penty}l \quad \text{Ph} \quad \text{H} + \text{penty}l \quad \text{P} \quad \text{H} \quad \text{penty}l \rightarrow \text{Mes}_2\text{Ge} = \text{GeMes}_2 \quad \text{Ph} \quad \text{P} \quad \text{H} + \text{penty}l \quad \text{Ph} \quad \text{H} + \text{penty}l \quad \text{P} \quad \text{H} \quad \text{penty}l
\]

**Scheme 44.** The addition of diphenylphosphine oxide to 32 to yield diphenylgermyl phosphinite 28.

The exchange phenomenon was not observed in the reverse reaction, the addition of dipentylphosphine oxide to diphenylgermyl phosphinite 28. In addition, the OP(OCH$_3$)$_2$ group of dimethylidisilyl phosphate 35 could not be exchanged with either OPPh$_2$ or OP(OPh)$_2$ groups.

Lastly, the mechanism for the exchange of the OP(pentyl)$_2$ group of 32 with a PPh$_2$ group was explored by adding diphenylphosphine oxide-$d_1$ to a crude sample of 32. Since the deuterium label was not incorporated into diphenylgermyl phosphinite 28, four plausible mechanisms can still be considered including mechanisms involving intermolecular abstraction of the Ge-H moiety or substitution mechanisms. However, more work is required to determine whether the Ge-H of 32 remains intact to distinguish between the plausible mechanisms remaining.

### 3.6 Experimental

#### 3.6.1 General Experimental Details

All reactions were carried out in an MBraun glovebox under an atmosphere of nitrogen. All anhydrous solvents were collected from an Innovative Technology solvent purification system and dried over 4 Å molecular sieves. All reagents were purchased from Millipore Sigma or Alfa Aesar. Disilene 4 was prepared by photolysis of Mes$_2$Si(Si(CH$_3$)$_3$)$_2$ in hexanes in a quartz tube with Ushio G8T5 Mercury UV-C lamps (254 nm) and cooled to -45 °C using a Thermo Scientific Neslab ULT 80 bath circulator. Digermene 5 was prepared through a similar procedure as 4, by the photolysis of (Mes$_2$Ge)$_3$ in THF at 350 nm. NMR spectra were acquired using a Varian INOVA I600 or I400 FT-NMR spectrometer or a Bruker AvIII HD 400 spectrometer. The $^1$H and $^{13}$C chemical shifts (δ) are listed in ppm against residual C$_6$D$_5$H (7.15 ppm) and C$_6$D$_6$ (128 ppm) relative to tetramethylsilane, respectively. The chemical shifts for the $^{31}$P{$^1$H} NMR spectrum
were referenced externally to 85% H$_3$PO$_4$. Triethylphosphine oxide was used as an internal standard inside a sealed capillary tube for reactions monitored by $^{31}$P{$^{1}$H} NMR spectroscopy, unless otherwise stated. The $^2$H chemical shifts are listed in ppm against residual C$_6$H$_5$D (7.15 ppm).

### 3.6.2 Addition of Diphenylphosphine Oxide-$d_I$ to Tetramesityldigermene 5

Diphenylphosphine oxide-$d_I$ (6.9 mg, 0.034 mmol) was added to a yellow solution of 5 (17 mg, 0.034 mmol) dissolved in C$_6$D$_6$. After 5 minutes of stirring the reaction at room temperature, the colour of the solution changed to light yellow. The C$_6$D$_6$ was evaporated under vacuum to yield a light yellow oil, which was redissolved in a minimal amount of hexanes and stored in the freezer (-20 °C) for 18 hours. A tan precipitate formed and 55 was isolated as a solid by decantation (20 mg, 61%). $^1$H NMR (C$_6$D$_6$, 600 MHz) δ 7.66 – 7.62 (m, 4H, Ph o-H), 7.10 – 7.05 (m, 4H, Ph m-H), 7.02 – 6.98 (m, 2H, Ph p-H), 6.68 (s, 4H, Mes m-H), 6.63 (s, 4H, Mes m-H), 5.98 (s, 0.2H, residual Ge-H from 28), [2.331, 2.328 (s, all together 24H, Mes o-CH$_3$)], [2.07, 2.06 (s, all together 12H, Mes p-CH$_3$)]; $^{31}$P{$^{1}$H} NMR (C$_6$D$_6$, 243 MHz) δ 104.8; $^2$H{$^{1}$H} NMR (C$_6$H$_6$, 92 MHz) 5.99 (Ge-D).

