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Doubly Bonded Derivatives of Si and Ge: Cycloaddition Reactions and Polymer Chemistry

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Abstract

(Di)tetrelenes are a fundamental class of unsaturated Group 14 compounds and play a central role in the synthesis of functional Group 14 compounds. The objective of this research was to investigate the various aspects of group 14 (di)tetrelenes ($R_2M{=}ER_2$, M = Si, Ge, and E = C, Si, Ge) reactivity.

The addition of a series of nitrone and nitro compounds to the group 14 (di)tetrelenes $Mes_2Si{=}SiMes_2$, $Mes_2Ge{=}GeMes_2$ and $Mes_2Ge{=}CH(CH_2\text{-}t\text{-}Bu)$, was examined. In general, the addition of the 1,3-dipolar nitrogen oxides to the (di)tetrelene gave 5-membered ring adducts via a formal [3+2] cycloaddition where the (di)tetrelene acts as the 2π component and the nitro/nitrone act as the 4π component. In some cases, the ring underwent rearrengment or cleavage to give secondary products.

Reactivity of (di)tetrelenes toward $R_2HP{=}O$ derivatives, where R = Ph, OPh, OCH_3, and R_3P:, where R = OCH_3, to tetramesityldigermene **1.2** and/or the germene **1.1** is reported in an effort to give a broader understanding of the chemistry of the addition of phosphine oxides to (di)tetrelenes. In general, a 1,2-adduct is formed which appears to be derived from the isomeric hydroxyphosphines. Notably, the phosphine oxides are reduced during the course of the reaction. A comparison to the analogous chemistry of alkenes and surface digermenes is made.

A variety of alkyllithium (R = Me, Bu, *t*-Bu) reagents and potassium *tert*-butoxide were added to the highly reactive silene $Mes_2Si{=}CHCH_2t\text{-}Bu$ and the germene $Mes_2Ge{=}CHCH_2t\text{-}Bu$, in diethyl ether. 1,2-Addition products were obtained regioselectively and in good yield after treatment with a weak acid with no evidence for any rearrangement products and no polymerization was observed. The reactivity of the silene and germene toward organometallic reagents is compared to previous studies of analogous silenes and germenes.

The characterization of polysilenes and polygermenes derived from the anionic polymerization of silenes and germenes, respectively, is reported. The molecular weight of the polygermene was determined by static light scattering (SLS) in THF which showed that M_W to be 41500 g mol^{-1}. The M_W determined by SLS was compared to the data obtained by GPC. Characterization of polysilene and polygermene by ESI-MS revealed the presence of oligomers ($n < 10$) of the polytetrelenes. The mass spectral data also reveal the presence of R-Ge and C-H end groups, consistent with a chain growth mechanism where the R group is derived from the anionic initiator. NMR spectroscopic analysis of the polysilene provided further evidence of a chain growth mechanism for the anionic polymerization of the silene without rearrangement during the polymerization.

Keywords: Cycloaddition, Nitro, Nitrone, (Di)tetrelene, Germene, Digermene, Disilene, Silene, 1,2-Addition, Polysilene, Polygermene, Static Light Scattering, ESI-MS.

Co-Authorship Statement

A version of Chapter 4 has been published as a full paper authored by Bahareh Farhadpour, Jiacheng Guo, Laura C. Pavelka, and Kim M. Baines. I am the primary author and conducted most of the experimental work under the supervision of Dr. Kim M. Baines. Jiacheng Guo and Laura C. Pavelka conducted some preliminary experiments.

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List of Abbreviations

Ad = admantyl

br = broad

Bu = butyl

calcd = calculated

d = doublet (NMR)

dm = doublet of multiplet (NMR)

DCM = dichloromethane

DFT = density functional theory

DSC = differential scanning calorimetry

EI = electron impact

ESI = electrospray ionization

Et = ethyl

FT = fourier transform

gCOSY = gradient correlation spectroscopy

gHMBC = gradient heteronuclear multiple bond correlation

gHMQC = gradient heteronuclear multiple quantum coherence

gHSQC = gradient homonuclear spin quantum coherence

GPC = gel permeation chromatography

HOMO = highest occupied molecular orbital

hr = hour

Hz = hertz

IR = infrared

J = coupling constant

LUMO = lowest unoccupied molecular orbital

m = multiplet (NMR); medium (IR)

MALDI = matrix-assisted laser desorption/ionization

Me = methyl

Mes = mesityl = 2,4,6-trimethylphenyl

MHz = megahertz

MO = molecular orbital

M_n = number-average molecular weight

M_w = number-average molecular weight

MS = mass spectrometry

m/z = mass-to-charge units

PDI = polydispersity index

Ph = phenyl

ppm = parts per million

RT = room temperature

s = singlet (NMR); strong (IR)

SEC = size-exclusion chromatography

SLS = static light scattering

t = triplet (NMR)

t-BuLi = *tertiary* butyllithium

t-Bu = *tertiary* butyl

THF = tetrahydrofuran

TMS = trimethylsilyl

TOF = time of flight

w = weak

δ = chemical shift

Chapter 1

1 Stable Doubly-Bonded Compounds of Silicon and Germanium

1.1 General Introduction

Compounds with homo- and heteronuclear multiple bonds of the heavy Group 14 elements have long been of interest. Despite much research into the synthesis and reactivity of (di)tetrelenes [referring to the heavy Group 14 derivatives: tetrelenes ($R_2M{=}CR_2$) and ditetrelenes ($R_2M{=}MR_2$) where M = Si, Ge, Sn and Pb], the quest for further understanding of the structural, spectroscopic properties and reactivity of these species continues. Given the numerous applications of alkene chemistry in organic synthesis and materials chemistry, it is not surprising that the applications of (di)tetrelene chemistry to polymer chemistry,[1] material science,[2] and catalysis[3] are now being explored.

1.2 Structure and Bonding of (Di)tetrelenes

The landmark syntheses of the first isolable disilene by West,[4] silene by Brook,[5] digermene by Masamune[6] and germene by Couret[7] were crucial breakthroughs in main group chemistry and allowed the development of this fundamental class of highly reactive organometallic compounds (**Scheme 1.1**).

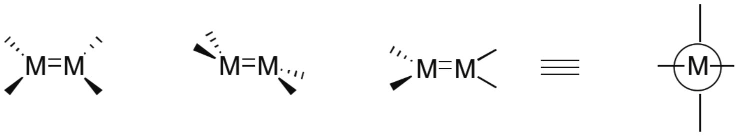
$Mes_2Si{=}SiMes_2$	$Ar_2Ge{=}GeAr_2$	$Ad(Me_3SiO)C{=}Si(SiMe_3)_2$	$Mes_2Ge{=}CR_2$
West *et al.*,1981	Masamune *et al.*,1982	Brook *et al.*, 1981	Couret *et al.*, 1987
Mes = 2,4,6-trimethylphenyl	Ar = 2,6-dimethylphenyl	Ad = 1-adamantyl	CR_2 = fluorenylidene

Scheme 1.1

The key to the isolation of these compounds lay in the utilization of bulky substituents to kinetically protect the double bonds and prevent dimerization.[8] The concept of steric protection has become widely accepted and has been employed to generate a number of isolable multiply-bonded main group compounds.[8g] On the basis of the central role of these compounds to this thesis, the structures and bonding of (di)-tetrelenes will be reviewed.

1.3 Structure and Bonding in (Di)tetrelenes

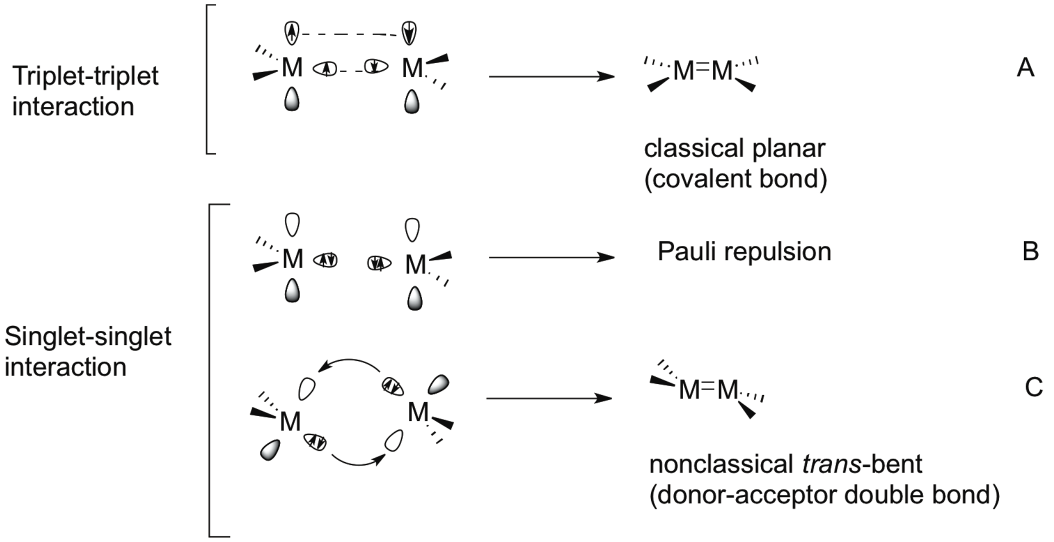
The most fundamental difference between alkenes and (di)tetrelenes is the difference in size of the covalent radii between the first and subsequent rows of the periodic table which is due to the different core electronic structures. While the molecular structure of tetrelenes exhibits a nearly planar geometry around the double bond, ditetrelenes exhibit a *trans*-bent geometry and a twisting about the double bond (**Scheme 1.2**).[9]



planar *trans*-bent twist form

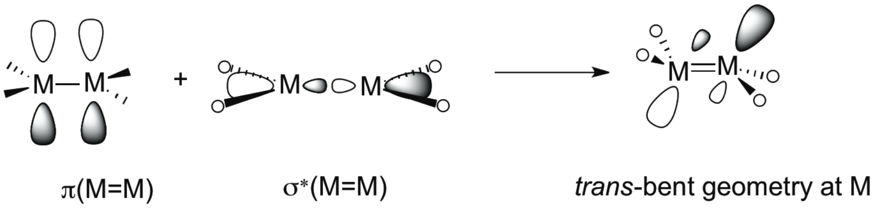
Scheme 1.2

The *trans*-bent geometry can be understood in terms of two different bonding models. One model is the formation of a double bond by the interaction of two monomeric divalent Group 14 units, with triplet ground states. Covalent interactions between the singly occupied molecular orbitals forms the classical planar C=C double bond (**Scheme 1.3, A**). In contrast, direct interaction between two ground state singlets would result in significant Pauli repulsions between the doubly occupied n-orbitals (**Scheme 1.3, B**). To form a classical M=M bond, initial excitation to the triplet state (the elevation of one electron from the *n*- to the p- level) is required. However, there is a significant energetic difference between the singlet and triplet states (ΔE_{ST}). Alternatively, the two heavy divalent fragments can interact with each other by donation of a pair of electrons from the *n*-orbital of one fragment to the empty p-orbital of the other fragment. As a consequence, a nonclassical M=M bond with a *trans*-bent geometry at the doubly-bonded M centre is formed (**Scheme 1.3, C**).[9,10]



Scheme 1.3[16a]

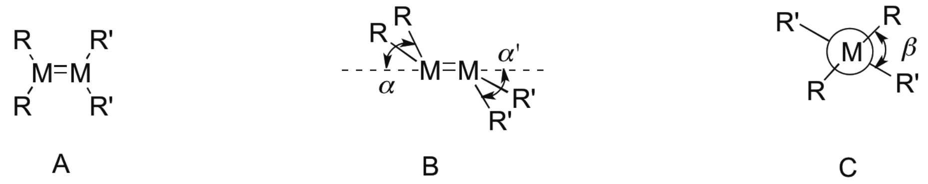
On the other hand, the *trans*-bent geometry of ditetrelenes can be understood in terms of an orbital interaction between the M=M π and σ^* -orbitals, which becomes attainable upon bending at the M centres. The stronger the π-σ^* interaction, the greater the degree of *trans*-bending (**Scheme 1.4**). The size of the π -σ^* energy gap notably decreases going down Group 14, which leads to stronger π-σ^* mixing and more significant bending at the M centres.[10]



Scheme 1.4[11]

The electronegativity of the substituents also plays a role on the degree of *trans*-bending of the heavy analogues of alkene. Electron-donating substituents, such as F, OH, NH_2, which increase the ΔE_{ST} gap and the degree of the π -σ^* orbital interaction, cause significant *trans*-bending at the M centre and weaken the M=M bond. Electron-accepting groups such as BH_2 and SiH_3, reduce the ΔE_{ST} gap, resulting in a smaller degree of bending at the M centre and a concomitant increase in the strength of the M=M bond.[11]

As mentioned above, structural deformations, specifically, bending at M (**Scheme 1.5, B**) and twisting (**Scheme 1.5, C)** around the M=M bond, are observable by molecular structure determination through X-ray diffraction analysis. The bending angles α/α\` are defined as the angles between the R-M-R/R\`-M-R\` mean planes and the M-M bond axis, whereas the twisting angle "β" is defined as the dihedral angle between the R-M-R and R\`-M-R\` mean planes.[9]



planar *trans*-bending (α/α`) twisting (β)

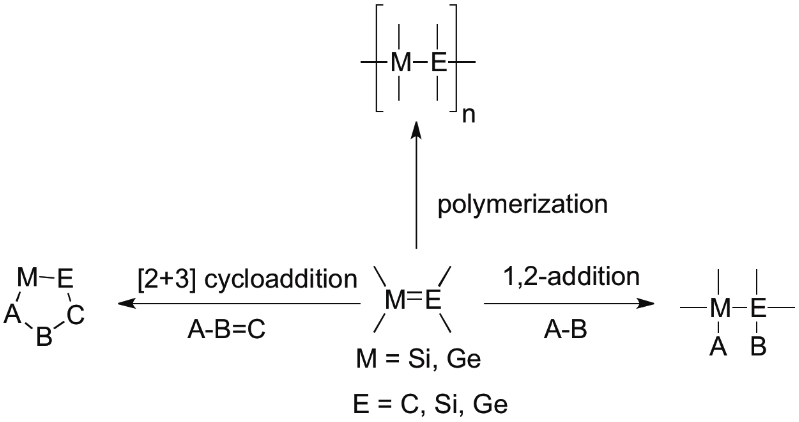
Scheme 1.5

1.4 Reactivity of (Di)tetrelenes

The reactivity of (di)tetrelenes has been studied extensively.[12,13,14,15] The high reactivity of (di)tetrelenes can be ascribed in part to the nature of the π bond, which is much weaker than the π bond in alkenes (estimated π-bond strengths (kcal/mol): C=C 65; Si=Si 25-30; Ge=Ge 20-22; Si=C 37-47).[16] In addition, the difference in electronegativity between germanium (χ = 1.9) or silicon (χ = 1.8) and carbon (χ = 2.5) gives rise to a polarized π bond which also contributes to the reactivity of silenes and germenes. The high reactivity of multiply-bonded Group 14 compounds leads to facile reactions. Although many doubly-bonded derivatives of the heavy Group 14 elements are stable, they have a high reactivity towards electrophilic or nucleophilic reagents, such as alcohols, amines, nitriles, and carbonyl compounds which react rapidly and often quantitatively.[17,18,19,20] A general scheme depicting several modes of reactivity of (di)tetrelenes is shown below (**Scheme 1.6**).

The most commonly used reagents to react with (di)tetrelenes are polar reagents such as water and alcohols. These σ-bonded reagents often undergo regioselective 1,2-

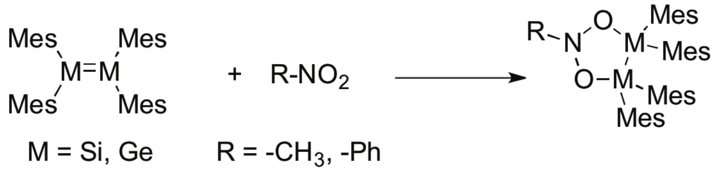
additions in the case of tetrelenes. In general, the more electronegative atom of the polar reagent adds to the germanium or silicon of the double bond.



Scheme 1.6

(Di)tetrelenes also undergo reactions with π-bonded reagents such as carbonyl compounds and their derivatives, unsaturated nitrogen compounds, alkenes and alkynes. Depending on the nature of the reagents, different modes of reactivity may occur including [2+2], [3+2], and [4+2] cycloaddition. Cycloaddition reactions of (di)tetrelenes have been utilized in the synthesis of new inorganic materials. For example, the formation of organosilicon hybrid polymers through a formal [2+2] cycloaddition reaction between a terminal alkyne and a disilene.[20b] Furthermore, the cycloaddition of heteronuclear π-bonded reagents such as aldehydes, ketones, or unsaturated nitrogen compounds to (di)tetrelenes generates new inorganic heterocycles composed of carbon, nitrogen, and/or oxygen which holds much potential for the synthesis of a wide variety of silicon/germanium heterocycles. 1,3-Dipolar cycloaddition (1,3-DC) reactions are one of the most effective methods for obtaining a wide range of five-membered functionalized compounds. 1,3-Dipolar cycloaddition reactions have also a high level of regio- and stereospecificity.

As an example, the addition of a variety of nitro compounds to ditetrelenes has been investigated in the Baines group.[21] Aliphatic and aromatic-substituted nitro compounds (namely, nitromethane, nitroethane, nitrobenzene) react with ditetrelenes in a [3+2] manner to give dioxazadisil- and digermolidine ring systems. The reactivity of ditetrelenes ($R_2M{=}MR_2$, M=Si, Ge) towards nitro compounds has been shown to parallel that of the Si (or Ge) dimers on the Si (or Ge) (100) 2 x 1 surface, and thus, can be useful in the understanding of the surface chemistry to facilitate the attachment of complex molecules and the subsequent development of devices.[21]

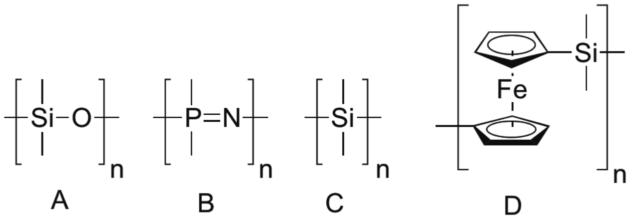


Scheme 1.7

Expanding the reactivity of M=E (M = Si, Ge; E = C) to polymer science has been of particular interest over the last 10 years. The development of this area of chemistry will be reviewed here.

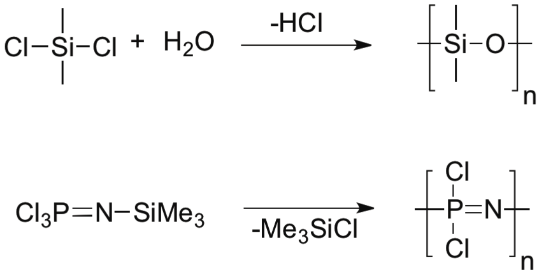
1.5 Incorporation of Heavier Group 14 Elements into Polymers

The synthesis and study of macromolecules containing inorganic elements in the main chain are of long-standing interest due to their novel properties and possible specialty applications. Notable examples include: polysiloxanes (A), polyphosphazenes (B), polysilanes (C), and poly(ferrocenylsilane)s (D) (**Scheme 1.8**).[22]



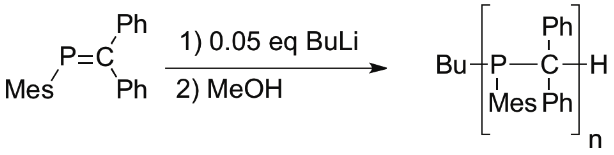
Scheme 1.8

Both addition and condensation polymerizations have been applied to the synthesis of inorganic polymers (**Scheme 1.9**).[22, 23] The most well-known and widely-used routes to high molecular weight polysiloxanes (A), polyphosphazenes (B) and polysilanes (C) involve a condensation polymerization reaction.



Scheme 1.9

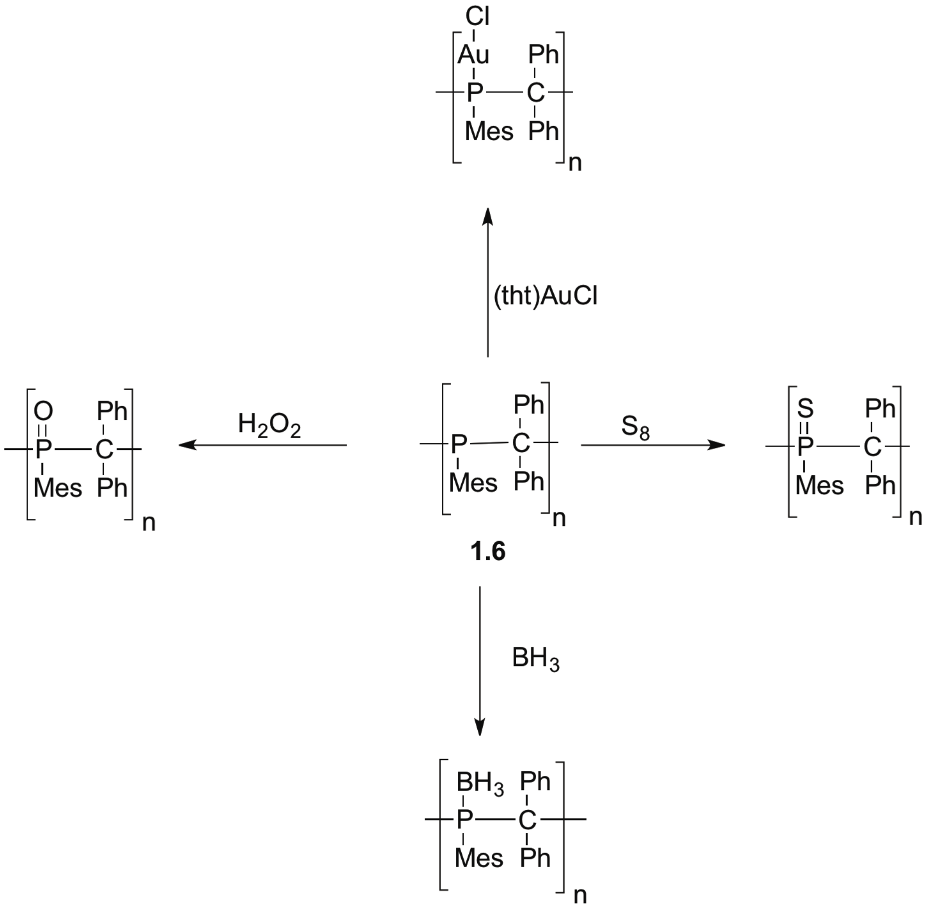
In an important advance in inorganic polymer chemistry, the addition polymerization of phosphene **1.5** to afford air- and moisture-stable polyphosphenes **1.6** was reported by Gates *et al.* (**Scheme 1.10**).[24] Phosphene **1.5** is a suitable monomer for polymerization since it is isolable but has minimal kinetic stabilization. The random copolymerization of phosphene **1.5** and styrene using a radical initiator was also reported.[25]



1.5 **1.6**

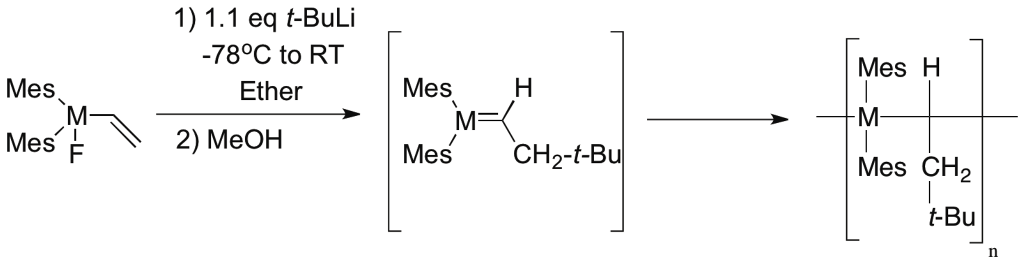
Scheme 1.10

Furthermore, conditions have been developed for the living anionic polymerization of phosphaalkene **1.5** using BuLi as the initiator.[26] Aspects of the chemistry of polyphosphenes have also been investigated: the phosphorus can be oxidized by either H_2O_2 or S_8[24] and the coordination chemistry of the backbone phosphine with either borane[27] or gold[28] was achieved (**Scheme 1.11**).



Scheme 1.11

Inspired by the rich chemistry of polyphosphenes, the addition polymerization of a stable germene, dimesitylneopentylgermene [1d] **1.1**, and a stable silene, 1,1-dimesitylneopentylsilene [1a] **1.4**, was investigated. Germene **1.1** and silene **1.4** were polymerized in presence of *t*-BuLi to give polygermene **1.7** (M_n = 36000 g mol^{-1} and 7100 g mol^{-1}, PDI = 1.1 and 1.5, respectively) or polysilene **1.8** (M_n = 28000 g mol^{-1}, PDI = 1.2), respectively (**Scheme 1.12**).

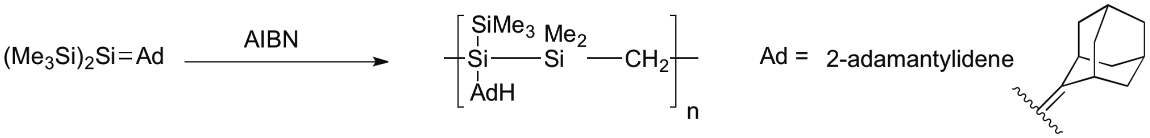


1.1: M= Ge
1.4: M= Si

1.7: M= Ge
1.8: M= Si

Scheme 1.12

The polymerization of the silene ((Me$_3$Si)$_2$Si=Ad, Ad = 2-adamantylidene) has also been reported.[1c] (Me$_3$Si)$_2$Si=Ad, produced by thermal dissociation of the head-to-tail dimer, was polymerized either thermally or in the presence of a radical to give a polymer (M_w = 11400 g mol^{-1}) (**Scheme 1.13**).



Scheme 1.13

1.6 Determination of the Molecular Weight of a Polymer

One of the most important pieces of characterization data, which provides insight into the physical properties and application of a polymer, is the molecular weight.[29] Gel permeation chromatography (GPC) also known as size-exclusion chromatography (SEC) is the most widely used technique for measuring the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of polymers. M_n is the mean molecular weight value, taken from the total weight of all the molecules divided by the total number of molecules (**Equation 1.1**). The M_w is a weighted average; the higher molecular weight molecules are weighted more heavily (**Equation 1.1**). The distribution of molecular weights in a given polymer sample is represented by the polydispersity index (PDI). PDI is determined by dividing the M_w by the M_n; a monodisperse polymer sample, where all polymer chains are the same length, would have a PDI of one. Notably, the molecular weight of the polymer is often underestimated by GPC (versus polystyrene standard).[24]

$$M_w = \frac{\sum N_i \times M_i^2}{\sum N_i \times M_i} \qquad M_n = \frac{\sum N_i \times M_i}{\sum N_i}$$

Equation 1.1 M_n and M_w

The use of soft ionization mass spectrometry (*i.e.* electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI)) has been widely applied in the characterization of polymers because the technique provides access to the absolute molecular weight of a sample without a reference standard as well as knowledge of the structure of the polymer including the identity of the end groups. Soft ionization techniques produce little or no fragmentation and can determine the molecular weight of large, intact macromolecules to the MDa range. Both MALDI and ESI-MS have been used to analyze some common organic polymers such as polystyrene and poly(methyl methacrylate).[30] ESI-MS experiments on polymers often use time-of-flight (TOF) mass analyzers which are widely available and also have capability of detecting ions with high mass-to-charge ratios (*m/z*).[31] Mass spectrometry can also be used to identify the structure of the chain end-groups, which provides essential information about the polymerization mechanism. With ESI-MS, the molecular weight, the molecular weight distribution, and the end-group can be rapidly and accurately determined.[32]

1.7 Scope of the Thesis

Much of the experimental research within this thesis has utilized the following prototypical substrates: germene Mes_2Ge=$CHCH_2$*t*-Bu, **1.1**, digermene Mes_2Ge=$GeMes_2$ (where Mes = 2, 4, 6-$Me_3C_6H_2$), **1.2**, and disilene Mes_2Si=$SiMes_2$, **1.3**.

Our group has long been interested in the reactivity of multiply-bonded Group 14 species with focus on cycloaddition reactions. Furthermore, multiply-bonded Group 14 species have proven to be used as building blocks in organometallic/inorganic synthesis. However, in order to achieve the full potential of these low valent main group compounds, it is very important to have a firm understanding of their reactivity. Two perspectives were investigated in the present work: the addition reaction of organometallic reagents, nitrones, nitro compounds, phosphites and/or phosphine oxides to Mes_2Si=$SiMes_2$ **1.3**, Mes_2Ge=$GeMes_2$ **1.2**, and Mes_2Ge=$CHCH_2$*t*-Bu **1.1** and the characterization of polygermene **1.7** and polysilene **1.8** using a variety of techniques.

In Chapter 2, the addition of a variety of nitrones including C,N-diphenylnitrone, N-*tert*-butyl-α-phenylnitrone and 5,5-dimethyl-1-pyrroline *N*-oxide to Mes_2Si=$SiMes_2$ **1.3**, Mes_2Ge=$GeMes_2$ **1.2**, and/or Mes_2Ge=$CHCH_2$*t*-Bu **1.1** and the addition of nitroalkanes (R = Me, Et) to Mes_2Ge=$CHCH_2$*t*-Bu **1.1** will be discussed. The structure elucidation of the products will be presented and the reactivity will be compared to other (di)tetrelene nitro/nitrone reactions.

In Chapter 3, the addition of a diphenylphosphine oxide, dimethyl phosphite, diphenyl phosphite, and/or trimethyl phosphite to $Mes_2Si=SiMes_2$ **1.3**, $Mes_2Ge=GeMes_2$ **1.2** and/or $Mes_2Ge=CHCH_2$*t*-Bu **1.1** is examined. The addition of trimethyl phosphite to **1.2** and **1.3** will be compared to the analogous chemistry of the Ge(100)- 2 × 1 surface.

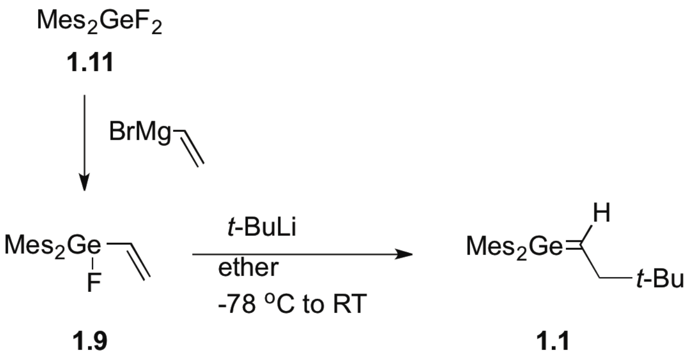
In Chapter 4, a variety of alkyllithium (R = Me, Bu, *t*-Bu) reagents and potassium tert-butoxide were added to the highly reactive silene, $Mes_2Si=CHCH_2$*t*-Bu **1.4**, and germene $Mes_2Ge=CHCH_2$*t*-Bu **1.1**. 1,2-Addition products were obtained regioselectively and in good yield after treatment with a weak acid with no evidence for any rearrangement products and no polymerization was observed. The reactivity of the silene **1.4** and germene **1.1** toward organometallic reagents is compared to previous studies of analogous silenes and germenes.

In Chapter 5, a comparison of various techniques (GPC, ESI-MS and SLS) for the molecular weight determination of polygermene **1.7** and polysilene **1.8** will be presented. Moreover, the primary structure of polysilene **1.8** will be explored by NMR spectroscopy. By using end group analysis, a mechanism for the polymerization will be proposed. The results will be compared to those obtained by Gates *et al.* for the analogous polyphosphene.[33]

1.8 Synthesis of Precursors

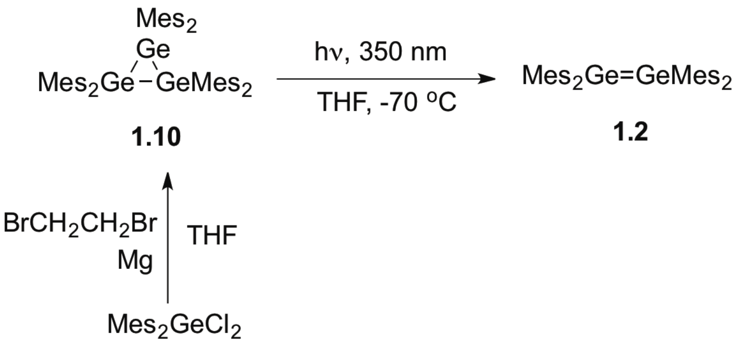
Since the focus of this thesis will be on the reactivity of (di)tetrelenes, the synthesis of the key compounds are presented here. Germene[34] **1.1** and silene[35] **1.4** were synthesized by the addition of *t*-BuLi to fluorodimesitylvinylgermane **1.9** or –silane **1.10**, respectively, in diethyl ether at ~ -78 °C and used in situ without purification. Germane

1.9 is synthesized from the addition of vinylmagnesium bromide to Mes_2GeF_2 (**1.11**) (**Scheme 1.14**).



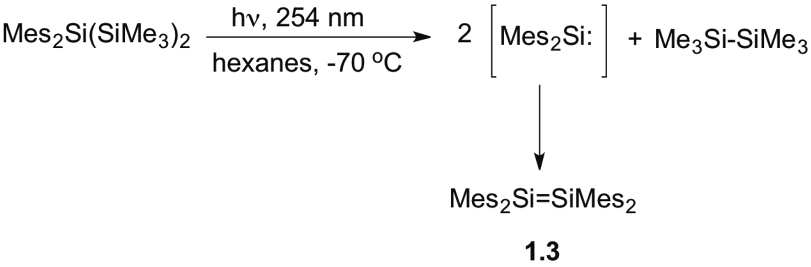
Scheme 1.14

Tetramesityldigermene **1.2** is easily prepared by irradiation of a THF solution of hexamesitylcyclotrigermane **1.10**. Digermene **1.2** is not stable in solution for extended periods of time (weeks) and slowly reverts back to cyclotrigermane. [36] Hexamesitylcyclotrigermane **1.10** was prepared by reductive coupling of Mes_2GeCl_2 with fine-powder magnesium and 1,2-dibromoethane in THF (**Scheme 1.15**).



Scheme 1.15

Disilene **1.3** $Mes_2Si{=}SiMes_2$ is synthesized by the photolysis of the trisilane, $Mes_2Si(SiMe_3)_2$, in hexanes solution (**Scheme 1.16**) at -70 °C. Tetramesityldisilene is stable at room temperature, in the absence of air. The accepted mechanism for the formation of disilene **1.3** is by dimerization of the divalent silicon intermediate.[4]



Scheme 1.16

1.9 References

1. Selected examples: (a) Pavelka, L. C.; Milnes, K. K.; Baines, K. M. *Chem. Mater.* **2008**, *20*, 5948; (b) Majumdar, M.; Bejan, L.; Huch, V.; White, A. J. P.; Whittell, G. R.; Schäfer, A.; Manners, I.; Scheschkewitz, D. *Chem. Eur. J.* **2014**, *20*, 9225; (c) Bravo-Zhivotovskii, D.; Melamed, S.; Molev, V.; Sigal, N.; Tumanskii, B.; Botoshansky, M.; Molev, G.; Apeloig, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 1834; (d) Pavelka, L. C.; Holder, S. J.; Baines, K. M. *Chem. Commun.* **2008**, 2346.

2. (a) Parke, S. M.; Boone, M. P.; Rivard, E. *Chem. Commun.* **2016**, *52*, 9485.; (b) Löfas̊, H.; Orthaber, A.; Jahn, O.B.; Rouf, M. A.; Grigoriev, A.; Ott, S.; Ahuja, R.; Ottosson, H. *J. Phys. Chem. C* **2013**, *117*, 10909; (c) Pola, J.; Urbanová, M.; Volnina, E. A.;

Bakardjieva, S.; Subrt, J.; Bastl, Z. *J. Mater. Chem.* **2003**, *13*, 394; (d) Pola, J. *Surf. Coat. Technol.* **1998**, *100−101*, 408.

3. For example: (a) Ermert, D. M.; Gordon, J.B.; Abboud, K. A.; Murray, L. J. *Organometallics* **2016**, *35*, 3651; (b) Hadlington, T. J.; Li, J.; Hermann, M.; Davey, A.; Frenking, G.; Jones, C. *Organometallics* **2015**, *34*, 3175; (c) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2014**, *136*, 3028; (d) Jana, A.; Tavcar, G.; Roesky, H. W.; John, M. *Dalton Trans.* **2010**, *39*, 9487.

4. (a) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343; (b) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

5. Brook, A.G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc. Chem. Commun.* **1981**, 191.

6. Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

7. Couret, C.; Satgé, J.; Escudié, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *27*, 828.

8. For reviews see: (a) Kays, D. L. *Chem. Soc. Rev.* **2016**, *45*, 1004; (b) Matsuo, T. Kobayashi M.; Tamao, K. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1201; (c) Power, P.P. *Organometallics* **2004**, 24, 3904; (d) Yoshifuji, M. *J. Organomet. Chem.* **2000**, 611, 210; (e) Wilfling, P.; Schittelkopf, K.; Flock, M.; Herber, R. H.; Power, P. P.; Fischer, R. C. *Organometallics* **2015**, *34*, 2222; (f) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354; (g) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047; (h) Driess, M.;

Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828; (i) Norman, N. C. *Polyhedron* **1993**, *12*, 2431; (j) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386.

9. Kira, M. *Proc. Jpn. Acad., Ser. B, Phys. Biol. Sci.* **2012**, 88, 167.

10. (a) Power, P.P. *Chem. Rev.* **1999**, *99*, 3463; (b) Karni, M.; Apeloig, Y.; Kapp, J. Schleyer, P. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons: New York, **2001**; Chichester, Vol. *3* Chapter 1; (c) Klinkhammer, K. W. *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Eds.; John Wiley & Sons, Ltd, **2002**; Chichester, Vol. *2*, Part 1, Chapter 4.

11. Lee, V. Y. *CheM* **2012**, *2*, 35.

12. For recent accounts on various aspects of silene chemistry: (a) Ottosson H.; Rouf, A. M. *Science of Synthesis: Knowledge Updates;* 2011/3, Oestreich, M., Eds.; Thieme, Stuttgart, **2011**; Chapters 4.4.25; (b) Baines, K. M. *Chem. Comm.* **2013**, *49*, 6366; (c) Ottosson H.; Eklof, A. M. *Coord. Chem. Rev.* **2008**, *252*, 1287; (d) Ottosson H.; Steel, P. G. *Chem. Eur. J.* **2006**, *12*, 1576; (e) Gusel'nikov, L. E. *Coord. Chem. Rev*. **2003**, *244*, 149; (f) Escudié, J.; Couret C.; Ranaivonjatovo, H. *Coord. Chem. Rev*. **1998**, *565,* 178.

13. For recent accounts on various aspects of disilene chemistry: (a) Iwamoto, T.; Ishida, S. *Struct. Bonding* **2014**, *156*, 125; (b) Sasamori; T.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1005; (c) Kira, M. *Proc. Jpn. Acad., Ser. B* **2012**, *88*, 167; (d) Matsuo, T. Kobayashi M.; Tamao, K. *Dalton Trans.* **2010**, *39*, 9203; (e) Abersfelder, K.; Scheschkewitz, D. *Pure Appl. Chem.* **2010**, *82*, 595; (f) Scheschkewitz, D. *Chem. Eur. J.*

2009, *15*, 2476; (g) Kira, M. *J. Organomet. Chem*. **2004**, *689*, 4475; (h) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348.

14. For recent accounts of the chemistry of germenes and digermenes see: (a) Plyusnin, V. F.; Kaletina M. V.; Leshina, T. V. *Russ. Chem. Rev*. **2007**, *76*, 931; (b) Takeda, N.; Tokitoh N.; Okazaki, R. *Science of Synthesis*; Moloney, M. G., Eds.; Thieme, Stuttgart, **2003**; Chapters 5.1.2.

15. Power, P.P. *Organometallics* **2007**, *26*, 4362.

16. General reviews: (a) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, S, and Pb, From Phantom Species to Stable Compounds*; John Wiley & Sons, Ltd, Chichester, **2010**; Chapter 5; (b) Lee V. Y.; Sekiguchi, A. *Organometallics* **2004**, *23*, 2822.

17. For reviews of the reactivity of silenes see: (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71; (b) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 71.

18. For reviews of the reactivity of disilenes see: (a) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73; (b) Weidenbruch, M. *The Chemistry of Organic Silicon Compounds,* ed. Z. Rappoport and Y. Apeloig, Wiley and Sons Ltd, New York, **2001**, ch. 5, vol. *3*; (c) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231.

19. For reviews of the reactivity of germenes and digermenes see: (a) Tokitoh, N.; Okazaki, R. *The Chemistry of Organic Germanium, Tin, and Lead Compounds*, ed. Z.

Rappoport, John Wiley and Sons Ltd, Chichester, **2002**, ch. 13, vol. *2*; (b) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113; (c) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

20. For some recent examples see: (a) Motomatsu, D.; Ishida, S.; Ohno, K.; Iwamoto, T.; *Chem. Eur. J.* **2014**, *20*, 9424; (b) Majumdar, M.; Bejan, I.; Huch, V.; White, A. J. P.; Whittell, G. R.; Schäfer, A.; Manners, I.; Scheschkewitz, D. *Chem. Eur. J.* **2014**, *20*, 9225; (c) Zhou, J.; Hall, M. B. *J. Organomet. Chem.* **2013**, *748*, 8; (d) Lee, V. Y.; McNiece, K.; Ito, Y.; Sekiguchi, A.; Geinik, N.; Becker, J. Y. *Heteroat. Chem.* **2014**, *25*, 313.

21. (a) Tashkandi, N. Y.; Parsons, F.; Guo, J.; Baines, K. M. *Angew. Chem. Int. Ed.* **2015**, *54,* 1612; (b) Tashkandi, N. Y. Cycloaddition Reactions of (Di)tetrelenes ,The University of Western Ontario, **2016**.

22. (a) Chivers, T.; Manners, I. *Inorganic Rings and Polymers of the p-Block Elements: from Fundamentals to Applications*, RSC Publishing, Cambridge, **2009**; (b) Archer, R. D. *Inorganic and Organometallic Polymers;* Wiley & Sons: New York, **2001**; (c) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers;* Oxford University Press: Oxford, **2005**.

23. Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P. *Chem. Soc. Rev.* **2016**, *45*, 922.

24. Tsang, C. W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003**, *125*, 1480.

25. Tsang, C. W.; Baharloo, B.; Riendl, D.; Yam, M.; Gates, D. P. *Angew. Chem. Int. Ed.* **2004**, *43,* 5682.

26. a) Noonan, K. J. T.; Gates, D. P. *Angew. Chem. Int. Ed.* **2006**, *45*, 7271; b) Noonan, K. J. T.; Gates, D. P. *Macromolecules*. **2008**, *41*, 1961.

27. Noonan, K. J. T.; Feldscher, B.; Bates, J. I.; Kingsley, J. J.; Yam, M. D. P. *Dalton Trans*. **2008**, 4451.

28. Gillon, B. H.; Patrick, B. O.; Gates, D. P. *Chem. Commun*. **2008**, 2161.

29. (a) Odian, G. *Principles of Ploymerization*; Wiley & Sons, **1991**; (b) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, Englewood Cliffs, **1981**.

30. (a) Montaudo, G.; Lattimer, R. P. *Mass Spectrometry of Polymers*; CRC Press: Florida, **2002**. (b) Liang, L. *MALDI Mass Spectrometry for Synthetic Polymer Analysis*; Wiley & Sons: New Jersey, **2009**. (c) Macha, S. F.; Limbach, P. A. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 213. (d) Stump, M. J.; Fleming, R. C.; Gong, W. H.; Jaber, A. J.; Jones, J. J.; Surber, C. W.; Wilkins, C. L. *Appl. Spectrosc. Rev.* **2002**, *37*, 275. (e) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527.

31. Hakkarainen, M. *Mass Spectrometry of Polymers-New Techniques*; Springer-Verlag Berlin Heidelberg, **2012**.

32. Crecelius, C. A.; Baumgaertel, A.; Schubert, S. U. *J. Mass Spectrom.*

2009, *44*, 1277.

33. (a) Serin, S. C.; Dake, G. R.; Gates, D. P. *Macromolecules.* **2016**, *49*, 4067; (b) Siu, P. W.; Serin, S. C.; Krummenacher, I.; Hey, T. W.; Gates, D. P. *Angew. Chem. Int. Ed.* **2013**, *52*, 6967; (c) Gillon, B. H.; Gates, D. P.; Henderson, M. A.; Janusson, E.; McIndoe, J. S. *Can. J. Chem.* **2017**, 95, 239

34. Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.

35. a) Delpon-Lacaze, G.; Couret, C. *J. Organomet. Chem.* **1994**, *480*, C14; b) Delpon-Lacaze, G.; de Battisti, C.; Couret, C. *J. Organomet. Chem.* **1996**, *514*, 59

36. Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics* **2007**, *26*, 5569.

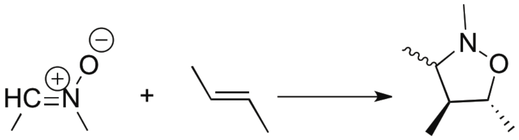
Chapter 2

2 The Addition of Nitrone and Nitro Compounds to Tetrelenes and Ditetrelenes

2.1 Introduction

Despite more than 35 years of research on the chemistry of unsaturated heavier group 14 compounds, the fundamental chemistry of these molecules remains relatively unexplored.[1,2] (Di)tetrelenes have proven to be useful building blocks in organometallic/inorganic synthesis[1,2] owing to the high reactivity of these doubly-bonded heavy group 14 compounds towards a variety of species.[3] The use of unsaturated main group compounds in coordination chemistry[4] and catalysis[5] has also received much attention in recent years. In particular, the cycloaddition reactions of group 14 (di)tetrelenes have been attracting the interest of chemists due to their high degree of regio- and stereospecificity. In this chapter, the cycloaddition of germene **1.1**, digermene **1.2**, and disilene **1.3** towards dipolar nitrogen oxides will be described.