### 3.6.3 Competition Kinetic Isotope Effect

A stock solution of diphenylphosphine oxide (0.05 M, 0.02 mmol) and 94% diphenylphosphine oxide-$d_I$ (0.05 M, 0.02 mmol) were added to a yellow solution of 5 dissolved in C$_6$D$_6$ (0.06M, 0.02 mmol) in an NMR tube. The colour of the solution faded to light yellow in 5 minutes. The reaction was monitored by $^{31}$P{$^{1}$H} NMR spectroscopy over 9 time points (5, 7, 10, 12, 15, 20, 30, 40 and 60 minutes).

### 3.6.4 Addition of Dipenty1- and Diphenylphosphine Oxide to Tetramesityldigermene 5

A mixture of diphenylphosphine oxide (33 mg, 0.17 mmol) and dipentylphosphine oxide (31 mg, 0.17 mmol) dissolved in C$_6$D$_6$ (2 mL) was added to a yellow solution of 5 (0.1 g, 0.17 mmol) dissolved in C$_6$D$_6$ (2 mL). The colour of the solution immediately faded to light yellow. An aliquot
of the solution was taken to monitor the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, without an internal standard, over 6 time points (5, 10, and 20 minutes, 1, 2, and 24 hours).

3.6.5 Addition of Diphenylphosphine Oxide to Dipentyldigermyl Phosphinite 32

A stock solution of diphenylphosphine oxide (0.3 M, 0.2 mmol) was added to 32 (17 mg, 0.021 mmol) in an NMR tube. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy over 7 time points (10, 12, 15, 18, 20 and 60 minutes, and 18 hours).

3.6.6 Addition of Dipentylphosphine Oxide to Diphenyldigermyl Phosphinite 28

A stock solution of dipentylphosphine oxide (0.2 M, 0.08 mmol) in C$_6$D$_6$ was added to 28 (8 mg, 0.01 mmol) in an NMR tube. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy over 7 time points (10, 20, 30, 40, 50 and 60 minutes, and 24 hours), however, no reaction was observed after 24 hours.

3.6.7 Addition of Diphenylphosphine Oxide to Dimethylidisilyl Phosphite 35

A stock solution of diphenylphosphine oxide (0.2 M, 0.09 mmol) in C$_6$D$_6$ was added to 35 (7 mg, 0.02 mmol) in an NMR tube. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy over 5 time points (10, 20, 30, and 60 min, and 22 hours), however, no reaction was observed after 22 hours.

3.6.8 Addition of Diphenyl Phosphite to Dimethylidisilyl Phosphite 35

A stock solution of diphenyl phosphite (0.3 M, 0.1 mmol) in C$_6$D$_6$, was added to 35 (0.01 g, 0.02 mmol) in an NMR tube. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy over 6 time points (12, 20, 30, 40 and 60 min, and 18 hours). After 18 hours, no reaction occurred at room temperature. The reaction was heated at 50 ºC for an additional 18 hours, but no reaction was observed.
3.6.9 The Addition of Diphenylphosphine Oxide-$d_1$ to Dipentyldigermyl Phosphininite 32

A stock solution of diphenylphosphine oxide-$d_1$ (0.2 M, 0.07 mmol) in C$_6$D$_6$ was added to 32 (14 mg, 0.017 mmol) in an NMR tube. The reaction was monitored by $^{31}$P{$^1$H} NMR spectroscopy over 9 time points (7, 10, 20, 30, 40, 50 and 60 minutes, 15 hours, and 3 days). $^2$H{$^1$H} (C$_6$H$_6$, 92 MHz) $\delta$ 7.80 (d, $J = 73$ Hz, Ph$_2$P(O)D), 7.33 (d, $J = 22$ Hz)$^a$, 6.60 (d, $J = 70$ Hz, pentyl$_2$P(O)D).

$^a$ Identity of compound is unknown.
3.7 References


Chapter 4

4 Conclusions and Future Work

4.1 Summary and Conclusions

This thesis has examined the reactivity of doubly bonded Group 14 species towards organophosphorus oxides. The addition of dialkyl and diaryl phosphine oxides and phosphites with ditetrelenes 4 and 5 was explored (Scheme 45), and in all cases examined, disilyl and digermyl phosphinite and phosphites (27, 28, 29, 30, 31, 32, 35 and 36) were isolated. The reaction results in a mild reduction of the P(V) centre of the phosphine oxides and phosphites to give a P centre in the phosphinite and phosphite derivatives that has an intermediate chemical state between R_3P=O and R_3P. The only other method for synthesizing the silyl phosphinite and phosphite derivatives is through the reaction of phosphine oxides or phosphites with chlorosilanes in the presence of amines at elevated temperatures. In the reactivity with disilene 4, the Lewis acid and Lewis base are contained within the same molecule and the reaction can be performed under neutral conditions at room temperature. The typical synthesis of germyl phosphinites and phosphites involves the salt metathesis reaction of the phosphine oxide or phosphite salt with chlorogermandanes at elevated temperatures. In the synthesis of digermyl phosphinite and phosphite derivatives using digermene 5, the Ge centre is directly involved in the partial reduction of the P(V) centre of the phosphine oxide and phosphite.

\[
\text{Mes}_2M\equiv\text{MMes}_2 + \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{Mes}_2M=\text{MMes}_2 \\
\text{R}_3\text{P}=\text{O} \\
\text{H} \\
\text{R}
\end{array}
\]

Scheme 45. The addition of organophosphorus oxides to ditetrelenes 4 and 5.

In the analogous reactivity with alkenes, the P-H bond of the phosphine oxide or phosphite adds across the C=C bond through activation of the P-H bond by a transition metal catalyst to form
a C-P and a C-H bond. In contrast, in the reaction of phosphine oxides and phosphites with ditetrelenes 4 or 5, an M-O bond is formed, without the use of heat or a catalyst. The reactivity of phosphine oxides and phosphites with ditetrelenes 4 and 5 provides an additional example of the activation of organic main group oxides by doubly bonded Group 14 species, which previously included nitromethane, arylsulfonyl chlorides, carbon monoxide and carbon dioxide.

In Chapter 3, the mechanism for the reaction of organophosphorus oxides with ditetrelenes 4 and 5 was explored. On the basis of the results from the KIE experiment, the mechanism was proposed to be a stepwise nucleophilic addition of the organophosphorus oxide across the M=M bond in the ditetrelene (Scheme 46). However, it is not clear whether one or two equivalents of the organophosphorus oxide is involved in the reaction mechanism.

![Scheme 46. Plausible mechanisms for the addition of organophosphorus oxides to 4 and 5.](image-url)

The relative rates of the reactions between dipentyl- or diphenylphosphine oxide with digermene 5 was also investigated by a competition experiment. Since diphenyldigermyl phosphinite 28 was formed in a larger amount, this indicates diphenylphosphine oxide reacts more rapidly with 5, suggesting higher nucleophilicity of the P⁺-O⁻ moiety in the diaryl-substituted phosphine oxide. Surprisingly, the relative ratio of products changed over time, with the concentration of 28 increasing and the concentration of 32 decreasing, suggesting the OP(pentyl)$_2$ moiety of 32 can be exchanged for a OPPh$_2$ group.
The exchange phenomenon was investigated further by adding excess diphenylphosphine oxide to 32 (Scheme 47). This competition experiment confirmed the exchange of the OPR₂ moieties. However, when the reverse reaction was attempted and when disilene derivatives were probed, no exchange occurred. In fact, of all the cases attempted, the only exchange observed was between the OP(pentyl)₂ moiety of 32 and the OPPh₂ group of diphenylphosphine oxide. The exchange seen in the dipentyldigermyl phosphinite derivative 32 may be due to instability of the product which has been proven to readily undergo secondary reactivity such as hydrolysis of the O-P bond on the Ge centre. The exchange with the OPPh₂ group would generate diphenyldigermyl phosphinite 28, which is a more stable adduct.