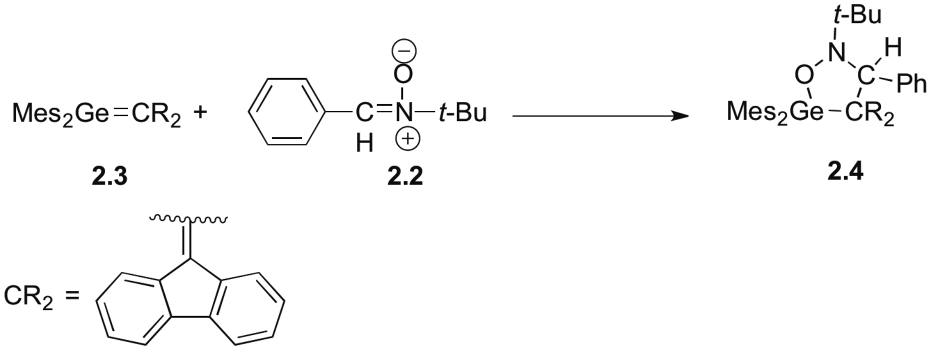
The nitrone-olefin [3+2] cycloaddition leading to isoxazolidines **2.1** is a well-known reaction in organic chemistry (**Scheme 2.1**).[6]



2.1

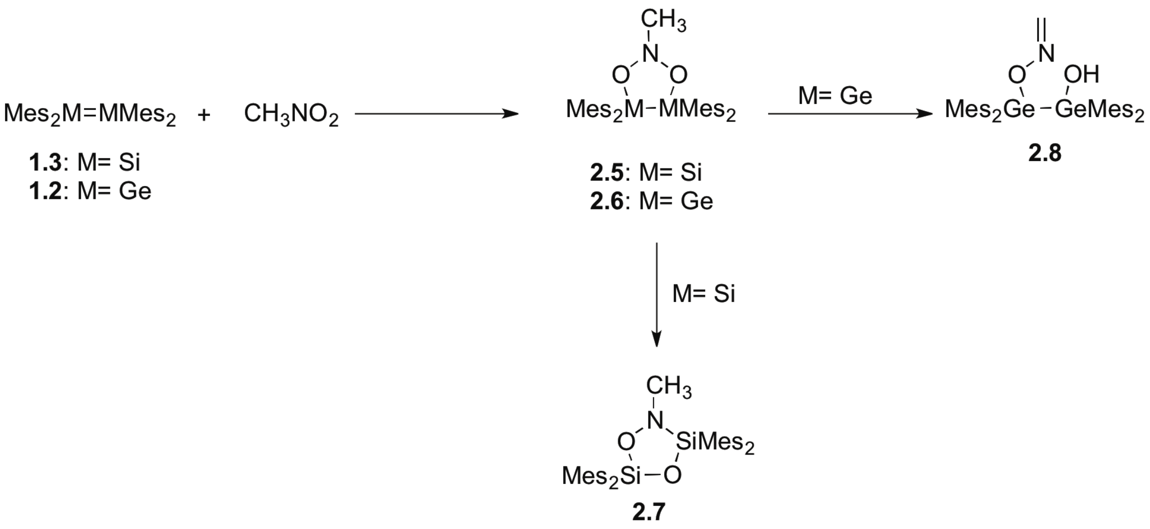
Scheme 2.1

However, the analogous reaction with Group 14 (di)tetrelenes is relatively unknown; only one reaction, between a germene and a nitrone, has been investigated to date. The addition of N-*tert*-butyl-α-phenylnitrone **2.2** to dimesitylfluorenylidenegermane **2.3**, $Mes_2Ge{=}CR_2$ (where CR_2= fluorenylidene), cleanly gives 1,2,5-oxazagermolidine **2.4**.[7]



Scheme 2.2

In related chemistry, nitro compounds are weak nucleophiles and, in general, require catalysts to react with alkenes; however, the reaction of nitro compounds with (di)tetrelenes proceeds smoothly. Recently, the facile preparation of **2.5** and **2.6** by the addition of nitromethane to tetramesityldisilene **1.3** or to tetramesityldigermene **1.2**, respectively was reported (**Scheme 2.3**).[8] 1,3,2,4,5-Dioxazadisilolidine **2.5** undergoes thermal rearrangement to **2.7** whereas the germanium analog, 1,3,2,4,5-dioxazadigermolidine **2.6**, cleanly isomerizes to the oxime isomer **2.8** (**Scheme 2.3**).[8]



Scheme 2.3

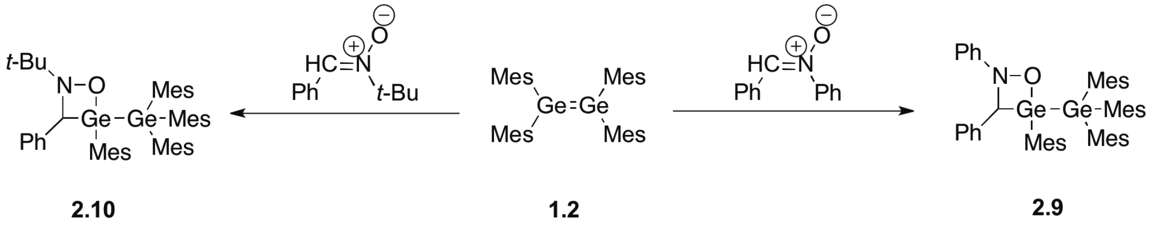
Given our extensive interest in the synthesis of new heterocyclic ring systems and to expand the scope of previous studies, we have investigated the addition of nitrones and/or nitro compounds to germene **1.1**, tetramesityldigermene **1.2**, and tetramesityldisilene **1.3**.

2.2 Results

Germene **1.1**,[9] digermene **1.2**,[10] and disilene **1.3**[11] were synthesized prior to each reaction in quantitative yield and used in *situ* without purification. Germene **1.1**, digermene **1.2** or disilene **1.3** was dissolved in C_6D_6 and the nitro/nitrone compound was added in excess. The reaction mixture was kept at room temperature and monitored by ^1H NMR spectroscopy. The products were isolated as either colourless or yellow oils/solids and were identified by ^1H, ^{13}C, ^1H-^1H COSY, ^{13}C-^1H gHSQC and ^{13}C-^1H gHMBC NMR spectroscopy, ESI-TOF mass spectrometry and, in some cases, single crystal X-ray diffraction.

2.2.1 Addition of Nitrone Compounds to Tetramesityldigermene 1.2

The addition of C,N-diphenylnitrone to the bright yellow solution of digermene **1.2** at room temperature gave a clear, pale yellow oil upon removal of the solvent. Crystallization from ether at -14 °C gave a white solid, **2.9**. The high resolution mass spectrum of **2.9** showed a signal at *m/z* 814.2861, which is consistent with a 1:1 adduct between digermene **1.2** and C,N-diphenylnitrone. The ^{1}H NMR spectrum of **2.9** revealed the presence of two chemically nonequivalent mesityl substituents in a ratio of 3:1. One sets of signals was assigned to three equivalent mesityl groups on one germanium atom (Mes_3Ge-). The ^{1}H NMR spectrum of **2.9** also revealed a singlet at 4.92 ppm that integrated to 1H which was assigned to a C**H**-Ph hydrogen on the basis of the observed correlation to the signal at 79.12 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum which was assigned to a C attached to N on the basis of its chemical shift. Crystals of **2.9** were grown from a concentrated THF solution and the molecular structure of **2.9** was determined by X-ray crystallography. Compound **2.9** was identified as 4-mesityl-2,3-diphenyl-4-(trimesitylgermyl)-1,2,4-oxazagermetidine (**Scheme 2.4, Figure 2.1**). All bond lengths and angles of **2.19** are within normal ranges.



Scheme 2.4

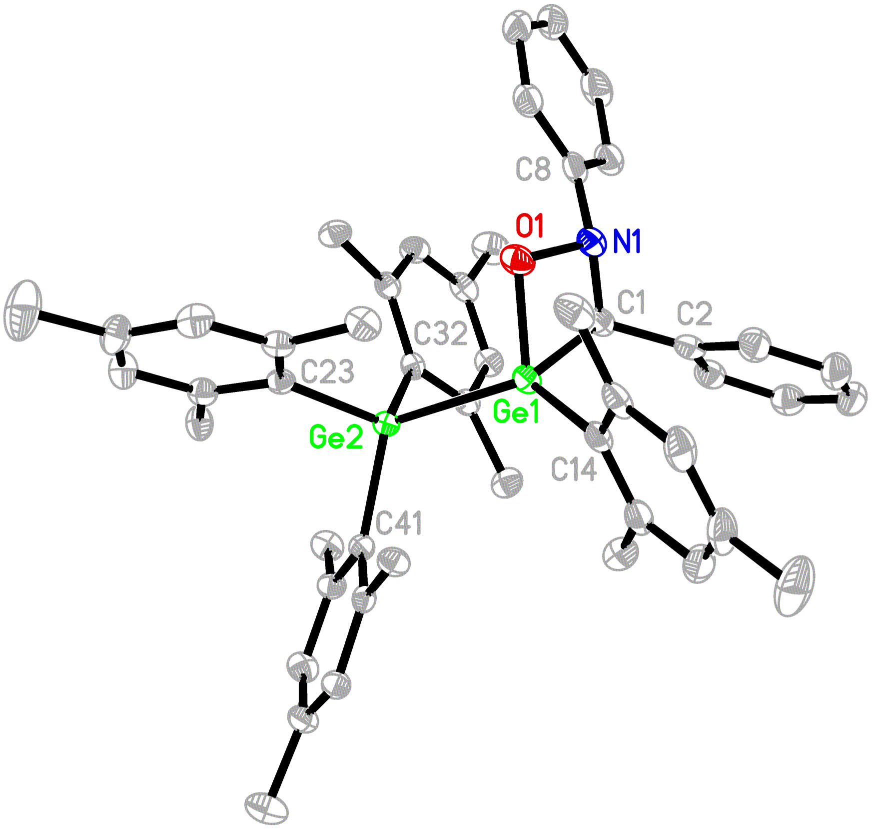
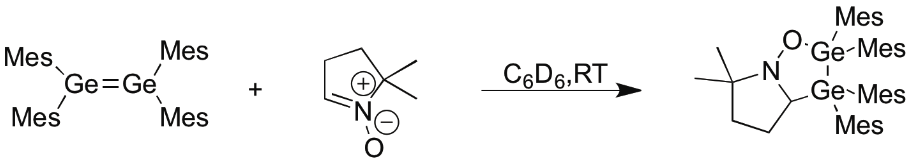


Figure 2.1 Thermal ellipsoid plot of **2.9** (50% probability surface; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge1-O1= 1.8552(14), Ge1-Ge2= 2.5044(7), Ge1-C1= 2.0180(19), O1-N1= 1.4804(19), N1-C1= 1.478(2), N1-C8= 1.408(2), O1-Ge1-Ge2= 105.63(5), N1- O1-Ge1= 92.92(9), N1-C1-Ge1= 86.69(11).

The addition of N-*tert*-butyl-α-phenylnitrone to digermene **1.2** in C_6D_6 at room temperature gave a clear oil, **2.10**, upon removal of the solvent (**Scheme 2.4**). The mass spectrum of **2.10** revealed a molecular ion at *m/z* 794.3160, which is consistent with a 1:1 adduct between N-*tert*-butyl-α-phenylnitrone and digermene **1.2**. The chemical shifts of signals in the ^{1}H NMR spectrum of **2.10** were in reasonable agreement with the chemical shifts of the analogous signals in the ^{1}H NMR of spectrum of **2.9**. Two sets of signals, assigned to two non-equivalent mesityl groups, and a sharp singlet at 0.87 ppm that integrated to 9H, assigned to a *t*-Bu group, were present. The ^{1}H NMR spectrum of **2.10** also showed a singlet at 4.98 ppm, which was assigned to the C<u>**H**</u>-Ph group. The signal at 61.76 ppm in the ^{13}C NMR spectrum of **2.10** was assigned to the quaternary carbon of the *t*Bu group which correlates to the singlet in the ^{1}H dimension at 4.98 ppm. The signal at 4.98 ppm also correlates to a signal in the ^{13}C dimension assigned to the *ipso*-carbon of a mesityl substituent in the ^{13}C dimension of the ^{13}C-^{1}H gHMBC NMR spectrum of **2.10**. Furthermore, the singlet at 4.98 ppm in the ^{1}H dimension correlates to a signal at 73.13 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **2.10** and was assigned to the ring carbon. On the basis of the data, the structure of **2.10** was assigned.

The addition of an excess of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) to a solution of digermene **1.2** in C_6D_6 at room temperature gave **2.11** (**Scheme 2.5**). The high resolution mass spectral data of **2.11** and the isotopic pattern of the signal assigned to the molecular ion were consistent with the formation of a 1:1 adduct between 5,5-dimethyl-1-pyrroline *N*-oxide and digermene **1.2**.



2.11

Scheme 2.5

The ^{1}H and ^{13}C NMR data revealed the presence of four unique mesityl substituents in a 1:1:1:1 ratio. The signal assigned to the N-C<u>**H**</u> group appeared as a broad singlet at 4.17 ppm in the ^{1}H NMR spectrum of **2.11**. The sample was heated in the NMR spectrometer to 65 °C. The ^{1}H NMR spectrum of **2.11** at 65 °C displayed a triplet (rather than a broad singlet) at 4.14 ppm with *J* value equal to 9 Hz. The triplet at 4.14 ppm correlates to the signal at 63.11 ppm in the ^{13}C dimension of the ^{13}C-^{1}H HSQC NMR spectrum of **2.11** which was assigned to the ring carbon. Unambiguous identification of **2.11** in the solid-state was obtained using X-ray crystallographic methods (**Figure 2.2**). The structure also exhibited a region of disorder; the DMPO moiety was disordered about the two-fold rotation axis perpendicular to the Ge-Ge bond.

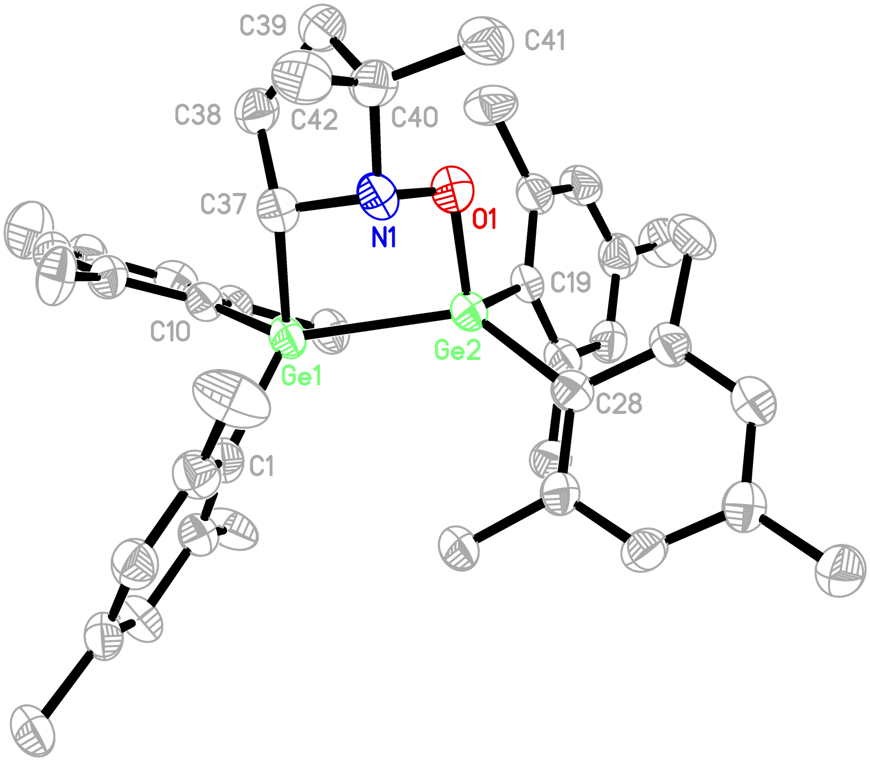


Figure 2.2 Thermal ellipsoid plot of **2.11** (50% probability surface; hydrogen atoms and the disorder are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge1-Ge2= 2.4787(7), Ge1-C37= 2.024(19), Ge2-O1= 1.760(10), O1-N1= 1.495(10), N1-C37= 1.462(15), N1-C40= 1.490(10), Ge1-C1= 1.977(4), Ge1-C10= 1.983(4), Ge2-C19=

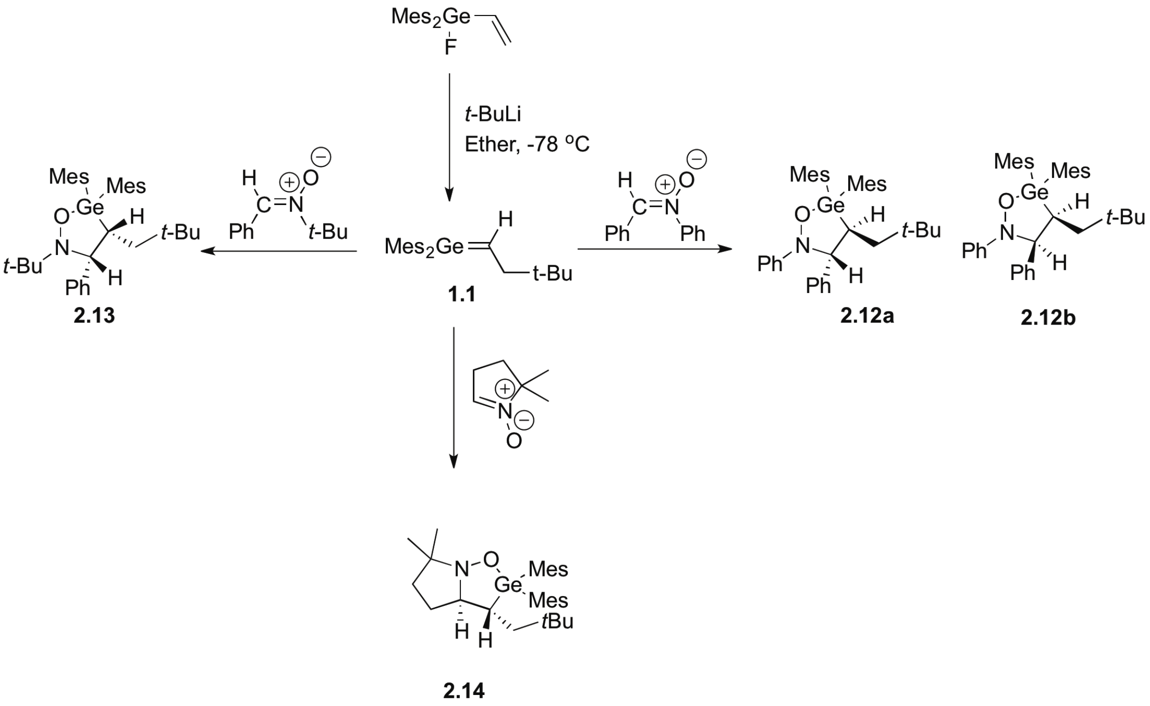
1.983(5), Ge2-C28= 1.983(4), O1-Ge2-Ge1= 88.6(3), C37-Ge1-Ge2= 86.6(5), O1-N1-C40= 104.6(9).

2.2.2 Addition of Nitrone Compounds to 1,1-Dimesitylneopentylgermene 1.1

Germene **1.1** was synthesized prior to each reaction and used in *situ* without purification. A colourless etheral solution of fluorovinylgermane **1.9** was cooled to -78 °C and then treated with *t*-BuLi. Upon warming to room temperature, the solution became yellow in colour and a fine precipitate appeared (LiF), indicating the formation of the germene. It was necessary to add slightly less than 1 equiv of *t*-BuLi to the fluorovinylgermane to prevent polymerization of the germene, and thus, germene **1.1** was always contaminated with residual fluorogermane (**Scheme 2.6**).[9] The addition of C,N-diphenylnitrone to 1,1-dimesitylneopentylgermene **1.1** in C_6D_6 yielded **2.12**. The ^{1}H NMR spectrum of **2.12** revealed the presence of two sets of signals in a ratio of 1:1 indicative of two different isomers (**2.12a**, **2.12b**), which were separated cleanly by thin-layer chromatography. The mass spectrum of **2.12b** revealed a signal at *m/z* 590.2832 which was assigned to a 1:1 adduct between germene **1.1** and C,N-diphenylnitrone ($M+H^+$). Two sets of signals assigned to two non-equivalent mesityl groups and a sharp singlet at 0.57 ppm, that integrated to 9H and was assigned to a *t*-Bu group, were present. The ^{1}H NMR spectrum of **2.12b** also showed a doublet at 5.07 and a quartet 2.79 ppm, which were assigned to the N-C**H** and Ge-C**H** hydrogens, on the basis of observed correlations to the signals at 73.72 ppm and 39.36 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum, respectively. The *J* values for both the doublet and the quartet were determined to be 4.8 Hz. Accordingly, a correlation was observed between these two doublets in the ^{1}H-^{1}H COSY NMR spectrum of **2.12b**. A correlation between the signals at 1.99 ppm and 1.88

ppm in the ^{1}H dimension and a signal at 38.16 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **2.12b** was observed and assigned to a CH_2 group. Together, the assignments are consistent with the structure of **2.12b** shown in the **Scheme 2.6**. Similarly, the same pattern, but different chemical shifts were observed for the other isomer, **2.12a**. The mass spectrum of **2.12a** revealed a signal at *m/z* 612.2653 which was assigned to a 1:1 adduct between germene **1.1** and C,N-diphenylnitrone (M+Na$^+$). Once again, two sets of signals were assigned to two non-equivalent mesityl groups. A singlet at 5.25 ppm and a doublet 2.90 ppm observed in the ^{1}H NMR spectrum of **2.12a** were assigned to the N-C$\underline{\mathbf{H}}$ and Ge-C$\underline{\mathbf{H}}$ moieties and were found to correlate to signals at 73.82 ppm and 40.78 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **2.12a**, respectively.

Close examination of the ^{1}H-^{1}H coupling constants between the hydrogens in the five-membered rings revealed the stereochemistry of rings **2.12a**, **b**. The $^3J_{H\text{-}H}$ values between the ring hydrogens for **2.12a** and **2.12b** are equal to <1 Hz and 4.8 Hz, respectively. Based on the Karplus curve established for cyclopentanes, a small *J* value establishes a *trans* relationship. Therefore, **2.12a** is assigned to the *trans* isomer whereas **2.12b** is the *cis* isomer.



Scheme 2.6

The addition of N-*tert*-butyl-α-phenylnitrone to 1,1-dimesitylneopentylgermene **1.1** in C_6D_6 yielded only one product **2.13**. The high resolution mass spectral data of **2.13** and the isotopic pattern of the signal assigned to the molecular ion were consistent with the molecular formula, $C_{35}H_{50}NO^{70}Ge$, which was consistent with a 1:1 adduct between N-*tert*-butyl-α-phenylnitrone and 1,1-dimesitylneopentylgermene **1.1**. A similar strategy was applied to elucidate the structure of **2.13**. The ^1H NMR spectrum of **2.13** revealed a doublet at 4.63 ppm with a *J* value of 5.4 Hz which was assigned to the C-**H** next to the N-*t*Bu moiety on the basis of its chemical shift and its similarity to the chemical shift of the analogous hydrogen in compound **2.12** (**Scheme 2.6**). The $^3J_{H\text{-}H}$ value, 5.4 Hz, establishes the chemistry about the five-membered ring to be *cis*. Two singlets, at 1.04 ppm and 0.94 ppm in the ^1H NMR spectrum of **2.13**, were assigned to the N-***t*Bu** and CH_2-***t*Bu** moieties. A correlation between the signal at 60.56 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHMBC NMR spectrum of **2.13** and the signal at 1.04 ppm in the ^{1}H dimension was observed, and thus, the signal at 60.56 ppm was assigned to the quaternary carbon of *t*Bu moiety on nitrogen. A correlation between the signals at 2.03 ppm and 1.73 ppm in the ^{1}H dimension and the signal at 37.26 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **2.13** was observed and assigned to a CH_2 group. On the basis of spectroscopic data of the product, the structure was assigned to **2.13** (**Scheme 2.6**). Close examination of the ^{1}H-^{1}H coupling constants in the five-membered ring of **2.13** revealed the stereochemistry of the ring.

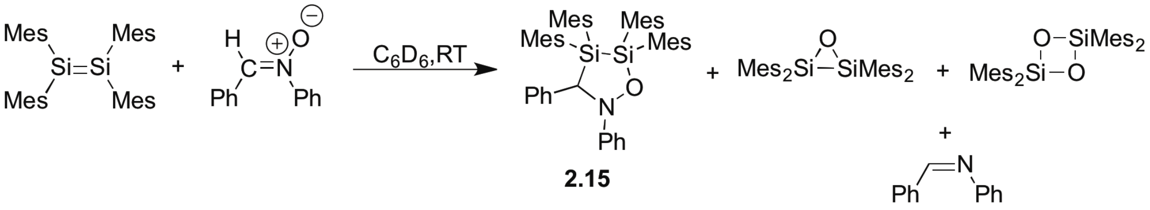
The addition of DMPO to germene **1.1** in diethyl ether results in the regioselective formation of the **2.14** in good to excellent yields (**Scheme 2.6**). The mass spectrum of **2.14** revealed a molecular ion at *m/z* 506.2807, which is consistent with a 1:1 adduct between 5,5-dimethyl-1-pyrroline *N*-oxide and germene **1.1**. The structure of **2.14** was evidenced by its NMR data. The characteristics of the spectroscopic data of **2.14** were similar to those of **2.11**, the adduct from the reaction of digermene **1.2** and DMPO. Two sets of signals assigned to two non-equivalent mesityl groups and a sharp singlet at 0.85 ppm that integrated to 9H assigned to a *t*-Bu group were present. The ^{1}H NMR spectrum of **2.14** displayed a broad triplet at 3.74 ppm, characteristic of a C$\underline{\mathbf{H}}$ group attached to nitrogen, as was observed at 4.17 ppm for adduct **2.11**. The signal assigned to the N-C$\underline{\mathbf{H}}$ showed correlation to the signal at 74.65 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC spectrum of **2.14**. The ^{1}H-^{1}H COSY NMR spectrum of **2.14** shows a correlation between the signal assigned to the N-C$\underline{\mathbf{H}}$ moiety and the signal assigned to attached C$\underline{\mathbf{H}_2}$. The signal at 1.10 ppm in the ^{1}H NMR spectrum of **2.14** was assigned to the GeC$\underline{\mathbf{H}}$. Notably, this signal is a singlet which establishes the stereochemistry of the 1,2,5-

oxazagermolidine ring as *trans*. The ^{1}H NMR spectrum of **2.14** also showed two singlets at 1.60 ppm and 1.15 ppm, which were assigned to the two CH_3 groups, on the basis of the observed correlations to the broad signals at 29.60 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum. Considering all assignments of the spectroscopic data of **2.14**, and the close agreement with adduct **2.11**, we conclude that the structure of **2.14** is that shown in **Scheme 2.6**.

2.2.3 Addition of Nitrone Compounds to Tetramesityldisilene 1.3

The addition of C,N-diphenylnitrone to a bright yellow solution of disilene **1.3** in C_6D_6 at room temperature gave a yellow solution with a white precipitate. Removal of the solvent yielded a mixture of white and yellow solids. ^{1}H NMR spectroscopic analysis of the crude mixture revealed the presence of compound **2.15**, along with at least two additional products which were identified as tetramesityloxadisilirane (Mes_4Si_2O)[12] and 1,3-tetramesityldioxadisilirane ($Mes_2Si_2O_2$)[12], in a ratio of 1:0.9:0.2 respectively. The presence of 1,2-diphenylimine was also confirmed by ^{1}H NMR spectroscopy and EI mass spectrometry (**Scheme 2.7**). The high resolution mass spectral data of **2.15** and the isotopic pattern of the signal assigned to the molecular ion were consistent with the molecular formula, $C_{49}H_{56}NOSi_2$, consistent with a 1:1 adduct between C,N-diphenylnitrone and disilene **1.3**. Due to the presence of the chiral carbon centre in **2.15**, the two mesityl groups on each silicon are diastereotopic. Accordingly, the ^{1}H NMR spectra of **2.15** revealed the presence of four nonequivalent mesityl groups. Furthermore, the ^{1}H NMR spectrum of **2.15** revealed a signal at 5.72 ppm which integrates for 1 H and was assigned to a C-H moiety. Correlation in the ^{1}H-^{13}C gHSQC NMR spectrum of **2.15** was observed between the signal at 66.86 ppm in the ^{13}C dimension and the singlet at

5.72 ppm in the ^{1}H dimension which is consistent with the CH group being attached to nitrogen. Furthermore, the singlet at 5.72 ppm in the ^{1}H dimension correlates to a signal at 130.84 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHMBC NMR spectrum which was assigned to the *ipso* carbon of a phenyl group. The observed correlations are consistent with a CH(Ph)N moiety. On the basis of the assignments of the signals in the NMR spectra and the high-resolution mass spectral data, the structure of **2.15** was determined to be that shown in the **Scheme 2.7**.



Scheme 2.7

Upon addition of N-*tert*-butyl-α-phenylnitrone to disilene **1.3**, no reaction was observed. The addition of excess of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) to a C_6D_6 solution of disilene **1.3** at room temperature gave **2.16** (**Scheme 2.8**). The high-resolution mass spectral data of **2.16** and the isotopic pattern of the signal assigned to the molecular ion were consistent with the molecular formula $C_{42}H_{56}NOSi_2$, a 1:1 adduct between 5,5-dimethyl-1-pyrroline *N*-oxide and disilene **1.3**. Compound **2.16** was characterized by NMR spectroscopy. Four sets of signals in the ^{1}H and ^{13}C NMR spectrum of **2.16** were assigned to four inequivalent mesityl groups. A characteristic triplet was observed on the ^{1}H NMR spectrum of **2.16** at 4.07 ppm and was assigned to the hydrogen on the carbon attached to silicon and nitrogen. Accordingly, the signal at 4.07 ppm correlates to the signal at 59.85 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum. Furthermore, the triplet at 4.07 ppm correlates to the signal at 28.49 ppm in the ^{13}C dimension of the ^{1}H-^{13}C gHMBC spectrum of **2.15**, which assigned to the CH$_2$ group next to C-H moiety. An X-ray structural determination study unambiguously established the structure of **2.16** (**Figure 2.3**). A long Si1-Si1A bond (2.4482(10) Å) was observed presumably due to the steric interactions between the mesityl groups. The structure also exhibited a region of disorder; the DMPO moiety was disordered about the two-fold rotation axis perpendicular to the Si-Si bond.

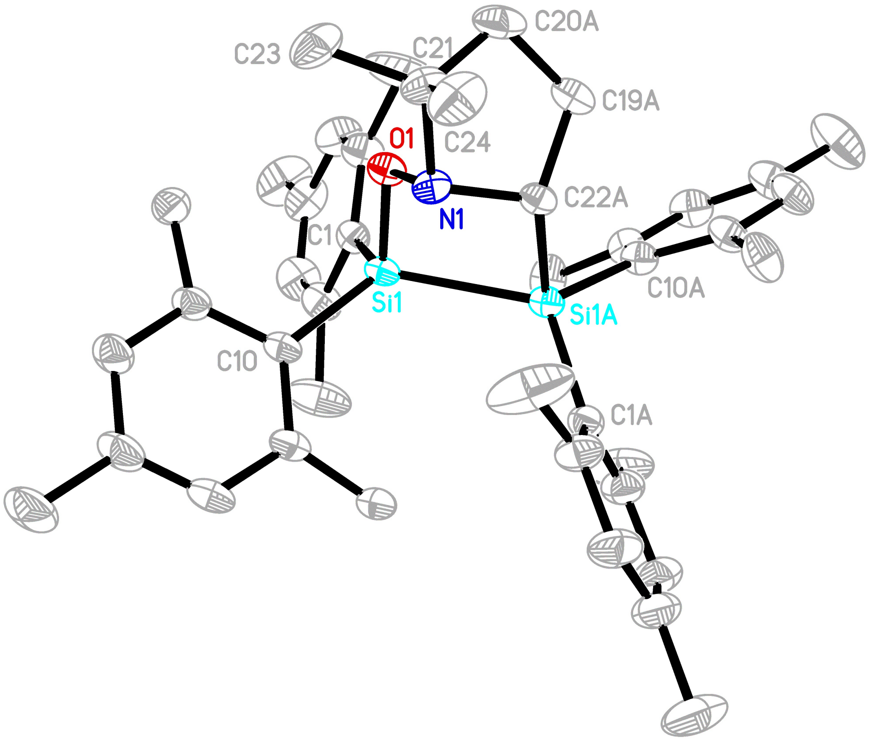
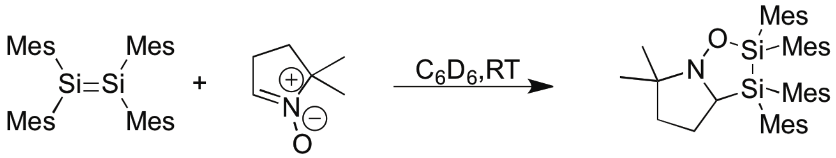


Figure 2.3 Thermal ellipsoid plot of **2.16** (50% probability surface; hydrogen atoms and the disorder are omitted for clarity). Selected bond lengths (Å) and angles (deg): Si1-Si1A=2.4482(10), Si1-O1=1.674(5), Si1-C22= 1.911(6), C19-C22= 1.543(6), C19-C20= 1.551(4), C20-C21= 1.528(5), C21-N1= 1.494(3), C22-N1= 1.203(6), N1-O1=1.573(6), O1-N1-C22= 103.7(3), C19-C22-Si1= 120.6(4), N1-C21-C20= 104.9(2).



2.16

Scheme 2.8

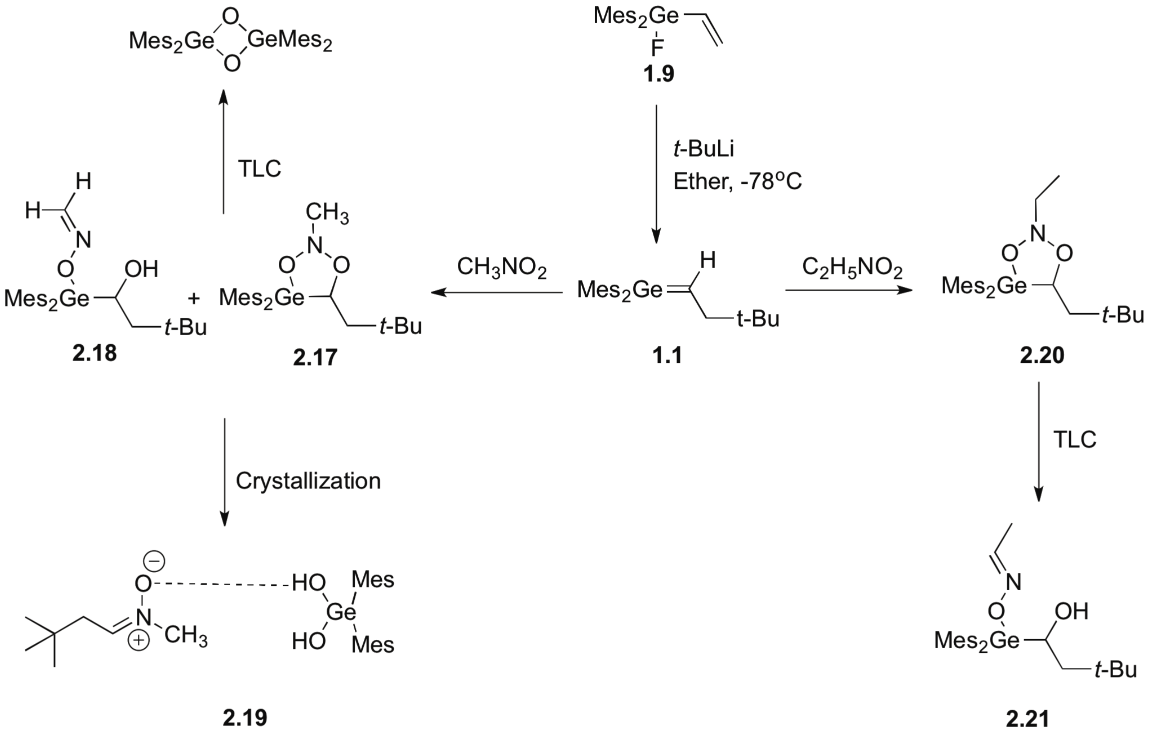
2.2.4 Addition of Nitro Compounds to 1,1-Dimesitylneopentylgermene 1.1

When excess of nitromethane was added to a yellow ethereal solution of germene **1.1** cooled to -78 °C, the colour disappeared immediately. Removal of the solvent yielded a clear, colourless oil and analysis of the product by ^{1}H NMR spectroscopy revealed the presence of compound **2.17** along with minor amounts of at least one additional product, **2.18**, in a 1:0.1 ratio, respectively (**Scheme 2.9**). The high resolution mass spectral data of **2.17** and the isotopic pattern of the signal assigned to the molecular ion were consistent with the molecular formula, $C_{25}H_{37}NO_2{}^{70}Ge$ (M+Na$^+$), a 1:1 adduct between germene **1.1** and nitromethane. The ^{1}H NMR spectrum of **2.17** revealed the presence of two sets of signals assigned to two non-equivalent mesityl groups and a singlet at 3.12 ppm that integrated to 3H, indicating the presence of a methyl group, most likely attached to nitrogen. Most noteworthy in the ^{1}H NMR spectrum of the **2.17** was a doublet of doublets at 5.14 ppm, which correlates to the signal at 75.01 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum and was assigned to Ge-C**H**. The spectrum also contains two doublet of doublets, at 2.10 ppm and 1.17 ppm, which were assigned to the hydrogens of the CH_2 attached to the *t*-Bu group. The signal assigned at 5.14 ppm in ^{1}H dimension (Ge-C**H)** also correlates to the signal at 44.35 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHMBC NMR spectrum which was assigned to the **C**H_2 group.

The isomeric oxime **2.18** is also present in crude product mixture. A broad absorption was observed in the IR spectrum of the crude product at 3300 cm^{-1}, consistent with the presence of a hydroxyl group. The ^{1}H and ^{13}C NMR spectra of **2.18** revealed the presence of two non-equivalent mesityl groups. Two doublets were present in the ^{1}H NMR spectrum of **2.18**, at 6.10 and 6.90 ppm, with a coupling constant of 9 Hz. These data are in closely agreement with the previously reported spectroscopic data for **2.8** **(Scheme 2.8)**.[8] The ^{1}H NMR spectrum of **2.18** revealed two doublets, at 5.87 and 6.68 ppm, with a coupling constant of 9 Hz. Due to the complexity of the ^{1}H NMR spectrum of the crude reaction mixture, it was difficult to fully characterize oxime **2.18**.

Attempt to crystallize **2.17** from a saturated hexanes solution at low temperature resulted in the formation of **2.19**. Single crystal X-ray diffraction revealed the structure of **2.19** (**Figure 2.4**). All bond lengths and angles in **2.19** are within normal ranges. Notably, the bond length of C20-N1 was 1.272(5) Å, indicating a double bond between nitrogen and carbon. The ^{1}H NMR spectrum of **2.19** revealed that **2.17** had been converted cleanly to **2.19** (a 1:1 hyrogen-bonded mixture of (*Z*)-*N*-(3,3-dimethylbutylidene)methanamine oxide and dimesitylgermanediol). The ^{1}H NMR spectrum of **2.19** showed the presence of only one set of signals assigned to two equivalent mesityl groups and a singlet at 0.78 ppm assigned to the *t*-Bu group (**Scheme 2.9**). Additionally, a triplet at 5.87 ppm, assigned to the vinylic hydrogen of the imine oxide was present and correlates to the signal at 134.55 ppm in the ^{13}C NMR dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **2.19** which was assigned to the iminic carbon. The spectrum also contains a multiplet at 2.34 ppm which was assigned to the CH_2 hydrogens attached to the vinylic group of imine oxide. These data further support the assigned structure of **2.19**.

1,3-Digermadioxetane $Mes_4Ge_2O_2$ [13] was the only compound isolated after preparative thin-layer chromatography of the mixture of **2.17** and **2.18**. Although, compound **2.17** could not be isolated in pure form, we are confident in its structural assignment as the spectral data are very similar to those of **2.5**[8] which has been previously characterized characterized by single crystal X-ray diffraction data in addition to NMR spectroscopy and mass spectrometry.[8]



Scheme 2.9

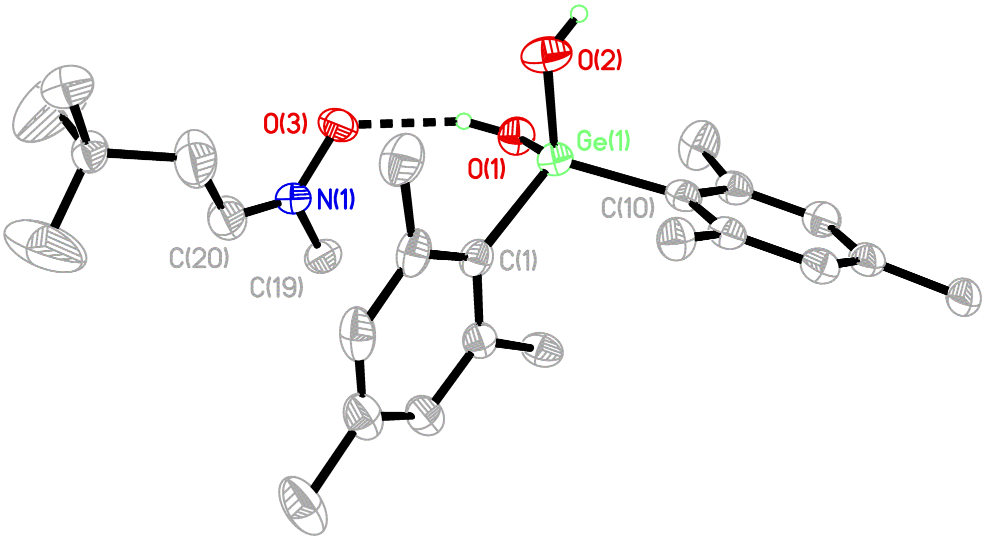


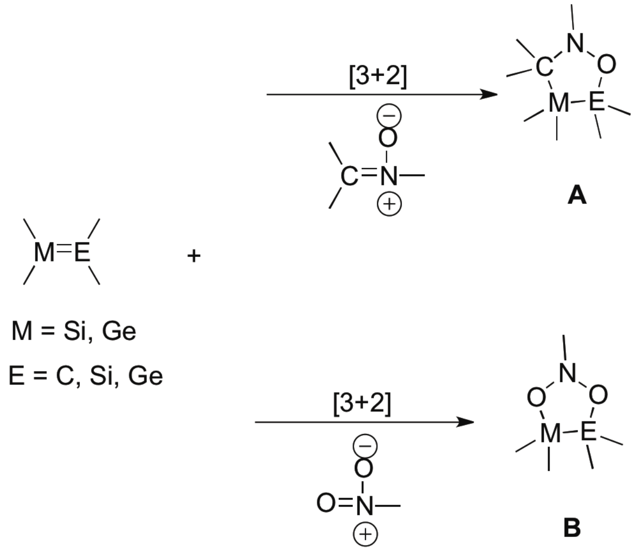
Figure 2.4 Thermal ellipsoid plot of **2.19** (50% probability surface; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge1-O1= 1.773(3), Ge1-O2= 1.771(3), N1-C20= 1.272(5), N1-O3= 1.324(4), N1-C19= 1.462(5), C20-C21= 1.488(6), O2-Ge1-O1= 108.00(12), O3-N1-C19= 115.4(3).

Nitroethane rapidly reacted with germene **1.1** to yield 1,3,2,4,5-oxazadigermolidine **2.20** contaminated with a minor product (**Scheme 2.9**). The ESI mass spectrum of the crude product mixture revealed a signal at *m/z* 490.2121 and the isotopic pattern of the signal assigned to the molecular ion was consistent with the molecular formula, $C_{26}H_{39}NO_2{}^{70}Ge$ (M+Na$^+$), a 1:1 adduct between germene **1.1** and nitroethane. The ^1H NMR spectrum of **2.20** revealed the presence of two sets of signals assigned to two non-equivalent mesityl groups and a singlet at 0.99 ppm that integrates to 9H indicating the presence of a *t*-Bu group. Similar to the ^1H spectral data of **2.17**, a doublet of doublet at 5.13 ppm that integrated to 1H, was assigned to the CH moiety. This signal was found to correlate to the signal at 74.45 ppm in the ^{13}C dimension of the ^{13}C-^1H gHSQC spectrum of **2.20**. The chemical shift of the Ge-C$\underline{\mathbf{H}}$-O signal of **2.20** is very similar to the chemical shift of the analogous signal assigned to the Ge-C**H**-O hydrogen in **2.17** (5.14 ppm). Additionally, two doublet of doublets (2.10 ppm and 1.18 ppm), assigned to the C**H**$_2$- *t*-Bu group, both correlate to the same carbon at 44.36 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **2.20**. The chemical shifts of the two doublet of doublets are quite similar to those assigned to the C**H**$_2$- *t*-Bu moiety of **2.17** (2.10 ppm and 1.17 ppm). The ^{1}H NMR spectrum also contains a quartet at 3.40 ppm and a triplet at 1.26 ppm which were assigned to the N-C**H**$_2$-CH$_3$ and N-CH$_2$-C**H**$_3$ groups, on the basis of observed correlations to signals at 56.93 ppm and 11.66 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum, respectively, and by correlations between these signals in the ^{1}H-^{1}H COSY NMR spectrum of **2.20**.