![Scheme 47](image)

Scheme 47. The addition of diphenylphosphine oxide to 32.

Using a deuterium labelling experiment, the mechanism of the exchange phenomenon was probed by adding diphenylphosphine oxide-d₁ to dipentyldigermyl phosphinite 32. The deuterium label was only incorporated in the dipentyldphosphine oxide that was regenerated. On the basis of the results from the deuterium labelling experiment, a direct substitution mechanism is proposed for the exchange of the OP(pentyl)₂ moiety of 32 with a OPPh₂ group (Scheme 48).

![Scheme 48](image)

Scheme 48. Plausible mechanism for the exchange phenomenon between 32 and diphenylphosphine oxide.

### 4.2 Future Work

The scope of this work includes reactions of dialkyl and diarylphosphine oxides and phosphites with ditetrelenes 4 and 5, however, the reaction scope may be increased by looking at
other compounds containing a P=O group. Potential organophosphorus oxides that could be explored include primary phosphine oxides and phosphites (RP(O)H$_2$) or diorganophosphinic chlorides (R$_2$P(O)Cl).

The reaction mechanism for the addition of organophosphorus oxides to 4 and 5 proceeds through a stepwise nucleophilic addition, as confirmed by KIE experiments. However, to determine whether one or two equivalents of diphenylphosphine oxide are required in the reaction mechanism, the order of phosphine oxide in the rate law could be investigated. Diphenylphosphine oxide could also be added to cyclic digermene$^9$ 58 (Scheme 49) to gain information on whether one or two equivalents of phosphine oxide are involved in the reaction mechanism. The reaction of 58 with diphenylphosphine oxide could proceed through two pathways, a syn-addition to form 59 or anti-addition to yield 60. If 59 is formed as the major product, an intramolecular proton abstraction seems more plausible. However, if a racemic mixture of 59 and 60 is observed, an intermolecular proton abstraction is more likely, since the second equivalent of phosphine oxide could be deprotonated on either face of the Ge=Ge bond.

Scheme 49. The addition of diphenylphosphine oxide to cyclic digermene 58.

The competition experiment between dipentyl- and diphenylphosphine oxide with digermene 4 should be monitored within the first 5 minutes of the reaction by NMR spectroscopy to determine whether diphenyldigermyl phosphinite 28 or dipentyldigermyl phosphinite 29 is the kinetic product. Since the exchange of the OP(pentyl)$_2$ moiety of 32 with a OPPh$_2$ group from diphenylphosphine oxide was successful, expanding on the scope of this reactivity is worthwhile. Diphenyl phosphite or dimethyl phosphite can be added to 32 to determine if an OP(OR)$_2$ group can also exchange with the OP(pentyl)$_2$ moiety.
Lastly, the mechanism for the exchange phenomenon can be investigated further by labeling the Ge-H moiety in 32 with deuterium. This labelling experiment would provide information on whether the Ge-H moiety is retained throughout the reaction. If the Ge-H moiety is retained, and the deuterium label is not transferred, this would provide evidence for a substitution mechanism.
4.3 References


Appendices

Appendix A: NMR Data

Note: $^1$H, $^{13}$C($^1$H) and $^1$H-$^{29}$Si gHMBC NMR spectra have been expanded to clearly show all signals assigned to the compounds of interest.

Figure A1: $^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of 27.
Figure A2: $^{31}$P{$^1$}H NMR spectrum (C$_6$D$_6$, 243 MHz) of 27.

Figure A3: $^{13}$C{$^1$}H NMR spectrum (C$_6$D$_6$, 151 MHz) of 27. The region of the spectrum from 30 to 120 ppm has been omitted.
Figure A4: $^1$H-$^{29}$Si gHMBC NMR spectrum (C$_6$D$_6$) of 27.

Figure A5: ATR-IR spectrum of 27.
Figure A6: $^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of 28.

Figure A7: $^{31}$P{$^1$H} NMR spectrum (C$_6$D$_6$, 243 MHz) of 28.
Figure A8: $^{13}$C($^1$H) NMR spectrum (C$_6$D$_6$, 151 MHz) of 28. The region of the spectrum from 40 to 115 ppm has been omitted.

Figure A9: $^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of 31.
**Figure A10:** $^{31}$P{H} NMR spectrum (C$_6$D$_6$, 162 MHz) of 31.

**Figure A11:** $^{13}$C{H} NMR spectrum (C$_6$D$_6$, 151 MHz) of 31. The region of the spectrum from 60 to 120 ppm has been omitted.
Figure A12: $^1$H–$^{29}$Si gHMBC NMR spectrum ($C_6D_6$) of 31.

Figure A13: $^1$H NMR spectrum ($C_6D_6$, 600 MHz) of 32.
Figure A14: $^{31}$P{$^1$H} NMR spectrum (C$_6$D$_6$, 162 MHz) of 32.

Figure A15: $^{13}$C{$^1$H} NMR spectrum (C$_6$D$_6$, 151 MHz) of 32.
Figure A16: $^1$H NMR spectrum (C$_6$D$_6$, 400 MHz) of 34.

Figure A17: $^{31}$P{$_^1$H} NMR spectrum (C$_6$D$_6$, 162 MHz) of 34.
Figure A18: $^{13}$C($^1$H) NMR spectrum (C$_6$D$_6$, 101 MHz) of 34. The region of the spectrum from 35 to 110 ppm has been omitted.

Figure A19: $^1$H-$^{29}$Si gHMBC NMR spectrum (C$_6$D$_6$) of 34.
Figure A20: $^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of 35.

Figure A21: $^{31}$P{$^1$H} NMR spectrum (C$_6$D$_6$, 162 MHz) of 35.
Figure A22: $^{13}$C{$_{1}$H} NMR spectrum (C$_6$D$_6$, 101 MHz) of 35. The region of the spectrum from 50 to 120 ppm has been omitted.

Figure A23: $^1$H-$^{29}$Si gHMBC NMR spectrum (C$_6$D$_6$) of 35.
Figure A24: ATR-IR spectrum of 35.

Figure A25: $^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of 36.
Figure A26: $^{31}$P{$^1$H} NMR spectrum (C$_6$D$_6$, 243 MHz) of 36.

Figure A27: $^{13}$C{$^1$H} NMR spectrum (C$_6$D$_6$, 151 MHz) of 36. The region of the spectrum from 30 to 115 ppm has been omitted.
Figure A28: $^1$H–$^{29}$Si gHMBC NMR spectrum (C$_6$D$_6$) of 36.

Figure A29: ATR-IR spectrum of 36.
Figure A30: $^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of 41.

Figure A31: $^{31}$P NMR spectrum (C$_6$D$_6$, 243 MHz) of 41.
Figure A32: $^{13}$C{$^1$H} NMR spectrum (C$_6$D$_6$, 151 MHz) of 41. The region of the spectrum from 55 to 115 ppm has been omitted.

Figure A33: $^1$H-$^{29}$Si gHMBC NMR spectrum (C$_6$D$_6$) of 41.
Appendix B: X-ray Crystallography Data

Appendix B1: X-ray crystallography data for 34.

Experimental for C_{40}H_{55}O_2Si_2 (n19016)

Data Collection and Processing. The sample (n19016) was submitted by Maissa Belcina of the Baines research group at the University of Western Ontario. The sample was mounted on a MiTeGen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker-Nonius KappaCCD Apex2 diffractometer at a temperature of 123 K. The unit cell dimensions were determined from a symmetry constrained fit of 7915 reflections with 7.08° < 2θ < 134.7°. The data collection strategy was a number of ω and φ scans which collected data up to 135.51° (2θ). The frame integration was performed using SAINT.\(^1\) The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.\(^2\)

Structure Solution and Refinement. The structure was solved by using a dual space methodology using the SHELXT program.\(^3\) All non-hydrogen atoms were obtained from the initial solution. The carbon bound hydrogen atoms were introduced at idealized positions and were allowed to ride on their parent atoms. The position of the hydrogen atom bound to the Si atom was obtained from a difference Fourier map and was allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on \(F^2\). The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELX suite of crystallographic software.\(^4\) Graphic plots were produced using the Mercury program suite.\(^5\) Additional information and other relevant literature references can be found in the reference section of this website (http://xray.chem.uwo.ca).