1,3,2,4-Dioxazagermolidine **2.20** decomposes upon adsorption to silica to give **2.21** (**Scheme 2.11**). Both *E* and *Z* isomers of oxime **2.21** are formed[14] in a 1:1 ratio. The spectroscopic data for **2.21** were similar to those reported for addition of nitroethane to digermene **1.2**.[14,20] The ^{1}H and ^{13}C NMR spectra of **2.21** revealed the presence of two non-equivalent mesityl groups. Correlations in the ^{1}H-^{1}H COSY spectra of **2.21** were utilized to construct the vinylic fragment of oxime structure. A quartet at 6.28 ppm in the ^{1}H NMR spectrum of **2.21** was assigned to the vinylic hydrogen of the *Z* isomer, whereas the vinylic hydrogen of the *E* isomer of **2.21** was more deshielded at 7.13 ppm.[8,14,20] The ^{1}H NMR spectrum of **2.21** also revealed the presence of two doublets at 1.48 ppm and 1.14 ppm with coupling constants of 5.4 Hz and 6 Hz, respectively. On the basis of the available evidence, compound **2.21** is assigned the structure shown in **Scheme 2.9**.

2.3 Discussion

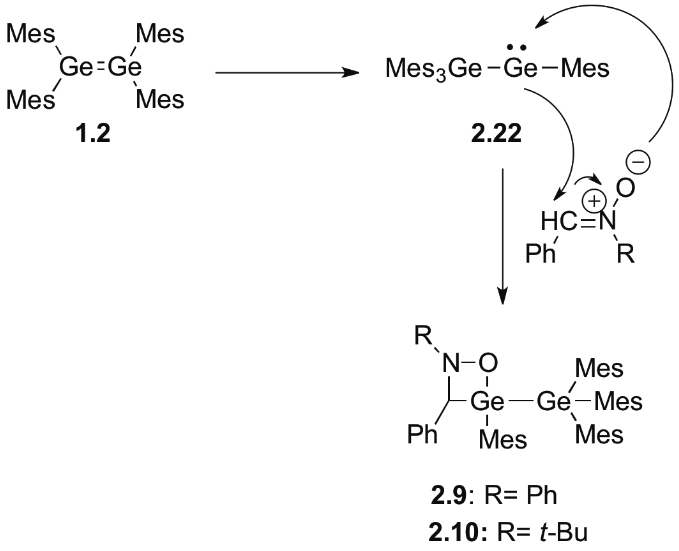
In general, the reaction of (di)tetrelenes with nitrones and nitro compounds follows the same reactivity trend: the initial adducts appear to be derived from a formal [3+2] cycloaddition between the nitrone or the nitro group and the Ge=Ge, Si=Si or the Ge=C bond to give a 1,2-oxazolidine (**A**) or a 1,3,2-dioxazolidine (**B**) ring system (**Scheme 2.10**).



Scheme 2.10

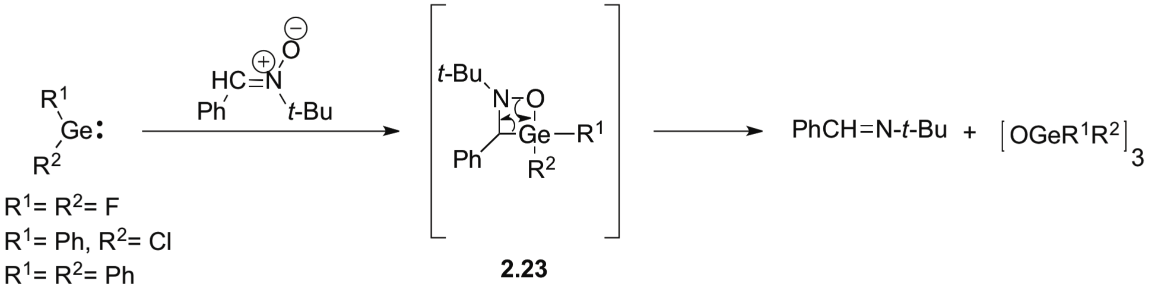
The additions of C,N-diphenylnitrone and N-*tert*-butyl-α-phenylnitrone to digermene **1.2** appear to be the exception. In these cases, the four-membered ring heterocycles **2.9** and **2.10** are formed in high yield. Notably, C,N-diphenylnitrone and N-*tert*-butyl-α-phenylnitrone react at considerably different rates: C,N-diphenylnitrone reacts instantly whereas N-*tert*-butyl-α-phenylnitrone reacts with **1.2** over a period of 24 hours. The formation of **2.9** and **2.10** may occur through initial rearrangement of digermene **1.2** to mesityl(trimesitylgermyl)germylene **2.22**,[15] which then reacts with the nitrone to form the unusual four-membered 1,2,4-oxazagermetidine ring system (**Scheme**

2.11). Notably, adducts **2.9** and **2.10** are air- and moisture stable, presumably due to bulky substituents.



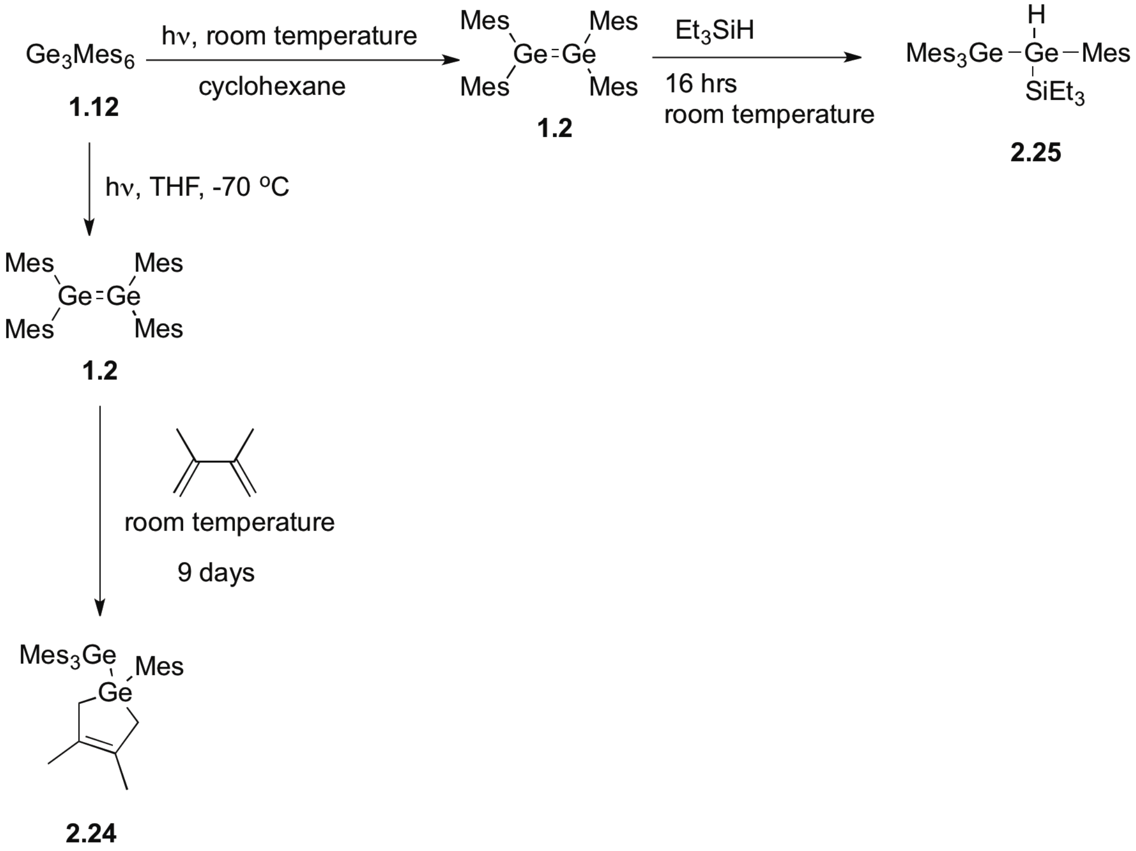
Scheme 2.11

The reaction of germylenes with *N*-*tert*-butyl-α-phenylnitrone has been reported by Satgé.[16] The reaction was postulated to occur by a 1,3-chelotropic cycloaddition between the germylene and the 1,3-dipole to afford 1,2,4-oxazagermetidine **2.23** as a transient intermediate (**Scheme 2.12**).[16] Adduct **2.23** was not isolated, rather **2.23** was postulated to undergo a rapid cycloreversion to give the corresponding imine and the cyclic trigermoxane.



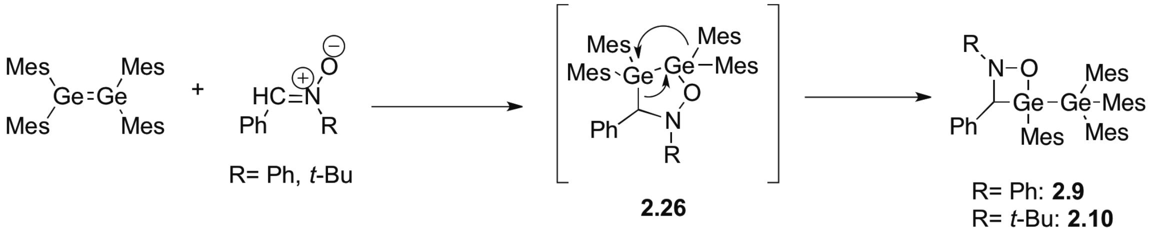
Scheme 2.12

Our group has previously examined the reactivity of **1.2** in THF at room temperature in the presence of a well-known germylene traps, 2,3-dimethylbutadiene and triethylsilane (**Scheme 2.13**).[10,15] In the reaction with the diene, the formation of mesityl(trimesitylgermyl)germacyclopentene **2.24** was observed over the course of nine days, indicating that a 1,2-shift of mesityl group in digermene **1.2** to give mesityl(trimesitylgermyl)germylene **2.22** had occurred, followed by subsequent trapping with diene.[10] Alternatively, when **1.2** was allowed to react with Et_3SiH at room temperature in cyclohexane, **2.25** was formed as the major product after 16 hours. Given the apparent slow rate of reaction of digermene **1.2** at room temperature with well-known germylene trapping agents and the rapid rate for the reaction of digermene **1.2** with C,N-diphenylnitrone, it appears unlikely that digermene **1.2** rearranges first to germylgermylene **2.22** followed by trapping with the nitrone, at least with the diphenylnitrone derivative. Given the qualitative difference in reaction rates, an alternative pathway for the formation of adducts **2.8** and **2.9** is proposed.



Scheme 2.13

Cycloaddition of the nitrone to digermene **1.2** may initially give a 1,2,4,5-oxazadigermolidine **(2.26)**, followed by a ring contraction, to form 1,2,4 - oxazagermetidines **2.9** and **2.10**. Such a rearrangement implies the migration of a C-Ge bond and a 1,2-mesityl shift. The rearrangement may be concerted as shown in **Scheme 2.14** or occur in a stepwise fashion. The difference in the qualitative rates of the reaction between digermene **1.2** and C,N-diphenylnitrone and N-*tert*-butyl-α-phenylnitrone may be attributed to the difference in the steric bulk of the nitrone. Evidently, increasing the bulk on the nitrone inhibits the reaction.

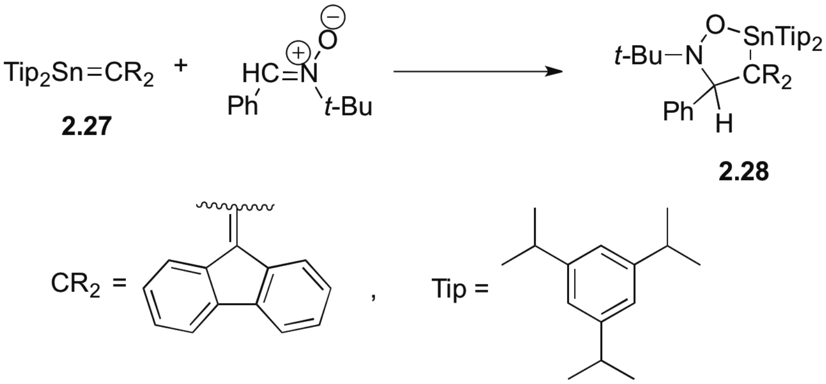


Scheme 2.14

The addition of DMPO to digermene **1.2** appears to be analogous to the addition of C,N-diphenylnitrone and N-*tert*-butyl-α-phenylnitrone nitrone to digermene **1.2** as postulated in **Scheme 2.14** even though the outcomes of their reactions are quite different (**Scheme 2.5**). The initial step in the reaction again appears to be formal [3+2] cycloaddition of DMPO to digermene **1.2**; however, in this case, the 5-membered ring is stable, possibly because the migration of an alkyl group is less favored compared to a benzyl group.

The results of the addition reaction of nitrones to digermene **1.2** are comparable to those of germene **1.1**. The formation of **2.12**, **2.13**, and **2.14** (**Scheme 2.6**) can be explained easily by [3+2] cycloaddition of the nitrone to the germene. The reaction is regioslective with the negative end of the dipolar nitrone (oxygen) adding to the partially positive germanium of the germene. The high Ge–O bond energy (~410 kJ/mol)[17] is believed to play a major role in the regioselectivity of the reaction (**Scheme 2.6**). As is evident from the ratio of two diastereomers obtained in the addition of C,N-diphenylnitrone to germene **1.1**, the reaction is not stereoselective. However, in the addition of N-*tert*-butyl-α-phenylnitrone and DMPO to germene **1.1**, only one isomer is formed demonstrating that the reactivity can be stereoselective. More research is required to understand how to control the stereoselectivity of the reaction.

A similar reaction has been reported by Escudié;[18] stannene **2.27** reacts with N-*tert*-butyl-α-phenylnitrone to give oxazastannolidine **2.28** in relatively high yield (69%). The formation of cycloadduct **2.28** is also best understood in terms of a [3+2] cycloaddition between stannene **2.27** and the 1,3-dipolar nitrone (**Scheme 2.15**). The structure of **2.28** was unambiguously determined by X-ray crystallography.[18] The regioselectivity of the reaction is again based on a match between the polarity of the stannene $Sn^{\delta+}=C^{\delta-}$ and the polarity of the nitrone.[18] The reactivity of the stannene closly parallels that of germene **1.1**.

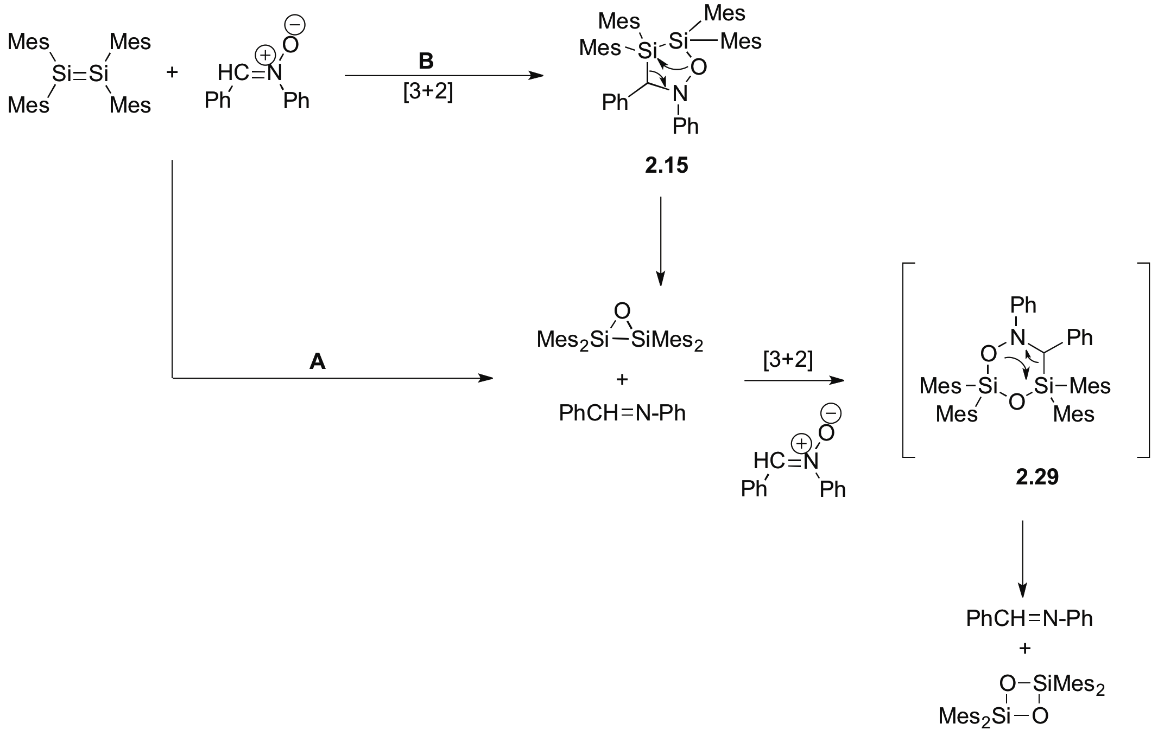


Scheme 2.15

The addition of DMPO to disilene **1.3** (**Scheme 2.8**) is analogous to the addition of DMPO to tetramesityldigermene **1.2** and germene **1.1**. Heterocycles **2.11**, **2.14** and **2.16** are stable; they do not react with air or moisture, and are stable upon adsorption to silica gel. The stability of **2.11**, **2.14** and **2.16** is probably due to steric protection (accordingly, the rotation of a mesityl group is hindered at room temperature in each isomer, as shown by ^{1}H NMR spectroscopy). Notably, only one isomer is obtained for the reaction of DMPO to germene **1.1**, and thus, the reaction is both diastereoselective, and regioselective.

The addition of C,N-diphenylnitrone to disilene **1.3** resulted in the formation of

2.15, tetramesityloxadisilirane (Mes_4Si_2O)[12], 1,3-tetramesityldioxadisilirane ($Mes_2Si_2O_2$)[12] and 1,2-diphenylimine. The formation of the oxadisilirane and the 1,3-dioxadisilirane, at first consideration, may appear to be the result of the reaction of the disilene with oxygen. However, the oxygenation of disilenes using oxygen (O_2) in solution typically gives the 1,2-disiladioxetane as the major product accompanied by a smaller quantity of the disilaoxirane.[12] The current results are not consistent with a reaction of oxygen with disilenes. In contrast, disilaoxiranes, are formed in good yield by reaction of a disilene with oxygen atom donors such as epoxides[19] and diphenylsulfone[20] and dinitrogen oxide (N_2O).[21] Thus, two different modes for the reaction of C,N-diphenylnitrone with disilene **1.3** are proposed. C,N-diphenylnitrone may react with disilene **1.3** directly by donation of an oxygen atom to give tetramesityloxadisilirane (Mes_4Si_2O) and PhCH=N-Ph (**Scheme 2.16**, **A**). Dipolar addition of a second equivalent of the nitrone to the tetramesityloxadisilirane (Mes_4Si_2O) would give the 6-membered heterocycle which can cleave to give 1,3-tetramesityldioxadisilirane ($Mes_2Si_2O_2$) and a second equivalent of the imine. Alternatively, [3+2] cycloaddition between disilene **1.3** and C,N-diphenylnitrone to give the 5-membered ring **2.15** followed by cycloreversion would give tetramesityloxadisilirane (Mes_4Si_2O) (**Scheme 2.16, B**). Again, the oxadisilirane can react with C,N-diphenylnitrone to give intermediate **2.29** which undergoes cycloreversion to give the 1,3-oxadisilirane and 1,2-diphenylimine. *Tert*-butyl-α-phenylnitrone did not react as an oxygen donor towards disilene **1.3**, whereas C,N-diphenylnitrone did. The difference in reactivity may be understood in terms of the relative stability of the two imines, PhCH=N-Ph and PhCH=N-*t*-Bu.



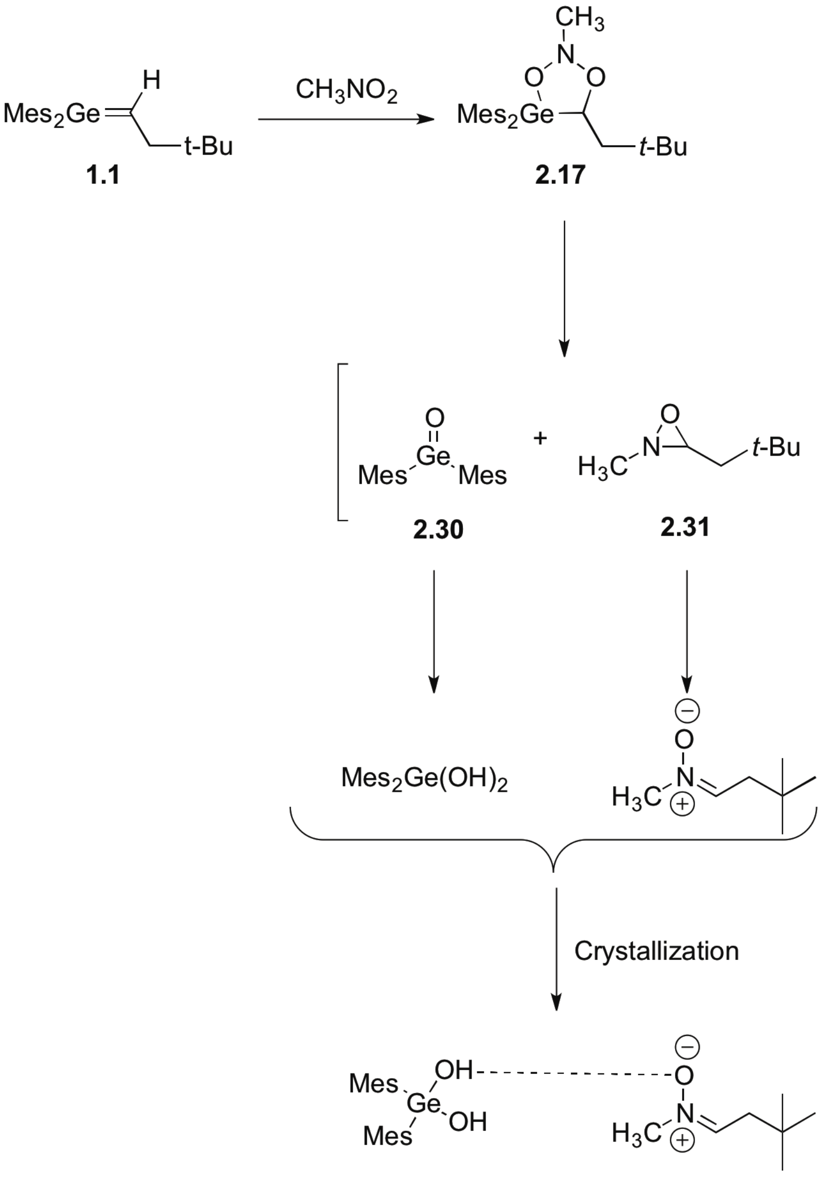
Scheme 2.16

The difference in the reactivity of disilene **1.3** compared to that of digermene **1.2** towards C,N-diphenylnitrone was somewhat surprising; however, may be attributed to the oxophilicity of silicon. The formation of the strong Si-O bond is thermodynamically favored; the relative strengths of the Si–O and Ge–O bonds are 492 kJ mol^{-1} and 410 kJ mol^{-1}, respectively.[17] Thus, the formation of multiple Si-O bond in tetramesityloxadisilirane (Mes_4Si_2O) and 1,3-tetramesityldioxadisilirane ($Mes_2Si_2O_2$) may be the driving force for the observed reactivity of C,N-diphenylnitrone with disilene **1.3**.

The addition of N-*tert*-butyl-α-phenylnitrone to a THF solution of tetramesityldisilene **1.3** did not result in the formation of an adduct, even upon prolonged heating at 100 °C. Increasing the bulk on the nitrogen hinders the reaction completely, although the *t*-Bu group is distant from the silicon of disilene **1.3**.

It is interesting to compare the chemistry of the digermenes and disilenes with nitrones to that of their lighter congeners, alkenes. The reaction of alkenes with nitrones generally proceeds by [3+2] cycloaddition.[22] However the 1,3 dipolar cycloaddition of nitrones and alkenes relies on the coordination of Lewis acids to the 1,3-dipole or to the alkene, to catalyze the cycloaddition.[6] In contrast, the reaction of (di)tetrelenes and nitrones proceeds with no catalyst. The high reactivity of (di)tetrelenes is due to the nature of its π bond compared to the π bond of an alkene. The π bond in (di)tetrelenes is inherently weak and many computational studies have focused on understanding the weakness of the π bond.[23] Furthermore, the group 14 elements are all oxophilic; silicon is particularly so.[22,24] The greater oxophilicity of silicon and germanium, in comparsion to carbon, certainly contributes to the observed rate of the reactions.

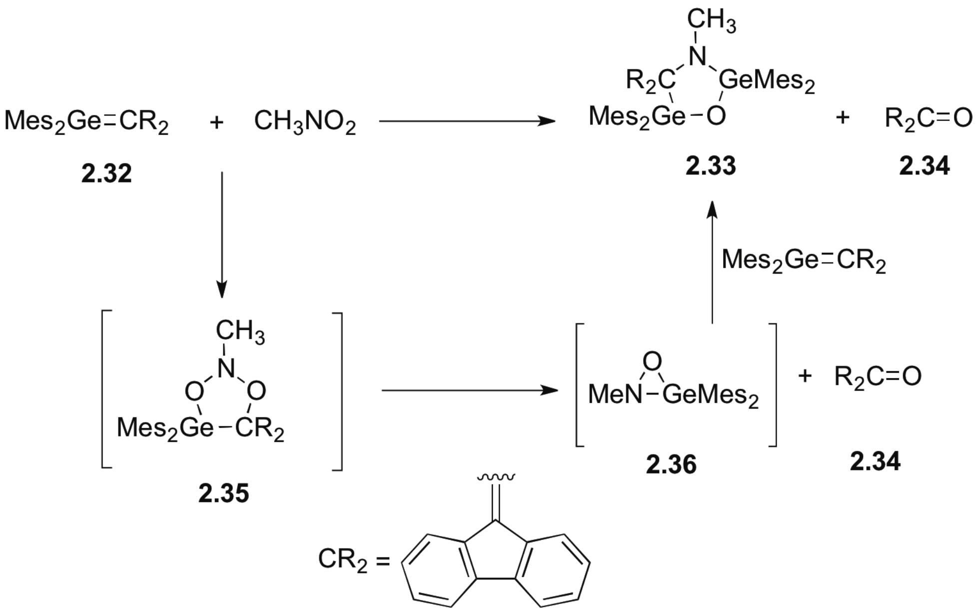
The addition of nitromethane and nitroethane to 1,1-dimesitylneopentylgermene **1.1** resulted in the formation of 1,3,2,4-dioxazagermolidines **2.17** and **2.19**, respectively (**Scheme 2.9**), mirroring the reactivity of disilene **1.3** and digermene **1.2** towards nitromethane.[8] Adducts **2.17** and **2.19** are derived from a formal [3+2] cycloaddition of the nitro group to the germene to give the 1,3,2-dioxazolidine ring system. Attempts to isolate **2.17** by crystallization failed, the formation of complex of **2.19** was observed. The following mechanism is proposed to account for the formation of the hydrogen-bonded complex between dimesitylgermanediol and (*Z*)-*N*-(3,3-dimethylbutylidene)methanamine oxide, **2.19** (**Scheme 2.17**). The initial step involves the [3+2] cycloaddition between nitromethane and germene **1.1** to give heterocycle **2.17**. Ring cleavage would give dimesitylgermanone **2.30** and 1,2-oxaziridine **2.31** followed by rearrangement of the latter to give the imine oxide. Hydration of the germanone would result in the formation of the germandiol. Upon crystallization, the hydrogen-bonded complex is formed. Attempts to purify **2.17** by chromatography lead only to the isolation of 1,3,2,4-dioxadigermetane, $Mes_4Ge_2O_2$,[13] derived from either dimerization of dimesitylgermanone (**2.30**) or condensation of germanediol.



Scheme 2.17

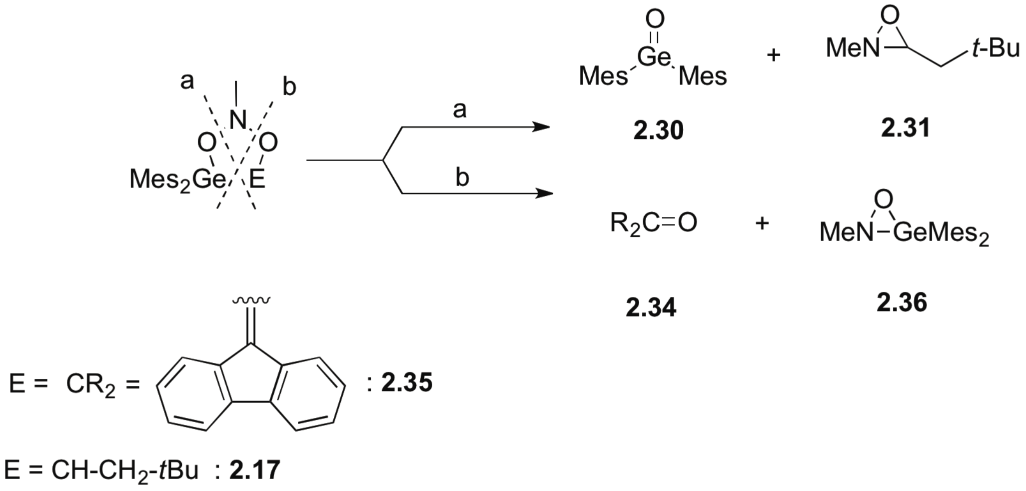
Compounds **2.17** and **2.20** are new heterocyclic ring systems containing the O-N-O moiety and are formed easily and in high yield. The addition reactions of nitromethane and nitroethane to germene **1.1** are undoubtedly facilitated by weakness of the Ge=C bond and the strength of Ge-O bond. The 1,3,2,4-dioxazagermolidine **2.20** undergoes ring opening to the isomeric oxime **2.21** upon preparative thin layer chromatography. Also, a trace of isomeric oxime **2.21** was present in the crude reaction. The formation of isomeric oximes was also reported in addition of nitromethane, nitroethane and *trans*-β-nitrostyrene to digermene **1.2**.[8,20] In the case of addition of nitromethane to digermene **1.2**, DFT calculations showed that oxime **2.8** is stabilized by 236 kJ mol^{-1} compared to the 1,3,2-dioxazolidine ring **2.6**.[8]

It is interesting to compare our results to those of the addition of nitromethane to dimesitylfluorenylidenegermane **2.32** as reported by Escudié.[25]



Scheme 2.18

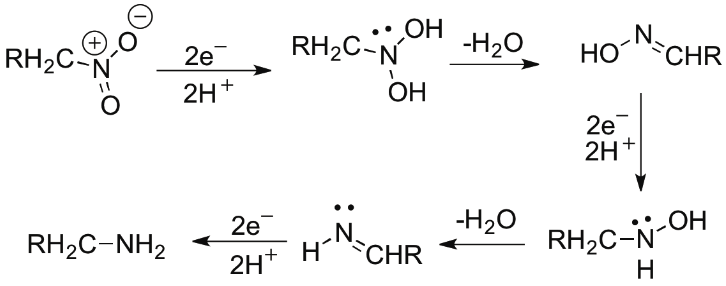
Compounds **2.33** and **2.34** were isolated from the addition of nitromethane to dimesitylfluorenyldienegermane **2.32** and were postulated to form from the [3+2] cycloadduct **2.35** which underwent subsequent fragmentation to ketone **2.34** and oxazagermiridine **2.36** (**Scheme 2.18**). Another equivalent of dimesitylfluorenyldienegermane **2.32** apparently then reacts with intermediate **2.36** to give the isolated product **2.33**. Although, both **2.17** and **2.35** arise from a [3+2] cycloaddition reaction, there is a difference in the cleavage mode of the 5-membered rings: adduct **2.17** cleaves to form germanone **2.30** and **2.31** and adduct **2.35** cleaves to form ketone **2.34** and **2.36** (**Scheme 2.19**).



Scheme 2.19

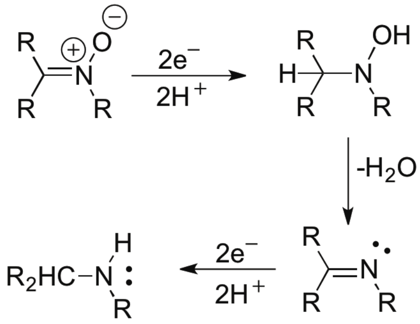
It is difficult to make any conclusive statements regarding the factors governing the pathway reactivity. A computational study is needed to study the thermodynamics of the reactions to understand the two fragmentation pathways and the influence of the substituents at carbon.

This study demonstrates that the reaction of germenes with nitroalkanes is a convenient chemical method for the conversion of a nitro functional group to the water adduct of the analogous oxime in a stepwise, controlled 2-electron reduction (**Scheme 2.20**). Our findings are consistent with the previous results of addition of the addition of nitroalkenes to disilenes and digermenes.[20]



Scheme 2.20

The reactivity of digermenes and disilenes towards nitrones is also a convenient chemical method for the conversion of a nitrone functional group to an hydroxylamine in a stepwise, controlled 2-electron reduction (**Scheme 2.21**).



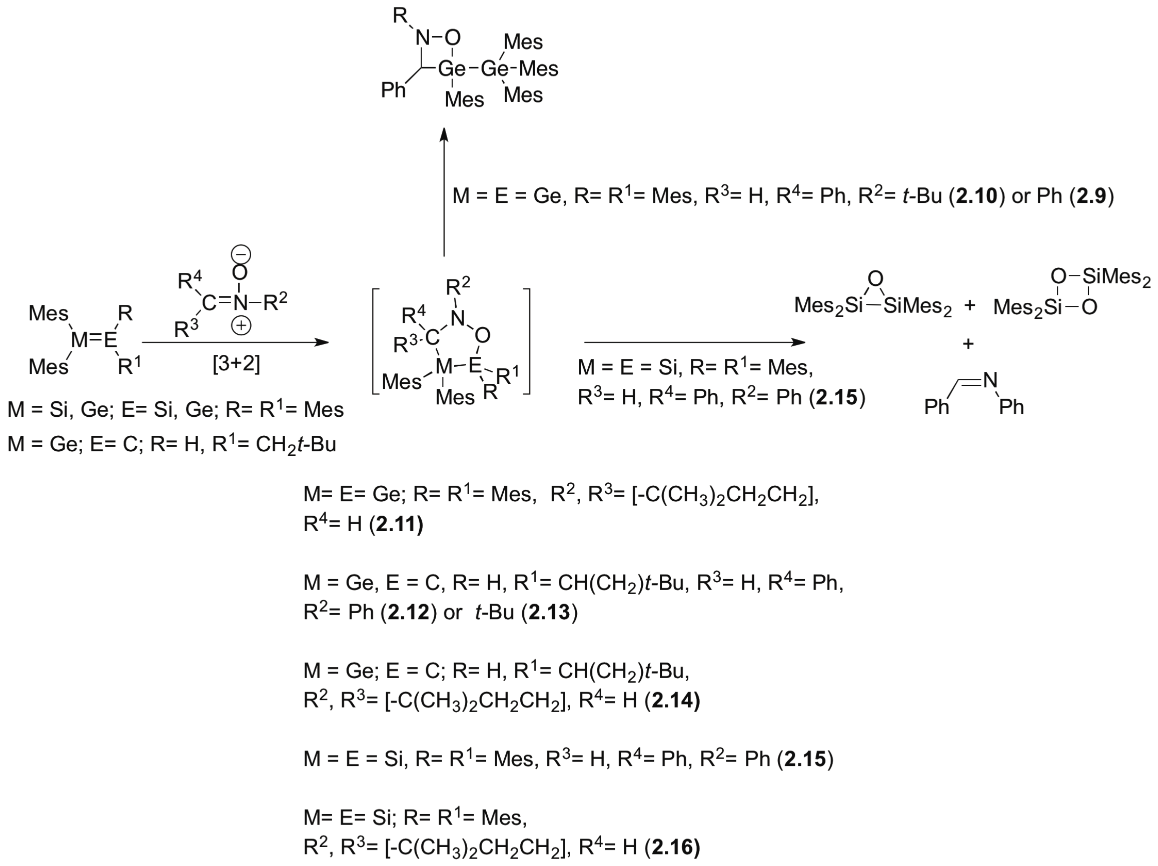
Scheme 2.21

Both reactions are selective, 2-electron reductions from nitro compounds to (essentially) an oxime, or an imine oxide to a hydroxylamine. Such selectivity is difficult to achieve using common reducing reducing agents; additional methods for the mild, convenient synthesis of oximes are needed.[8,20] Group 14 (di)tetrelenes may be exploited in the future for the selective reduction of nitrones and nitroalkenes.

2.4 Conclusions

In conclusion, this study illustrates the facile reaction between $Mes_2Si=SiMes_2$, $Mes_2Ge=GeMes_2$ and $Mes_2Ge=CH(CH_2$-*t*-Bu) and two main group oxides: nitrones and nitroalkanes. The reactions occur easily at room temperature and can be followed by the rapid disappearance of the deep yellow colour of the starting (di)tetrelene. The addition leads to the formation of 5-membered rings via an apparent [3+2] cycloaddition where the (di)tetrelene acts as a 2π component and the nitro/nitrone as the 4π component. Furthermore, these products can often be synthesized in good yield (**Scheme 2.22**). The chemistry of the nitrone additions is highly dependent upon the type of substituent bonded to the nitrone nitrogen and the (di)tetrelene used. In general, the germene **1.1** reacted with nitrones to give 1,2,5-oxazagermolidines. On the other hand, digermene **1.2** and disilene **1.3** reacted with nitrones to give 1,2,4,5-oxazadigerm- or disilolidines, respectively. In the case of germanium, the 1,2,4,5-oxazadigermolidines which rearranged to 1,2,4-oxazagermetidines. In the case of silicon, the nitrone may act as an oxygen donating reagent. In the addition of nitromethane and nitroethane to germene **1.1**, 1,3,2,4-dioxazagermolidines were obtained as the first formed products. However, both ring systems were susceptible to ring opening reactions: the nitroethane adduct **2.20** underwent isomerization to the oxime and the nitromethane adduct underwent cycloreversion.

The results presented in this chapter further reveal the rich chemistry of (di)tetrelenes. In the future it is hoped that the compounds formed in this study, by the reaction of nitrogen oxides with (di)tetrelenes, can be utilized in technological applications.



Scheme 2.22

2.5 Experimental

2.5.1 General Experimental Details

All air and moisture sensitive reactions were carried out in flame-dried Schlenk tubes under an argon atmosphere. C_6D_6 was stored over 4 Å molecular sieves. All other solvents were dried using a solvent purification system (Innovative Technology Ltd) by passing the solvent through an alumina column. All reagents were purchased from the Aldrich Chemical Co. and were used as received. Ge_3Mes_6[9] and $(Me_3Si)_2SiMes_2$[11] and $Mes_2Ge(F)CH=CH_2$ [26] were synthesized according to the literature procedures.

Tetramesityldigermene[9] –disilene[11] and 1,1-dimesitylneopentylgermene[9] were synthesized prior to each reaction in quantitative yield and used *in situ* without purification. Nuclear Magnetic Resonance (NMR) spectra was recorded on a Varian INOVA 600 MHz spectrometer (^{1}H 600 MHz, ^{13}C{^{1}H} 150.8 MHz). Spectra were referenced to the residual hydrogens in the deuterated solvent relative to tetramethylsilane (C_6D_5H; ^{1}H δ = 7.15 ppm) or the central transition of C_6D_6 (128.00 ppm) for ^{13}C NMR spectra. All NMR experiments were performed at 25 °C unless indicated. Mass spectral data are reported in mass-to-charge ratios (*m/z*). ESI mass spectra were recorded on a Bruker micrOTOF II mass spectrometer with an electrospray interface in positive ion mode.

2.5.2 Addition of C,N-Diphenylnitrone to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.05 g, 0.05 mmol) was placed in a quartz tube[a] and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 ^{o}C for ~18 h to give a bright yellow solution. The solution was cooled during the irradiation by circulating methanol in the quartz Dewar. The solvent was removed under reduced pressure and bright yellow residue was dissolved in C_6D_6 (1 mL). C,N-diphenylnitrone compound (0.02 g, 0.12 mmol) was added to solution and the reaction was allowed to stir at room temperature less than five minutes. The colour of the reaction mixture faded almost immediately. The solvent was evaporated to give pale yellow oil which was dissolved in a minimum amount of ether. The flask was placed in a freezer (-14 ^{o}C), yielding crystalline material, which was isolated by decantation. The crude material was purified by thin-layer chromatography (80:20 DCM/hexanes) (43 mg, 72% yield).

[a] A quartz tube and Dewar were used but a Pyrex Dewar can be used instead.

2.9: Yellow oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 7.45 (d, *J* = 7.2, 2H, Ph *o*-H), 6.97-6.94 (m, 4H, Ph *m*-H), 6.85-6.78 (m, 3H, Ph *o*-H, Ph *p*-H), [6.72-6.64 (m, Ph *p*-H), 6.68 (s, Mes *m*-H) all together 3H], 6.59 (s, 6H, Mes *m*-H), 4.92 (s, 1H, CH), 2.48 (s, 18H, Mes *o*-CH_3), 2.42 (s, 6H, Mes *o*-CH_3), 2.01 (s, 3H, Mes *p*-CH_3), 2.00 (s, 9H, Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 151 MHz) δ 156.37 (Ph *i*-C), 144.12 (Ge-Mes *o*-C), 143.83 (Ge-Mes_3 *o*-C), 141.68 (Ph *o*-C), 138.61 (Ge-Mes *p*-C, *i*-C), 138.47 (Ge-Mes_3 *p*-C, *i*-C), 130.12 (Ge-Mes *m*-C), 129.77 (br, Ge-Mes_3 *m*-C, Ph *p*-C), 127.71 (Ph *m*-C), 126.24 (Ph *p*-C), 121.27 (Ph *i*-C), 119.76 (Ph *o*-C), 113.25 (Ph, *m*-C), 79.12 (N-CH), 25.28 (Mes *o*-CH_3), 25.17 (Mes *o*-CH_3), 20.99 (Mes, *p*-CH_3), 20.79 (Mes *p*-CH_3); high resolution ESI-MS *m/z* for $C_{49}H_{56}NO^{70}Ge_2$ ($M+H^+$) Calc. 814.2847, found 814.2861.

2.5.3 Addition of N-*tert*-Butyl-α-phenylnitrone to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.05 g, 0.05 mmol) was placed in a quartz tube and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 °C for ~18 h to give a yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The solvent was removed under reduced pressure and the bright yellow residue was dissolved in C_6D_6 (1 mL). N-*tert*-Butyl-α-phenylnitrone (0.02 g, 0.12 mmol) was added and the solution was allowed to stir at room temperature. After 24 h, the deep yellow solution had faded to pale yellow. The solvent was evaporated to give clear oil. An attempt was made to purify the product by thin-layer chromatography (80:20 DCM/hexanes), however, no compounds were isolated from the plate.

2.10: clear oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 7.16-7.15 (obscured by solvent, Ph *o*-H), 7.10 (t, *J* = 7.8 Hz, 1H, Ph *p*-H), 6.85 (t, 1H, *J* = 7.2 Hz, 2H, Ph *m*-H), 6.99 (s, 1H, Mes *m*-H), 6.71 (s, 6H, Mes *m*-H), 6.35 (s, 1H, Mes *m*-H), 4.98 (s, 1H, CH), 3.28 (s, 3H, Mes *o*-CH_3), 2.47 (s, 18H, Mes *o*-CH_3), 2.11 (s, 3H, Mes *o*-CH_3), 2.07 (s, 9H, Mes *p*-CH_3), 1.39 (s, 3H, Mes *p*-CH_3), 0.87 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 145.86 (Ge-Mes *o*-C), 144.29 (Ge-Mes_3 *o*-C), 143.37 (Ge-Mes *o*-C), 142.75 (Ph *i*-C), 139.12 (Ge-Mes_3 *i*-C), 138.94 (Ge-Mes *p*-C), 138.39 (Ge-Mes_3 *p*-C), 136.70 (Ge-Mes *i*-C), 130.66 (Ge-Mes CH), 129.76 (Ge-Mes_3 CH), 128.64 (Ph *o*-C), 128.53 (Ph *m*-C), 127.5 (Ge-Mes CH)[b], 125.90 (Ph *p*-CH), 73.13 (CH), 61.76 ($N\underline{C}(CH_3)_3$), 25.08 (Mes_3 *o*-CH_3), 24.64 ($NC(\underline{C}H_3)_3$), 22.70 (Mes *o*-CH_3), 21.85 (Mes *o*-CH_3), 21.08 (Mes *p*-CH_3), 20.95 (Mes_3 *p*-CH_3); high resolution ESI-MS *m/z* for $C_{47}H_{60}NO^{70}Ge_2$ ($M+H^+$) Calc. 794.3160, found 794.3160.

2.5.4 Addition of 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.05 g, 0.05 mmol) was placed in a quartz tube and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 °C for ~18 h to give a yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The solvent was removed under reduced pressure and the bright yellow residue was dissolved in C_6D_6 (1 mL). DMPO (0.01 g, 0.12 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir for less than five minutes. The solution decolourized immediately. The benzene was removed under reduced pressure to give a pale yellow powder which was dissolved in a minimum amount of THF. The flask was placed in the freezer (-14 °C) for 24 h. Colourless, clear crystals precipitated (73 mg, 82%). The residue from the mother liquor was purified by

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[b] Chemical shift extracted from the ^{13}C-^{1}H HMBC spectrum.

thin-layer chromatography (60:40 DCM/hexanes) to yield compound **2.11** as a yellow solid (0.02 g, 16%).