\(^1\) Bruker-AXS, SAINT version 2013.8, 2013, Bruker-AXS, Madison, WI 53711, USA
\(^2\) Bruker-AXS, SADABS version 2012.1, 2012, Bruker-AXS, Madison, WI 53711, USA
\(^3\) Sheldrick, G. M., Acta Cryst. 2015, A71, 3-8
\(^4\) Sheldrick, G. M., Acta Cryst. 2015, C71, 3-8
**Table 1. Summary of Crystal Data for n19016**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{C}<em>{40}\text{H}</em>{55}\text{O}_2\text{PSi}_2$</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>654.99</td>
</tr>
<tr>
<td>Crystal Dimensions (mm)</td>
<td>$0.390 \times 0.234 \times 0.072$</td>
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<tr>
<td>Crystal Color and Habit</td>
<td>colourless prism</td>
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<tr>
<td>Crystal System</td>
<td>monoclinic</td>
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<tr>
<td>Space Group</td>
<td>$\text{P } 2_1/n$</td>
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<tr>
<td>Temperature, K</td>
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<td>$a$, Å</td>
<td>11.421(2)</td>
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<tr>
<td>$b$, Å</td>
<td>20.397(4)</td>
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<tr>
<td>$c$, Å</td>
<td>16.635(3)</td>
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<tr>
<td>$\alpha$, °</td>
<td>90</td>
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<tr>
<td>$\beta$, °</td>
<td>108.314(8)</td>
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<tr>
<td>$\gamma$, °</td>
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<td>$V$, Å$^3$</td>
<td>3678.9(13)</td>
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<tr>
<td>Number of reflections to determine final unit cell</td>
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<td>Min and Max 2θ for cell determination, °</td>
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<td>$Z$</td>
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<td>$F(000)$</td>
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<td>$\rho$ (g/cm$^3$)</td>
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<td>$\lambda$, Å (CuK$\alpha$)</td>
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<td>Value</td>
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<td>--------------------------------------------</td>
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<td>Scan Type(s)</td>
<td>phi and omega scans</td>
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<td>Max 2θ for data collection, °</td>
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<td>Measured fraction of data</td>
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<td>Number of reflections measured</td>
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<td>Unique reflections measured</td>
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<tr>
<td>(R_{\text{merge}})</td>
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</tr>
<tr>
<td>Number of reflections included in refinement</td>
<td>6519</td>
</tr>
<tr>
<td>Cut off Threshold Expression</td>
<td>(I &gt; 2\sigma(I))</td>
</tr>
<tr>
<td>Structure refined using</td>
<td>full matrix least-squares using (F^2)</td>
</tr>
<tr>
<td>Weighting Scheme</td>
<td>(w = 1/[\sigma^2(Fo^2) + (0.0628P)^2 + 1.14 (35P)]) where (P = (Fo^2 + 2Fc^2)/3)</td>
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<td>Number of parameters in least-squares</td>
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<tr>
<td>(\omega R_2)</td>
<td>0.1108</td>
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<tr>
<td>(R_1) (all data)</td>
<td>0.0692</td>
</tr>
<tr>
<td>(\omega R_2) (all data)</td>
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<td>Maximum shift/error</td>
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<tr>
<td>Min &amp; Max peak heights on final (\Delta F) Map ((e/\AA))</td>
<td>-0.341, 0.303</td>
</tr>
</tbody>
</table>

Where:

\[R_1 = \frac{\Sigma (|F_o| - |F_c|)}{\Sigma F_o}\]

\[\omega R_2 = \left( \frac{\Sigma \omega(F_o^2 - F_c^2)^2}{\Sigma(\omega F_o^4)} \right)^{\frac{1}{2}}\]
GOF = [ \sum \omega (F_o^2 - F_c^2)^2 / (\text{No. of reflns.} - \text{No. of params.}) ]^{1/2}

**Appendix B2:** X-ray crystallography data for 35.

**Experimental for C_{38}H_{51}O_3PSi_2 (b19206)**

*Data Collection and Processing.* The sample (b19206) was submitted by Maissa of the Baines research group at the University of Western Ontario. The sample was mounted on a MiTeGen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9860 reflections with 5.46° < 2θ < 61.94°. The data collection strategy was a number of ω and φ scans which collected data up to 63.316° (20). The frame integration was performed using SAINT. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.