2.11: Yellow solid; ^{1}H NMR (C_6D_6, 600 MHz) δ 6.74 (s, 2H, Mes *m*-H), 6.72 (s, 2H, Mes *m*-H), 6.69 (s, 2H, Mes *m*-H), 6.61 (s, 2H, Mes *m*-H), 4.17 (br, 1H, Ge-CH), 2.54 (s, 6H, Mes *o*-CH_3), 2.40 (s, 6H, Mes *o*-CH_3), 2.22 (s, 6H, Mes *o*-CH_3), 2.11 (s, 6H, Mes *p*-CH_3), 2.07 (s, 3H, Mes *p*-CH_3), 1.98 (s, 3H, Mes *p*-CH_3), 1.87-1.83 (m, 2H, CH_2), 1.95-1.73 (m, 3H), 1.57 (s, 3H, CH_3), 1.54-1.48 (m, 1H, CH), 1.08 (s, 3H, CH_3); ^{1}H NMR (C_6D_6, 600 MHz, 65 °C) δ 6.74 (s, 2H, Mes *m*-H), 6.71, 6.70 (each s, 4H total, Mes *m*-H), 6.61 (2H, Mes *m*-H), 4.14 (t, *J* = 9 Hz, 1H, Ge-CH), 2.53 (s, 6H, Mes *o*-CH_3), 2.37 (s, 12H, Mes *o*-CH_3), 2.22 (s, 6H, Mes *o*-CH_3), 2.12, 2.11 (each s, 6H total, Mes *p*-CH_3), 2.08 (s, 3H, Mes *p*-CH_3), 2.00 (s, 3H, Mes *p*-CH_3), 1.91-1.76 (m, 3 x CH), 1.57-1.53 (m, 1H, CH), 1.52 (s, 3H, CH_3), 1.10 (s, 3H, CH_3); ^{13}C NMR (C_6D_6, 151 MHz) δ 143.92 (br, Mes *o*-C), 143.59 (br, Mes *o*-C), 140.24 (br, Mes *i*-C), 139.14 (br, Mes *i*-C), 138.63 (Mes *p*-C), 138.46 (Mes *p*-C), 138.06 (Mes *p*-C), 138.03 (Mes *p*-C), 129.62 (Mes *m*-C), 129.47 (Mes *m*-C), 129.10 (Mes *m*-C), 62.73 (N-C-H), 36.87 (CH_2), 30.19 (CH_2), 26.93 (br, $C(\underline{C}H_3)_2$), 25.67 (br, Mes *o*-CH_3), 25.31 (Mes *o*-CH_3), 24.37 (Mes *o*-CH_3), 20.98 (Mes *p*-CH_3), 20.96 (Mes *p*-CH_3), 20.88 (Mes *p*-CH_3), 20.86 (Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 151 MHz, 65 °C) δ 143.03 (Mes *o*-C), 143.91(br, Mes *o*-C), 143.80 (br, Mes *o*-C), 143.68 (Mes *o*-C), 143.47 (Mes *i*-C), 143.33(Mes *i*-C), 140.42 (Mes *i*-C), 139.26 (Mes *i*-C), 138.66 (Mes *p*-C), 138.46 (Mes *p*-C), 138.11 (Mes *p*-C), 138.07 (Mes *p*-C), 129.58 (Mes *m*-C), 129.43 (Mes *m*-C), 129.21 (Mes *m*-C), 129.14 (Mes *m*-C), 63.11 (N-C-H), 37.20 (CH_2), 30.11 (CH_2), 26.95 ($C(\underline{C}H_3)_2$), 25.61 (br, Mes *o*-CH_3), 25.26 (Mes *o*-CH_3), 24.30 (Mes *o*-CH_3), 24.06 (br, Mes *o*-CH_3), 20.90 (Mes *p*-CH_3), 20.87 (Mes *p*-CH_3), 20.81

(Mes *p*-CH_3), 20.79 (Mes *p*-CH_3); high resolution ESI-MS *m/z* for $C_{42}H_{56}NO^{70}Ge_2$ ($M+H^+$) Calc. 730.2847, found 730.2861.

2.5.5 Addition of C,N-Diphenylnitrone to 1,1-Dimesitylneopentylgermene 1.1

tert-Butyllithium (1.7 M in pentane, 0.15 mL, 0.26 mmol) was added to a solution of **1.9** (100 mg, 0.28 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and solvent was removed under vacuum to give an orange solid. The solid was transferred to the glove box and dissolved in C_6D_6 (1 mL). C,N-Diphenylnitrone (0.05 g, 0.28 mmol) was added to the solution and allowed to stir under an inert atmosphere for 30 minutes. The solvent removed under reduced pressure to give yellow oil which was identified as a mixture of **2.12a** and **2.12b** in a ratio of 1:1.6 (0.14 g, 85%). The crude product was purified by thin-layer chromatography (40:60 DCM/hexanes), to give **2.12a** (0.01g, 6%) and **2.12b** (0.01 g, 6%). The samples are contaminated with hydrocarbon grease.

2.12a: ^1H NMR (C_6D_6, 600 MHz) δ 7.54 (d, *J* = 7.2 Hz, 2H, CPh *o*-H), 7.41 (d, *J* = 7.2 Hz, 2H, NPh *o*-H), 7.15 (obscured by solvent, NPh *m*-H), 6.84-6.76 (m, 3H, CPh *m*-H, *p*-H), 6.74-6.70 (m, 1H, NPh *p*-H), 6.68 (s, 2H, Mes CH), 6.64 (s, 2H, Mes CH), 5.25 (s, 1H, NCH), 2.90 (d, *J* = 8.4 Hz, 1H, GeCH), 2.53 (s, 6H, Mes *o*-CH_3), 2.39 (s, 6H, Mes *o*-CH_3), 2.06 (s, 3H, Mes *p*-CH_3), 2.02 (s, 3H, Mes *p*-CH_3), 1.84 (dd, *J* = 9, 15 Hz, 1H, CH of CH_2), 1.66 (dd, J = 1.8, 15 Hz, 1H, CH of CH_2), 0.95 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 151.26 (NPh *i*-C), 143.19 (Mes *o*-C), 142.81 (Mes *o*-C), 141.24 (CPh *i*-C), 139.42 (Mes *p*-C), 139.34 (Mes *p*-C), 135.67 (Mes *i*-C), 133.13 (Mes i-C), 129.47 (Mes *m*-C), 129.29 (Mes *m*-C),128.76 (CPh *o*-C), 128.90 (NPh *m*-C), 128.25 (CPh *m*-CH), 126.95 (CPh *p*-C), 119.83 (NPh *p*-C), 116.10 (NPh *o*-C), 73.82 (N-CH), 45.47 ($\underline{C}H_2$-

$C(CH_3)_3$), 40.78 (HC-Ge), 32.14 ($\underline{C}(CH_3)_3$), 29.92 ($C(\underline{C}H_3)_3$), 24.02 (Mes *o*-CH_3), 22.64 (Mes *o*-CH_3), 20.99 (Mes *p*-CH_3), 20.96 (Mes *p*-CH_3); high resolution ESI-MS *m/z* for $C_{37}H_{45}NNaO^{70}Ge$ ($M+Na^+$) Calc. 612.2641, found 612.2653.

2.12b: ^1H NMR (C_6D_6, 600 MHz) δ 7.40-7.36 (m, 4H, NPh *o*-H, CPh *o*-H), 7.00-6.95 (m, 4H, CPh *m*-H, NPh *m*-H), 6.90-6.87 (br, 1H, CPh *p*-H), 6.75 (s, 2H, Mes CH), 6.72 (t, *J* = 7.2, 1H, NPh *p*-H), 6.69 (s, 2H, Mes CH), 5.07 (d, *J* = 4.8 Hz, 1H, NCH), 2.79 (q, *J* = 4.8 Hz, 1H, GeCH), 2.63 (s, 6H, Mes *o*-CH_3), 2.59 (s, 6H, Mes *o*-CH_3), 2.07 (s, 3H, Mes *p*-CH_3), 2.06 (s, 3H, Mes *p*-CH_3), 1.99 (dd, *J* = 4.8, 15 Hz, 1H, CH of CH_2), 1.88 (dd, *J* = 4.2, 14.4 Hz, 1H, CH of CH_2), 0.57 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 151.86 (*i*-Ph-N), 143.66 (Mes *o*-C), 142.34 (Mes *o*-C), 139.50 (CPh *i*-C), 139.35 (Mes *i*-C), 139.20 (Mes *i*-C), 137.12 (Mes *p*-C), 134.20 (Mes *p*-C), 129.8 (Mes *m*-C), 129.55 (Mes *m*-C), 129.44 (br, CPh *o*-C), 128.44 (NPh *m*-C), 128.28 (CPh *m*-CH), 127.20 (CPh *p*-C), 123.31 (NPh *p*-C), 121.69 (NPh *o*-C), 73.72 (N-CH), 39.36 (HC-Ge), 38.16 ($\underline{C}H_2$-$C(CH_3)_3$), 31.09 ($\underline{C}(CH_3)_3$), 29.19 ($C(\underline{C}H_3)_3$), 23.98 (Mes *o*-CH_3), 23.76 (Mes *o*-CH_3), 20.99 (2 x Mes *p*-CH_3); high resolution ESI-MS *m/z* for $C_{37}H_{46}NO^{70}Ge$ ($M+H^+$) Calc. 590.2822, found 590.2832.

2.5.6 Addition of N-*tert*-Butyl-α-phenylnitrone to 1,1-Dimesitylneopentylgermene 1.1

tert-Butyllithium (1.7 M in pentane, 0.15 mL, 0.26 mmol) was added to a solution of **1.9** (100 mg, 0.28 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and solvent was removed under reduced pressure to give a mixture of an orange solid and a white solid. The solid was transferred to the glove box and dissolved in C_6D_6 (1 mL). N-*tert*-Butyl-α-phenylnitrone (0.04 g, 0.28 mmol) was added to the solution. The deep yellow solution decolourized immediately to give a pale yellow solution and the solution was allowed to stir under an inert atmosphere for 30 minutes. The solvent was removed under reduced pressure; a pale yellow solid was obtained (0.15 g, 93%). The crude product was purified by thin layer chromatography (30:70 DCM/hexanes) which yielded compound **2.13** (60 mg, 37%) as a yellow oil.[c]

2.13: Yellow oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 7.47–7.46 (br d, 2 H, *J* = 7.2 Hz, Ph *o*-H), 7.09 (t, 2H, *J* = 7.8 Hz, Ph *m*-H), 7.05–7.01 (m, 1 H, Ph *p*-H), 6.77 (s, 2H, Mes CH), 6.74 (s, 2H, Mes CH), 4.63 (d, 1H, *J* = 5.4 Hz, NCH), [2.57-2.68 (m, CH-Ge), 2.64 (s, Mes *o*-CH_3), all together 13H], 2.10 (s, 3H, Mes *p*-CH_3), 2.06 (s, 3H, Mes *p*-CH_3), 2.03 (dd, 2H, *J* = 15 Hz, 3.9 Hz, CH of CH_2), 1.73 (dd, 2H, *J* = 15 Hz, 5.1 Hz, CH of CH_2), 1.04 (s, 9H, N-*t*-Bu), 0.94 (s, 9H, CH_2-*t*-$\underline{\text{Bu}}$); ^{13}C NMR (C_6D_6, 151 MHz) δ 142.23 (2 x Mes *o*-C), 142.15 (Ph *i*-C), 139.22 (Mes *p*-C), 138.88 (Mes *p*-C), 137.63 (Mes *i*-C), 133.78 (Mes *i*-C), 130.29 (Ph *o*-C), 129.57 (Mes *m*-C), 129.35 (Mes *m*-C), 127.63 (Ph *m*-C), 125.08 (Ph *p*-C), 70.38 ($N\underline{C}HPh$), 60.56 ($N\underline{C}(CH_3)$), 40.31 (HCGe), 37.26 (CH_2), 30.89 ($CH_2\underline{C}(CH_3)$)), 28.95 ($CH_2C(\underline{C}H_3)_3$), 27.74 ($NC(\underline{C}H_3)_3$), 23.84, 23.68 (Mes *o*-CH_3), 21.05, 21.01 (Mes *p*-CH_3); high resolution ESI-MS *m/z* for $C_{35}H_{50}NO^{70}Ge$ ($M+H^+$) Calc. 570.3135, found 570.3146; low resolution ESI-MS *m/z* 574 (MH^+), 400 (MH^+-*t*$BuCH_2CH=CHPh$), 327 (Mes_2GeMe^+).

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[c] The ^{1}H NMR spectrum of **2.13** also has signals at 6.73, 6.71, 2.57, 2.45, 2.11, 2.08, 1.15, 0.81 which may be a diastereomer of **2.13**.

2.5.7 Addition of 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) to 1,1-Dimesitylneopentylgermene 1.1

tert-Butyllithium (1.7 M in pentane, 0.15 mL, 0.26 mmol) was added to a colourless solution of **1.9** (100 mg, 0.28 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and the solvent was removed under vacuum to give dimesitylneopentylgermene **1.1** as an orange powder. The sample was then transferred to the glove box and dissolved in C_6D_6 (1 mL). DMPO (0.03 g, 0.28 mmol) was added to the solution. The deep yellow solution decolourized immediately to give a pale yellow solution. The solvent was removed under vacuum; a pale yellow solid was obtained (0.15 g, 93%). The crude product was purified by thin layer chromatography (30:70 DCM/hexanes), to yield compound **2.14** (60 mg, 37%) as a yellow oil, contaminated with $Mes_2GeOH(CH{=}CH_2)$ in a ratio of (1:2).

2.14: Yellow oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 6.73 (s, 2H, Mes *m*-H), 6.68 (s, 2H, Mes *m*-H), 3.74 (br, t, *J* = 9 Hz, 1H, NCH), 2.67 (br, 6H, *o*-Mes), 2.61 (s, 6H, Mes *o*-CH_3), [2.050 (s, Mes *p*-CH_3), 2.047 (s, Mes *p*-CH_3), all together 6H], 1.92-1.80 (br, 2H, CH_2), 1.78-1.70 (br, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.4-1.36 (br, 2H, CH_2), 1.15 (s, 3H, CH_3), 1.10 (s, 1H, GeCH), 0.86 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 143.75 (Mes *o*-C), 142.68 (Mes *o*-C), 141.38 (Mes *p*-C), 141.36 (Mes *p*-C), 136.44 (Mes *i*-C), 133.61 (Mes *i*-C), 129.45 (Mes *m*-C), 129.32 (Mes *m*-C), 74.65 (NCH), 69.05 ($\underline{C}(CH_3)_2$), 36.60 ($\underline{C}H_2C(CH_3)_2$), 35.61 ($\underline{C}(CH_3)_3$), 31.97 ($CH_2$-*t*-Bu), 30.01 (NCH-$\underline{C}H_2$), 29.60 (br, 2 x CH_3), 29.26 ($C(\underline{C}H_3)_3$), 26.24 (Ge-CH), 24.46 (br, Mes *o*-CH_3), 22.81 (br, Mes *o*-CH_3), 21.01 (Mes *p*-CH_3), 20.96 (Mes *p*-CH_3); high resolution ESI-MS *m/z* for $C_{30}H_{46}NO^{70}Ge$ ($M+H^+$) Calc. 506.2822, found 506.2807.

2.5.8 Addition of C,N-Diphenylnitrone to Tetramesityldisilene 1.3

$Mes_2Si(SiMe_3)_2$ (0.2 g, 0.48 mmol) was placed in a quartz tube and dissolved in hexanes (5 mL) and irradiated ($\lambda = 254$ nm) in a quartz Dewar at -60 ^{o}C for ~18 h to give a yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The solvent was removed under reduced pressure and the bright yellow residue was dissolved in C_6D_6 (1 mL). C,N-Diphenylnitrone (0.25 g, 0.48 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir for one minutes. Immediately, a fine precipitate formed while the solution remained yellow. The solvent was removed under reduced pressure; a pale yellow solid was obtained (0.086 g, 90%). The crude product was purified by thin layer chromatography (20:80 DCM/hexanes) to yield compound **2.15** (0.02 g, 22%) as a pale yellow oil, contaminated with $Mes_4Si_2O_2$[12] and Mes_4Si_2O[12] in a ratio of 1:0.9:0.2, respectively.

2.15: Pale yellow oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 7.33 (br d, $J = 8.4$, 2H, Ph *o*-H), 7.08-7.03 (m, 2H, Ph *m*-H), 6.82 (s, 2H, Mes *m*-H), [6.70-6.69 (m, Ph *o*-H, Ph *p*-H), (s, Mes *m*-H) all together 5H], 6.64-6.63 (m, 1H, Ph *p*-H), 6.50 (s, 2H, Mes *m*-H), 6.40 (s, 2H, Mes *m*-H), 5.72 (s, 1H, CH), 2.92 (s, 6H, Mes *o*-CH_3), 2.49 (s, 6H, Mes *o*-CH_3), 2.42 (s, 6H, Mes *o*-CH_3), 2.15 (s, 3H, Mes *p*-CH_3), 2.13 (s, 3H, Mes *p*-CH_3), 2.11 (s, 6H, Mes *o*-CH_3), 1.93 (s, 3H, Mes *p*-CH_3), 1.87 (s, 3H, Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 151 MHz) δ 152.38 (Ph *i*-C), 144.92 (Mes *o*-C), 144.62 (Mes *o*-C), 144.19 (Mes *o*-C), 143.67 (Mes *o*-C), 139.33 (Mes *p*-C), 138.90 (Ph *p*-C), 138.71 (Mes *p*-C), 138.33 (Mes *p*-C), 138.31 (Mes *p*-C), 135.18 (Mes *i*-C), 133.89 (Mes *i*-C), 132.88 (Mes *i*-C), 132.80 (Mes *i*-C), 130.84 (Ph *i*-C), 129.95 (Mes *m*-C), 129.78 (Mes *m*-C), 129.58 (Ph *m*-C), 129.25 (Mes *m*-C), 128.75 (Mes *m*-C), 128.54 (Ph *m*-C), 126.58 (Mes, *m*-C), 125.82 (Ph *p*-C), 122.16

(Ph, *o*-C), 118.76 (Ph, *o*-C), 66.86 (N-CH), 26.28 (Mes *o*-CH_3), 25.90 (Mes *o*-CH_3), 23.71 (Mes *o*-CH_3), 22.92 (Mes *o*-CH_3), 21.01 (Mes, *p*-CH_3), 20.93 (Mes *p*-CH_3), 20.77 (Mes, *p*-CH_3) , 20.75 (Mes *p*-CH_3); ^{29}Si NMR (C_6D_6,119 MHz) δ -0.5 (SiCHPh), -31.01 (SiON); high resolution ESI-MS *m/z* for $C_{49}H_{56}NOSi_2$ ($M{+}H^+$) Calc. 730.3900, found 730.3912.

2.5.9 Addition of 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) to Tetramesityldisilene 1.3

$Mes_2Si(SiMe_3)_2$ (100 mg, 0.24 mmol) was placed in a quartz tube and dissolved in hexanes (5 mL) and the solution was irradiated (λ = 254 nm) in a quartz Dewar at -60 ^{o}C for ~18 h. The solvent was removed under reduced pressure and the bright yellow residue was dissolved in C_6D_6 (2 mL). DMPO (27 mg, 0.24 mmol) was added and the reaction mixture was allowed to stir at room temperature. The solution decolourized to pale yellow immediately. The solvent was removed to give a yellow solid which was dissolved in a minimum amount of hexanes. The flask was placed in the freezer (-14 ^{o}C). Clear, colourless crystals formed which were isolated by decantation (0.12 g, 72%). The residue from the mother liquor was purified by thin layer chromatography (70:30 hexanes/DCM), to give a yellow solid (27 mg, 17%).

2.16: Yellow solid; ^{1}H NMR (C_6D_6, 600 MHz, 65 ^{o}C) δ 6.75 (s, 2H, Mes *m*-H), 6.71 (s, 2H, Mes *m*-H), 6.67 (s, 2H, Mes *m*-H), 6.65 (s, 2H, Mes *m*-H), 4.07 (t, *J* = 9.6 Hz, 1H, SiCH), 2.45 (br, 6H, *o*-Mes), [2.40 (s, Mes *o*-CH_3), 2.39 (s, Mes *o*-CH_3), all together 6H], 2.28 (br, 6H, Mes *o*-CH_3), 2.25 (br, 6H, Mes *o*-CH_3), 2.11 (s, 3H, Mes *p*-CH_3), 2.10 (s, 3H, Mes *p*-CH_3), 2.09 (s, 3H, Mes *p*-CH_3), 2.03 (s, 3H, Mes *p*-CH_3), 1.90-1.77 (br, 2H, CH/CH), 1.77-1.67 (br, 1H, CH), 1.56-1.45 (br, 4H, CH_3/CH), 1.05 (s, 3H, CH_3); ^{13}C

NMR (C_6D_6, 151 MHz) δ 146.39 (Mes *o*-C), 145.25 (Mes *o*-C), 145.09 (Mes *o*-C), 144.53 (Mes *o*-C), 144.24 (Mes *o*-C), 139.36 (Mes *p*-C), 138.76 (Mes *p*-C), 138.47 (Mes *p*-C), 138.21 (Mes *p*-C), 135.79 (Mes *i*-C), 135.44 (Mes *i*-C), 132.81 (Mes *i*-C), 132.54 (Mes *i*-C), 129.93 (Mes *m*-C), 129.68 (Mes *m*-C), 129.57 (Mes *m*-C), 129.39 (Mes *m*-C), 128.97 (Mes *m*-C), 71 (br, $\underline{C}(CH_3)_2$), 59.85 (NCH), 37.15 ($\underline{C}H_2C(CH_3)_2$), 28.49 ($CH_2$), 27.29 ($CH_3$), 26.20 ($CH_3$), 25.6 (br, Mes *o*-$CH_3$), 25.57 (Mes *o*-$CH_3$), 25.19 (Mes *o*-$CH_3$)[d], 23.69 (Mes *o*-$CH_3$)[d], 22.72 (Mes *o*-$CH_3$)[d], 21.02 (Mes *p*-$CH_3$), 20.98 (Mes *p*-$CH_3$), 20.91 (Mes *p*-$CH_3$), 20.83 (Mes *p*-$CH_3$); high resolution ESI-MS *m/z* for $C_{42}H_{56}NOSi_2$ ($M+H^+$) Calc. 646.3900, found 646.3920.

2.5.10 Addition of N-*tert*-Butyl-α-phenylnitrone to Tetramesityldisilene 1.3

$Mes_2Si(SiMe_3)_2$ (50 mg, 0.12 mmol) was placed in a quartz tube and dissolved in hexanes (5 mL) and the solution was irradiated ($\lambda = 254$ nm) in a quartz Dewar at -60 ^oC for ~18 h. The solvent was removed under reduced pressure and the bright yellow residue was dissolved in C_6D_6 (2 mL). N-*tert*-Butyl-α-phenylnitrone (0.02 g, 0.12 mmol) was added to the yellow solution at room temperature. The reaction was allowed to stir for 3 days under an inert atmosphere and was monitored by ^1H NMR spectroscopy. No reaction was observed.

2.5.11 Addition of Nitromethane to 1,1- Dimesitylneopentylgermene 1.1

tert-Butyllithium (1.7 M in pentane, 0.15 mL, 0.26 mmol) was added to a solution of **1.9** (100 mg, 0.28 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and solvent was removed

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[d] Correlates to a signal in the ^{1} H NMR spectrum of **2.16** which integrates for 3H.

under vacuum to give a mixture of an orange solid and a white solid. The solid was transferred to the glove box and then dissolved in C_6D_6 (1 mL). Nitromethane (0.02 g, 0.28 mmol) was added to the solution. The deep yellow solution decolourized immediately. The solvent was removed under vacuum and a clear, colourless oil was obtained (0.11 g, 84%). The oil was dissolved in a minimum amount of pentane. The flask was placed in a freezer (-14 ^{o}C); just one crystal was obtained by crystallization. The crude material was contaminated with at least two unidentified compounds. Attempts to purify **2.17** by chromatography (50:50 hexanes: DCM) gave only 1,3-$Mes_4Ge_2O_2$.[13]

2.17: colourless oil contaminated with two unknown products and fluorodimesitylvinylgermane **1.9**; ^{1}H NMR (C_6D_6, 600 MHz) δ 6.69 (s, 2H, *m*-Mes), 6.63 (s, 2H, *m*-Mes), 5.14 (dd, *J* = 1.2, 11 Hz, 1H, Ge-CH), 3.12 (s, 3H, NCH_3), 2.50 (s, 6H, Mes *o*-CH_3), 2.48 (s, 6H, Mes *o*-CH_3), 2.10 (dd, *J* = 11, 15 Hz, 1H, CH of CH_2), 2.04 (s, 6H, Mes *p*-CH_3), 1.17 (dd, *J* = 1.2, 15 Hz, 1H, CH of CH_2), 0.10 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 143.04 (Mes *o*-C), 142.97 (Mes *o*-C), 139.60 (Mes *p*-C), 139.24 (Mes *p*-C), 134.11 (Mes *i*-C), 133.53 (Mes *i*-C), 129.36 (Mes *m*-C), 129.34 (Mes *m*-C), 75.01 (CH-O), 49.66 (N-CH_3), 44.35 ($\underline{C}H_2$-*t*Bu), 30.03 ($C(\underline{C}H_3)_3$), 24.13 (Mes *o*-CH_3), 22.65 (Mes *o*-CH_3), 21.00 (Mes *p*-CH_3), 20.97 (Mes *p*-CH_3); FTIR (thin film, cm^{-1}) 2924 (s), 1603 (s), 1450 (s), 1029 (m), 847 (s), 685 (m), 547 (m); high resolution ESI-MS *m/z* for $C_{25}H_{37}NO_2{}^{70}Ge$ ($M+Na^+$) Calc. 476.1965, found 476.1956.

2.19: colourless solid obtained by crystallization from the hexanes reaction mixture, contaminated with trace of **2.16**. ^{1}H NMR (C_6D_6, 600 MHz) δ 6.68 (s, 4H, *m*-Mes), 5.87 (t, *J* = 5.4, 1H, N=CH), 2.96 (s, 3H, N-CH_3), 2.55 (s, 12H, Mes *o*-CH_3), 2.34 (dm, *J* = 6.6 Hz, 2H, CH_2), 2.06 (s, 6H, Mes *p*-CH_3), 0.78 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ

143.48 (Mes *o*-C), 143.36 (Mes *o*-C), 139.52 (Mes *p*-C), 139.01 (Mes *p*-C), 134.55 (CH=N), 132.14 (Mes *i*-C), 129.57 (Mes *i*-C), 129.49 (Mes *m*-C), 129.34 (Mes *m*-C), 51.96 (NCH_3), 40.23 (CH_2), 30.17 ($\underline{C}(CH_3)_3$), 29.45 ($C(\underline{C}H_3)_3$), 23.31 (Mes *o*-CH_3), 23.12 (Mes *o*-CH_3), 21.00 (Mes *p*-CH_3).

2.5.12 Addition of Nitroethane to 1,1-Dimesitylneopentylgermene 1.1

tert-Butyllithium (1.7 M in pentane, 0.15 mL, 0.26 mmol) was added to a solution of **1.9** (100 mg, 0.28 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and the solvent was removed under reduced pressure to give a mixture of an orange solid and a white solid. The solid was transferred to the glove box and dissolved in C_6D_6 (1 mL). Nitroethane (0.02 g, 0.28 mmol) was added to the solution. The deep yellow solution decolourized immediately. The solvent was removed under reduced pressure to give a colourless oil. Compound **2.20** was contaminated with **1.9** in a ratio of 1:0.2 and with an unknown compound (0.13 g). The crude product was purified by thin layer chromatography (50:50 DCM/hexanes) which yielded compound **2.20** (0.03 g, 27%) as a clear oil.

2.20: clear oil contaminated with one unknown product and fluorodimesitylvinylgermane **1.9**; ^{1}H NMR (C_6D_6, 600 MHz) δ 6.7 (br, s, 2H, Mes *m*-CH), 6.64 (s, 2H, Mes *m*-CH), 5.13 (dd, 1H, *J* = 1.2, 11 Hz, Ge-CH), 3.40 (q, 2H, *J* = 7.8 Hz, CH_2N), 2.51 (s, 6H, Mes *o*-CH_3), 2.48 (s, 6H, Mes *o*-CH_3), 2.05 (s, 3H, Mes *p*-CH_3), 2.04 (s, 3H, Mes *p*-CH_3), 1.26 (t, 3H, *J* = 7.2 Hz, CH_3), 2.10 (dd, 1H, *J* = 11 Hz, 15 Hz, CH of CH_2), 1.18 (dd, 1H, *J* = 1.2, 15 Hz, CH of CH_2), 0.99 (s, 9H, CH_2-*t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 143.11 (Mes *o*-C), 142.97 (Mes *o*-C), 139.58 (Mes *p*-C), 139.23 (Mes *p*-C), 134.01 (Mes *i*-C), 133.62 (Mes *i*-C), 129.36 (Mes *m*-C), 129.31 (Mes *m*-C), 74.45 (CH-O), 65.86

($\underline{C}(CH_3)_3$), 56.93 (N-$\underline{C}H_2$-CH_3), 44.36 ($\underline{C}H_2$-*t*Bu), 30.04 ($C(\underline{C}H_3)_3$), 24.13 (Mes *o*-CH_3), 22.72 (Mes *o*-CH_3), 21.00 (Mes *p*-CH_3), 20.94 (Mes *p*-CH_3), 11.66 (N-CH_2-$\underline{C}H_3$); FTIR (thin film, cm^{-1}) 2954 (m), 1603 (m), 1448 (m), 1029 (w), 848 (s), 670 (w), 626 (w), 590 (w), 546 (m), 497 (s); high resolution ESI-MS *m/z* for $C_{26}H_{39}NO_2{}^{70}Ge$ ($M+Na^+$) Calc. 490.2121, found 490.2101.

2.21: Mixture of two *Z* and *E* isomers in 1:1 ratio, colourless oil; ^1H NMR (C_6D_6, 600 MHz) δ 7.13 (q, 1H, J = 5.4 Hz, $=CH_E$), 6.73 (s, 2H, Mes *m*-H_E), 6.71 (s, 2H, Mes *m*-H_E), 6.69 (s, 2H, Mes *m*-H_Z), 6.67 (s, 2H, Mes *m*-H_Z), 6.28 (q, 1H, J = 5.4 Hz, $=CH_Z$), 4.97-4.92 (m, 1H, $CH_{E/Z}$), 4.74-4.68 (m, 1H, O-$H_{E/Z}$), [2.70 (s, Mes *o*-CH_{3E}), 2.68 (s, Mes *o*-CH_{3Z}), 2.57 (s, Mes *o*-CH_{3E}), 2.54 (s, Mes *o*-CH_{3Z}) all together 12H], 2.21-2.17 (m, 1H, CH of $CH_{2E/Z}$), [2.06 (br s, Mes *p*-CH_{3E}), 2.05 (br s, Mes *p*-CH_{3Z}) all together 6H], 1.85-1.80 (m, 1H, CH of $CH_{2E/Z}$), 1.48 (d, 3H, J = 5.4 Hz, CH_{3Z}), 1.14 (d, J = 6Hz , 2H, CH_{3E}), 1.05 (s, 9H, *t*-$Bu_{E/Z}$); ^{13}C NMR (C_6D_6, 151 MHz) δ 149.33 ($=CH_{E+Z}$), 143.71 (Mes *o*-C_E), 143.00 (Mes *o*-C_Z), 142.92 (Mes *o*-C_Z), 139.25 (Mes *p*-$C_{E\text{ or }Z}$), 139.08 (Mes *p*-$C_{E\text{ or }Z}$), 135.31 (Mes *i*-$C_{E\text{ or }Z}$), 134.97 (Mes *i*-$C_{E\text{ or }Z}$), 129.53 (Mes *m*-$CH_{E\text{ or }Z}$), 129.44 (Mes *m*-$CH_{E\text{ or }Z}$), 71.20 ($CH(OH)_{E\text{ or }Z}$), 48.23 ($CH_{2E,Z}$), 31.66 ($\underline{C}(CH_3)_3$), 30.23 ($C(\underline{C}H_3)_3$), 23.57 (Mes *o*-CH_{3E+Z}), 23.34 (Mes *o*-CH_{3E+Z}), 21.00 (Mes *p*-$CH_{3E\text{ or }Z}$), 20.95 (Mes *p*-$CH_{3E\text{ or }Z}$), 15.02 (CH_{3E}), 11.36 (CH_{3Z}).

2.6 Single Crystal X-ray Diffraction Experimental Details[e]

Data Collection and Processing. The samples were 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 or a Nonius Bruker KappaCCD Apex2

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[e] The X-ray structure determination experiments were performed by Jeremy L. Bourque.

diffractometer at a temperature of 110 K. The frame integration was performed using SAINT.[27] The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[28]

Structure Solution and Refinement. The structure was solved by using a dual space methodology using the SHELXT program.[29] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom.

For **2.11**, the data demonstrated an area of disorder around the substrate. The disorder was found to be approximately a 180° rotation perpendicular to the Ge-Ge bond. The disorder refined to a normalized occupancy value of 0.573(6).

For **2.16**, the structure was centered on a two-fold rotation axis which was found to be perpendicular to the Si-Si plane. This resulted in a region of disorder, where the DMPO moiety was disordered about the two-fold rotation axis.

The structural models were fit to the data using full matrix least-squares based on F^2. The calculated structure factors include corrections for anomalous dispersion from the usual tabulation. The structures were refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.[30] Graphic plots were produced using the XP program.[31]

Table 2.1 Crystallographic data of compounds **2.9**, **2.11**, **2.16**, **2.19**

Data	**2.9**	**2.11**	**2.16**	**2.19**
Formula	$C_{49}H_{55}Ge_2NO$	$C_{45.67}H_{62.35}Ge_2NO_{1.92}$	$C_{42}H_{55}NOSi_2$	$C_{25}H_{39}GeNO_3$
Formula Weight (*g/mol*)	819.12	801.24	646.05	474.16
Crystal System	monoclinic	monoclinic	monoclinic	orthorhombic
Space Group	$P\ 2_1/c$	$P\ 2_1/c$	C 2/c	P b c a
a, Å	18.816(6)	11.8144(19)	10.810(3)	9.424(4)
b, Å	12.722(4)	20.272(4)	21.560(7)	20.275(10)
c, Å	17.224(5)	17.183(4)	16.553(5)	26.401(11)
α,°	90	90	90	90
ß,°	96.444(15)	92.149(12)	106.383(8)	90
γ,°	90	90	90	90
V, $Å^3$	4097(2)	4112.6(14)	3701(2)	5045(4)
Z	4	4	4	8
R_1	0.0490	0.0539	0.0487	0.0496
wR_2	0.0350	0.1376	0.1356	0.1156
R_1 (all data)	0.0699	0.0771	0.0741	0.0882
wR_2 (all data)	0.0721	0.1564	0.1511	0.1327
GOF	0.908	1.050	1.032	1.033

2.7 References

1. For recent accounts on various aspects of disilene chemistry: (a) Iwamoto, T.; Ishida, S. *Struct. Bonding* **2014**, *156*, 125; (b) Sasamori, T.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1005.; (c) Kira, M. *Proc. Jpn. Acad., Ser. B* **2012**, *88*, 167; (d) T Matsuo, T. Kobayashi M.; Tamao, K. *Dalton Trans.* **2010**, *39*, 9203; (e) Abersfelder, K.;

Scheschkewitz, D. *Pure Appl. Chem.* **2010**, *82*, 595; (f) Scheschkewitz, D. *Chem. Eur. J.* **2009**, *15*, 2476; (g) Kira, M. *J. Organomet. Chem*. **2004**, *689*, 4475; (h) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348.

2. For recent accounts of the chemistry of germenes and digermenes see: (a) Plyusnin, V. F.; Kaletina, M. V.; Leshina, T. V. *Russ. Chem. Rev.*, **2007**, *76*, 931; (b) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178–180*, 565; (c) Takeda, N.; Tokitoh N.; Okazaki, R. *Science of Synthesis*; Moloney, M. G., Eds.; Thieme, Stuttgart, **2003**; Chapters 5.1.2.

3. For some recent examples see: (a) Milnes, K. K.; Pavelka, L. C.; Baines, K. M. *Chem. Soc. Rev.* **2016**, *45*, 1019; (b) Majumdar, M.; Bejan, I.; Huch, V.; White, A. J. P.; Whittell, G. R.; Schäfer, A.; Manners, I.; Scheschkewitz, D. *Chem. Eur. J.* **2014**, *20*, 9225; (c) Zhou, J.; Hall, M. B. *J. Organomet. Chem.* **2013**, *748*, 8; (d) Lee, V. Y.; McNiece, K.; Ito, Y.; Sekiguchi, A.; Geinik, N.; Becker, J. Y. *Heteroat. Chem.* **2014**, *25*, 313; (d) Hardwick, J. A.; Baines, K. M. *Chem. Eur. J.* **2015**, *21*, 2480.

4. Iwamoto, T.; Ishida, S. *Coord. Chem. Rev.* **2016**, *314*, 34

5. (a) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627; (b) Power, P. P. *Nature* **2010**, *463*, 171.

6. (a) Gothelf, K. V.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 863; (b) Hashimoto, T.; Maruoka, K. *Chem. Rev.* **2015**, *115*, 5366; (c) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137.

7. Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc*. **1987**, *109*, 441.

8. Tashkandi, N. Y.; Parsons, F.; Guo, J.; Baines, K. M. *Angew. Chem. Int. Ed*. **2015**, *54*, 1612; *Angew. Chem.* **2015**, *127*, 1632.

9. Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.

10. Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics,* **2007**, *26*, 5569.

11. Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *Organometallics* **1984,** *3*, 793.

12. (a) McKillop, K. L.; Gillette, G. R.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1992***, 114,* 5203; (b) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865; (c) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5***,** 531.

13. (a) Duverneuil, G.; Mazerolles, P.; Perrier, E. *Appl. Organomet. Chem.* **1994**, *8*, 119; (b) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *J. Organomet. Chem.* **2001**, *636*, 130.

14. Assignment of the configuration about the C=N double bond was made based on a comparison of the chemical shifts of vinylic hydrogen in structurally-related compounds: Pretsch, E.; Buhlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds*; Springer, 2009; 4th edition.

15. Baines, K. M.; Cooke, J. A.; Vittal, J. J. *J. Chem. Soc.*, *Chem. Commun*. **1992**, 1484.

16. Riviere, P.; Satgé, J.; Castel, A.; Cazes, A. *J. Organomet. Chem*. **1979**, *177*, 171.

17. Mosey, N. J.; Baines, K. M.; Woo, T.K. *J. Am. Chem. Soc.* **2002**, *124*, 13306.

18. Fatah, A.; Ghereg, D.; Escudié, J.; Saffon, N.; Ladeira, S.; Ranaivonjatovo, H. *Organometallics* **2012**, *31*, 6148.

19. (a) Mangette, J. E.; Powell, D. R.; Calabrese, J. C.; West, R. *Organometallics* **1995**, *14*, 4064; (b) Mangette, J. E.; Powell, D. R.; Firman, T. K.; West, R. *Organometallics* **1996**, *521*, 363.

20. Tashkandi, N. Y. Cycloaddition Reactions of (Di)tetrelenes, The University of Western Ontario, **2016**.

21. Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc*. **1987**, *109*, 6866.

22. Torssell, K.; Feuer, H. *Nitrile oxides, Nitrones, and Nitronates in Organic Synthesis: Novel Strategies in Synthesis*, Wiley-Interscience, Hoboken, **2008**, pp. 129-434.

23. (a) Power, P.P. *Chem. Rev.* **1999**, *99*, 3463; (b) Karni, M.; Apeloig, Y.; Kapp, J. Schleyer, P. *The Chemistry of Organic Silicon Compounds*; Rapport ,Z.; Apeloig, Y., Eds.; John Wiley & Sons: New York, **2001**; Chichester, Vol. *3* Chapter 1; (c) Klinkammer, K. W. *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Eds.; John Wiley & Sons, Ltd, **2002**; Chichester, Vol. *2*, Part 1, Chapter 4.

24. Ghosh, A.; Berg, S. *Group 14 Elements*, John Wiley & Sons, Ltd, **2014**, Chapter 4.

25. El Kettani, S.; Lazraq, M.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Gornitzka, H.; Atmani, A. *Organometallics* **2005**, *24*, 5364.

26. Farhadpour, B.; Guo, J.; Pavelka, L.C.; Baines, K. M. *Organometallics* **2015**, *34*, 3748.

27. Bruker-AXS, SAINT version 2013.8, **2013**, Bruker-AXS, Madison, WI 53711, USA.

28. Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA.

29. Sheldrick, G. M. **2014**, University of Göttingen.

30. Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.

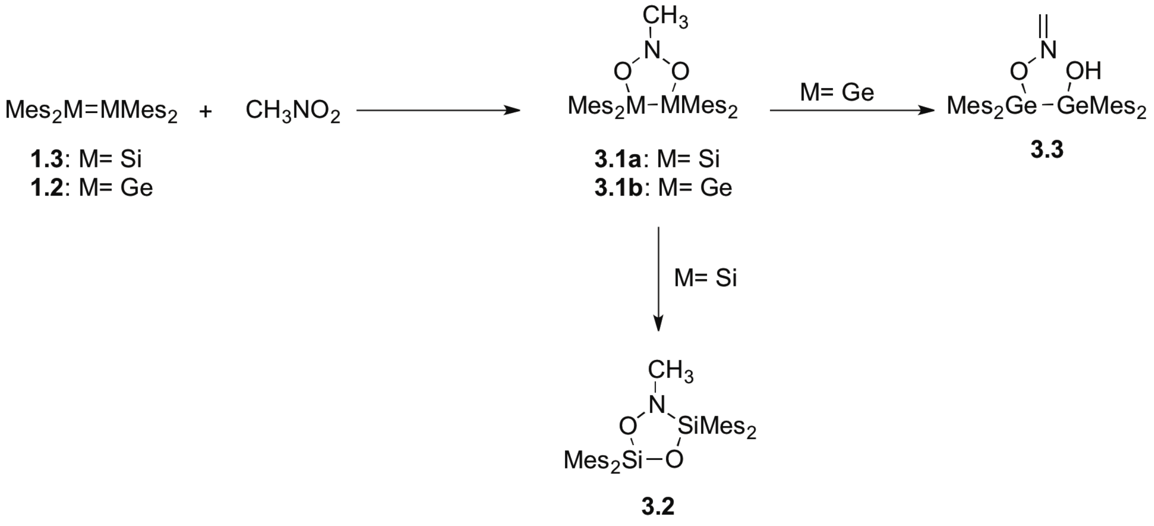
31. Bruker-AXS, XP version 2013.1, **2013**, Bruker-AXS, Madison, WI 53711, USA.

Chapter 3

3 Reactivity of (Di)tetrelenes Toward Phosphorus Oxide Compounds

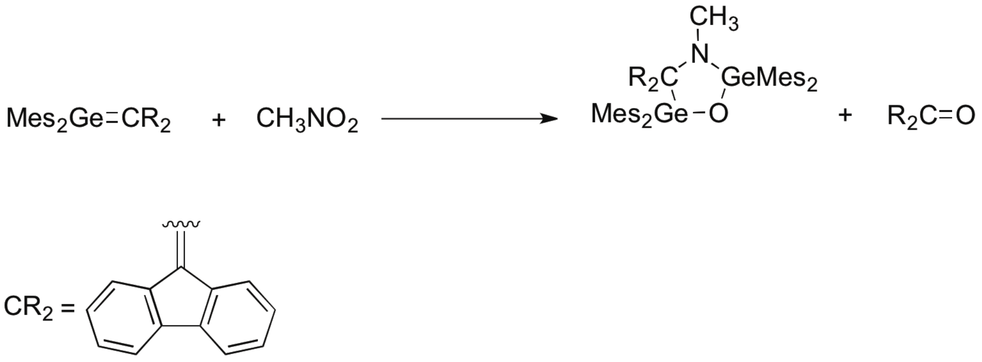
3.1 Introduction

Significant advances have been achieved over the past four decades regarding the reactivity of Si=Si or Ge=Ge double bonds.[1] Although Group 14 (di)tetrelenes, $R_2M=ER_2$, where M = Si, Ge and E = C, Si, Ge, are known to react with a variety of compounds, reactions with main group oxides are relatively unknown. In addition to the fundamental importance of such reactivity studies in molecular (di)tetrelene chemistry, the result of such investigations are also relevant in studies of the chemistry of Ge (100)-2 × 1 and Si (100)-2 × 1 surfaces. For example, in a recent study, the addition of nitromethane to tetramesityldisilene **1.3** and tetramesityldigermene **1.2** lead to the facile formation of the five-membered rings, 1,3,2,4,5-dioxazadisilolidine **3.1a** and 1,3,2,4,5-dioxazadigermolidine **3.1b**, respectively. Interestingly, compound **3.1b** undergoes a quantitative isomerization to the oxime, **3.3**, whereas **3.1a** rearranges to the **3.2** (**Scheme 3.1**).[2] A comparison between the reactivity of nitro compounds and the Si(100)-2 × 1 and Ge(100)-2 × 1 surfaces was made in terms of the type of adducts formed and their reactivity.[2] In the case of silicon, the results provided supporting evidence for the reactivity of the surface dimers. However, for germanium, a new potential reaction pathway at the Ge(100)-2 × 1 surface was revealed.



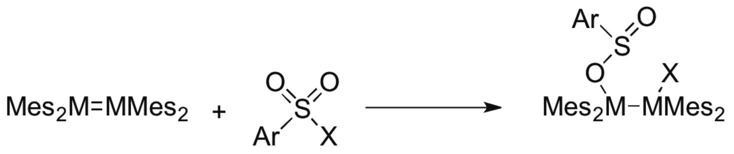
Scheme 3.1

Furthermore, the ease of reduction of the nitro functional group in the reaction of nitro compounds with disilenes and digermenes is notable[3] and may have application in organic synthesis. There is only one other report of a reaction between an organic nitrogen oxide and a (di)tetrelene in the literature. Escudié *et. al.* has also reported the [3+2] cycloaddition of nitromethane to dimesitylfluorenylidenegermane (**Scheme 3.2**).[4]



Scheme 3.2

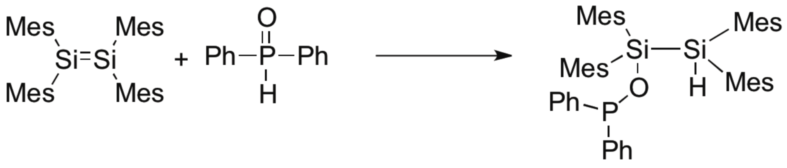
More recently, the reactivity RSO_2X derivatives, where R = Ph, Tol; X = Cl, F, OH, Ph, towards ditetrelenes was reported.[3] Specifically, the addition of sulfonyl chlorides to digermenes and disilenes resulted in the facile formation of sulfinates **3.4** and **3.5**, respectively (**Scheme 3.3**). The formation of sulfinate compounds again displayed an interesting, mild, two-electron reduction of the sulfur centre.[3]



3.4 : M = Ge; Ar = Ph; X = Cl
3.5 : M = Si; Ar = Ph, Tol; X= Cl

Scheme 3.3

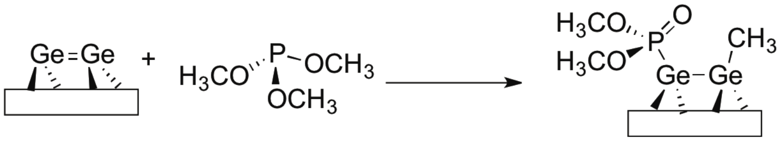
These recent examples have inspired us to further explore the reactivity of main group oxide compounds toward ditetrelenes. The application of phosphorus-based compounds in catalysis has received much attention in recent years[5], which has tremendously impacted chemical synthesis. Of particular relevance is the utilization of the P(III) to P(V) redox cycle.[6] Recently, the addition of a diphenylphosphine oxide ($Ph_2HP=O$) to disilene **1.3** has been reported (**Scheme 3.4**).[3] In this reaction the phosphorus is readily reduced from the P(V) to the P(III) oxidation state. In this study, the addition of phosphine oxides ($R_2HP=O$; R = Ph) and phosphites $(RO)_2HP=O$; R = Ph, CH_3) to (di)tetrelenes will be examined and the results compared to the addition of other main group oxides.



3.6

Scheme 3.4

The adsorption of trimethyl phosphite to the Ge(100)-2 × 1 surface has been examined; IR, XPS and DFT calculations were used to identify the surface adducts.[7] Although several possible reaction products were considered, the structure of the surface adduct was assigned as **3.7** (**Scheme 3.5**) with a covalent bond between a surface germanium and phosphorus.



3.7

Scheme 3.5

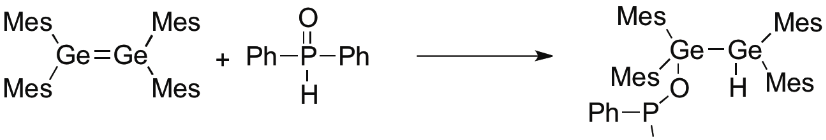
The reactivity of molecular tetramesityldigermene **1.2** and tetramesityldisilene **1.3** has been shown to provide valuable insights into the chemistry of the Ge and Si dimers at the Ge(100)-2 × 1 and Si(100)-2 × 1 surfaces, respectively, including the structure of surface adducts.[7,8] With this objective in mind, we have also investigated the reaction of trimethyl phosphite with tetramesityldigermene **1.2** and tetramesityldisilene **1.3**.

3.2 Results

Germene **1.1**[9], digermene **1.2**[10], and disilene **1.3**[11] were synthesized prior to each reaction in quantitative yield and used in *situ* without purification. Digermene **1.2**, disilene **1.3**, and/or germene **1.1** were dissolved in C_6D_6 and the phosphine oxide was added in excess. The reaction mixtures were kept at room temperature and monitored by ^1H NMR spectroscopy. The products were isolated as either colourless or yellow oils/solids and were identified by ^1H, ^{13}C, ^1H-^1H-COSY, ^{13}C-^1H gHSQC and ^{13}C-^1H gHMBC NMR spectroscopy, and ESI-TOF mass spectrometry.

3.2.1 Addition of Diphenylphosphine Oxide to Tetramesityldigermene 1.2

The addition of diphenylphosphine oxide to a solution of tetramesityldigermene (**1.2**) at room temperature gave a white powder, **3.8**, upon removal of the solvent (**Scheme 3.6**). ^1H NMR spectroscopic analysis of the crude product revealed that **3.8** is the only product formed. The mass spectrum of **3.8** revealed a molecular ion at *m/z* 841.2398, which is consistent with a 1:1 adduct between digermene **1.2** and diphenylphosphine oxide. The ^1H NMR spectrum of **3.8** revealed two sets of signals assigned to two non-equivalent mesityl groups, and one signal assigned to hydrogen attached to germanium atom (Ge-H) at 5.97 ppm. The region between 7.0-7.7 ppm contained signals where were assigned to two equivalent phenyl groups. In the ^{13}C- ^1H HMBC spectrum of **3.8**, two correlations were observed between the signals assigned to the two *ortho*-C of the Mes groups in the ^{13}C dimension and the signal assigned to the one hydrogen attached to germanium atom. The ^{31}P NMR spectrum of **3.8** revealed a signal at 104.69 ppm which is in closely agreement with the ^{31}P chemical shift of **3.6** reported previously (107.19 ppm).[3] Furthermore, the ^{31}P NMR spectrum of Ph_2P-O-$Si(CH_3)_3$ exhibits a singlet at 94.4 ppm,[12] which, again, is consistent with the ^{31}P chemical shift of **3.8**. Notably, the ^{31}P chemical shift of **3.8** is quite different from the reagent, diphenylphosphine oxide (~15 ppm). The IR spectrum of **3.8** revealed an absorption at 2918 cm^{-1} which was assigned to a Ge-H stretching vibration. On the basis of the data the structure of **3.8** was assigned. Although, compound **3.8** could not be isolated in pure form, we are confident in its structural assignment as the spectral data, is very similar to that of **3.6**[3] which has been previously characterized by single crystal X-ray diffraction data in addition to NMR spectroscopy and mass spectrometry.[3]

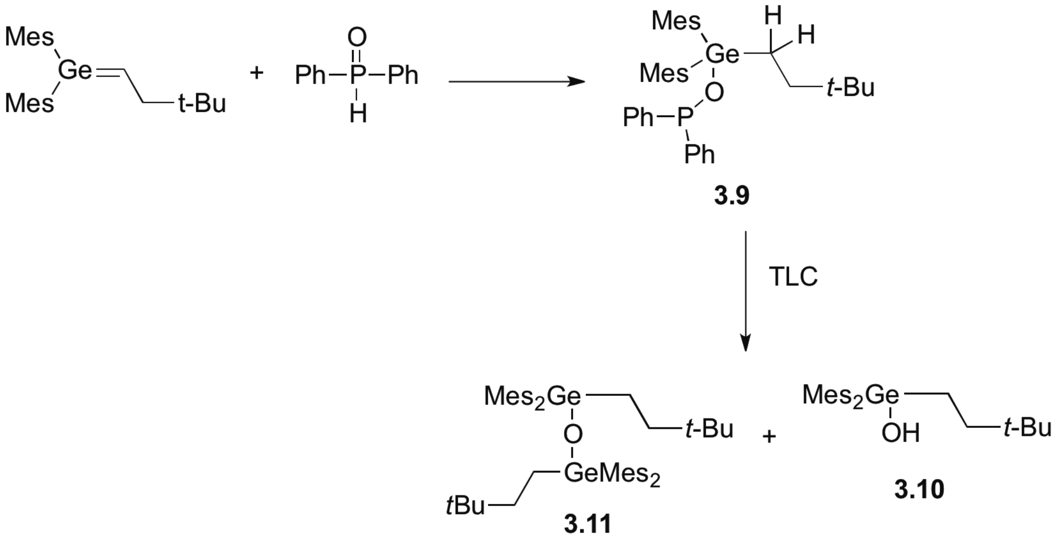


1.2 **3.8**

Scheme 3.6

3.2.2 Addition of Diphenylphosphine Oxide to Dimesitylneopentylgermene 1.1

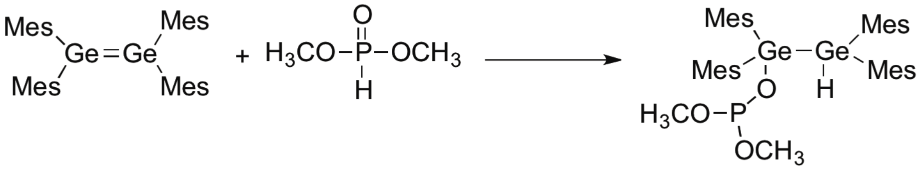
Treatment of an ethereal solution of germene **1.1** with diphenylphosphine oxide yielded compound **3.9**. The exact mass of the signal assigned to the molecular ion in the mass spectrum of **3.9** was determined to be at *m/z* 593.2348, which corresponds to a 1:1 adduct between diphenylphosphine oxide and germene **1.1**. The ^{1}H NMR spectrum of **3.9** showed one set of signals assigned to a mesityl group and a singlet at 0.76 ppm assigned to *t*-Bu moiety. The ^{1}H- ^{1}H gCOSY NMR spectrum of **3.9** revealed a correlation between the ^{1}H signals at 1.76-1.73 (2H) and 1.57-1.54 (2H). On the basis of the observed correlations, integrations, the multiplicity and chemical shifts of the signals, these signals were assigned to a CH_2-CH_2 group. Furthermore, the aromatic region of the ^1H NMR spectrum of **3.9** showed one set of signals assigned to two phenyl moieties, on the basis of the splitting patterns, chemical shifts, and the correlations observed by 2D NMR spectroscopy. The ^{31}P NMR spectrum of **3.9** revealed a signal at 101.35 ppm. In comparison, the ^{31}P NMR chemical shift of Ph-Si(OPPh$_2$)$_3$ is at 100.93 ppm (d_8-THF)[13] which is in close agreement with that of **3.9**. Taken together, these data lead to the assignment of the structure shown in **Scheme 3.7**. Attempted isolation of **3.9** by chromatography yielded germanol[9] **3.10** and digermoxane[9] **3.11**.



Scheme 3.7

3.2.3 Addition of Dimethyl Phosphite to Tetramesityldigermene 1.2

The addition of dimethyl phosphite to a C_6D_6 solution of tetramesityldigermene **1.2** at room temperature gave a pale yellow oil (**3.13**) upon removal of solvent (**Scheme 3.8**). The mass spectrum of **3.13** revealed a molecular ion at *m/z* 749.1962, which is consistent with a 1:1 adduct between digermene **1.2** and dimethyl phosphite. Two sets of signals assigned to two different mesityl groups were evident in both the ^{1}H and the ^{13}C NMR spectra of **3.13**. The ^{1}H NMR spectrum of **3.13** also revealed a singlet at 5.92 ppm that integrated to 1H which was assigned to the Ge-H hydrogen. In the ^{13}C- ^{1}H HMBC spectrum of **3.13**, a correlation between the signal assigned to the *ipso*-C of the Mes group in the ^{13}C dimension and the signal assigned to the hydrogen attached to germanium moiety was observed consistent with the assigned structure. Furthermore, the ^{1}H NMR spectrum of **3.13** contained a doublet at 3.32 ppm which was assigned to the methoxy groups. Accordingly, these signals correlate to two signals at 47.50 ppm and 47.48 ppm in the ^{13}C dimension of the ^{13}C-^{1}H gHSQC NMR spectrum of **3.13**. The IR spectrum of **3.13** revealed an absorption at 2921 cm^{-1} which was assigned to a Ge-H stretching vibration. The ^{31}P NMR spectrum of **3.13** showed only one signal at 138.31 ppm. Similarity, the ^{31}P NMR spectrum of $((CH_3O)_2PO)_2SiPh_2$ contains a signal at 126.2 ppm[14] in the region expected for tertiary phosphites.[15]

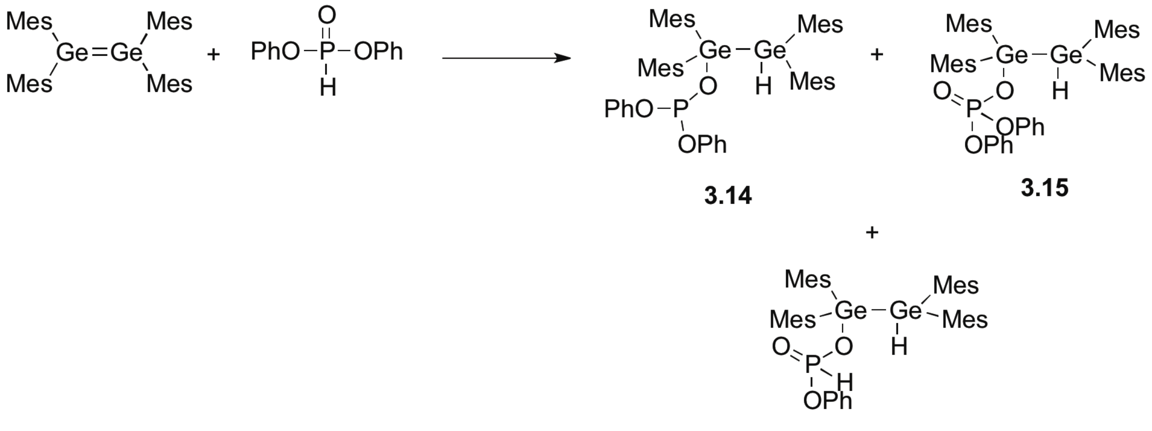


3.13

Scheme 3.8

3.2.4 Addition of Diphenyl Phosphite to Tetramesityldigermene 1.2

The product formed in the addition of excess diphenyl phosphite to digermene **1.2** appears to be analogous in structure to the product formed in the addition of dimethyl phosphite to the same digermene (**Scheme 3.9**). The ^{1}H NMR spectrum of **3.14** showed two sets of mesityl signals and a singlet at 5.95 ppm, which was assigned to a Ge-H bond. The high resolution mass spectral data, and the isotopic pattern of the signal assigned to the molecular ion, were consistent with the molecular formula, $C_{48}H_{55}O_3P^{70}Ge_2Na$ ($M+Na^+$) corresponding to a 1:1 adduct between tetramesityldigermene **1.2** and diphenylphosphosphite (plus a sodium ion). The ^{31}P NMR spectrum of **3.14** showed a singlet at 138.21 ppm which is in the expected chemical shift range of tertiary phosphines.[15] As an example, the ^{31}P NMR spectrum of $(PhO)_2P(OSiMe_3)$ revealed a signal at 123.3 ppm.[16]



Scheme 3.9

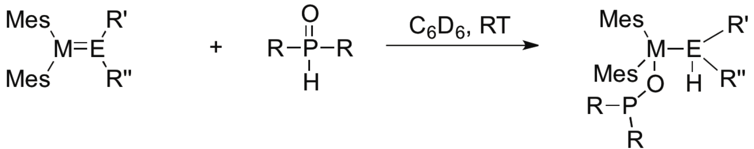
The crude product mixture contains a small amount of **3.15**, which was identified by ^{31}P NMR and ESI mass spectrometry. The ^{31}P NMR spectrum of **3.15** exhibits a singlet at 37.4 ppm which is more shielded (ca. 100 ppm) than that of **3.14**. The ^{31}P NMR chemical shift of **3.15** is close to that of $GeOP(=O)Ph_2$ (δ 19.90 ppm).[17] The high-resolution mass spectrum of **3.15** revealed a signal at *m/z* 797.1952 which is consistent with the molecular formula $C_{48}H_{55}O_4P^{72}Ge^{74}GeNa$ ($M+Na^+$). Upon attempted purification by chromatography, **3.14** oxidied completely to **3.15**. Therefore, adduct **3.14** was characterized without purification. Adduct **3.16** was also isolated upon chromatography. Given that the reagent, diphenyl phosphite, was not purified before use, adduct **3.16** may arise from addition of (PhO)HP=O(OH) to digermene **1.2**.

3.2.5 Addition of Trimethyl Phosphite to Tetramesityldigermene 1.2 and Tetramesityldisilene 1.3

The addition of trimethyl phosphite (TMP) to a solution of tetramesityldigermene (**1.2**) or tetramesityldisilene (**1.3**) did not result in the formation of an adduct; no reaction was observed.

3.3 Discussion

The results of the addition of the phosphorus oxides to disilene **1.3**, digermene **1.2**, or germene **1.1** are shown in the **Scheme 3.10**.

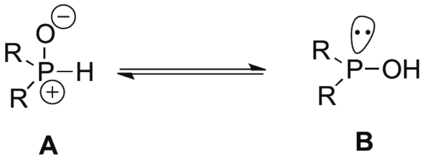


M = E = Ge, R' = R'' = Mes: **1.2**
M = E = Si, R' = R'' = Mes: **1.3**
M = Ge, E= C, R' = H, R'' = CH_2-*t*-Bu : **1.1**

M = E = Si, R' = R'' = Mes, R = Ph: **3.6**
M = E = Ge, R' = R'' = Mes, R = Ph : **3.8**
M = Ge, E= C, R' = H, R'' = CH_2-*t*-Bu, R = Ph : **3.9**
M = E = Ge, R' = R'' = Mes, R = OCH_3 : **3.13**
M = E = Ge, R' = R'' = Mes, R = OPh : **3.14**

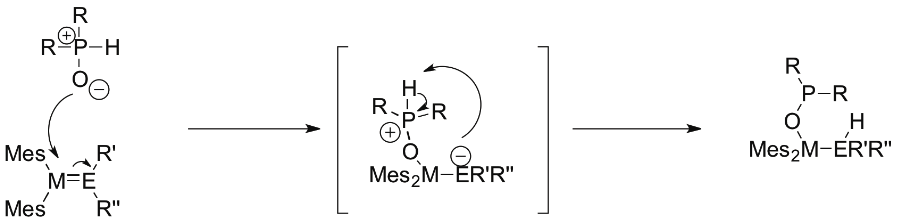
Scheme 3.10

Although phosphine oxides or phosphites were added to the (di)tetrelene, the products appear to be drived from the isomeric hydroxyphosphines. An equilibrium exists between the pentavalent and the trivalent phosphorus oxides[18]; diphenylphosphine oxide (**A**) is a weak acid and can tautomerize in solution to give hydroxydiphenylphosphine (**B**)[19] (**Scheme 3.11**).[20] When R= Ph, the equilibrium lies strongly in favour of diphenylphophine oxide **A** under neutral conditions.[21]



Scheme 3.11

Two mechanisms can be envisioned for the formation of **3.8**, **3.9**, **3.13,** and **3.14**; although both are quite similar. Recent investigations have concluded that the P=O bond is best described as a highly polarized, short, and strong ionic bond.[22] Accordingly, the addition of diphenylphosphine oxide or dialkyl phosphite **A** to the (di)germene may begin with nucleophilic attack by the oxygen in **A** on the germanium of digermene **1.2** or germene **1.1** to form a zwitterionic intermediate followed by hydrogen abstraction by the germyl anion and/or carbanion to generate the addition products. Alternatively, addition of hydroxydiphenylphosphine, and/or hydroxydialkylphosphite **B**, may begin with nucleophilic attack by the oxygen in **B** to the germanium of digermene **1.2** or germene **1.1** followed by abstraction of the hydrogen by the germyl anion or the carbanion to give the observed products. The same pathway has been postulated for the formation of adduct **3.6**.[3] The reactions may be concerted rather than stepwise. Although, it is unclear whether the (di)germene reacts with isomer **A** or **B**, in either case, the phosphorus is reduced from 5+ to 3+.

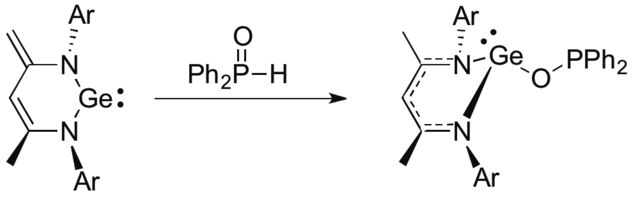


M = E = Ge, R' = R" = Mes: **1.2**
M = Ge, E= C, R' = H, R" = CH_2-*t*-Bu : **1.1**

M = E = Ge, R' = R" = Mes, R = Ph : **3.8**
M = Ge, E= C, R' = H, R" = CH_2-*t*-Bu, R = Ph : **3.9**
M = E = Ge, R' = R" = Mes, R = OCH_3 : **3.13**
M = E = Ge, R' = R" = Mes, R = OPh : **3.14**

Scheme 3.12

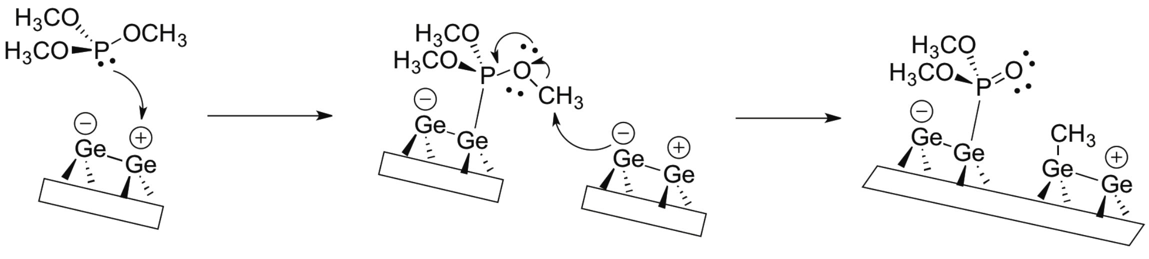
Notably, the addition of diphenylphosphine oxide to the N-heterocyclic germylene **3.16** afforded the direct 1,4-addition product **3.17** in relatively high yield (67%) where the phosphine oxide exhibits similar behavior (**Scheme 3.13**).[17] The structure of **3.17** has been unambigusly determined by X-ray crystallogrphy. Again, tricoordinated phosphorus(III) species is produced rather than the isomeric product ($N_2GeP(O)Ph_2$). Similarly, it was proposed that diphenylphosphine oxide undergoes intramolecular tautomerism during the reaction; the reactivity closely parallels that observed for the ditetrelenes.



3.16 **3.17**

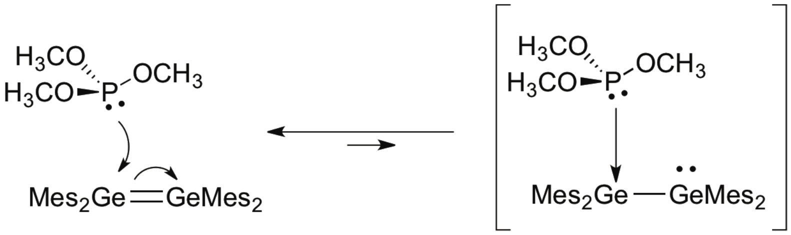
Scheme 3.13

The addition of trimethyl phosphite to digermene **1.2** and disilene **1.3** did not yield a product. Our findings are not consistent with the formation of the surface adduct **3.7** generated by the addition of trimethyl phosphite to the Ge(100) 2 × 1 reconstructed surface (**Scheme 3.5**).[7] Bent and coworkers provided a possible mechanism for the reaction of trimethyl phosphite at the Ge(100)-2 × 1 surface (**Scheme 3.14**). Surface digermenes have been shown to be tilted producing a zwitterionic species on the surface.[23] Adsorption of trimethyl phosphite to the surface dimer may occur by nucleophilic attack of the phosphorus at the electron-deficient Ge of the tilted surface dimer to form a Ge-P dative bond. Abstraction of a methyl group by the adjacent electron-rich germanium would give dimethyl germylphosphonate **3.18**. The difference in reactivity may be due to the difference in the electronic structure of a surface digermene compared to a molecular digermene or also be related to the geometry of substituents on the surface dimer compared to the molecular dimer. In contrast to the *trans*-bent geometry of the bulky mesityl substituents on digermene **1.2**,[24] the underlying germyl substituents on the surface dimers of the Ge(100)- 2 × 1 surface are *cis*-bent. The increased bulk of the substituents of digermene **1.2** as a result of its stabilizing ligands may prevent the formation of an adduct with trimethyl phosphite.



Scheme 3.14

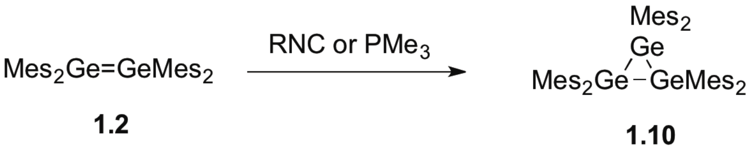
No evidence for a dimethyl germylphosphonate type adduct was observed in the addition of any phosphorus containing compounds to the molecular (di)tetrelenes. Considering the well-known nucleophilicity of phosphorus in phosphites, one can envisioned that the initial step may occur by coordination of the phosphorus to one of the germanium atoms of digermene **1.2** to give a germyl(germylene)-phosphite complex **3.19**. Given that we did not observe any adduct formation, we postulate that complex **3.19**, if formed, is in equilibrium with the reactants and the equilibrium lies more towards the free digermene **1.2** and the phosphite (**Scheme 3.15**).



3.19

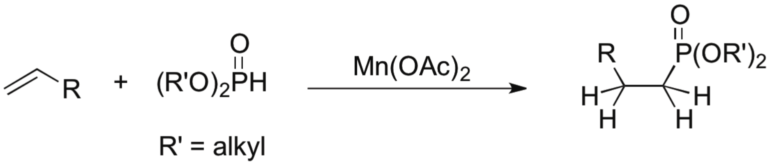
Scheme 3.15

The coordination of donor molecules to unsaturated heavier main group compounds is known. In this context, the addition of Me_3P to digermene **1.2** has been reported to accelerate the conversion of digermene **1.2** to hexamesitylcyclotrigermane **1.10**. [25] Similarly, the addition of 2,6-dimethylphenyl- or *tert*-butyl isocyanide to digermene **1.2** catalyzes the conversion of digermene **1.2** to cyclotrigermane **1.10** presumably through a donor interaction **(Scheme 3.16)**. [26] Trialkylphosphines are relatively weak bases but strong nucleophiles and are effective catalysts for many reactions in organic synthesis.[27] The proton affinities of the tervalent $P(CH_3)_3$ decreases with increasing electron-withdrawing ability of the substituents (ie. $P(OCH_3)_3$).[28] Pearson calculated relative reactivity parameters (or Swain– Scott parameters; termed *n*) to provide a nucleophilicity scale for phosphines.[27,29] On that basis, $P(OCH_3)_3$ ($n = 5.2$) is less nucleophilic than $P(CH_3)_3$ ($n = 8.7$). Therefore, $P(CH_3)_3$ is a better donor and the reactivity towards be digermene **1.2** can understood.



Scheme 3.16

It is interesting to compare the observed reactivity of (di)tetrelenes towards dialkyl phosphites with the chemistry of the analogous alkenes. Dialkyl phosphites and phosphine oxides add to alkenes to form a C-P bond and require the use of transition metal catalyst.[30] As an example, the hydrophosphorylation of alkenes with dialkyl phosphites catalyzed by species such as $Mn(OAc)_2$ led to the formation of dialkyl phosphonates (**Scheme 3.17**).[31] The reaction between dialkyl phosphites and alkenes is believed to proceed through radical process.



Scheme 3.17

In contrast, the addition of phosphorus oxides, $(RO)_2HP{=}O$ and/or $(R)_2HP{=}O$, to (di)tetrelenes proceeds rapidly without a catalyst or heat. The formation of the strong

M-O (M = Si, Ge) bond is thermodynamically favorable, and thus, the M-O bond is preferentially formed over the weaker M-P bond. Moreover, the phosphorus in the phosphine adducts **3.6**, **3.8**, **3.9**, **3.13,** and **3.14** has been reduced from the +5 to the +3 oxidation state. The use of (di)tetrelenes as reducing agents is not widespread. Other examples include the reduction of nitro compounds by ditetrelenes[2,3] where the nitrogen of the nitro moiety is reduced (**3.1** and **3.2**; **Scheme 3.1**), the addition of nitroalkanes (R= Me, Et) to germene **1.1** (Chapter **2**, **Scheme 2.9**), and the facile and clean reduction of sulfonyl chlorides (RSO_2Cl) by ditetrelenes[3] where the sulfur is reduced from the +6 to the +4 oxidation state (**Scheme 3.3**). Similarly, the sulfur in diphenyl sulfoxide (Ph_2SO) has an oxidation number of +4 and is reduced to +2 to diphenylsulfide through the reaction with the disilene **1.3** (**Scheme 3.13**).[3]

These reactions reveal a potential application of ditetrelenes as effective and selective reducing agents for main group oxides. The reductions occur rapidly and under mild conditions. Investigations into this aspect of the chemistry of (di)tetrelenes has not been explored extensively. This study has highlighted the theme of ditetrelenes as reducing agents which might bring new possibilities in organic/inorganic and organometallic synthesis.

3.4 Conclusions

The addition of phosphine oxide and phosphite compounds to tetramesityldigermene **1.2** and 1,1-dimesitylneopentylgermene **1.1** leads to the facile formation of the 1,2-addition products. We propose that the first step in these reactions is nucleophilic attack by the oxygen atom of either **A** or **B** to the germanium of **1.1** or **1.2** followed by hydrogen abstraction. Our findings parallel the results of a recent study of the reactivity of the analogous disilene **1.2** which also showed the formation of an 1,2-addition product.[3] The addition trimethyl phosphite to digermene **1.2** and disilene **1.3** did not give a product. Lack of reactivity reveals the limitations of using a molecular ditetrelene as a model for surface dimers as the different electronic structures lead to different reactions, in some cases. The formation of oxyphosphine compounds (**3.6, 3.8** and **3.9)** as well as the phosphite compounds (**3.13** and **3.14**) revealed an interesting, mild 2-electron reduction of the phosphorus centres using (di)tetrelenes. The addition reactions of phosphine oxide and phosphite compounds illustrate the potential use of (di)tetrelenes as effective reducing agents as the reductions occur rapidly, at room temperature and under mild conditions. Forming phosphorus(III) compounds via the addition of phosphorus(V) compounds by reaction of a (di)tetrelene represent a relatively simple, one step reaction under very mild conditions which does not require the use of heat or a catalyst.

3.5 Experimental

3.5.1 General Experimental Details

All manipulations were performed in flame-dried Schlenk tubes, or NMR tubes sealed with a septum under an inert atmosphere of argon. Benzene-d_6 was distilled from $LiAlH_4$, stored over 4 Å molecular sieves, and degassed prior to use. All reagents were purchased from the Aldrich Chemical Co. and were used as received. Tetramesityldigermene[10] and 1,1-dimesitylneopentylgermene[9] were synthesized prior to each reaction in quantitative yield and used in *situ* without purification. $Mes_2Ge(F)CH{=}CH_2$,[32] and Ge_3Mes_6[33] and $(Me_3Si)_2SiMes_2$[11] were synthesized according to the literature procedure. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian INOVA 600 MHz spectrometer (^{1}H 600 MHz, ^{13}C{^{1}H} 151 MHz). Samples for ^{1}H NMR spectroscopy were referenced to the residual protons in the deuterated solvent relative to tetramethylsilane (C_6D_5H; ^{1}H δ = 7.15 ppm). The chemical shifts for ^{31}P{H} NMR spectroscopy were referenced using an external standard (85% H_3PO_4: δ = 0.0 ppm). Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). IR spectra were recorded (cm^{-1}) from thin films on a Bruker Tensor 27 FT-IR spectrometer and absorptions are reported in cm^{-1}. Electrospray ionization mass spectra were recorded on a Bruker micrOTOF II mass spectrometer. Mass spectral data are reported in mass-to-charge units, *m/z*.

3.5.2 Addition of Diphenylphosphine Oxide to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.05 g, 0.05 mmol) was placed in a quartz tube[a] and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 °C for ~18 h to give yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The THF was evaporated and the residue was dissolved in C_6D_6 (1 mL). Diphenylphosphine oxide (0.02 g, 0.12 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir. The solution decolourized after 3-4 minutes. The benzene was evaporated to give a white powder (0.08 g, 72%). Compound **3.8** was contaminated with diphenylphosphine oxide.

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[a] A quartz tube and Dewar were used but a Pyrex Dewar can be used instead.

3.8: white powder; ^{1}H NMR (C_6D_6, 600 MHz) δ 7.64 (t, *J* = 7.2 Hz, 4H, Ph *o*-H), 7.08 (t, *J* = 7.8 Hz, 4H, Ph *m*-H), 7.01-6.99 (m, 2H, Ph *p*-H), 6.68 (s, 4H, Mes *m*-H), 6.63 (s, 4H, Mes *m*-H), 5.97 (s, 1H, Ge-H), 2.329, 2.325 (each s, 24H total, Mes *o*-CH_3), 2.064, 2.059 (each s, 12H total, Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 151 MHz) δ 147.06 (d, *J* = 24 Hz, Ph *i*-C), 144.01 (Mes *o*-C), 143.17 (Mes *o*-C), 139.07 (Mes *p*-C), 138.31 (Mes *i*-C and *p*-C), 134.99 (Mes *i*-C), 133.75 (Ph *i*-C), 130.89 (m, Ph *o*-CH), 129.68 (d, *J* = 4.7 Hz, Mes *m*-CH), 128.96 (d, *J* = 5.7 Hz, Mes *m*-CH), 128.63 (Ph *p*-CH), 128.12 (Ph *m*-CH), 25.23 (br, Mes *o*-CH_3), 24.62 (br, Mes *o*-CH_3), 20.98 (br, Mes *p*-CH_3); ^{31}P (C_6D_6, 162 MHz) δ 104.69 ppm; FTIR (thin film, cm^{-1}) 2917 (m), 2024 (m), 1600 (m), 1555 (m), 1436 (s), 1290 (w), 1186 (s), 1122 (m), 1026 (m), 952 (m), 845 (s), 737 (s), 693 (s); high resolution ESI-MS *m/z* for $C_{48}H_{55}OP^{70}Ge_2$ (M+Na) Calc. 841.2373, found 841.2398.

3.5.3 Addition of Diphenylphosphine Oxide to 1,1-Dimesitylneopentylgermene 1.1

tert-Butyllithium (1.7 M in pentane, 0.15 mL, 0.26 mmol) was added to a solution of **1.9** (100 mg, 0.28 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and solvent was removed under vacuum to give an orange solid. The solid was transferred to the glove box and dissolved in C_6D_6 (1mL). Diphenylphosphine oxide (0.05 g, 0.28 mmol) was added to the solution. The solvent was evaporated to give a clear, colourless oil (0.72 g, 85%) containing **3.9**, $Ph_2PH{=}O$, $Mes_2Ge(OH)CH_2CH_2$*t*-Bu and an unknown in a 1:0.08:0.2 ratio. Attempts were made to purify **3.9** by thin-layer chromatography (60:40 DCM/hexanes); however, only $Mes_2Ge(OH)CH_2CH_2$-*t*-Bu[32a] was isolated from the plate.

3.9: ^{1}H NMR (C_6D_6, 600 MHz) δ 7.64 (t, *J* = 7.8 Hz, 4H, Ph *o*-H), 7.09 (t, *J* = 7.2 Hz, 4H, Ph *m*-H), 7.03-7.00 (m, 2H, Ph *p*-H), 6.67 (s, 4H, Mes *m*-H), 2.45 (s, 12H, Mes *o*-CH_3), 2.06 (s, 6H, Mes *p*-CH_3), 1.76-1.73 (m, 2H, CH_2), 1.57-1.54 (m, 2H, CH_2), 0.76 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6, 151 MHz) δ 146.54 (d, *J* = 23 Hz, Ph *i*-C), 142.95 (Mes *o*-C), 139.14 (Mes *p*-C), 135.41 (d, *J* = 3.5 Hz, Mes *i*-C), 130.64 (Ph *o*-CH), 129.58 (Mes *m*-CH), 128.75 (Ph *p*-CH), 128.24 (Ph *m*-CH), 38.47 ($\underline{C}H_2$-*t*-Bu), 31.14 ($\underline{C}(CH_3)_3$), 28.81 ($C(\underline{C}H_3)_3$), 23.80 (br s, Mes *o*-CH_3), 20.98 (br s, Mes *p*-CH_3), 20.07 (Ge-CH_2); ^{31}P (C_6D_6,162 MHz) δ 101.35 ppm; high resolution ESI-MS *m/z* for $C_{36}H_{44}OP^{70}Ge$ ($M+H^+$) Calc. 593.2372, found 593.2348.

3.5.4 Addition of Dimethyl Phosphite to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.03 g, 0.03 mmol) was placed in a quartz tube and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 °C for ~18 h to give yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The THF was evaporated and the residue was dissolved in C_6D_6 (1 mL). Dimethyl phosphite (0.007 g, 0.06 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir. The solution changed from dark yellow to slightly pale yellow after 30 minutes. The benzene was evaporated to give pale yellow oil (0.02 g, 52%).

3.13: pale yellow oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 6.73 (s, 4H, Mes *m*-H), 6.66 (s, 4H, Mes *m*-H), 5.92 (s, 1H, Ge-H), 3.32 (d, *J* = 11 Hz, 3H, O-CH_3), 2.45 (s, 12H, Mes *o*-CH_3), 2.39 (s, 12H, Mes *o*-CH_3), 2.08 (s, 6H, Mes *p*-CH_3), 2.08 (s, 6H, Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 151 MHz) δ 144.17 (Mes *o*-CH_3), 143.09 (Mes *o*-CH_3), 139.15 (Mes *p*-C), 138.47 (Mes *p*-C), 137.76 (Mes *i*- C), 134.60 (Mes *i*-C), 129.70 (Mes *m*-CH), 129.02 (Mes *m*-CH), 47.50 (O-CH_3), 24.91 (Mes *o*-CH_3), 24.04 (Mes *o*-CH_3), 21.01 (Mes *p*-CH_3), 20.96 (Mes *p*-CH_3); ^{31}P (C_6D_6, 162 MHz) δ 138.31 ppm; FTIR (thin film, cm^{-1}) 2920 (m), 1734 (m), 1449 (m), 1170 (m), 1092 (m), 1037 (s), 924 (m), 848 (m), 731 (m), 546 (m); high resolution ESI-MS *m/z* for $C_{38}H_{51}O_3P^{70}Ge_2Na$ ($M+Na^+$) Calc.749.1959, found 749.1962.

3.5.5 Addition of Diphenyl Phosphite to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.06 g, 0.06 mmol) was placed in a quartz tube and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 °C for ~18 h to give yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The THF was evaporated and the residue was dissolved in C_6D_6 (2 mL). Diphenylphosphine oxide (0.03 g, 0.14 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir for 24 hours. The colour of the solution changed gradually from dark yellow to bright yellow. The benzene was evaporated to give a pale yellow oil (110 mg, 97%) which contained **3.14**, $Mes_2Ge(OH)Ge(H)Mes_2$ in a ratio of 1: 0.3 and possibly **3.15**[b]. The crude product was purified by thin-layer chromatography (80:20 DCM/hexanes) to yield **3.14** as a clear, colourless oil (0.01 g, 9%), adduct **3.15** (0.03 g, 21%) and **3.16** which was contaminated with $Mes_2Ge(OH)Ge(H)Mes_2$ and $(PhO)_2P(=O)H$ in a 1: 0.2: 1.5 ratio.

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[b] The presence of adduct **3.15** in crude mixture is based on the ^{31}P NMR spectrum, ESI-MS data and the FT-IR spectrum.

3.14: clear oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 7.12-7.09 (m, 4H, Ph *o*-H)[c], 7.01-7.00 (m, 4H, Ph *m*-H)[c], 6.85-6.78 (m, 2H, Ph *p*-H)[c], 6.69 (s, 4H, Mes *m*-H), 6.63 (s, 4H, Mes *m*-H), 5.95 (s, 1H, Ge-H), 2.44 (br s, 12H, Mes *o*-CH_3), 2.38 (br s, 12H, Mes *o*-CH_3), 2.06 (br s, 6H, Mes *p*-CH_3), 2.04 (br s, 6H, Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 151 MHz) δ 153.53 (d, J = 5.7 Hz, Ph *i*-C), 144.14 (Mes *o*-C), 143.02 (Mes *o*-C), 139.39 (Mes *p*-C), 138.60 (Mes *p*-C), 137.58 (Mes *i*-C), 134.17 (br Mes *o*-C), 129.81 (br, Mes *m*-C), 129.70 (Ph, *o*-C), 129.58 (Ph *m*-C), 129.07 (br, Mes *m*-C), 124.41 (Ph *p*-C)[d], 24.86 (br, Mes *o*-CH_3), 24.14 (br Mes *o*-CH_3), 20.98 (Mes, *p*-CH_3) , 20.93 (Mes *p*-CH_3); ^{31}P (C_6D_6,162 MHz) δ 138.18 ppm; FTIR (thin film, cm^{-1}) 3322 (w); high resolution ESI-MS *m/z* for $C_{48}H_{55}O_3P^{70}Ge_2Na$ (M+Na$^+$) Calc. 873.2272, found 873.2249.

3.15: clear, colourless oil: ^{1}H NMR (C_6D_6, 600 MHz) δ 7.08-7.06 (m, 4H, Ph *o*-H), 6.69-6.89 (m, 4H, Ph *m*-H), 6.78-6.76 (m, 2H, Ph *p*-H), 6.69 (s, 4H, Mes *m*-H), 6.65 (s, 4H, Mes *m*-H), 6.23 (d, J = 36.6 Hz, 1H, Ge-H), 2.47 (s, 12H, Mes *o*-CH_3), 2.45 (br s, 12H, Mes *o*-CH_3), 2.07 (s, 6H, Mes *p*-CH_3), 2.05 (s, 6H, Mes *p*-CH_3); ^{13}C NMR δ (C_6D_6, 151 MHz) 151.70 (d, J = 15 Hz, Ph *i*-C), 144.18 (br, Mes *o*-C), 138.91 (Mes *p*-C), 138.50 (Mes *p*-C), 135.2 (br, Mes *i*-C), 135.00 (br, Mes *i*-C), 129.80 (br, Mes *m*-C), 129.36 (Ph *m*-C), 129.23 (br, Mes *m*-C), 124.43 (Ph *p*-C), 121.57 (d, J = 3.5 Hz, Ph, *o*-C), 25.49 (Mes *o*-CH_3), 24.72 (br, Mes *o*-CH_3), 20.98 (br, Mes, *p*-CH_3) , 20.85 (Mes *p*-CH_3); ^{31}P (C_6D_6, 243 MHz) δ 37.23 ppm; high resolution ESI-MS *m/z* for $C_{48}H_{55}O_4P^{72}Ge^{74}Ge$ (M+Na$^+$) Calc. 895.2168, found 895.2177.

3.16: ^{1}H NMR (C_6D_6, 600 MHz) δ 7.11 (d, 1H, J = 690 Hz, P-H), 7.07-7.06 (m, Ph *o*-H), 6.97 (t, J = 8.4 Hz, 2H, Ph *m*-H), 6.82-6.80 (m, Ph *p*-H), 6.685, 6.690 (each s, 4H total,

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[c] These assignments are tentative.

[d] These assignments are tentative

Mes *m*-H), 6.62 (s, 2H, Mes *m*-H), 6.61 (s, 2H, Mes *m*-H), 5.97 (d, *J* = 2.4 Hz, 1H, Ge-H), 2.414, 2.411 (each s, 12H total, Mes *o*-CH_3), 2.33 (br s, 12H, Mes *o*-CH_3), 2.066, 2.062 (each s, 6H total, Mes *p*-CH_3), 2.02 (s, 6H, Mes *p*-CH_3); ^{13}C NMR δ (C_6D_6, 151 MHz) 151.0 (br, Ph *i*-C), 143.70 (Mes *o*-C), 143.63 (Mes *o*-C), 142.61 (Mes *o*-C), 142.55 (Mes *o*-C), 139.56 (Mes *p*-C), 139.55 (Mes *p*-C), 138.59 (2 × Mes *p*-C), 136.08 (Mes *i*-C), 136.02 (Mes, *i*-C), 133.18 (Mes *i*-C), 133.03 (Mes *i*-C), 129.62 (Mes *m*-C), 129.58 (Mes *m*-C), 129.43 (Ph *m*-C), 128.89 (br, 2 × Mes *m*-C), 120.37 (Ph *o*-C), 115.44 (Ph *p*-C)[c], 24.33 (Mes *o*-CH_3), 23.46 (br, Mes *o*-CH_3), 20.62 (br, Mes *p*-CH_3); ^{31}P (C_6D_6, 243 MHz) δ -17.27 ppm.

3.5.6 Addition of Trimethyl Phosphite to Tetramesityldisilene 1.3

$Mes_2Si(SiMe_3)_2$ (100 mg, 0.24 mmol) was placed in a quartz tube and dissolved in hexanes (5 mL) and the solution was irradiated (λ = 254 nm) in a quartz Dewar at -60 °C for ~18 h. The hexanes were evaporated; a yellow solid was obtained, then dissolved in C_6D_6 (2 mL). Trimethyl phosphite (0.03 g, 0.24 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir for at least 24 h. The reaction was monitored by ^1H NMR spectroscopy; no reaction was observed.

3.5.7 Addition of Trimethyl Phosphite to Tetramesityldigermene 1.2

Ge_3Mes_6 (0.05 g, 0.05 mmol) was placed in a quartz tube and dissolved in THF (5 mL) and irradiated (λ = 350 nm) in a quartz Dewar at -60 °C for ~18 h to give yellow solution. The solution was cooled during the irradiation by circulating cold methanol in the quartz Dewar. The THF was evaporated and the residue was dissolved in C_6D_6 (1 mL). Trimethyl phosphite (0.01 g, 0.12mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir at least 24 h. The reaction was monitored by ^{1}H NMR spectroscopy; no reaction was observed.