*Structure Solution and Refinement.* The structure was solved by using a dual space methodology using the SHELXT program. All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were treated in a mixed fashion. The structural model was fit to the data using full matrix least-squares based on $F^2$. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELXTL suite of crystallographic software. Graphic plots were produced using the Mercury program suite. Additional information and other relevant literature references can be found in the reference section of this website ([http://xray.chem.uwo.ca](http://xray.chem.uwo.ca)).

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6 Bruker-AXS, SAINT version 2013.8, 2013, Bruker-AXS, Madison, WI 53711, USA
7 Bruker-AXS, SADABS version 2012.1, 2012, Bruker-AXS, Madison, WI 53711, USA
9 Sheldrick, G. M., *Acta Cryst.* 2015, C71, 3-8
**Table 1. Summary of Crystal Data for b19206**

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<thead>
<tr>
<th>Property</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{38}$H$</em>{51}$O$_3$PSi$_2$</td>
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<td>Formula Weight (g/mol)</td>
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<td>Crystal Dimensions (mm)</td>
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<td>Crystal System</td>
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<td>Space Group</td>
<td>$P \ 2_1/c$</td>
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<td>Temperature, K</td>
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<td>$a$, Å</td>
<td>11.509(3)</td>
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<td>$b$, Å</td>
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<td>$c$, Å</td>
<td>14.804(4)</td>
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<tr>
<td>$\alpha$,°</td>
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<td>$\beta$,°</td>
<td>106.380(9)</td>
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<td>$\gamma$,°</td>
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<td>$V$, Å$^3$</td>
<td>3563.8(16)</td>
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<td>$F(000)$</td>
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<td>Diffractometer Type</td>
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<td>Cut off Threshold Expression</td>
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<td>Structure refined using</td>
<td>full matrix least-squares using $F^2$</td>
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<tr>
<td>Weighting Scheme</td>
<td>$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 1.71$</td>
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<tr>
<td></td>
<td>$70P]$ where $P = (F_o^2 + 2F_c^2)/3$</td>
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<tr>
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<tr>
<td>$\omega R_2$</td>
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<td>$R_1$ (all data)</td>
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<td>$\omega R_2$ (all data)</td>
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<td>GOF</td>
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<td>Maximum shift/error</td>
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<tr>
<td>Min &amp; Max peak heights on final ΔF Map (e/Å)</td>
<td>-0.568, 0.597</td>
</tr>
</tbody>
</table>

Where:

$$R_1 = \frac{\sum (F_o - |F_c|)}{\sum F_o}$$

$$\omega R_2 = \left[ \frac{\sum (\omega (F_o^2 - F_c^2)^2)}{\sum (\omega F_o^4)} \right]^{1/2}$$
GOF = \[ \Sigma (\omega (F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})^{1/2} \]
Curriculum Vitae

Education

B.Sc. Honors Chemistry

The University of Western Ontario

2013 – 2017

4491 Supervisor: Dr. Kim Baines

Presentations

“Addition of Phosphorus Oxides to Ditetrelenes” Maissa Belcina, Bahareh Farhadpour, Nada Y. Tashkandi, and Kim M. Baines*, CSC 2018

Related Experience

Research Assistant

Baines Group

May 2017 – August 2017

Graduate Teaching Assistant

2017 – 2019

Courses: Chemistry 2213 (Organic Chemistry for Life Sciences), Chemistry 2223 (Organic Chemistry of Biological Molecules), Chemistry 3373 (Organic Chemistry III: Reactions and Strategies for Synthesis)

Course Grades

9503R (Advanced NMR Spectroscopy I) – 83

9507Q (Advanced Chemical Communications) – 90

9521S (Catalysis) – 87

9603S (Advanced NMR Spectroscopy II) – 87

9657 (Seminar) – PASS