3.6 References

1. For selected recent reviews and papers on reactivity of group 14 (di)tetrelene: (a) Tashkandi, N. Y.; Cook, E. E; Bourque, J. L; Baines, M. K. *Chem. Eur. J.* **2016**, *22*, 14006; (b) Milnes, K. K.; Pavelka, L. C.; Baines, K. M. *Chem. Soc. Rev.* **2016**, *45*, 1019; (c) Farhadpour, B.; Guo, J.; Pavelka, L. C.; Baines, K. M. *Organometallics* **2015**, *34*, 3748; (d) Hardwick, J. A.; Baines, K. M. *Chem. Eur. J.* **2015**, *21*, 2480; (e) Hardwick, J. A.; Pavelka, L. C.; Baines, K. M. *Dalton Transactions* **2012**, *41*, 609; (f) Scheschkewitz, D. *Chem. Lett.* **2011**, *40*, 2; (g) Allan, C. J.; Reinhold, C. R. W.; Pavelka, L. C.; Baines, K. M. *Organometallics* **2011**, *30*, 3010.

2. Tashkandi, N. Y.; Parsons, F.; Guo, J.; Baines, K. M. *Angew. Chem. Int. Ed.* **2015**, *54,* 1612.

3. Tashkandi, N. Y. Cycloaddition Reactions of (Di)tetrelenes ,The University of Western Ontario, **2016**.

4. El Kettani, S.; Lazraq, M.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Gornitzka, H.; Atmani, A. *Organometallics* **2005**, *24*, 5364.

5. Coyle, E. E.; O'Brien, C. J. *Nat. Chem.* **2012**, *4*, 779; (b) Bayne, J. M.; Stephan, D. W. *Chem. Soc. Rev.* **2016**, *45*, 765; (c) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134*, 11330.

6. Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992.

7. Wong, K. T.; Shong, B.; Sun, W.; Bent, S. F. *J. Phys. Chem. C* **2013**, *117*, 26628.

8. (a) Hardwick, J. A.; Pavelka, L. C.; Baines, K. M. *Dalton Trans.* **2012**, *41*, 609; (b) Hurni, K. L.; Baines, K. M. *Chem. Comm.* **2011**, *47*, 8382; (c) Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics* **2007**, *26*, 5569; (d) Gottschling, S. E.; Milnes, K. K.; Jennings, M. C.; Baines, K. M. *Organometallics* **2005**, *24*, 3811; (e) Gottschling, S. E.; Jennings, M. C.; Baines, K. M. *Can. J. Chem.* **2005**, *83*, 1568; (f) Samuel, M. S.; Baines, K. M. *J. Am Chem. Soc.* **2003**, *125*, 12702; (g) Samuel, M. S.; Jenkins, H. A.; Hughes, D. W.; Baines, K. M. *Organometallics* **2003**, *22*, 1603.

9. Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.

10. K. L. Hurni, P. A. Rupar, N. C. Payne, K. M. Baines, *Organometallics* **2007**, *26***,** 5569.

11 . Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *Organometallics* **1984,** *3*, 793.

12. Morgalyuka, V. P.; Strelkovaa, T. V.; Nifant'eva, E. E.; Brel, V. K. *Phosphorus, Sulfur, and Silicon* **2016**, *191*, 1462.

13. Alicia Aloisi, A.; Berthet, J. C.; Pierre Thuéry, C. G.; Cantat, T. *Dalton Trans.* **2016**, *45*, 14774.

14. Kee, T. P.; Patel, M. T. *Polyhedron* **1992**, *11*, 135.

15. Gorenstein, D. G. *Phosphorus-31 NMR: Principles and Applications*, **1984**, Academic Press, New York, Chapter. 18.

16. Chojnowski, J.; Cypryk, M.; Michalski, J. *J. Org.Chem.* **1981**, *215*, 355.

17. Wu,Y.; Liu, L.; Su, J.; Yan, K.; Wang, T,; Zhu, J.; Gao, X,; Gao,Y.; Zhao, Y. *Inorg. Chem.* **2015**, *54*, 4423.

18. Shaikh, T. M.; Weng, C.-M.; Hong, F.-E. *Coord. Chem. Rev.* **2012**, *256* (9−10), 771.

19. Grayson, M.; Farley, C. E.; Streuli, C. A. *Tetrahedron* **1967**, *23,* 1065

20. Chatt, J.; Heaton, B. T. *J. Chem. Soc. A* **1968**, 2745.

21. Dixon, K. R.; Rattray, A. D. *Can. J. Chem.* **1971**, *49*, 3997.

22. D. B. Chesnut, *J. Phys. Chem. A* **2003**, *107*, 4307.

23. Kachian, J. S.; Wong, K. T.; Bent, S. F. *Acc. Chem. Res.* **2010**, *43*, 346.

24. Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics* **2007**, *26*, 5569.

25. Rupar, P. A. Intermolecular Complexes of Germanium (II), The University of Western Ontario, **2009**.

26. Tashkandi, N. Y.; Cook, E. E.; Bourque, J. L.; Baines, K. M. *Chem. Eur. J.* **2016**, *22*, 14006.

27. Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035.

28. Hodges, R. V.; McDonnell, T. J.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102 (4)*, 1327.

29. Rahman, M. M.; Liu, H. –Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics*, **1989**, *8*, 1.

30. Queffelec, C.; Petit, M.; Janvier, P.; Knight, D. A.; Bujoli, B. *Chem. Rev.* **2012**, *112*, 3777.

31 . Tayama, O.; Nakano, A.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.*, **2004**, *69*, 5494.

32. (a) Couret, C.; Escudié, J.; Delpon-Lacaze,G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.; (b) Farhadpour, B.; Guo, J.; Pavelka, L.C.; Baines, K. M. *Organometallics* **2015**, *34*, 3748.

33. Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics* **2007**, *26*, 5569.

Chapter 4

4 Addition of Organometallic Reagents to a Stable Silene and Germene[a]

4.1 Introduction

After a quarter century of active research on the synthesis, characterization and reactivity of silenes[1,2] applications of this chemistry are now being explored in diverse areas such as organic synthesis,[1f, 3] polymer chemistry,[4,5] and materials science.[6,7] Pertinent to these applications is the study of the reactivity of silenes toward organometallic reagents for the purpose of creating new Si-C bonds to either increase functionality in molecular compounds for applications in synthesis or materials chemistry or to initiate anionic polymerizations. However, there are, for the most part, only isolated reports on the addition of organometallic reagents to silenes and, furthermore, the types of substrates and conditions of the reactions are quite variable.

The reactions of Grignard reagents with stable Brook-type silenes ($(Me_3Si)_2Si{=}(OSiMe_3)R$) are complicated by the lability of the trimethylsilyl group[8] and the addition of MeLi/MgBr or *t*-BuLi to transient 1,1-dialkylsilenes often leads to side products due to loss or migration of hydride.[9,10] In one instance, Ishikawa was able to isolate the simple products of addition (after hydrolysis of the initially formed organometallic adducts) of 1,1-dialkylsilenes in low yield (20-40%, GPC yields): MeLi

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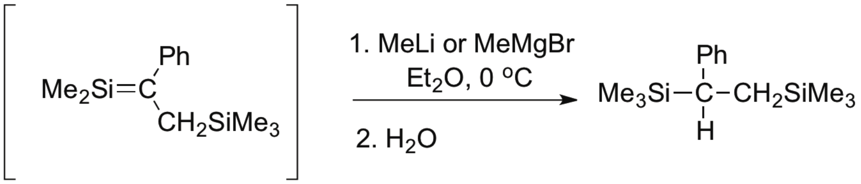
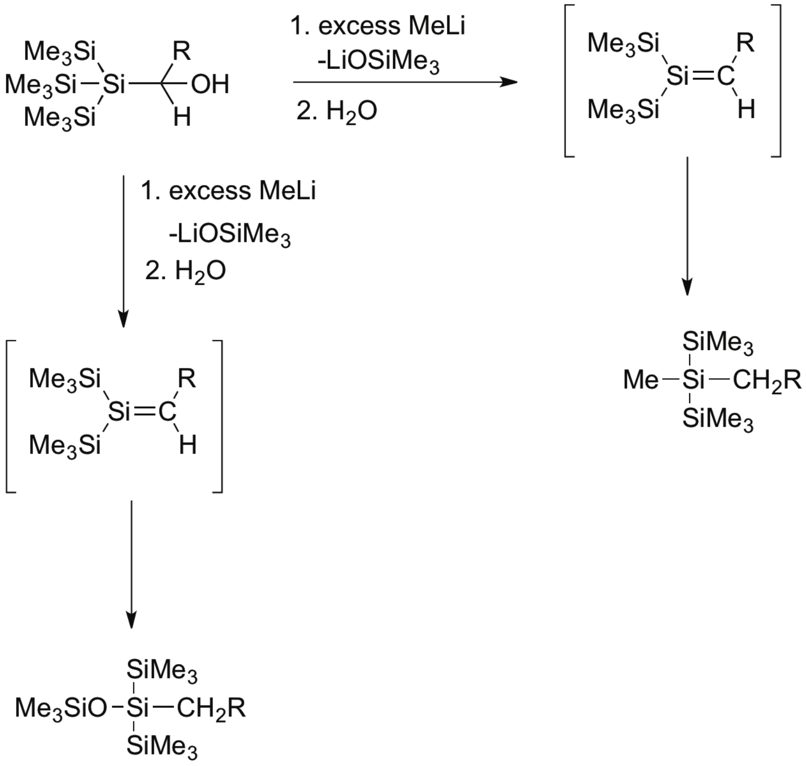
[a] A version of chapter 4 has been published. Farhadpour, B.; Guo, J.; Pavelka, L.C.; Baines, K. M. Addition of Organometallic Reagents to a Stable Silene and Germene. *Organometallics* **2015**, *34*, 3748.

(or MeMgBr) added to the transient $Me_2Si{=}CPh(CH_2SiMe_3)$ regioselectively with the organic group adding to the silicon atom of the silene (**Scheme 4.1**).[9]

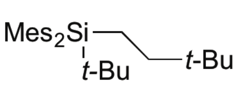


Scheme 4.1[9]

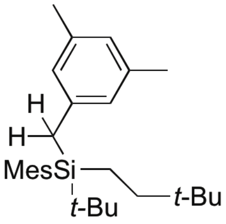
The most extensive study of the addition of organometallic reagents to silenes to date was reported by Oehme. His group studied the addition of organometallic reagents to transient 1,1-bis(trimethylsilyl)silenes ($(Me_3Si)_2Si{=}CR_2$), generated by Petersen elimination of the corresponding carbinols upon treatment with organolithium reagents.[11,12,13,14,15] In most cases, the excess organolithium reagent or the released lithium silanolate adds regioselectively to the silicon of the transient silene to give 1,2-additon products in moderate to good yields after hydrolysis (**Scheme 4.2**), although, on occasion, migration of the silyl substituents was observed.[14] Only a few studies of the addition of organometallic reagents to stable, naturally polarized silenes have been reported. When excess *t*-BuLi was added to 1,1-dimesitylneopentylsilene ($Mes_2Si{=}CHCH_2$*t*-Bu, **1.4**)[16] in diethyl ether at 0 °C quantitative and regioselective formation of Mes_2Si(*t*-Bu)CH_2CH_2*t*-Bu (**4.1**), was observed.[5] Interestingly, at room temperature in diethyl ether, a rearrangement took place to give **4.2** (**Chart 4.1**).[5] In contrast, the addition of excess *t*-BuLi to 1,1-dimesitylneopentylgermene ($Mes_2Ge{=}CHCH_2$*t*-Bu, **1.1**) at room temperature in diethyl ether gave Mes_2Ge(*t*-Bu)CH_2CH_2*t*-Bu regioselectively;[17] no evidence for any rearrangement was noted. Alternatively, when excess *t*-BuLi was added to silene **1.4** or germene **1.1** dissolved in pentane, polymeric material was formed in each case rather than simple addition products.[5,18]



Scheme 4.2[11-15]



4.1



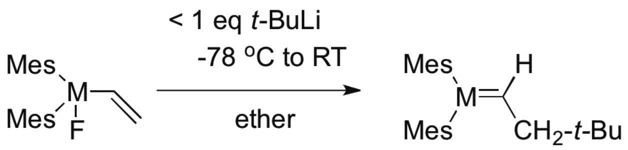
4.2

Chart 4.1

Given the potential usefulness of the addition of organometallic reagents to silenes in synthesis and materials chemistry, we wished to examine the reaction under a consistent set of reaction conditions to determine if addition products could reliably be obtained in good yields. Therefore, the addition of a variety of organometallic reagents to the solution-stable silene $Mes_2Si{=}CHCH_2t$-Bu, **1.4**, in diethyl ether at room temperature is reported and, for comparison purposes, we have also examined the addition of the same organometallic reagents to the analogous solution-stable germene, $Mes_2Ge{=}CHCH_2t$-Bu, **1.1**. We selected diethyl ether as the solvent since we previously reported that the addition of *t*-BuLi to **1.4** or **1.1** in a hydrocarbon solvent, pentane, leads to the formation of polymers. Given the well-known stability of aryl- and silyl-substituted silyl (or germyl) anions, we have always been intrigued by the *exclusive* regioselectivity of the isolated reports on the addition of organometallic reagents to transient and stable silenes and wished to determine if the same regiochemistry persisted with germenes as well. Finally, the addition of *t*-BuLi to the stable silene **1.4** has been re-examined in an effort to understand the different chemistry observed at low (0 °C) and at room temperature in diethyl ether.

4.2 Results and Discussion

Silene **1.4**[16] and germene **1.1**[17] were synthesized by the addition of *t*-BuLi to fluorodimesitylvinylsilane (**4.3**) or –germane (**1.9**) in diethyl ether in the cold (Dry Ice/acetone) prior to each reaction and used *in situ* without purification (**Scheme 4.3**).



4.3: M= Si
1.9: M= Ge

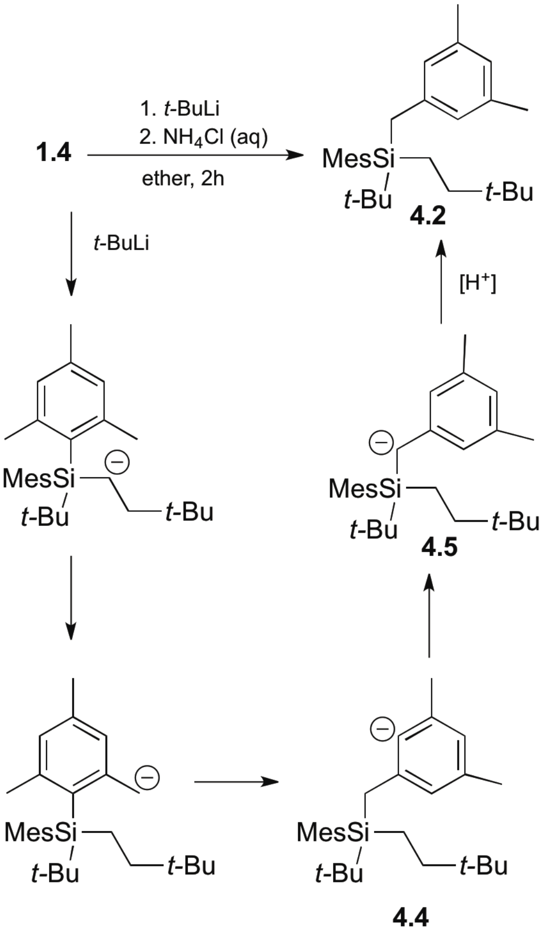
1.4: M= Si
1.1: M= Ge

Scheme 4.3

We have improved the overall yield for the synthesis of the precursor germane **1.9** from approximately 50%[17,19] to approximately 84% by synthesizing difluorodimesitylgermane, the required starting material for the synthesis of **1.9**, in one step from dichlorodimesitylgermane using silver tetrafluoroborate rather than in two steps via dimesityldimethoxygermane. Germane **1.9** is then made from the addition of vinylmagnesium bromide to Mes_2GeF_2 according to the published procedure.[17] As a precaution, slightly less than 1 equiv of *t*-BuLi was used in the addition of *t*-BuLi to fluorovinylsilane **4.3** (or -germane **1.9**) to prevent polymerization of the tetrelene. After addition of the organometallic reagent to the tetrelene and quenching of the reaction mixture with methanol, all products were purified by preparative thin layer chromatography and characterized by IR and NMR spectroscopy and mass spectrometry.

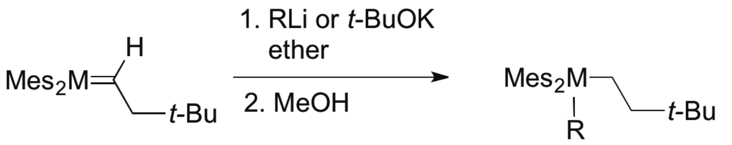
As previously reported, to prepare $Mes_2Si(t\text{-}Bu)CH_2CH_2t\text{-}Bu$, **4.1**, the addition of *t*-BuLi to silene **1.4** was performed in cold diethyl ether (0 °C); however, at room temperature, the isomeric *t*-butylsilane **4.2** was produced quantitatively (**Chart 4.1**).[5] We reasoned that the initial α-silyl anion, formed by the regioselective addition of *t*-butyllithium to silene **1.4**, removed a proton from an *o*-methyl group of the mesityl substituent to form a benzylic anion, followed by a 1,3-silyl shift to form intermediate **4.4**

(**Scheme 4.4**). Anion **4.4** could abstract a hydrogen to form the more stable benzylic, α-silyl substituted anion **4.5**. To test the validity of the hypothesis and to unequivocally determine the identity of the anion in solution immediately prior to quenching (i.e. **4.4** or **4.5**), the reaction of silene **1.4** with excess *t*-butyllithium in diethyl ether at room temperature was quenched with D_2O; silane **4.2** was isolated with a deuterium at the benzylic position (**4.2D**). The ^{1}H NMR spectrum of **4.2** contained an AB spin system (J = 15 Hz) at 2.61 ppm and 2.65 ppm, which was assigned to the inequivalent hydrogens of the benzyl moiety.[5] The AB pattern was not apparent in the ^{1}H NMR spectrum of **4.2D** and only a singlet was observed at approximately the same chemical shift (2.65 ppm). The ^{2}H NMR spectrum of **4.2D** also revealed a signal at 2.60 ppm. The results demonstrate that **4.5** is indeed the anion quenched in the reaction. The strain around silicon is likely the major driving force for the rearrangement. Conversely, the previously reported addition of *t*-BuLi to germene **1.1** in diethyl ether at room temperature does not yield any rearrangement products. Undoubtedly, the longer bonds to germanium ease the steric strain around the central metalloid, and thus, the driving force for rearrangement is diminished. We hypothesized that the use of less bulky organometallic reagents, such as MeLi, BuLi, and even *t*-BuOK, may avoid rearrangement at room temperature by relieving the congestion at silicon in the initially formed anion.



Scheme 4.4

The addition of MeLi, BuLi, or *t*-BuOK to silene **1.4** or germene **1.1** in diethyl ether results in the regioselective formation of simple 1,2-addition products which, after treatment with a weak acid, gave the corresponding silanes **4.6-4.8** or germanes **4.9-4.11**, respectively, in good to excellent yields (**Scheme 4.5**). Silanes **4.6-4.8** and germanes **4.9-4.11** were the *only* products derived from the tetrelenes isolated.



1.4: M = Si
1.1: M = Ge

4.6: M = Si, R = Me
4.7: M = Si, R = Bu
4.8: M = Si, R = O*t*-Bu
4.9: M = Ge, R = Me
4.10: M = Ge, R = Bu
4.11: M = Ge, R = O*t*-Bu

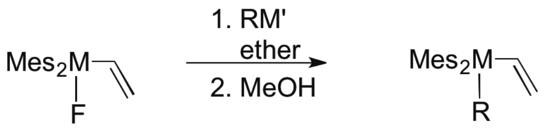
Scheme 4.5

No rearrangement products were observed in the reactions in contrast to the addition of organometallic reagents to some 1,1-bis(trimethylsilyl)silenes[8,14] or the addition of *t*-BuLi to the same silene (**1.4**) at room temperature. The lack of rearrangement in the systems studied here is likely because of the absence of substituents which readily migrate, such as a silyl group. Although the previously reported addition of *t*-BuLi to silene **1.4** did result in the formation of a rearranged product (**4.2**),[5] our results now demonstrate that such a rearrangement can easily be avoided by the use of less sterically demanding organometallic reagents which supports our earlier hypothesis that the driving force of the rearrangement to give **4.2** is indeed the relief of steric strain about the silicon.

Polysilane or polygermane were also not formed in the addition of MeLi, BuLi or *t*-BuOK to silene **1.4** or germene **1.1**, respectively. The complete lack of polymer formation under these conditions is in stark contrast to the addition of *t*-BuLi to either the silene or germene in pentane which results in the rapid formation of the polysilane,[18] or –germane, respectively.[5] In preliminary experiments, we have demonstrated that both silene **1.4** and germene **1.1** do polymerize under anionic conditions in ether, and thus, we do not believe that the lack of polymer formation in these experiments is solely due to the solvent. We propose that the use of a less bulky anionic reagent likely increases the rate of addition of the reagent to the tetrelene relative to the subsequent dimerization (oligomerization), and thus, no polymer is formed when excess organometallic reagent is added. These are the conditions needed to achieve a controlled anionic polymerization and the use of less bulky anionic initiators for the controlled polymerization of silenes and germenes will be the subject of further research in this laboratory.

In all reports of the addition of organometallic reagents to silenes and germenes, including the results presented in this study, the addition is completely regioselective with the organometallic reagent adding to the silicon (or germanium) atom. We found the regioselectivity to be somewhat surprising since the reverse regiochemistry would result in the formation of relatively stable diaryl- or bis(silyl)-substituted silyl (or germyl) anions. There have been few mechanistic studies on the addition of nucleophiles to silenes. Water and alcohols have been shown to undergo nucleophilic addition to silenes.[1h,i] Again, the reaction is regioselective with the nucleophilic moiety adding to the silicon. The bond polarity of the Si=C bond is the most important factor governing the reactivity of the silene and plays a significant role in the regioselectivity of the addition of water and alcohols. For silenes of natural polarity, such as silene **1.4** or $Me_2Si=CPh(CH_2SiMe_3)$ studied by Ishikawa,[9] or even silenes of reduced polarity, such as the bis(silyl)-substituted silenes studied by Oehme,[11,12,13,14,15] the regiochemistry might be expected. On the other hand, the complete regioselectivity of the addition of organometallic reagents to Brook silenes ($(Me_3Si)_2Si=C(OSiMe_3)R$) which have reversed polarity is, at first, surprising. Interestingly, it was noted in the addition of alcohols[1h] or water[20] to silenes that the regiochemistry of the addition is *substituent-independent* and that the silicon atom is always the most electrophilic atom in the double bond of a range of substituted silenes. Thus, it appears as if the addition of organometallic reagents to silenes follows the same reactivity pattern; although the reaction may be further complicated by the influence of the solvent and the counter ion on the nature and aggregation of the organometallic reagent. The same factors appear to govern the regiochemistry of the addition of organometallic reagents towards germenes.

The reactions shown in **Scheme 4.5** are complicated because of the salt elimination method used to make silene **1.4** and germene **1.1**. It can be difficult to achieve high conversions of fluorosilane **4.3** to silene **1.4** or fluorogermane **1.9** to germene **1.1** (**Scheme 4.3**) while, at the same time, avoiding polymerization of the tetrelenes. Therefore, the presence of residual fluorosilane and -germane in the reaction mixtures is unavoidable and the amount present is directly related to the degree of conversion achieved in a given reaction. Not surprisingly, the fluorosilane and germane also react with the organometallic reagent (MeLi, BuLi and *t*-BuOK), added in the second step of the reaction sequence, to give by-products[21] which can be difficult to separate from the products derived from the silene (or germene) because of the similarities in the polarities of the two compounds. To unambiguously identify all possible products, the anticipated by-products were synthesized directly by treatment of fluorosilane **4.3** and fluorogermane **1.9** with MeLi, BuLi or *t*-BuOK (**Scheme 4.6**).



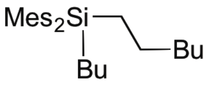
4.3: M = Si
1.9: M = Ge

R = Me, Bu, *t*-BuO
M' = Li or K

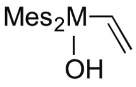
4.12: M = Si, R = Me
4.13: M = Ge, R= Me
4.14: M = Ge, R = Bu
4.15: M = Ge, R = O*t*-Bu

Scheme 4.6

Indeed vinylsilane **4.12** and vinylgermanes **4.13-4.15** were present in the crude product mixtures. Vinylgermanes **4.13** and **4.14** could not be separated from the products derived from the germene (i.e. **4.9** and **4.10**); however, in each of the other cases, separation was achieved. Interestingly, in the addition of excess BuLi to silene **1.4**, derived from **4.3**, in diethyl ether, butylhexyldimesitylsilane **4.16** (**Chart 4.2**) was formed in addition to silane **4.7**. Silane **4.16** was clearly formed by the reaction of *two* equivalents of BuLi to fluorovinylsilane **4.3** as demonstrated by the direct synthesis of **4.16** from the addition of excess BuLi to silane **4.3** in diethyl ether. Interestingly, when an excess of BuLi was added to silane **4.3** in pentane, only one equivalent of BuLi added to give Mes_2Si Bu($CH=CH_2$). Finally, in the addition of *t*-BuOK to silene **1.4** (or germene **1.1**), silanol **4.17** (or germanol **4.18**) was also present in the crude reaction mixture and presumably arises from direct reaction of hydroxide present in the alkoxide reagent with residual **4.3** (or **1.9**).



4.16



4.17: M = Si
4.18: M = Ge

Chart 4.2

4.3 Conclusions

We have examined the reactivity of the naturally polarized silene **1.4** and germene **1.1** toward organometallic reagents in diethyl ether. The organometallic reagent adds regioselectively to the tetrelene, with the organic moiety always adding to the Group 14 atom of the unsaturated bond. In combination with previously published results on silene chemistry, the addition is always regioselective despite a range of substituents on the silicon. As in the addition of oxygen nucleophiles to silenes, the electrophilicity of the unsaturated Group 14 element appears to be the governing factor in the regiochemistry of the reaction. Rearrangements are possible after initial addition of the organometallic moiety if there is a substituent which readily undergoes migration, such as a silyl substituent, or if there is considerable congestion about the Group 14 atom. The straightforward, selective addition of organometallic reagents to silenes and germenes makes this reaction synthetically useful and may be used to introduce functionality into the compound. However, as we and others have observed, the nature of the solvent and the reaction temperature may influence the reaction pathway followed, and thus, appropriate caution must be exercised.[8,12,14] No polymer was observed during addition of MeLi, BuLi and *t*-BuOK to silene **1.4** and germene **1.1** suggesting that the rate of addition to the tetrelene is significantly faster than the rate of propagation most likely due to the decrease in bulk of the organometallic reagent. Further studies are needed to examine the effect of the use of MeLi and BuLi in comparison with *t*-BuLi as anionic initiators in the polymerization of silenes and germenes.

4.4 Experimental

4.4.1 General Experimental Details

All air and moisture sensitive reactions were carried out in flame-dried Schlenk tubes under an argon atmosphere. C_6D_6 was distilled from $LiAlH_4$, stored over 4 Å molecular sieves, and degassed prior to use. All other solvents were dried using a solvent purification system (Innovative Technology Ltd) by passing the solvent through an alumina column. All reagents were purchased from the Aldrich Chemical Co. and were used as received. 1,1-Dimesitylneopentylsilene, **1.4**,[16b] fluorovinylsilane, **4.3**,[16b] 1,1-dimesitylneopentylgermene, **1.1**,[17] and fluorovinylgermane, **1.9**,[17] were prepared according to the previously reported procedures.

^1H NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer, a Varian Inova 400 MHz spectrometer or a Varian Inova 600 MHz spectrometer and are referenced to residual C_6D_5H (7.15 ppm) or $CHCl_3$ (7.25 ppm). IR spectra were recorded (cm^{-1}) from thin films on a Bruker Tensor 27 FT-IR spectrometer. Electron impact mass spectra were obtained using a MAT model 8400 mass spectrometer. Mass spectral data are reported in mass-to-charge ratios (*m/z*).

4.4.2 Synthesis of Difluorodimesitylgermane

Silver tetrafluoroborate (1.94 g, 9.96 mmol) was added to a solution of dichlorodimesitylgermane (1.0 g, 2.6 mmol) dissolved in dichloromethane (75 mL) under an inert atmosphere. The solid immediately dissolved and a white precipitate was observed. The mixture was allowed to stir for 3-4 min. Water (10 mL) was then added and the mixture filtered. The organic layer and the aqueous layer were separated. The aqueous layer was washed with dichloromethane (3 × 10 mL). The combined organic phase was dried using $MgSO_4$. The solids were removed by filtration and the solvent was removed on a rotary evaporator to give a white solid in quantitative yield. The isolated yield depends on the number of times the product is washed with water. The ^1H NMR data of Mes_2GeF_2 in $CDCl_3$ agreed with those published in the literature.[19]

Mes_2GeF_2: ^1H NMR (C_6D_6) δ 1.98 (s, 6 H, p-Me), 2.45 (s, 12 H, o-Me), 6.58 (s, 4 H, MesH).

4.4.3 Representative procedure for the addition of MeLi to 1.4[b]

t-Butyllithium (1.7 M, 0.09 mL, 0.15 mmol) was added to a solution of **4.3** (57 mg, 0.17 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and then stirred for 1.5 hr. Methyllithium (1.6 M, 0.30 mL, 0.48 mmol) was added to the solution, which was then allowed to stir for 10 min. Methanol (1 drop) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3 x 10 mL). The combined aqueous solution was washed with diethyl ether (3 x 10 mL). The combined organic solution was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give viscous, light yellow oil consisting of a mixture of 9, 15, and the water adduct of the silene (53 mg). **4.6** (20 mg, 31% yield) and **4.12** (4 mg, 6% yield) were separated by thin layer chromatography (80:20 hexanes: DCM) to give each as a clear oil.

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[b] The synthesis of compounds **4.6**, **4.7**, **4.8**, **4.10** and **4.16** were performed by J. Guo.

$Mes_2Si(Me)CH_2CH_2$*t*-Bu (**4.6**): ^1H NMR (C_6D_6) δ 0.74 (s, 3 H, $SiC\underline{H}_3$), 0.82 (s, 9 H, $C(C\underline{H}_3)_3$), 1.25 - 1.31 (AA'XX' spin system, 4 H, $SiC\underline{H}_2C\underline{H}_2$), 2.09 (s, 6 H, Mes *p*-$C\underline{H}_3$), 2.34 (s, 12 H, Mes *o*-$C\underline{H}_3$), 6.71 (s, 4 H, Mes-H); ^{13}C NMR (C_6D_6) δ 4.3 ($Si\underline{C}H_3$), 15.62 ($Si\underline{C}H_2CH_2$), 20.93 (Mes *p*-$\underline{C}H_3$), 24.36 (Mes *o*-$\underline{C}H_3$), 28.97 ($C(\underline{C}H_3)_3$), 31.09 ($\underline{C}(CH_3)_3$), 39.03 ($SiCH_2\underline{C}H_2$), 129.73 (Mes *m*-C), 134.78 (Mes *i*-C), 138.19 (Mes *p*-C), 143.36 (Mes *o*-C); ^{29}Si NMR (C_6D_6) δ -6.7; EI-MS *m/z* 366 (M^+, 6%), 351 (M^+-CH_3, 4%), 281 (M^+-$CH_2CH_2C(CH_3)_3$, 100%), 246 (M^+-Mes, 44%); High-resolution EI-MS for $C_{25}H_{38}Si$ *m/z* calcd 366.2743, found 366.2732.

$Mes_2Si(Me)CH{=}CH_2$ (**4.12**): IR (cm^{-1}) 793 (m), 847 (m), 1285 (m), 1449 (m), 1605 (m), 2978 (s); ^1H NMR (C_6D_6) δ 0.76 (s, 3 H, $SiC\underline{H}_3$), 2.10 (s, 6 H, Mes *p*-$C\underline{H}_3$), 2.29 (s, 12 H, Mes *o*-$C\underline{H}_3$), 5.63 (dd, J = 5, 20 Hz, 1 H, $SiCH{=}C\underline{H}_2$), 5.86 (dd, J = 4, 14 Hz, 1 H, $SiCH{=}C\underline{H}_2$), 6.68 (dd, J = 5, 20 Hz, 1 H, $SiC\underline{H}{=}CH_2$), 6.70 (s, 4 H, Mes-H); ^{13}C NMR (C_6D_6) δ 4.18 ($Si\underline{C}H_3$), 21.00 (Mes *p*-$\underline{C}H_3$), 24.63 (Mes *o*-$\underline{C}H_3$), 129.64 (Mes *m*-C), 130.48 ($SiCH{=}\underline{C}H_2$), 133.58 (Mes *i*-C), 138.43 (Mes *p*-C), 141.48 ($Si\underline{C}H{=}CH_2$), 143.59 (Mes *o*-C); EI-MS *m/z* 308 (M^+, 28%), 293 (M^+-CH_3, 24%), 281 (M^+-$CH_2{=}CH_2$, 7%), 188 (M^+-MesH, 100%); High-resolution EI-MS for $C_{21}H_{28}Si$ *m/z* calcd 308.1960, found 308.1971.

In the addition of MeLi to **1.1**, a viscous, colorless oil, identified as a mixture of **4.9** and **4.13**, was obtained in a ratio of 1: 0.03 (10 mg, 92% yield).

$Mes_2Ge(Me)CH_2CH_2$*t*-Bu (**4.9**): ^1H NMR (C_6D_6) δ: 0.825 and 0.829 (s, $C(C\underline{H}_3)_3$ and s, $GeC\underline{H}_3$, 12H), 1.23 - 1.33 (XX' of an AA'XX' spin system, 2H, $GeCH_2C\underline{H}_2$), 1.46 – 1.50 (AA' of an AA'XX' spin system, 2 H, $GeC\underline{H}_2CH_2$), 2.10 (s, 6 H, Mes *p*-$C\underline{H}_3$), 2.33 (s, 12H, Mes *o*-$\mathrm{C\underline{H}_3}$), 6.72 (s, 4H, Mes-H); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 4.16 ($\mathrm{Ge\underline{C}H_3}$), 17.46 ($\mathrm{Ge\underline{C}H_2CH_2}$), 20.93 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.19 (Mes *o*-$\mathrm{\underline{C}H_3}$), 28.96 ($\mathrm{C(\underline{C}H_3)_3}$), 31.21 ($\mathrm{\underline{C}(CH_3)_3}$), 39.78 ($\mathrm{GeCH_2\underline{C}H_2}$), 129.41 (Mes *m*-C), 137.53 (Mes *p*-C), 137.71 (Mes *i*-C), 142.79 (Mes *o*-C); EI-MS *m/z* 411 ($\mathrm{M^+}$, 11%), 397 ($\mathrm{M^+}$-$\mathrm{CH_3}$, 41%), 293 ($\mathrm{M^+}$-$\mathrm{CH_2CH_2C(CH_3)_3}$, 100%); High-resolution EI-MS for $\mathrm{C_{25}H_{38}{}^{70}Ge}$ *m/z* calcd 407.2138, found 407.2130.

$\mathrm{Mes_2Ge(CH{=}CH_2)Me}$ (**4.13**): IR ($\mathrm{cm^{-1}}$) 799 (s), 848 (s), 946 (m), 1009 (s), 1239 (m), 1261 (m), 1449 (m), 1603 (s), 2804 (w); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.84 (s, 3H, $\mathrm{GeC\underline{H}_3}$), 2.11 (s, 6H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.29 (s, 12H, Mes *o*-$\mathrm{C\underline{H}_3}$), 5.58 (dd, *J* = 3, 20 Hz, 1 H, $\mathrm{GeCH{=}C\underline{H}_2}$), 5.85 (dd, *J* = 3, 13 Hz, 1H, $\mathrm{GeCH{=}C\underline{H}_2}$), 6.71 (s, 4H, Mes-H), 6.78 (dd, *J* = 13, 20 Hz, 1H, $\mathrm{GeC\underline{H}{=}CH_2}$). ^{13}C NMR ($\mathrm{C_6D_6}$) δ 4.53 ($\mathrm{Ge\underline{C}H_3}$), 20.98 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.42 (Mes *o*-$\mathrm{\underline{C}H_3}$), 128.18 ($\mathrm{GeCH{=}\underline{C}H_2}$), 129.38 (Mes *m*-C), 136.39 (Mes *i*-C), 137.94 (Mes *p*-C), 142.76 ($\mathrm{Ge\underline{C}H{=}CH_2}$), 142.96 (Mes *o*-C); EI-MS *m/z* 354 ($\mathrm{M^+}$, 11%), 339 ($\mathrm{M^+}$-$\mathrm{CH_3}$, 70%), 327 ($\mathrm{M^+}$-$\mathrm{CH_2{=}CH_2}$, 33%), 234 ($\mathrm{M^+}$-Mes, 81%), 219 ($\mathrm{M^+}$-$\mathrm{CH_3}$-Mes, 100%); High-resolution EI-MS for $\mathrm{C_{21}H_{28}{}^{74}Ge}$ *m/z* calcd 354.1407, found 354.1402.

4.4.4 Synthesis of $\mathrm{Mes_2Si(CH{=}CH_2)CH_3}$ 4.12

Methyllithium (1.6 M in hexane, 0.40 mL, 0.64 mmol) was added to a solution of **4.3** (100 mg, 0.32 mmol) dissolved in diethyl ether (6 mL). The solution was allowed to stir overnight at room temperature. An ammonium chloride solution (2 mL) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3 x 10 mL). The combined aqueous solution was washed with diethyl ether (3 x 10 mL). The combined organic phase was dried over $\mathrm{MgSO_4}$ and filtered. The solvent was removed under vacuum to give **4.12** as a viscous, colorless liquid (10 mg, 10% yield). Similarly, the addition of methyllithium to **1.9** gave **4.13** (58 mg, 59% yield).

4.4.5 Representative procedure for the addition of BuLi to 1.4

t-Butyllithium (1.7 M, 0.10 mL, 0.17 mmol) was added to a solution of **4.3** (58 mg, 0.18 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and then stirred for 1.5 hr. Butyllithium (1.6 M, 0.34 mL, 0.54 mmol) was added to the solution, which was then allowed to stir for 10 min. Methanol (1 drop) was added to the reaction. The solution was washed with a saturated ammonium chloride solution (3 x 10 mL). The combined aqueous solution was washed with diethyl ether (3 x 10 mL). The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give a viscous, colorless oil (58 mg, 78% yield) identified as a mixture of **4.7** and **4.16** in a ratio of 1:1. The mixture was purified by thin layer chromatography (70:30 hexane: DCM) to give a clear oil (38 mg).

$\mathrm{Mes_2Si(Bu)CH_2CH_2}$*t*-Bu (**4.7**): ^{1}H NMR (C_6D_6) δ: 0.83 (t, 3 H, *J* = 7 Hz, $\mathrm{Si(CH_2)_3C\underline{H}_3}$), 0.84 (s, 9H, $\mathrm{C(C\underline{H}_3)_3}$), 1.46-1.15 (m, $\mathrm{SiC\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3}$), 2.09 (s, 6 H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.38 (s, 12 H, Mes *o*-$\mathrm{C\underline{H}_3}$), 6.71 (s, 4 H, Mes-H); ^{13}C NMR (C_6D_6) δ 9.14, 13.15 ($\mathrm{Si\underline{C}H_2CH_2}$ and $\mathrm{Si\underline{C}H_2CH_2CH_2CH_3}$), 18.70, 27.06, 27.43 ($\mathrm{SiCH_2\underline{C}H_2CH_2CH_3}$, $\mathrm{SiCH_2CH_2\underline{C}H_2CH_3}$ and $\mathrm{SiCH_2CH_2CH_2\underline{C}H_3}$), 20.94 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.52 (Mes *o*-$\mathrm{\underline{C}H_3}$), 28.97 ($\mathrm{C(\underline{C}H_3)_3}$), 31.13 ($\mathrm{\underline{C}(CH_3)_3}$), 39.14 ($\mathrm{SiCH_2\underline{C}H_2}$), 129.76 (Mes *m*-C), 134.30 (Mes *i*-C), 138.17 (Mes *p*-C), 143.59 (Mes *o*-C); ^{29}Si NMR (C_6D_6) δ -4.1; EI-MS *m/z* 408 (M^+, 1%), 351 (M^+-

$(CH_2)_3CH_3$, 14%), 323 (M^+-$(CH_2)_5CH_3$, 18%), 288 (M^+-MesH, 26%), 267 (Mes_2Si^+, 100%); High-resolution EI-MS for $C_{28}H_{44}Si$ *m/z* calcd 408.3212, found 408.3214.

$Mes_2Si(Bu)Hex$ (**4.16**): ^1H NMR (C_6D_6) δ 0.815 (t, *J* = 7 Hz) 0.821 (t, *J* = 7 Hz) (6H, $Si(CH_2)_3C\underline{H}_3$ and $Si(CH_2)_5C\underline{H}_3$), 1.16 - 1.21 (br, 4 H, $SiC\underline{H}_2$), 1.30 – 1.46 (m, $SiCH_2(C\underline{H}_2)_2CH_3$ and $SiCH_2(C\underline{H}_2)_4CH_3$), 2.10 (s, 6 H, Mes *p*-$C\underline{H}_3$), 2.37 (s, 12 H, Mes *o*-$C\underline{H}_3$), 6.71 (s, 4 H, Mes-H); ^{13}C NMR (C_6D_6) δ 13.90, 14.25 ($Si\underline{C}H_2CH_2CH_2CH_3$ and $Si\underline{C}H_2(CH_2)_4CH_3$), 18.98, 19.24 ($SiCH_2\underline{C}H_2CH_2CH_3$ and $SiCH_2\underline{C}H_2(CH_2)_3CH_3$), 20.95 (Mes *p*-$\underline{C}H_3$), 22.98, 25.24 ($Si(CH_2)_3\underline{C}H_2CH_2CH_3$ and $Si(CH_2)_2\underline{C}H_2(CH_2)_2CH_3$), 24.56 (Mes *o*-$\underline{C}H_3$), 27.48, 31.82 ($SiCH_2CH_2\underline{C}H_2CH_3$ and $Si(CH_2)_4\underline{C}H_2CH_3$), 27.14, 33.96 ($SiCH_2CH_2CH_2\underline{C}H_3$ and $Si(CH_2)_5\underline{C}H_3$), 129.75 (Mes *m*-C), 134.40 (Mes *i*-C), 138.14 (Mes *p*-C), 143.58 (Mes *o*-C); ^{29}Si NMR (C_6D_6) δ -5.1; EI-MS *m/z* 408 (M^+, 1%), 351 (M^+-$(CH_2)_3CH_3$, 10%), 323 (M^+-$(CH_2)_5CH_3$, 13%), 288 (M^+-MesH, 13%), 267 (Mes_2Si^+, 100%); High-resolution EI-MS for $C_{28}H_{44}Si$ *m/z* calcd 408.3212, found 408.3205.

In the addition of BuLi to **1.1**, a viscous, colorless oil identified as a mixture of **4.10** and **4.14** was obtained in a ratio of 1: 0.2 (28 mg, 47% yield).

$Mes_2Ge(Bu)CH_2CH_2$*t*-Bu (**4.10**): ^1H NMR (C_6D_6) δ 0.82 (m, 3H, *J* = 7 Hz, $Ge(CH_2)_3C\underline{H}_3$), 0.84 (s, 9H, $C(C\underline{H}_3)_3$), 1.29 – 1.63 (m, $GeC\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 2.10 (s, 6 H, Mes *p*-$C\underline{H}_3$), 2.37 (s, 12H, Mes *o*-$C\underline{H}_3$), 6.73 (s, 4H, Mes-$\underline{H}$); ^{13}C NMR (C_6D_6) δ 13.84 ($GeCH_2CH_2CH_2\underline{C}H_3$), 15.09 ($Ge\underline{C}H_2CH_2$*t-Bu*), 20.26 ($Ge\underline{C}H_2CH_2CH_2CH_3$), 20.94 (Mes *p*-$\underline{C}H_3$), 24.35 (Mes *o*-$\underline{C}H_3$), 26.75 ($GeCH_2CH_2\underline{C}H_2CH_3$), 28.30 ($GeCH_2\underline{C}H_2CH_2CH_3$), 28.97 ($C(\underline{C}H_3)_3$), 31.26 ($\underline{C}(CH_3)_3$), 39.94 ($GeCH_2\underline{C}H_2$*t-Bu*), 129.40 (Mes *m*-C), 137.11 (Mes *i*-C), 137.68 (Mes *p*-C), 142.99 (Mes *o*-C); EI-MS *m/z* 454 (M^+, 1%), 397 (M^+-

$(CH_2)_3CH_3$, 55%), 369 (M^+-$(CH_2)_2(CH_3)_3$, 67%), 191 (M^+-MesH, 26%), 313 ($Mes_2{}^{74}Ge^+H$, 100%); High-resolution EI-MS for $C_{28}H_{43}{}^{74}Ge$ *m/z* calcd 453.2582, found 453.2594.

4.4.6 Synthesis of $Mes_2Si(Bu)Hex$ 4.16

Butyllithium (1.6 M in hexane, 0.5 mL, 0.8 mmol) was added to a solution of **4.3** (47 mg, 0.15 mmol) dissolved in diethyl ether (3 mL). The solution was allowed to stir for 2 hr at room temperature. Methanol (1 drop) was added to the reaction mixture. The solution was washed with saturated ammonium chloride (3 x 10 mL). The combined aqueous solution was washed with diethyl ether (3 x 10 mL). The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give a viscous, colorless liquid (55 mg, 90% yield). **4.16** was purified by thin layer chromatography (70:30 hexanes: DCM) to give a colorless oil (37 mg, 61% yield).

4.4.7 Synthesis of $Mes_2Si(CH{=}CH_2)Bu$

Butyllithium (1.6 M in hexane, 0.50 mL, 0.80 mmol) was added to a solution of **4.3** (47 mg, 0.15 mmol) dissolved in pentane (3 mL). The solution was allowed to stir for 2 hr at room temperature. Methanol (1 drop) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3 x 10 mL). The combined aqueous solution was washed with diethyl ether (3 x 10 mL). The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give a viscous, colorless liquid (50 mg, 96% yield). $Mes_2Si(CH{=}CH_2)Bu$ was purified by thin layer chromatography (80:20 hexanes: DCM) to give a clear oil (38 mg, 72% yield).

Vinylgermane **4.14** was synthesized in a similar manner to give a viscous, colorless oil (55 mg, 50% yield).

$\mathrm{Mes_2Si(CH{=}CH_2)Bu}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.80 (t, *J* = 7 Hz, 3H, $\mathrm{SiCH_2CH_2CH_2C\underline{H}_3}$), 1.29-1.43 (m, $\mathrm{SiC\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3}$), 2.10 (s, 6 H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.32 (s, 12 H, Mes *o*-$\mathrm{C\underline{H}_3}$), 5.65 (dd, *J* = 3, 20 Hz, 1 H, $\mathrm{SiCH{=}C\underline{H}_2}$), 5.91 (dd, *J* = 4, 14 Hz, 1 H, $\mathrm{SiCH{=}C\underline{H}_2}$), 6.71 (s, 4 H, Mes-H), 6.82 (dd, *J* = 14, 20 Hz, 1 H, $\mathrm{SiC\underline{H}{=}CH_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 13.84 ($\mathrm{Si\underline{C}H_2CH_2CH_2CH_3}$), 20.03 ($\mathrm{SiCH_2\underline{C}H_2CH_2CH_3}$), 20.99 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.76 (Mes *o*-$\mathrm{\underline{C}H_3}$), 27.09 ($\mathrm{SiCH_2CH_2\underline{C}H_2CH_3}$), 27.58 ($\mathrm{SiCH_2CH_2CH_2\underline{C}H_3}$), 129.63 (Mes *m*-C), 130.83 ($\mathrm{SiCH{=}\underline{C}H_2}$), 133.05 (Mes *i*-C), 138.42 (Mes *p*-C), 140.11 ($\mathrm{Si\underline{C}H{=}CH_2}$), 143.87 (Mes *o*-C); ^{29}Si NMR ($\mathrm{C_6D_6}$) δ -13.8; EI-MS *m/z* 350 ($\mathrm{M^+}$, 33%), 335 ($\mathrm{M^+}$-$\mathrm{CH_3}$, 10%), 293 ($\mathrm{M^+}$-$\mathrm{C_4H_9}$, 100%), 230 ($\mathrm{M^+}$-MesH, 30%); High-resolution EI-MS for $\mathrm{C_{24}H_{34}Si}$ *m/z* calcd 350.2430, found 350.2441.

$\mathrm{Mes_2GeBu(CH{=}CH_2)}$ (**4.14**): IR (cm^{-1}) 697 (s), 847 (m), 1008 (m), 1289 (w), 1377 (m), 1392 (m), 1450 (s), 1603 (s), 2731 (w), 2858 (m), 2924 (s), 2957 (s);^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.79 (t, *J* = 7 Hz, 3H, $\mathrm{GeCH_2CH_2CH_2C\underline{H}_3}$), 1.25-1.60 (m, $\mathrm{GeC\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3}$), 2.11 (s, 6H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.31 (s, 12H, Mes *o*-$\mathrm{C\underline{H}_3}$), 5.60 (dd, *J* = 3, 19 Hz, 1H, $\mathrm{GeCH{=}C\underline{H}_2}$), 5.90 (dd, *J* = 3, 13 Hz, 1 H, $\mathrm{GeCH{=}C\underline{H}_2}$), 6.72 (s, 4H, Mes-H), 6.93 (dd, *J* = 13, 19 Hz, 1H, $\mathrm{GeC\underline{H}{=}CH_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 13.80 ($\mathrm{GeCH_2CH_2CH_2\underline{C}H_3}$), 20.97 (Mes *p* -$\mathrm{\underline{C}H_3}$), 22.00 ($\mathrm{Ge\underline{C}H_2CH_2CH_2CH_3}$), 24.55 (Mes *o*-$\mathrm{\underline{C}H_3}$), 26.74 ($\mathrm{GeCH_2CH_2\underline{C}H_2CH_3}$), 28.43 ($\mathrm{GeCH_2\underline{C}H_2CH_2CH_3}$), 128.48 ($\mathrm{GeCH{=}\underline{C}H_2}$), 129.35 (Mes *m*-C), 135.91 (Mes *i*-C), 137.93 (Mes *p*-C), 141.49 ($\mathrm{Ge\underline{C}H{=}CH_2}$), 143.19 (Mes *o*-C); EI-MS *m/z* 396 ($\mathrm{M^+}$, 2%), 369 ($\mathrm{M^+}$-$\mathrm{CH{=}CH_2}$, 1%), 339 ($\mathrm{M^+}$-$\mathrm{C_4H_9}$, 100%), 276 ($\mathrm{M^+}$-MesH, 11%); High-resolution EI-MS for $\mathrm{C_{24}H_{34}{}^{74}Ge}$ *m/z* calcd 396.1877, found 396.1869.

4.4.8 Representative procedure for the addition of KO*t*-Bu to 1.4

t-Butyllithium (1.7 M, 0.1 mL, 0.2 mmol) was added to a solution of **4.3** (57.8 mg, 0.18 mmol) dissolved in diethyl ether (3 mL) and cooled in a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and then stirred for 1.5 hr. Potassium *t*-butoxide (90 mg, 0.80 mmol) was added to the solution, which was then allowed to stir for 10 min. The potassium *t*-butoxide did not dissolve completely. Methanol (1 drop) was added to the reaction. The solution was washed with a saturated ammonium chloride solution (3 x 10 mL). The combined aqueous solution was washed with diethyl ether (3 x 10 mL). The combined organic phase was dried over $\mathrm{MgSO_4}$ and filtered. The solvent was removed under vacuum to give a clear, colorless liquid (60 mg). The liquid consisted of **4.8** and **4.17** in a 1:2 ratio as determined by ^{1}H NMR spectroscopy. The mixture was separated twice by thin layer chromatography (80:20 hexane: DCM) to give **4.8** (17 mg, 23% yield) and **4.17** (13 mg, 17%). Compound **4.8** remains contaminated with trace amounts of an unknown.

$\mathrm{Mes_2Si(O}\textit{t}\text{-}\mathrm{Bu)CH_2CH_2}\textit{t}\text{-}\mathrm{Bu}$ (**4.8**): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.87 (s, 9 H, $\mathrm{C(C\underline{H}_3)_3}$), 1.23 (s, 9 H, $\mathrm{OC(C\underline{H}_3)_3}$), 1.33 - 1.35 (XX' portion of an AA'XX' spin system, 2 H, $\mathrm{SiC\underline{H}_2CH_2}$), 1.48 - 1.50 (AA' portion of an AA'XX' spin system, 2 H, $\mathrm{SiCH_2C\underline{H}_2}$), 2.09 (s, 6 H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.48 (s, 12 H, Mes *o*-$\mathrm{C\underline{H}_3}$), 6.73 (s, 4 H, Mes-H); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 18.53 ($\mathrm{Si\underline{C}H_2CH_2}$), 21.02 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.29 (Mes *o*-$\mathrm{\underline{C}H_3}$), 29.08 ($\mathrm{C(\underline{C}H_3)_3}$), 31.04 ($\mathrm{\underline{C}(CH_3)_3}$), 31.69 ($\mathrm{OC(\underline{C}H_3)_3}$), 38.31 ($\mathrm{SiCH_2\underline{C}H_2}$), 74.16 ($\mathrm{O\underline{C}(CH_3)_3}$), 129.89 (Mes *m*-C), 134.88 (Mes *i*-C), 138.46 (Mes *p*-C), 143.64 (Mes *o*-C); ^{29}Si NMR ($\mathrm{C_6D_6}$) δ -8.1; EI-MS *m/z* 424 ($\mathrm{M^+}$, 0.1%), 339 ($\mathrm{M^+}$- $\mathrm{CH_2CH_2C(CH_3)_3}$, 55%), 283 ($\mathrm{Mes_2SiO^+}$, 100%); High-resolution EI-MS for $\mathrm{C_{28}H_{44}OSi}$ *m/z* calcd 424.3161, found 424.3156.

$Mes_2Si(OH)CH{=}CH_2$ (**4.17**): IR (cm^{-1}) 632 (m), 801 (m), 1179 (w), 1234 (m), 1263 (s), 1405 (m), 1448 (m), 1548 (m), 1605 (s), 2734 (w), 2860 (m), 2922 (s), 2965 (s); ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, Mes p-$C\underline{H}_3$), 2.37 (s, 12 H, Mes o-$C\underline{H}_3$), 5.81 (dd, J = 4, 20 Hz, 1 H, $SiCH{=}C\underline{H}_2$), 5.91 (dd, J = 4, 14 Hz, 1 H, $SiCH{=}C\underline{H}_2$), 6.57 (dd, J = 14, 20 Hz, 1 H, $SiC\underline{H}{=}CH_2$), 6.70 (s, 4 H, Mes-H); ^{13}C NMR (C_6D_6) δ, 21.05 (Mes p-$\underline{C}H_3$), 24.18 (Mes o-$\underline{C}H_3$), 129.56 (Mes m-C), 131.61 ($SiCH{=}\underline{C}H_2$), 132.97 (Mes i-C), 139.06 (Mes p-C), 140.78 ($Si\underline{C}H{=}CH_2$), 143.97 (Mes o-C); EI-MS m/z 310 (M^+, 12%), 283 (M^+- $CH_2{=}CH_2$, 8%), 191 (M^+ – Mes, 14%), 84 (100%); High-resolution EI-MS for $C_{20}H_{26}OSi$ m/z calcd 310.1753, found 310.1748.

In the addition of potassium t-butoxide to **1.1**, a clear oil was obtained which was identified as a mixture of **4.11**, **4.15** and **4.18** (in a ratio of 1:0.5:0.5) and a trace of an unknown. The mixture was purified by thin layer chromatography (80:20 hexanes:DCM) to give **4.11** as a clear oil contaminated with a minor impurity (15 mg, 12% yield).

$Mes_2Ge(Ot\text{-}Bu)CH_2CH_2t\text{-}Bu$ (**4.11**): IR (cm^{-1}) 848 (m), 1021 (m), 1466 (m), 1604 (m), 2965 (s); ^{1}H NMR (C_6D_6) δ 0.83 (s, 9 H, $C(C\underline{H}_3)_3$), 1.19 - 1.21 (XX' portion of an AA'XX' spin system, 2 H, $GeC\underline{H}_2CH_2$), 1.32 (s, 9 H, $OC(C\underline{H}_3)_3$), 1.6 - 1.62 (AA' portion of an AA'XX' spin system, 2 H, $GeCH_2C\underline{H}_2$), 2.10 (s, 6 H, Mes p-$C\underline{H}_3$), 2.32 (s, 12 H, Mes o-$C\underline{H}_3$), 6.73 (s, 4 H, Mes-H); ^{13}C NMR (C_6D_6) δ 14.82 ($Ge\underline{C}H_2CH_2$), 20.87 (Mes p-$\underline{C}H_3$), 25.32 (Mes o-$\underline{C}H_3$), 28.99 ($C(\underline{C}H_3)_3$), 30.01 ($\underline{C}(CH_3)_3$), 31.44 ($OC(\underline{C}H_3)_3$), 41.08 ($GeCH_2\underline{C}H_2$), 84.06 ($O\underline{C}(CH_3)_3$), 129.44 (Mes m-C), 137.31 (Mes p-C), 142.62 (Mes o-C); EI-MS m/z 395 (M^+-Ot-Bu, 66%), 312 (Mes_2Ge^+, 81%), 84 (100%).

4.4.9 Synthesis of $Mes_2Ge(OH)CH{=}CH_2$ 4.18

Aqueous sodium hydroxide (15%, 5.0 mL, 1.4 mmol) was added to a solution of **1.9** (50 mg, 0.14 mmol) dissolved in THF (20 mL), which was then allowed to stir to for 1 hr at room temperature. The aqueous solution was washed with diethyl ether (3 x 10 mL) and the organic layer was washed with water (3 x 10 mL). The combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give a viscous, colorless oil (25.0 mg, 50% yield). The oil consisted of **4.18** and **1.1** in a ratio of 1: 0.04. The mixture was purified by thin layer chromatography on silica gel (50:50 hexane: DCM) to give **4.18** as clear oil (2.2 mg). Silanol **4.17** was synthesized using the same procedure (99 mg, 98% yield).

$Mes_2Ge(OH)CH{=}CH_2$ (**4.18**): IR (cm^{-1}) 848 (s), 962 (m), 1449 (s), 1602 (s), 2922 (s) 3430 (br, m); ^1H NMR (C_6D_6) δ 2.08 (s, 6H, Mes p-$C\underline{H}_3$), 2.40 (s, 12H, Mes o-$C\underline{H}_3$), 5.77 (dd, J = 3, 20 Hz, 1H, $GeCH{=}C\underline{H}_2$), 5.87 (dd, J = 3, 13 Hz, 1H, $GeCH{=}C\underline{H}_2$), 6.65 (dd, J = 13, 20 Hz, 1H, $GeC\underline{H}{=}CH_2$), 6.69 (s, 4 H, Mes-H). ^{13}C NMR (C_6D_6) δ, 20.99 (Mes p-$\underline{C}H_3$), 23.77 (Mes o-$\underline{C}H_3$), 129.43 (Mes m-C), 130.02 ($GeCH{=}\underline{C}H_2$), 134.97 (Mes i-C), 138.99 (Mes p-C), 141.37 ($Ge\underline{C}H{=}CH_2$), 143.25 (Mes o-C); EI-MS m/z 356 (M^+, 7%), 338 (M^+-OH, 11%), 329 (M^+- $CH_2{=}CH_2$, 26%), 236 (M^+-Mes-H, 52%), 145 (M^+-Mes $CH{=}CH_2$, 100%); High-resolution EI-MS for $C_{20}H_{26}O^{74}Ge$ m/z calcd 356.1200, found 356.1189.

4.4.10 Synthesis of $Mes_2Si(CH{=}CH_2)Ot$-Bu

Potassium t-butoxide (153 mg, 1.37 mmol) was added to a solution of **4.3** (94 mg, 0.30 mmol) dissolved in THF (9 mL). The solution was allowed to stir for 24 hrs. Saturated ammonium chloride (1 drop) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3 x 10 mL). The combined aqueous solution was washed with THF (3 x 10 mL). The combined organic phase was dried over $\mathrm{MgSO_4}$ and filtered. The solvent was removed under vacuum to give an orange powder (100 mg, 90% yield). The powder consisted of $\mathrm{Mes_2Si(CH{=}CH_2)O}$*t*-Bu and a small amount of an unknown. The mixture was purified by thin layer chromatography on silica gel (70:30 hexane: DCM) to give $\mathrm{Mes_2Si(CH{=}CH_2)O}$*t*-Bu (59 mg, 53%). Vinylgermane **4.15** was synthesized in a similar manner to give a viscous, colorless oil (106 mg, 92% yield) consisting of **4.15** and **4.18** in the ratio of (1:0.06).

$\mathrm{Mes_2Si(CH{=}CH_2)O}$*t*-Bu: IR ($\mathrm{cm^{-1}}$) 632 (s), 697 (s), 848 (m), 959 (m), 1021 (s), 1040 (s), 1189 (s), 1363 (m), 1450 (m), 1605 (m), 2799 (m), 2948 (m), 3100 (br, s); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.20 (s, 9H, $\mathrm{OC(C\underline{H}_3)_3}$), 2.11 (s, 6H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.44 (s, 12H, Mes *o*-$\mathrm{C\underline{H}_3}$), 5.70 (dd, $J = 3, 20$ Hz, 1H, $\mathrm{SiCH{=}C\underline{H}_2}$), 5.90 (dd, $J = 3, 14$ Hz, 1H, $\mathrm{SiCH{=}C\underline{H}_2}$), 6.73 (s, 4H, Mes-H), 6.76 (dd, $J = 14, 20$ Hz, 1H, $\mathrm{SiC\underline{H}{=}CH_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 21.07 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.52 (Mes *o*-$\mathrm{\underline{C}H_3}$), 31.80 ($\mathrm{C(\underline{C}H_3)_3}$), 74.20 ($\mathrm{O\underline{C}(CH_3)_3}$), 129.73 (Mes *m*-C), 131.45 ($\mathrm{GeCH{=}\underline{C}H_2}$), 133.64 (Mes *i*-C), 138.72 (Mes *p*-C), 141.77 ($\mathrm{Si\underline{C}H{=}CH_2}$), 144.08 (Mes *o*-C); EI-MS *m/z* 366 ($\mathrm{M^+}$, 58%), 190 (100%), 293 ($\mathrm{M^+{-}C_4H_9O}$, 13%), 246 (M-Mes-$\mathrm{H^+}$, 37%); High-resolution EI-MS for $\mathrm{C_{24}H_{34}OSi}$ *m/z* calcd 366.2379, found 366.2389.

$\mathrm{Mes_2Ge(CH{=}CH_2)O}$*t*-Bu (**4.15**): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.26 (s, 9H, $\mathrm{OC(C\underline{H}_3)_3}$), 2.09 (s, 6H, Mes *p*-$\mathrm{C\underline{H}_3}$), 2.46 (s, 12H, Mes *o*-$\mathrm{C\underline{H}_3}$), 5.64 (dd, $J = 3, 20$ Hz, 1H, $\mathrm{GeCH{=}C\underline{H}_2}$), 5.86 (dd, $J = 3, 13$ Hz, 1H, $\mathrm{GeCH{=}C\underline{H}_2}$), 6.72 (s, 4H, Mes-H), 6.88 (dd, $J = 13, 20$ Hz, 1H, $\mathrm{GeC\underline{H}{=}CH_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 21.03 (Mes *p*-$\mathrm{\underline{C}H_3}$), 24.05 (Mes *o*-$\mathrm{\underline{C}H_3}$), 32.65

$(C(\underline{C}H_3)_3)$, 73.53 $(O\underline{C}(CH_3)_3)$, 129.60 (Mes *m*-CH), 130.10 $(GeCH{=}\underline{C}H_2)$, 135.55 (Mes *i*-C), 138.69 (Mes *p*-C), 142.62 $(Ge\underline{C}H{=}CH_2)$, 143.43 (Mes *o*-C); EI-MS *m/z* 412 (M^+, 0.5%), 385 (M^+-$CH_2{=}CH_2$, 4%), 339 (M^+-C_4H_9O, 100%), 311 (Mes_2Ge-H^+, 24%); High-resolution EI-MS for $C_{24}H_{34}O^{70}Ge$ *m/z* calcd 408.1852, found 408.1857.

4.5 References

1. For general reviews on silenes see: (a) Ottosson, H.; Ohshita, J. In *Science of Synthesis: Knowledge Updates 2011/3*; Oestreich, M., Ed.; Thieme: Stuttgart, **2011**; pp 47.; (b) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb, From Phantom Species to Stable Compounds*, Wiley, Chichester, **2010**; pp 246.; (c) Baines, K. M. *Chem. Commun.* **2013**, *49*, 6366.; (d) Scheschkewitz, D. *Chem. Eur. J.* **2009**, *15*, 2476.; (e) Ottosson, H.; Eklof, A. M. *Coord. Chem. Rev.* **2008**, *252*, 1287.; (f) Ottosson, H.; Steel, P. G. *Chem. Eur. J.* **2006**, *12*, 1576.; (g) Gusel'nikov, L. E. *Coord. Chem. Rev.* **2003**, *244*, 149.; (h) Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, *34*, 129.; (i) Morkin, T. L.; Owens, T. R.; Leigh, W. J. in *The Chemistry of Organic Silicon Compounds*, Rappoport, Z., Apeloig, Y. Eds., Wiley, Chichester, **2001**, Vol. *3*, pp 949.; (j) Escudie, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178-180*, 565.

2. For recent references on the synthesis of new silenes see: (a) Haas, M.; Fischer, R.; Flock, M.; Mueller, S.; Raush, M.; Saf, R.; Torvisco, A.; Stueger, H. *Organometallics* **2014**, *33*, 5956.; (b) Stueger, H.; Hasken, B.; Hass, M.; Rausch, M.; Fischer, R.;

Torvisco, A. *Organometallics* **2014**, *33*, 231.; (c) Nakata, N.; Rodriguez, R.; Troadec, T.; Saffon-Merceron, N.; Sotiropoulos, J.; Baceiredo, A.; Kato, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 10840.; (d) Zborovsky, L.; Dobrovetsky, R.; Botoshansky, M.; Bravo-Zhivotovskii, D.; Apeloig, Y. *J. Am. Chem. Soc.* **2012**, *134*, 18229.; (e) Cowley, M. J.; Ohmori, Y.; Huch, V.; Ichinohe, M.; Sekiguchi, A.; Scheschkewitz, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 13247.; (f) Majumdar, M.; Huch, V.; Bejan, I.; Meltzer, A.; Scheschkewitz, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 3516.; (g) Dobrovetsky, R.; Zborovsky, L.; Sheberla, D.; Botoshansky, M.; Bravo-Zhivotovskii, D.; Apeloig, Y. *Angew. Chem. Int. Ed.* **2010**, *49*, 4084.; (h) Bejan, I.; Gueclue, D.; Inoue, S.; Ichinohe, M.; Sekiguchi, A.; Scheschkewitz, D. *Angew. Chem. Int. Ed.* **2007**, *46*, 3349.

3. (a) Czyzewski, M.; Sellars, J. D.; Guliashvili, T.; Tibbelin, J.; Johnstone, L.; Bower, J.; Box, M.; Davies, R. D. M.; Ottosson, H.; Steel, P. G. *Chem. Commun.* **2014**, *50*, 2919; (b) Czyzewski, M.; Bower, J.; Box, M.; Ottosson, H.; Steel, P. G. *Chem. Sci.* **2011**, *2*, 2367; (c) Guliashvili, T.; Tibbelin, J.; Ryua, J.; Ottosson, H. *Dalton Trans.* **2010**, *39*, 9379; (d) Sellars, J. D.; Steel; P. G. *Tetrahedron* **2009**, *65*, 5588; (e) Pullin, R. C. D.; Sellars, J. D.; Steel, P. G. *Org. Biomol. Chem.* **2007**, *5*, 3201; (f) Hughes, J. N.; Pullin, R. C. D.; Sanganee, M. J.; Sellars, J. D.; Steel, P. G.; Turner, M. J. *Org. Biomol. Chem.* **2007**, *5*, 2841.

4. Bravo-Zhivotovskii, D.; Melamed, S.; Molev, V.; Sigal, N.; Tumanskii, B.; Botoshansky, M.; Molev, G.; Apeloig, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 1834.

5. Pavelka, L. C.; Milnes, K. K.; Baines, K. M. *Chem. Mat.* **2008**, *20*, 5948.

6. Löfås, H.; Orthaber, A.; Jahn, O. B.; Rouf, M. A.; Grigoriev, A.; Ott, S.; Ahuja, R.; Ottosson, H. *J. Phys. Chem. C* **2013**, *117*, 10909.

7. (a) Pola, J.; Urbanová, M.; Volnina, E. A.; Bakardjieva, S.; Šubrt, J.; Bastl, Z. *J. Mat. Chem.* **2003**, *13*, 394.; (b) Pola, J. *Surf. Coat. Technol.* **1998**, *100-101*, 408.

8. Brook, A. G.; Chiu, P.; McClenaghnan, J.; Lough, A. J. *Organometallics*, **1991**, *10*, 3292.

9. Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1979**, *173*, 117.

10. Auner, N. *Z. Anorg. Allg. Chem.*, **1988**, *558*, 87.

11. Krempner, C.; Oehme, H. *J. Organomet. Chem.*, **1994**, *464*, C7.

12. Luderer, F.; Reinke, H.; Oehme, H. *J. Organomet. Chem.* **1996**, *510*, 181.

13. Schmohl, K.; Blacha, M.; Reinkea, H.; Kempe, R.; Oehme, H. *Eur. J. Inorg. Chem.*, **1998**, 1667.

14. Sternberg, K.; Reinke, H.; Oehme, H. *Z. Anorg. Allg. Chem.*, **1999**, *625*, 467.

15. Hoffman, D.; Reinke, H.; Oehme, H. *J. Organomet. Chem.* **1999**, *585*, 189.

16. (a) Delpon-Lacaze, G.; Couret, C. *J. Organomet. Chem.* **1994**, *480*, C14; (b) Delpon-Lacaze, G.; de Battisti, C.; Couret, C. *J. Organomet.Chem.* **1996**, *514*, 59.

17. Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.

18. Pavelka, L. C.; Holder, S. J.; Baines, K. M. *Chem. Commun.* **2008**, *20*, 2346.

19. Riviere, P.; Riviere-Baudet, M.; Castel, A.; Desor, D.; Abdennadher, C. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1991**, *61*, 189.

20. Bendikov, M.; Quadt, S. R.; Rabin, O.; Apeloig, Y. *Organometallics* **2002**, *21*, 3930.

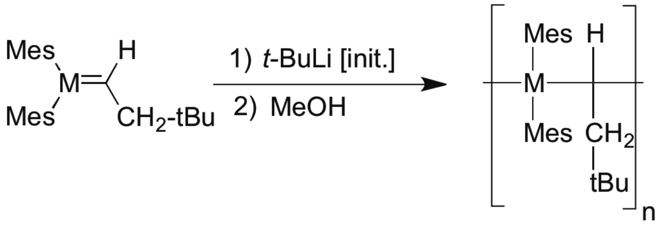
21. Jones, P. R.; Cheng, A. H. B; Albanesi, T. E. *Organometallics* **1984**, *3*, 78.

Chapter 5

5 Structural Analysis and Characterization of Polysilenes and Polygermenes

5.1 Introduction

In recent years, there has been significant interest in the synthesis and study of inorganic polymers[1] because of their unique properties and potential applications.[2] In an important advance, the anionic polymerization of phosphenes was reported by Gates *et al.*[3] Phosphenes undergo polymerization under a variety of conditions to afford air- and moisture-stable polyphosphenes with a regular alternating phosphorus-carbon backbone.[4] In the same vein, the incorporation of silicon and germanium into the polymer backbone to provide polysilene **1.8**[5] and polygermene **1.7**[6] was accomplished by the anion-initiated polymerization of the kinetically stable 1,1-dimesitylneopentylsilene **1.4** or 1,1-dimesitylneopentylgermene **1.1**, respectively (**Scheme 5.1**).

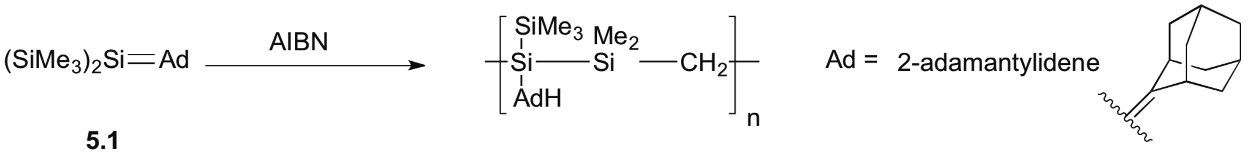


1.4: M= Si
1.1: M= Ge

1.8: M= Si
1.7: M= Ge

Scheme 5.1

The radical polymerization of the relatively stable silene **5.1** $(Me_3Si)_2Si=Ad$ (Ad= 2-adamantylidene) to give a polymer with $[(Me_3Si)(AdH)Si\text{-}SiMe_2CH_2]$ as the repeating unit, has also been reported.[7] The polymer is believed to be produced by the addition of a radical to the Si=C double bond, followed by hydrogen transfer from a Me_3Si group to the adamantyl substituent (**Scheme 5.2**).[7]

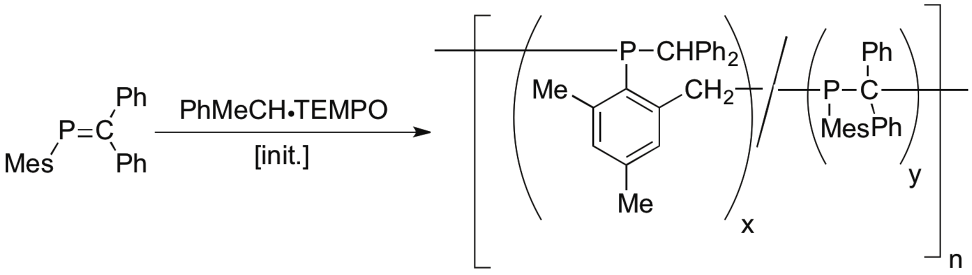


Scheme 5.2

Polysilenes have attracted much attention due to their ability to be easily converted into silicon carbide ceramics for use in a variety of technologies.[8] In addition to synthesis by the anionic polymerization of silenes, they have also been synthesized using metal-catalyzed ring-opening polymerization (ROP) of 1,3-disilacyclobutanes,[9a] or silacyclobutanes[9b-e], as well as the anion-initiated ROP of silacyclopropanes.[9f] Inspired by the unexplored chemistry and potential applications[10] of polymers incorporating germanium or silicon into the backbone and realizing the important relationship between structure and function, a detailed characterization study of these tetrel-containing polymers was carried out and the results of the study are reported herein.

The molecular weight of a polymer provides important insights into the physical properties and function of the material and is often determined using gel permeation chromatography (GPC) (versus a polystyrene standard); however, the molecular weight can be underestimated using this technique.[3a] The use of soft ionization mass spectrometric techniques, such as electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI), has been widely applied in the characterization of the molecular weight of organic polymers and provides access to the absolute molecular weight of a sample without a reference standard. These soft ionization techniques produce little or no fragmentation and can determine the molecular weight of large, intact macromolecules to the MDa range. Furthermore, information regarding the structure of the polymer, including end-groups, and the polymerization mechanism can also be derived from mass spectral data.

Polysilene **1.8** and polygermene **1.7** have been previously characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).[5,6] A regularly alternating silicon (or germanium) and carbon backbone structure was proposed on the basis of a comparsion of ^{1}H and ^{13}C NMR spectral data to those of model compounds. Interestingly, the structure of polyphosphene **5.3** was also originally proposed to be a regular alternating polymer;[11] however, recent work has shown that, in the radical-initiated addition polymerization of phosphene **5.2**, the NMR data of the resulting polymer, **5.3**, are more consistent with the structure shown in **Scheme 5.3**, where the propagating radical is apparently derived from a methyl group in the ortho position of the mesityl substituent.

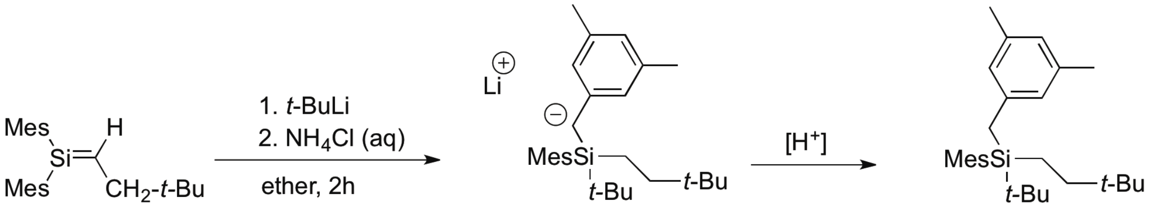


5.2

5.3

Scheme 5.3

Given the recent findings by Gates regarding the primary structure of polyphosphene **5.3** and the reported formation of **4.2** under similar experimental conditions as the formation of polysilene **1.8** (**Scheme 5.4**)[12]; the primary structure of polysilene **1.8** has been carefully re-examined using 2D NMR spectroscopy and is reported here.



1.4

4.2

Scheme 5.4

Both MALDI and ESI-MS have been used to analyze some common organic polymers such as polystyrene and poly(methyl methacrylate),[13] as well as inorganic polymers such as poly(N-methylamineboranes)[14] and a selenophene-fluorene co-polymer.[15] ESI-MS experiments on inorganic polymers often use time-of-flight (TOF) mass analyzers, which are widely available and also have the capability of detecting ions with high mass-to-charge ratios (*m/z*).[16] Gates and coworkers have previously demonstrated that the molecular weight of polyphosphenes may be underestimated when using polystyrene as a standard in GPC[3a] and have shown that MALDI-MS can be successfully used for analysis of low molecular weight polyphosphenes.[17] Furthermore, the mass spectral data of the polyphosphenes provided evidence for a chain growth mechanism in solution at ambient temperature.[17] Recently, the same group has demonstrated that ESI mass spectrometry can also be used to effectively characterize oligomeric phosphenes.[18] Given that the structures of polygermene **1.7** and polysilene **1.8** are somewhat similar to polystyrene and polyphosphene **5.3** (they all have pendant aryl substituents that could strongly interact with a cationization reagent), the use of a ESI-MS as a method for the analysis of the molecular weights of polysilene **1.8** and polygermene **1.7** has now been investigated. In addition, the absolute molecular weight of polygermene **1.7** was also assessed using static light scattering.

5.2 Results and Discussion

5.2.1 Characterization of Polysilene 1.8 by ESI-MS

GPC analysis of the molecular weight of polysilene **1.8** revealed an M_n and M_w at 1767 and 2354 Da, respectively, giving a polydispersity index of 1.33. The same polymer sample was then analysed by ESI-MS. The sample was dissolved in THF and cesium iodide was added as cationization agent. The ESI mass spectrum of polysilene **1.8** is depicted in **Figure 5.1.**

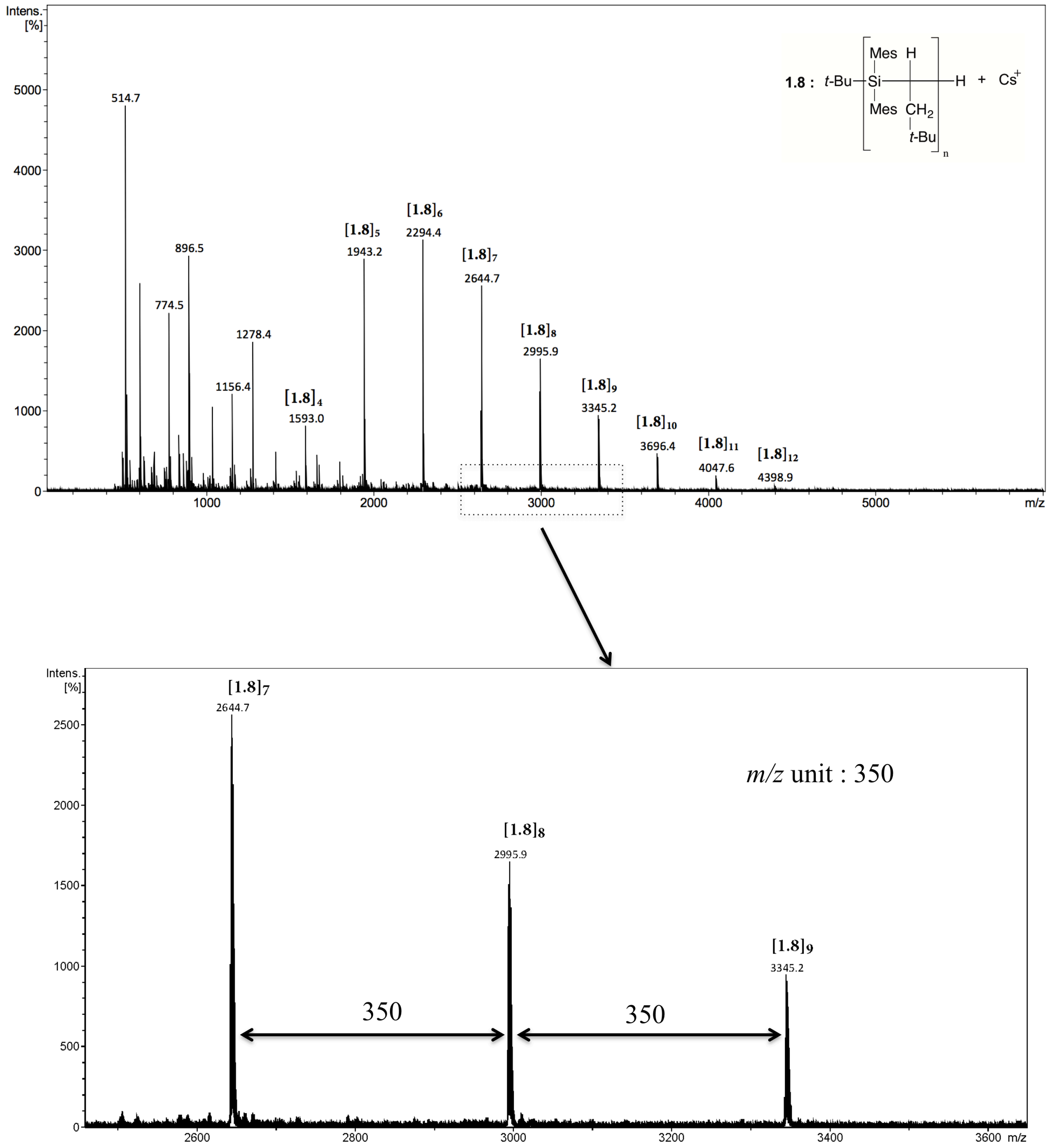


Figure 5.1 ESI-mass spectrum of polysilene **1.8** with an expansion from *m/z* 2600 to *m/z* 3600

Twelve clusters of signals which can be attributed to the sample were observed from *m/z* 1593.0 to 4398.9 in the mass spectrum of polysilene **1.8**; each cluster was separated by *m/z* 350 units, which corresponds to the mass of the silene monomer; [Mes_2Si-C(H)(CH_2-C(*t*-Bu)], (see **Figure 1.1**). No signals which could be attributed to oligomers below n = 4 or above n = 13 were observed, and the distribution maximizes at n = 6.

An expansion of the signal at *m/z* 2294.4 is shown in **Figure 5.2**. The *m/z* ratios and the relative intensities of signals within the isotopic cluster at 2294.4 *m/z* matches well (± 0.1 Dalton) with the calculated isotopic cluster of a hexamer of the *t*-Bu-initiated polysilene ($C_{148}H_{214}Si_6Cs$) (**Figure 5.2**). Furthermore, to determine the *m/z* of the end groups, the *m/z* of six repeating units and the cationzation agent (Cs^+) were subtracted from *m/z* 2294.4 giving a mass of 58. Given the polymerization was initiated using *t*-BuLi and quenched using MeOH, the end groups can be assigned to *t*-Bu and H.

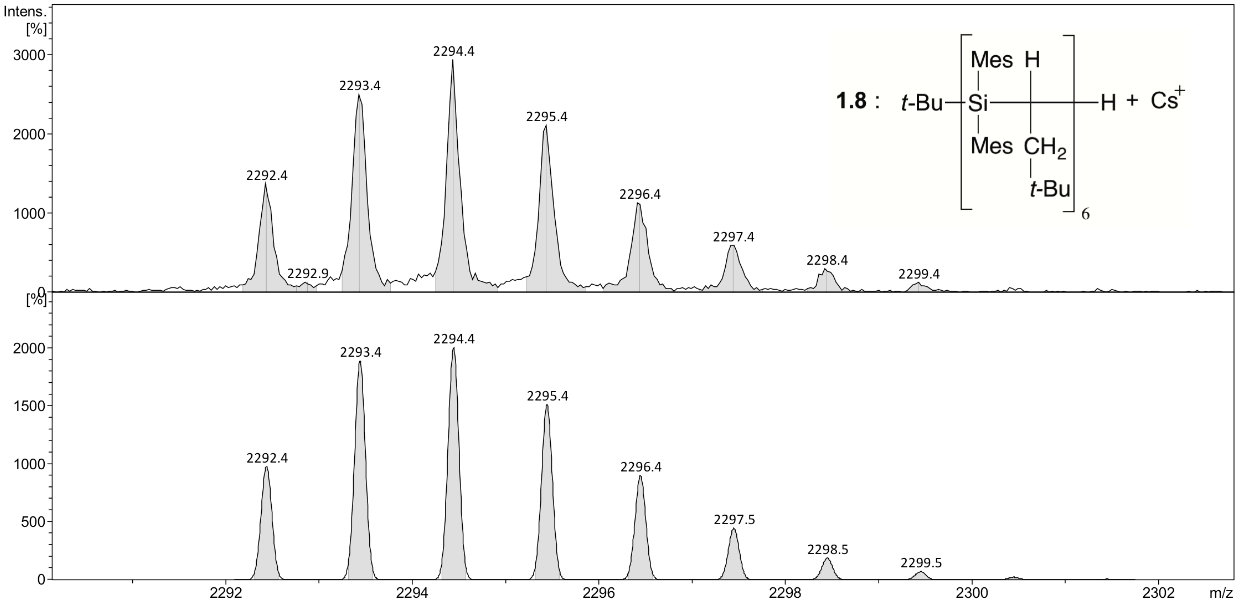
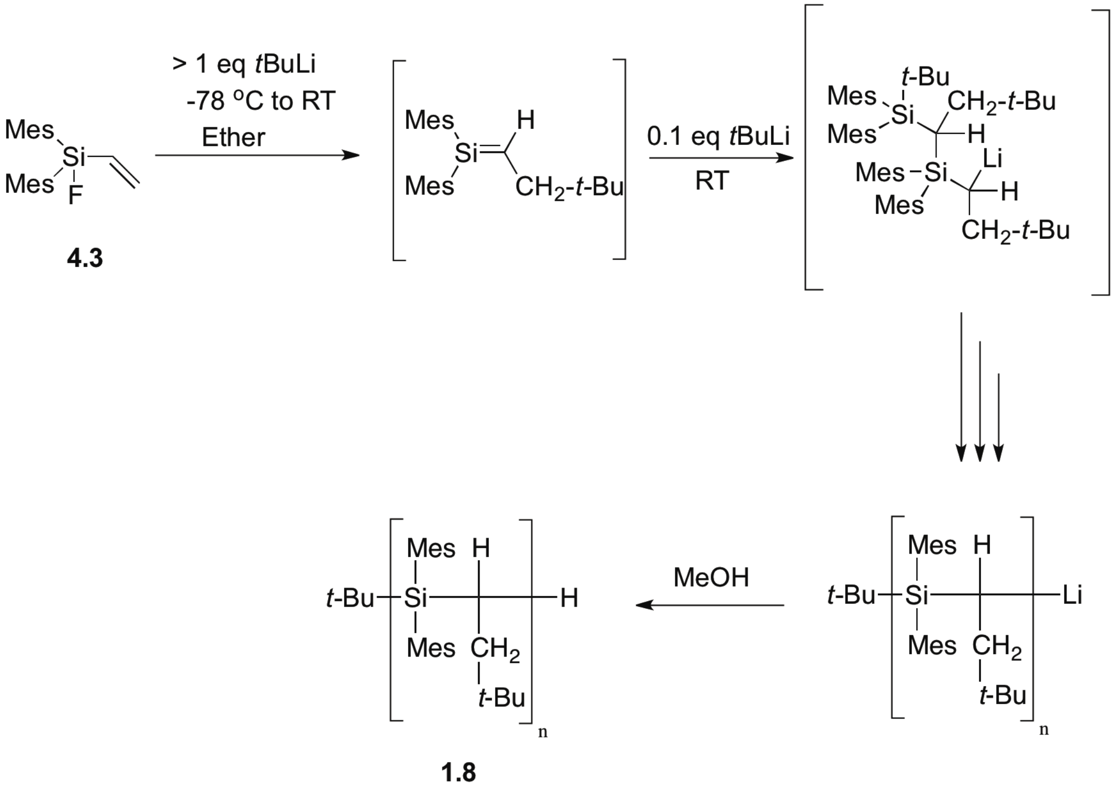


Figure 5.2 Isotopic pattern of *m/z* 2294.4 and calculated isotopic pattern

The observed molecular weight of polymer **1.8** as determined by GPC ($DP_n \cong$ 6-7) is lower than the molecular weight as determined by ESI-MS ($DP_n \cong$ 12). This is in agreement with Gates observations[18] that GPC can undestimate the molecular weight of this type of polymers. The identification of the end groups suggests a chain growth mechanism for the formation of the polymer (**Scheme 5.5**). The polymerization of silene **1.4** proceeds by the regioselctive addition of *t*-BuLi to the electrophilic silicon of the silene. The initial carbanion, adds to the silicon of a second silene to propagate the growth of the polymer.[5,19]



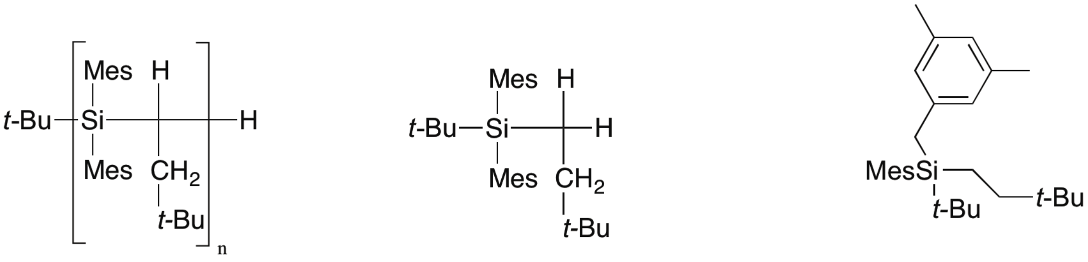
Scheme 5.5

5.2.2 Characterization of Polysilene 1.8 by ^{1}H NMR Spectroscopy

Recently, Gates *et al.* have shown that the radical- or anion-initiated addition polymerization of phosphaalkene **5.2** affords polyphosphenes with the primary structure shown in **Scheme 5.3**.[11,20] This discovery has called into question the primary structure of polysilene **1.8** derived from **1.4**, particulary since the addition of *t*-BuLi to **1.4** at room temperature gives **4.2** after quenching of the reaction mixture (**Chart 5.1**). Therefore, we probed the primary structure of polymer **1.8** using 2D ^{1}H-^{13}C correlation spectroscopy on a 600 MHz NMR spectrometer equipped with a high sensitivity cryoprobe. The correlations were phased to give positive correlations for signals which arise from CH/CH_3 carbons and negative correlations for signals arising from CH_2 carbons (**Figure 5.3**). To aid in the analysis of the structure of **1.8**, compounds **4.2** and **4.3** were used as model compounds of the repeating units of **1.8** (**Chart 5.1**).[5,12] In the original structureal assignment of the polymer, all of the signals in the ^{1}H NMR spectrum of **1.8** were assigned on the basis of their chemical shift and integration and were consistent with the proposed structure as modeled by **4.1**. The relevant ^{1}H and ^{13}C NMR chemical shifts of **4.1** and **4.2** and polymer **1.8** are given in **Table 5.1**.

The *o*- and *p*-CH_3 groups and the *m*-CH of the mesityl moieties of **1.8** showed three sets of signals in the ^{1}H–^{13}C gHSQC spectrum of polysilene **1.8** (**Figure 5.3**). The correlation at δ (^{13}C) = 20.6, δ (^{1}H) = 1.8 - 2.4) was assigned to the *p*-CH_3 groups and the correlation at δ (^{13}C) = 25.0, δ (^{1}H) = 2.0 – 2.5) was assigned to the *o*-CH_3 groups of the mesityl substituents. The broad resonance at δ (^{13}C) = 28.9, δ (^{1}H) = 0.7 was assigned to the backbone *t*-Bu group in the repeating unit of **1.8**. Examination of the ^{1}H–^{13}C HSQC

NMR spectrum of **1.8** also revealed correlations that can be assigned to the Si-CH moiety (δ (^{13}C) = 14.3, δ (^{1}H) = 0.9) and a CH_2 moiety (δ (^{13}C) = 39, δ (^{1}H) = 0.9) of the repeating unit in **1.8** (**Figure 5.3** and **Table 5.2**). The chemical shifts of these moieties displayed very similar chemical shifts to compound **4.1 (**Si-CH_2 (δ (^{13}C) = 11.91, δ (^{1}H) ~ 1.3 and CH_2*t*Bu at δ (^{13}C) = 39.9, δ(^{1}H) = 0.9. Furthermore, correlations can also be assigned to the end groups of polymer **1.8** at δ (^{13}C) = 14.7, δ (^{1}H) = 1.5 assigned to the SiCH_2 moiety, δ (^{13}C) = 39, δ (^{1}H) = 1.3 assigned to the CH_2*t*Bu moiety and δ (^{13}C) = 30, δ (^{1}H) = 1.3 assigned to the *t*BuSi moiety (**Table 5.2**). Notably, no correlations were observed in the region expected for a $SiCH_2Ar$ moiety (δ (^{13}C) = 23.8, δ (^{1}H) = 2.6) (**Table 5.1**). Although, there are a few unassigned weak correlations, we conclude that rearrangement to structures similar to compound **4.2** does not occur during the anionic polymerization of **1.8** and that propagation occurs through the former silenic carbon.



1.8 **4.1** **4.2**

Chart 5.1

Table 5.1 ^{1}H and ^{13}C NMR chemical shifts in ppm for **4.1**, **4.2** and **1.8**. Assignments were made with the aid of ^{13}C{^{1}H}-HSQC NMR experiments.

Compound	**4.1**		**4.2**		**1.8**	
Chemical shift	**^{1}H**	**^{13}C**	**^{1}H**	**^{13}C**	**^{1}H**	**^{13}C**
$CH_2C(\underline{CH_3})_3$	0.79	28.88	0.70	28.77	0.70	28.9
$SiC(\underline{CH_3})_3$	1.17	29.92	1.03	28.68	0.70	28.9
$SiCH_2\underline{CH_2}\textit{t}Bu$	0.88-0.94	39.86	0.98-1.10	37.14	0.8-1.4	38.2
$Si\underline{CH_2}CH_2\textit{t}Bu$	1.23-1.28	11.91	0.78-0.93	9.14	0.8-1.4	14.0
$CH_2\underline{C}(CH_3)_3$	____	31.21	____	31.08	____	31.0
$Si\underline{C}(CH_3)_3$	____	24.03	____	20.08	____	31.0
$SiCH_2Ar$	____	____	2.66, 2.62	23.80	____	____
$ArCH_3$	____	____	2.20	21.23	____	____

Table 5.2 ^{1}H-^{13}C{^{1}H} HSQC NMR spectra (600 MHz for ^{1}H, C_6D_6, 25 °C) of polysilene **1.8**. Data extracted from the HSQC spectra were collected with multiplicity editing during the selection step permitting assignments of CH/CH_3 *vs* CH_2 moieties.

Assignment	**Correlation** ^{1}H dimension/^{13}C dimension	**Phase**
_____	2.1/29	CH_2
_____	0.9/19	CH_2
Repeating unit $\mathrm{Si\underline{CH}CH_2}$*t*Bu	0.9/14.3	CH/CH_3
Repeating unit $\mathrm{\underline{CH_2}}$*t*Bu	0.9/39	CH_2
_____	1.5/28.9	CH_2
End group $\mathrm{Si\underline{CH_2}CH_2}$*t*Bu	1.5/14.7	CH_2
_____	1.3/29.9	CH_2
End group $\mathrm{SiCH_2\underline{CH_2}}$*t*Bu	1.3/39	CH_2
End group $\mathrm{SiC(\underline{CH_3})_3}$	1.3/30	CH/CH_3

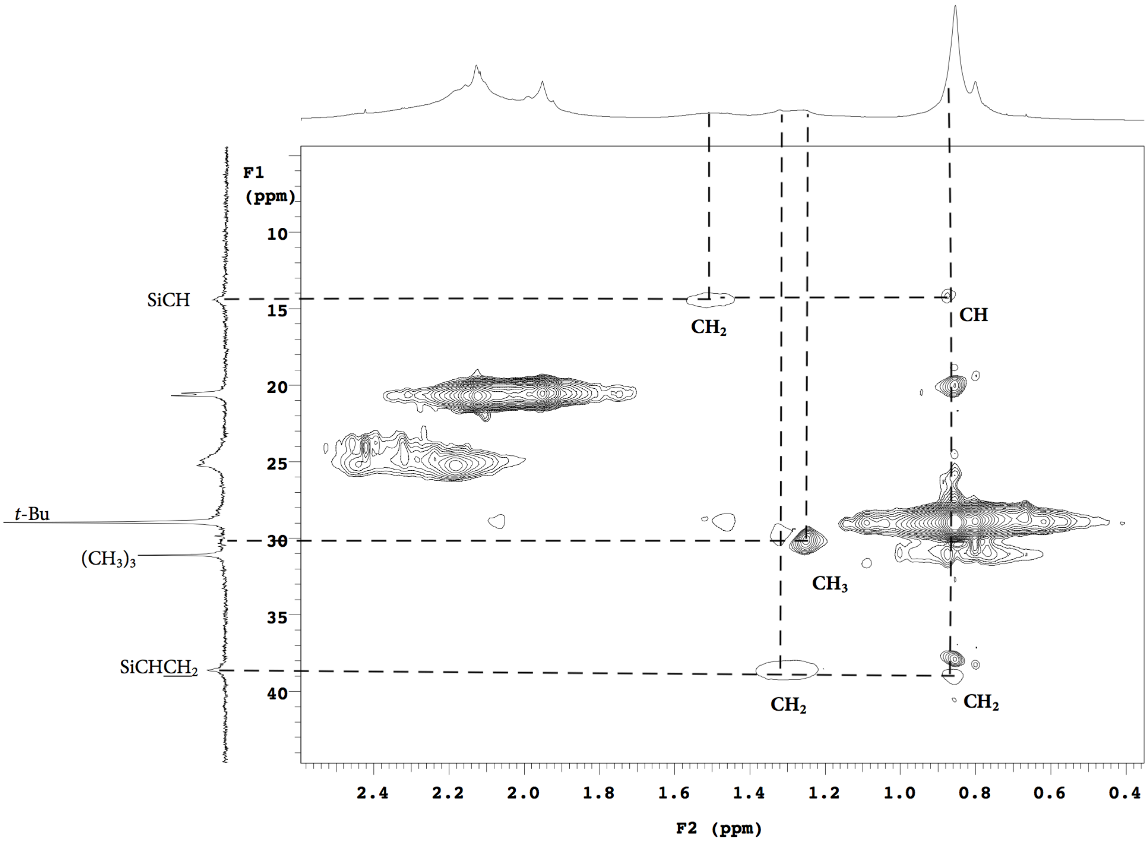


Figure 5.3 ^{1}H-^{13}C HSQC NMR spectra (600 MHz for ^{1}H, C_6D_6, 25 °C). The region from 2.5- 10 ppm in the ^{1}H dimension is not shown.

5.2.3 Polygermene 1.7 Preparation and Characterization by GPC

The polymerization of germene **1.1** was accomplished by the addition of excess *t*-BuLi (1.1 equiv) to an ethereal solution of fluorodimesitylvinylgermane at -78 °C. After addition of *t*-butyllithium, the solution was warmed to room temperature and the colour of the solution changed from pale to bright yellow. After 15 minutes, methanol was added and the bright yellow colour immediately disappeared. The solvents were removed and the residue was dissolved in CH_2Cl_2. The polymer was isolated as a white, air-stable solid after precipitation with MeOH (**Scheme 5.1**).

The ^{1}H NMR spectrum of the solid displayed broad resonances consistent with a polymeric substance. The number-average molecular weight (M_n) was determined by GPC (relative to polystyrene) in THF; two fractions were observed indicating a bimodal molecular weight distribution. The number average molecular weights (M_n) of the fractions were determined to be 41000 gmol^{-1} and 17000 gmol^{-1} with a polydispersity index (PDI) of 1.3, and 1.03 respectively. The data are consistent with previous results:[6] 26000 gmol^{-1}, 3340 gmol^{-1} with a polydispersity index (PDI) of 1.6, and 1.1, respectively.

5.2.4 Characterization of Polygermene 1.7 by ESI-MS

Polygermene **1.7** was analyzed using ESI-MS in positive ion mode. The sample was dissolved in tetrahydrofuran (THF) and sodium iodide was added as a cationization reagent. The spectrum was scanned from *m/z* 50 to *m/z* 20,000. The ESI-MS mass spectrum of the polygermene is shown in **Figure 5.4**. Signals that can be attributed to polygermene **1.7** were observed from *m/z* 4000 to 600 in the mass spectrum (**Figure 5.4**). Ten well-resolved clusters can be distinguished; the clusters were separated each by *m/z* 394 units, which corresponds to the mass of the germene monomer, [Mes_2Ge-C(H)(CH_2-C(*t*-Bu)]$_n$. Notably, no signals were observed from ~ *m/z* 5,000 to *m/z* 20,000, the upper limit of the instrument. The molecular weight of the polymer, as determined by GPC, exceeds the mass limit of the instrument and the cluster at n = 10 appears to be reaching the signal to noise limit. Similar observations were reported by Manners *et al.* in the attempted characterization of high molecular weight polyaminoboranes (M_W= 214000, PDI= 2.0 by GPC) by ESI-MS. The highest mass cluster of the polyaminoborane was observed at approximatly *m/z* 3000 and they concluded that ESI-MS does not permit a realistic molecular weight measurement for high molecular weight polymers.[21] Thus, the high molecular weight fraction of polygermene **1.7** observed by GPC (41000 g mol^{-1}) was not corroborated by ESI-MS. The maximum observed mass was around *m/z* 4000, corresponding to a degree of polymerization of about 10.

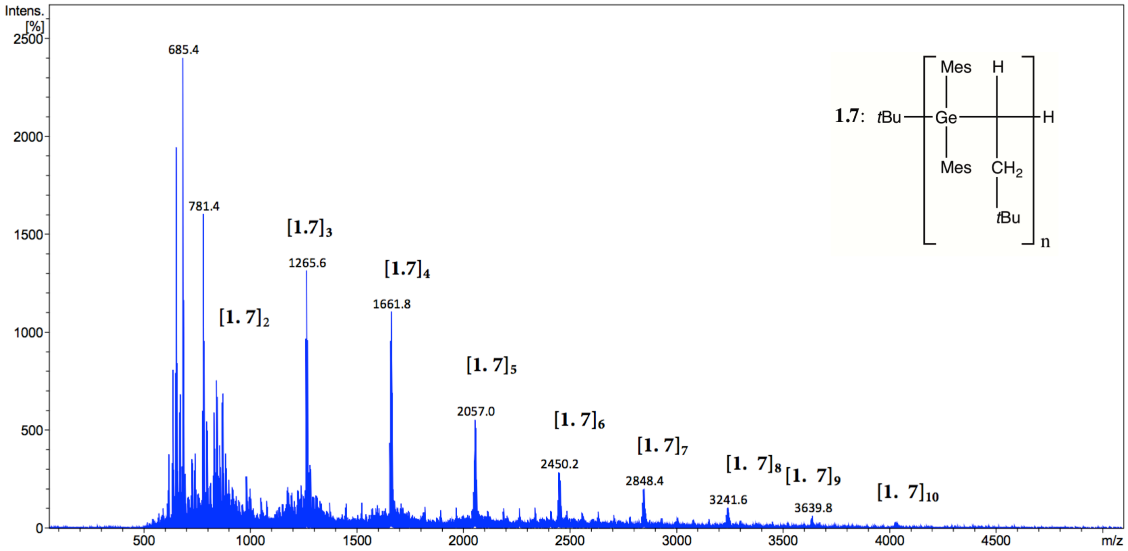


Figure 5.4 Positive ion ESI-MS of polygermene **1.7**

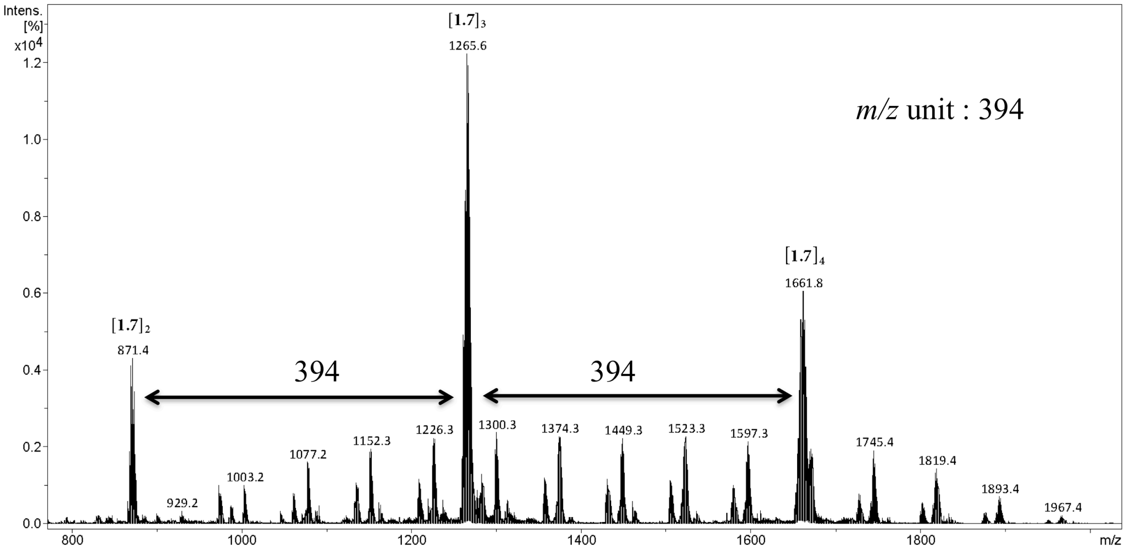


Figure 5.5 ESI-mass spectrum of polygermene **1.7** with an expansion from *m/z* 800 to *m/z* 2000. Also visible are a series of peaks with narrowly spaced lines with indicates the presence of silicone grease.

The ESI-MS of polygermene **1.7** from *m/z* 2000 to 800 is shown in **Figure 5.5**. In this spectrum, in which the sensitivity of the instrument was optimized for lower m/z values, three distinct clusters were observed which correspond to the dimer, trimer and tetramer, respectively. Additional lower intensity signals are also evident. On the basis of the regular spacing of *m/z* 74, these signals were assigned to silicone grease. Silicone grease is a dimethylsiloxane-based polymer, $(Me_2SiO)_x$,[22] that is routinely used to seal ground glass joints in the glassware used during the synthesis of air- and moisture- sensitive organometallic compounds[23] and is a common contaminant in products as observed by NMR spectroscopy and now by mass spectrometry. The separation of *m/z* 74 corresponds to the mass of the repeat unit of the siloxane monomer.

An expansion of the signal centred at *m/z* 871.4 is shown in **Figure 5.6**. The isotopic pattern of the signal at *m/z* 871.4 matches quite well with the calculated isotopic ratio for $C_{52}H_{78}{}^{72}Ge^{74}GeNa^+$ and can be assigned to a dimer of germene **1.1**. Furthermore, to determine the *m/z* of the end groups, the *m/z* of two repeating units of the polymer and the cationization agent (Na^+) were subtracted from *m/z* 871.4. Thus, the end groups had a mass of 58. Given the polymerization was initiated use *t*-BuLi and quenched using MeOH, the end groups can be assigned to *t*-Bu and H.

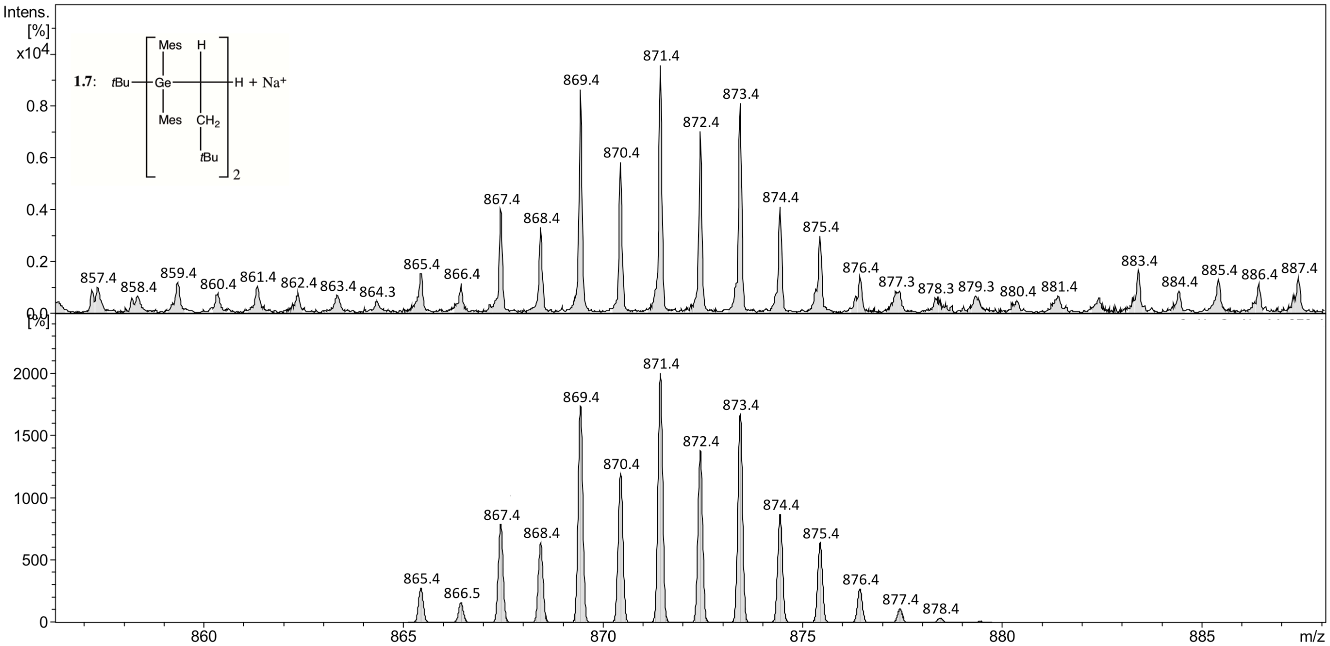


Figure 5.6 Experimental and calculated isotopic distribution for $(C_{25}H_{78}Ge_2Na^+)$

Table 5.3 Signal assignment for the mass spectrum of polygermene **1.7**

Oligomer tBu$[GeMes_2CHCH_2t\text{Bu}]_nH$	Exact mass (calc.)	Exact mass (exp.)	Error (ppm)
n = 2	871.4434	871.4444	1
n = 3	1265.6345	1265.6343	0.5
n = 4	1661.8194	1661.8242	0.7

The calculated and experimental exact masses of the three prominent signals assigned to the dimer, trimer and tetramer with *t*-Bu and H as the end groups in the mass spectrum of **1.7** (**Figure 5.4**) are given in **Table 5.3**. The agreement between the two numbers is excellent and we can assign the molecular formulation with confidence.

5.2.5 Characterization of Polygermene 1.7 by Static Light Scattering

Due to the noted inaccuracies of molecular weights using GPC,[3a] and the apparent inability of ESI-MS to determine the absolute molecular weight of high molecular weight inorganic polymers, the absolute molecular weight of polygermene **1.7** was determined using static light scattering (SLS). Because of the nature of the light scattering technique, the data reflect the true M_w of the samples in contrast to molecular weight determined by relative calibrations, such as GPC. The relative molecular weight determined by GPC more closely reflect the hydrodynamic size of a polymer and can be influenced by other effects such as interactions with the column.[24b] The absolute weight-average molecular weight of polygermene **1.7** in THF was determined to be M_w= 41500 gmol^{-1}. The molecular weights indicated by GPC (M_w =41000 gmol^{-1}, 17000 gmol^{-1} with a polydispersity index (PDI) of 1.3, and 1.03 respectively) and SLS (41500 gmol^{-1}) correspond to approximatly 43-104 repeat units. The static light scattering data agrees very well with the molecular weight obtained by GPC results for high molecular weight fraction of polygermene **1.7**.

5.3 Conclusions

We have described the structural characterization of polymers **1.7** and **1.8** by three different methods. The framework of polysilene **1.8** was investigated using 2D NMR spectroscopy to confirm the structure of the backbone of the polymers, and to provide evidence for the identity of the end groups. The ESI-MS data of polysilene **1.7** and polygermene **1.8** provided additional convincing evidence for the structure of the end groups. The structure of the polymers suggests a chain growth mechanism for the anionic polymerization of the two tetrelenes.

Characterization of polysilene **1.8** and polygermene **1.7** by ESI-MS revealed only the presence of oligomers ($n < 10$) of the polytetrelenes. ESI-MS appears to be a useful method for the characterization of inorganic oligomers such as poly(aminoborane)s[14], polyphosphaalkenes[17], as well as polysilenes and polygermenes, although the technique cannot be used for the molecular weight characterization of the high molecular weight fraction of a polymer sample. The use of CsI and NaI as cationization agents is very promising; this approach should be generally suitable for the characterization of inorganic polymers by ESI-MS. The absolute molecular weight of polygermene **1.7** by static light scattering was reported. GPC and SLS remain the best methods for the characterization of the molecular weight of high molecular weight polymers; however, ESI-MS is very useful for the identification of the end groups and a confirmation of the formulation of the polymer.

5.4 Experimental

5.4.1 General Experimental Details

Polysilene[5] **1.8** and polygermene[6] **1.7** were synthesized following the established procedures, using standard double-manifold Schlenk line techniques. ESI mass spectra were recorded on a Bruker micrOTOF II mass spectrometer with an electrospray interface in positive ion mode. The polygermene samples were dissolved in THF. A NaI solution (in acetone at 10 g $\cdot L^{-1}$, 2 μL) was added to the solutions of polymers. The polysilene samples were dissolved in THF and a CsI solution was added to the solution of polymers. The samples were directly injected into the ion source. Data are reported in mass-to-charge units (*m/z*). The ESI-MS experiments were carried out at a capillary voltage of 4500 V and a dry heater temperature of 180 °C and data were acquired over the range *m/z* 50-20000. An internal calibration was performed using NaI or CsI to improve the accuracy of the mass measurement leading to a precise identification of the *m/z* of the signals. Isotope distributions were simulated using the Bruker Compass DataAnlysis 4.0. ^{1}H, $^{13}C\{^{1}H\}$ and ^{1}H-^{13}C HSQCAD were acquired at 25 °C using a Varian Inova 600 multi-resonance NMR spectrometer equipped with a Varian 5mm helium-cooled HCN cryoprobe.

5.4.2 Molecular weight determination

The Gel Permeation Chromatography (GPC) instrument used to characterise polysilene **1.8** was equipped with a Viscotek GPC Max VE2001 solvent module. Samples were analyzed using the Viscotek VE3580 RI detector operating at 30 °C, and triple detection Malvern 270 Dual detector. The separation technique employed two Agilent Polypore (300 x 7.5mm) columns connected in series and to a Polypore guard column (50 x 7.5mm). Samples were dissolved in THF (glass distilled grade) in approximately 5 mg/mL concentrations and filtered through 0.22 µm syringe filters. Samples were injected using a 100µL loop. The THF eluent was filtered and eluted at 1 mL/min for a total of 30 minutes. A calibration curve was obtained using polystyrene samples with molecular weight ranges of 1,540-1,126,000/mol.

The Gel Permeation Chromatography (GPC) instrument used to characterise polygermene **1.7** was equipped with a Waters 515 HPLC pump and a Waters In-line Degasser AF. Samples were analyzed using the Wyatt miniDawn Treos Light Scattering detector, and a Wyatt Optilab Rex RI detector operating at 658 nm and 25 ^{o}C. The separation technique employed two Agilent Polypore (300 X 7.5mm) columns connected in series to a Polypore guard column. Samples were dissolved in THF (glass-distilled) at approximately 5 mg/mL concentrations and filtered through 0.22 μm syringe filters. Sample were injected using a 50 μL loop (56 μL volume). The THF eluent was filtered and eluted at 1mL/min for a total of 30 minutes. A calibration curve obtained from polystyrene samples with molecular weight ranges of 580-3,250,000 g/mol. The dn/dc value of polystyrene in THF used was 0.185 mL/g and was used in the conventional molecular weight analysis.

The dn/dc value for polygermene was measured directly by preparing a series of polygermene solutions in different concentrations ranging from 30 mg/mL- 0.5 mg/mL in THF using an Abbé refractometer manufactured by Bausch and Lomb. The polygermene samples were run at least two times to ensure reproducibility of the calculated dn/dc.

For the determination of M_w by light scattering, time-averaged light scattering intensities were measured for each polymer at a series of concentrations from 0.2 to 1.1 mg/mL in THF using a Malvern Zetasizer Nano-ZS instrument. The solutions were prepared and injected into a light scattering cell without filtration. Due to solvent evaporation and dilution, the amount of THF that might remain in the solution was considered as negligible. Toluene was used as a standard. Using these data, the M_w for each polymer was determined from the Rayleigh equation: $KC/R_\theta = (1/M_w + 2A_2C)P(\theta)$ using a Debye plot: KC/R_θ versus C, allowing $1/M_w$ to be determined as the y-intercept and where C = polymer concentration; R_θ = excess Rayleigh ratio − the ratio of scattered and incident light intensity; A_2 = second viral coefficient, which is a measure of solute-solvent interactions; $P(\theta)$ = scattering function, which relates the angular variation in scattering intensity to the mean square radius of the particle; $K = 4\pi^2/\lambda_o^4 N_A[n_o(\mathrm{dn/dc})]^2$ where λ_0 = vacuum wavelength of incident light; N_A = Avogadro's number; n_0 = solvent refractive index and the dn/dc is the refractive index increment in THF.[24] Refractive index increment measurements were carried out at five different concentrations in THF at room temperature. We have measured the refractive index increment to be 0.1968.

5.5 References

1. (a) Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P. *Chem. Soc. Rev.* **2016**, *45*, 922; (b) Scheschkewitz, D.; Präsang, C. *Chem. Soc. Rev.* **2016**, *45*, 900.

2. (a) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. *Nat. Mater.* **2011**, *10*, 176; (b) Lodhe, M., Babu, N.; Selvam, A.; Balasubramanian, M. *J. Adv. Ceram.* **2015**, *4*, 307.

3. (a) Tsang, C. W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003**, *125*, 1480; (b) Noonan, K. J. T.; Patrick, B. O.; Gates, D. P. *Chem. Commun.* **2007**, 3658.

4. (a) Noonan, K. J. T.; Gates, D. P. *Angew. Chem. Int. Ed.* **2006**, *45*, 7271; (b) Noonan, K. J. T.; Gates, D. P. *Macromolecules*. **2008**, *41*, 1961.

5. Pavelka, L. C.; Milnes, K. K.; Baines, K. M. *Chem. Mat.* **2008**, *20*, 5948.

6. Pavelka, L. C.; Holder, S. J.; Baines, K. M. *Chem. Commun*. **2008**, 2346.

7. Bravo-Zhivotovskii, D.; Melamed, S.; Molev, V.; Sigal, N.; Tumanskii, B.; Botoshansky, M.; Molev, G.; Apeloig, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 1834.

8. Colombo, P.; Mera, G.; Riedel, R.; Sorarù, G. D. *J. Am. Ceram. Soc.* **2010**, *93*, 1805.

9. (a) Wu, X.; Neckers, D. C. *Macromolecules*, **1999**, *32*, 6003; (b) Matsumoto, K.; Shinohata, M.; Yamaoka, H. *Polym. J.* **2000**, *32*, 1022; (c) Matsumoto, K.; Shinohata, M.; Yamaoka, H. *Polym. J.* **2000**, *32*, 354; (d) Matsumoto, K.; Deguchi, M.; Nakano, M.; Yamaoka, H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2699; (e) Liao, C.; Weber, W. *Polym. Bull.* **1992**, *28*, 281; (f) Matsumoto, K.; Matsuoka, H. *Macromolecules*, **2003**, *36*, 1474; (g) Bravo-Zhivotovskii, D.; Melamed, S.; Molev, V.; Sigal, N.; Tumanskii, B.; Botoshansky, M.; Molev, G.; Apeloig, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 1834.

10. (a) Birot, M.; Pillot, J. P.; Dunogues, J. *Chem. Rev.* **1995**, *95*, 1443; (b) Liu, Q.; Wu, H. J.; Lewis, R.; Maciel, G. E.; Interrante, L. V. *Chem. Mater*. **1999**, *11*, 2038; (c) Cheng, Q. M.; Interrante, L. V.; Lienhard, M.; Shen, Q.; Wu, Z. *J. Eur. Ceram. Soc.* **2005**, 25, 233; (d) Brefort, J.L.; Corriu, R. J. P.; Guerin, C.; Henner, B. J. L. *J. Organomet. Chem.* **1994**, *464*, 133.

11. Siu, P. W.; Serin, S. C.; Krummenacher, I.; Hey, T. W.; Gates, D. P. *Angew. Chem. Int. Ed.* **2013**, *52*, 6967.

12. Farhadpour, B.; Guo, J.; Pavelka, L.C.; Baines, K. M. *Organometallics* **2015**, *34*, 3748.

13. (a) Montaudo, G.; Lattimer, R. P. *Mass Spectrometry of Polymers*; CRC Press: Florida, **2002**; (b) Liang, L. *MALDI Mass Spectrometry for Synthetic Polymer Analysis*; Wiley & Sons: New Jersey, **2009**; (c) Macha, S. F.; Limbach, P. A. *Curr. Opin. Solid State Mater. Sci.*, **2002**, *6*, 213; (d) Stump, M. J.; Fleming, R. C.; Gong, W. H.; Jaber, A. J.; Jones, J. J.; Surber, C. W.; Wilkins, C. L. *Appl. Spectrosc. Rev.* **2002**, *37*, 275; (e) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527.

14. Metters, O. J.; Chapman, A. M.; Robertson, A, P. M.; Woodall, C. H.; Gates, J. P.; Wass, D. F.; Manners, I. *Chem. Commun.* **2014**, *50*, 12146.

15. He, G.; Kang, L.; Delgado, W. T.; Shynkaruk, O.; Ferguson, M. J.; McDonald, R.; Rivard, E. *J. Am. Chem. Soc.* **2013**, *135*, 5360.

16 . (a) Henderson, W.; McIndoe, J. S., *Mass Spectrometry of Inorganic and Organometallic Compounds: Tools — Techniques — Tips*. John Wiley & Sons: Chicester, **2005**. (b) Yunker, L. P. E.; Stoddard, R. L.; McIndoe, J. S. *J. Mass Spectrom.* **2014**, *49*, 1.

17. Gillon, B. H.; Gates, D. P. *Chem. Commun.* **2004**, 1868.

18. Gillon, B. H.; Gates, D. P.; Henderson, M. A.; Janusson, E.; McIndoe, J. S. *Can. J. Chem.* **2017**, 95, 239.

19. Pavelka, L. C. A Study of E=C Compound Reactivity: Alkyne Addition and Polymerization, The University of Western Ontario, **2009**.

20. Serin, S. C.; Dake, G. R.; Gates, D. P. *Macromolecules.* **2016**, *49*, 4067.

21. Staubitz, A.; Sloan, M. E.; Robertson, A. P. M.; Friedrich, A.; Schneider, S., Gates, P. J.; Schmedt auf der Günne, J.; Manners, I. *J. Am. Chem. Soc*. **2010**, *132*, 13332.

22. Manners, I. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1602.

23. Haiduc, I. *Organometallics* **2004**, *23*, 3.

24. (a) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669; (b) Bonduelle, C. V.; Karamdoust, S.; Gillies, E. R. *Macromolecules.* **2011**, *44*, 6405.

Chapter 6

6 Summary, Conclusions and Future Directions

6.1 Summary and Conclusions

This thesis has examined the reactivity of doubly-bonded Group 14 species with a focus on two areas: their reactivity towards main group oxides and the physical characteristics of polymers derived from them.

In Chapters 2 and 3, the addition of a variety of main group oxides to tetramesityldigermene, tetramesityldisilene and 1,1-dimesitylneopentylgermene were examined. In Chapter 2, the reactions of several nitrones and nitro compounds with (di)tetrelenes were described. The results can be most easily understood in terms of a [3+2] cycloaddition where the (di)tetrelene acts as the 2π component and the nitro/nitrone acts as the 4π component. The reaction between digermene **1.2** and C,N-diphenyl nitrone and *N*-*tert*-butyl-α-phenylnitrone revealed the formation of an interesting four-membered hetereocycle which involved a mesityl migration. In contrast, the analogous reaction with germene **1.1** yielded a 5-membered ring which does not involve a mesityl migration. The addition of C,N-diphenyl nitrone to disilene **1.3** resulted in the formation of 5-membered ring and additional side products; Mes_4SiO[1] and $Mes_4Si_2O_2$[1]. The difference in reactivity between the disilene and the doubly-bonded germanium derivatives is likely due to the difference in the Si-O versus the Ge-O bond strengths. Interestingly, the addition of DMPO to germene **1.1**, digermene **1.2**, and disilene **1.3** lead to the facile formation of highly stable 5-membered ring adducts. The addition of nitromethane and nitroethane to germene **1.1** revealed the formation of 1,3,2,4-dioxazagermolidine ring systems, mirroring the reactivity of disilenes and digermenes towards nitroalkanes.[2,3] The 1,3,2,4-dioxazagermolidines are derived from a formal [3+2] cycloaddition of the nitro group to the germene. Upon preparative thin-layer chromatography, 1,3,2,4-dioxazagermolidines undergo ring opening reactions. In the case of the addition of nitromethane to germene **1.1**, attempts to isolate the heterocycle by crystallization failed, and instead, a hydrogen-bonded complex was formed. Our results were compered with those reported by Escudié[4] and previously by our group.[2]

In Chapter 3, the addition of a phosphine oxides and phosphites to the Group 14 (di)tetrelenes, $Mes_2Si=SiMes_2$, $Mes_2Ge=GeMes_2$ and $Mes_2Ge=CH(CH_2$-*t*-Bu), was examined and resulted in the formation of 1,2-addition products. The initial step of the the addition of phosphonyl compounds to digermene **1.2** and germene **1.1** was proposed to occur by nucleophilic attack of the oxygen to the germanium of the digermene and/or the germene to form a zwitterionic intermediate. Abstraction of the hydrogen by the germyl anion, or the carbanion, gives the observed products. Our findings paralleled the results of a recent study of the reactivity of the analogous disilene with diphenylphosphine oxide which also showed the formation of 1,2-addition products.[3] The formation of the oxyphosphine adducts revealed an interesting, mild 2-electron reduction of the phosphorus centres using (di)tetrelenes. The addition reactions of phosphine oxides and phosphites illustrates the potential use of (di)tetrelenes as effective reducing agents as the reductions occur rapidly, at room temperature and under mild conditions. The addition of trimethyl phosphite to the molecular digermene and disilene did not form any adduct. Our findings were not consistent with the results of the analogous surface digermenes. The difference in reactivity between molecular digermenes and their surface counterparts was attributed to the difference in their electronic structures and the arrangements of the substituents about the Ge=Ge double bonds.

Overall, the reactivity of (di)tetrelenes towards main group oxides, such as nitrones, nitro compounds, phosphine oxides and phosphites, revealed the formation of new compounds. In general, two modes of reactivity were observed: 1,2- addition and 1,3-cycloaddition across the M=E double bond. The reactions of several aryl and alkyl-substituted derivatives of nitrone and nitro compounds are represented and the products can be synthesized in good yield. Thus, the addition of main group oxides to ditetrelenes offers a simple, direct route to new heterocycles from readily available starting materials. The formation of phosphorus(III) by the addition of phosphorus(V) compounds to ditetrelenes represents a relatively simple and new reaction. The compounds are formed in a one step reaction without the use of heat or a catalyst under very mild conditions. Furthermore, our work emphasizes that heavy main group unsaturated compounds can be powerful building blocks in organometallic/inorganic synthesis just as alkenes and alkynes have shown to be in organic synthesis. To achieve the potential applications of these new Group 14 compounds, the study of the reactivity of these intriguing species must be continued to give us a broad and comprehensive understanding of their chemistry. Only in this way can novel applications for the chemistry be developed.

In Chapter 4, the reactivity of the naturally polarized tetrelenes toward a variety of organometallic reagents has been reported.[5] The organometallic reagent added regioselectively to the highly reactive silene **1.4** and germene **1.1**, with the organic moiety always adding to the Group 14 atom of the unsaturated bond. 1,2-addition products formed in good yield and no evidence for rearrengment was observed. The staightforward, selective addition of commercially available organometallic reagents to silenes and germenes makes this reaction synthetically useful and may be used to introduce functionality into the compound. No polymer was observed during the addition of MeLi, BuLi and *t*-BuOK to silene **1.4** and germene **1.1**. Thus, we concluded that the rate of addition to the tetrelene is significantly faster than the rate of propagation. Presumably, this is due to the decrease in bulk of the organometallic reagent.

In Chapter 5, with the high level of interest in the potential applications of main group polymers, we have investigated the primary structure and molecular weights of polygermene **1.7** and polysilene **1.8**. Mass spectrometric and NMR spectroscopy analysis of polygermene **1.7** and polysilene **1.8**, prepared by polymerizing $Mes_2M{=}CHCH_2t$-Bu (M= Si, Ge) using *t*-BuLi as the initiator, revealed important insights into the structure and mechanism of these new inorganic polymers. The results demonstrate the presence of R-Ge and C-H end groups, consistent with a chain growth mechanism where the R group is derived from the anionic initiator. The absolute weight-average molecular weight of polygermene **1.7** was determined by static light scattering (SLS) in THF which showed that M_w to be 41500 g mol^{-1}.

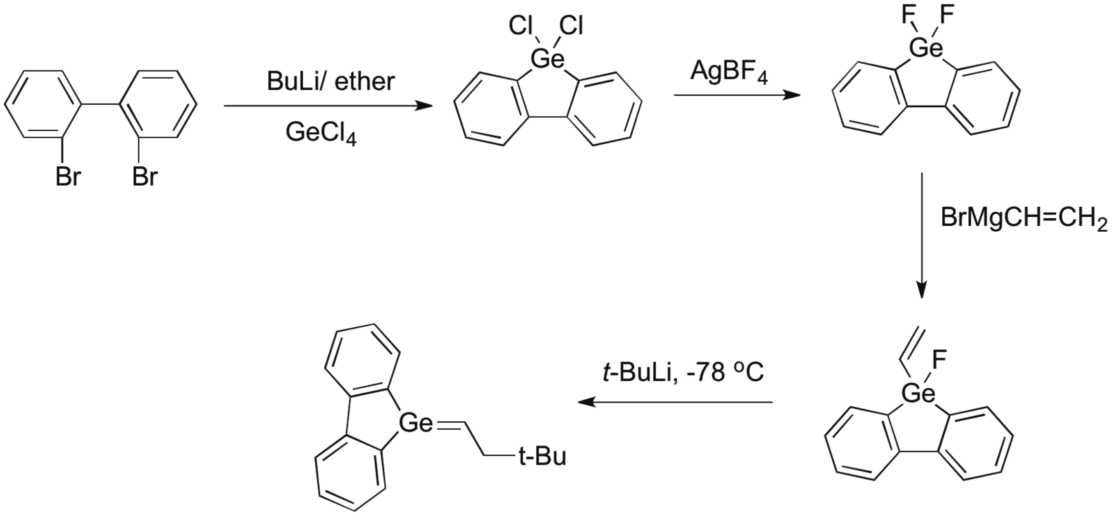
Our results now give us confidence in our ability to determine these important characterstics of these inorganic polymers and the methods can be broadly applied to newly synthesized main group polymers. Our results have opened the door to investigations of the unique physical and chemical properties of main group polymers containing silicon and germanium that may lead us to potential applications in the future.

6.2 Future Work

The addition of a variety of nitro compounds to ditetrelenes has been reported previously.[2,3] All reactions proceed via a 1,3-cycloaddition reaction. Except for nitromethane and nitroethane as reported in this thesis, the reactivity of nitro compounds towards germenes as well as silenes has not been investigated. We have carried out a preliminary study of the addition on nitrobenzene to germene **1.1** and obtained promising results. Further study of the addition of nitro compounds to silenes and germenes is required to determine the generality and scope of the reaction.

Very little is known about the addition of phosphorus-containing reagents to (di)tetrelenes. This study is the first example of the addition of phosphorus oxides to doubly-bonded germanium compounds. In the future, the reactivity of ditetrelenes towards other phosphorus reagents, such as di-tert-butylphosphine oxide and di-*tert*-butylphosphinic chloride, should be explored and compared to our results and those of the analogous sulfur derivatives.

Few stable germenes have been reported in the literature.[6] The synthesis of new germenes provides further opportunities for investigations into their reactivities, structure and bonding. Some preliminary results have been obtained. The proposed synthesis of a new germene is presented in **Scheme 6.1**. The installation of the fluorenyl substituent on germanium should be possible and will enable of a germene with potentially interesting photophysical properties.[7] The photophysical properties of a polymer derived from this germene should also be interesting.



Scheme 6.1

Different aspects of the chemistry of polygermene **1.7** and polysilene **1.8** can be pursued. The living polymerization of both polymers should be investigated in an effort to obtain a polymer with low polydispersities. The living anionic polymerization and atom transfer radical polymerization (ATRP) of germene **1.1** were attempted; however, further work is required to optimize the conditions of these reactions. Similar polymerization methods of silene **1.4** have not yet been attempted. The ability to synthesize living polymers enables the synthesis of a variety of block copolymers such as polygermene/polysilene block copolymers. Although much work still remains to be done, there is a significant potential to prepare main group polymers with unique characteristics for technological applications.

6.3 References

1. (a) McKillop, K. L.; Gillette, G. R.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1992**, *114,* 5203; (b) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865; (c) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5,* 531.

2. Tashkandi, N. Y.; Parsons, F.; Guo, J.; Baines, K. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 1612; *Angew. Chem.* **2015**, *127*, 1632.;

3. Tashkandi, N. Y. Cycloaddition Reactions of (Di)tetrelenes ,The University of Western Ontario, **2016**.

4. El Kettani, S.; Lazraq, M.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Gornitzka, H.; Atmani, A. *Organometallics* **2005**, *24*, 5364.

5. Farhadpour, B.; Guo, J.; Pavelka, L. C.; Baines, K. M. *Organometallics* **2015**, *34*, 3748.

6. (a) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.; (b) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113.

7. (a) Mei, J.; Leung, L. C.; Kwok, R. T.K.; Lam, J. W.; Tang, B. Z. *Chem. Rev.* **2015**, *115* (21), 11718; (b) Hong, Y.; Lam, W. Y. J.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361.

7 Appendix

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2. Farhadpour, B.; Bourque, J. L.; Baines, K. M. “The Addition of Nitrone and Nitro Compounds to Tetrelenes and Ditetrelenes,” manuscript in preparation.

3. Farhadpour, B.; Tashkandi, N. Y.; Bourque, J. L.; Baines, K. M. ”Reactivity of (Di)tetrelenes Toward Phosphorus Oxide Compounds,” manuscript in preparation.

4. Farhadpour, B.; Guo, J.; Pavelka, L. C.; Baines. M. K. “Addition of Organometallic Reagents to a Stable Silene and Germene”, Organometallics. **2015**, *34*, 3748-3755.

5. Hosseini, H.; Simiari, J.; Farhadpour, B. " Chemical and Electrochemical Grafting of Polyaniline on to Chitosan", Iranian Polymer Journal, **2009**, *18*, 3-13.

6. Pourjavadi, A.; Farhadpour, B.; Seidi, F. "Synthesis and Investigation of Swelling Behavior of New Agar Based Superabsorbent Hydrogel as a Candidate for Agrochemical Delivery", Journal of Polymer Research, **2009**, *16*, 655-665.

7. Pourjavadi, A.; Farhadpour, B. "Synthesis and investigation of swelling behavior of grafted alginate/alumina superabsorbent composite, Starch / Starke, **2008**, *60*, 457-466.

Presentations (Oral and poster):

1. Farhadpour, B.; Guo, J.; Baines, K. M. "Addition of Organometallic Reagents to a Stable Silene and Germene", Poster, 98th Canadian Chemistry Conference and Exhibition, Ottawa, Ontario, June 13-17, **2015**.

2. Farhadpour, B.; Baines, K. M. "The Anionic Polymerization of 1,1-Dimesitylneopentylgermene", 14th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead (GTL 2013), Baddeck, Nova Scotia, July **2013**.

3. Farhadpour, B.; Pavelka, L. C.; Baines, K. M. "The Anionic Polymerization of 1,1-Dimesitylneopentylgermene", 44 th Silicon Symposium, St. Catherines, Ontario, Canada, June15-17, **2012**.