Advances in the chemistry of base-stabilized germanium(II) compounds towards C-C bond formation

Ong, Melissa Xin Yi

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**Advances in the Chemistry of Base-Stabilized Germanium(I)
Compounds Towards C-C Bond Formation**

ONG XIN YI MELISSA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

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**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of Master of Science

2020

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Statement of Originality

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Abstract

The synthesis of base-stabilized germanium(I) dimers and a silagermyne were reported. In addition, the application of the base-stabilized germanium(I) dimers toward catalytic C-C bond formation of α,β -unsaturated carbonyl compounds was described. In Chapter 1, a brief introduction of low-valent heavier group 14 element carbene analogues and multiple bonded heavier group 14 element compounds was described. The small energy difference between the HOMO and LUMO facilitates their capability of transition-metal like reactivity in small molecules activation. In Chapter 2, the synthesis of base-stabilized germanium(I) dimers and their application toward C-C bond formation of α,β -unsaturated carbonyl compounds was reported. First, treatment of the amidinate-stabilized chlorogermylene and the 2-imino-5,6-methylenedioxyphenyl chlorogermylene with potassium graphite (KC₈) afforded the amidinato germanium(I) dimer [RGeGeR] and the 2-imino-5,6-methylenedioxyphenyl germanium(I) dimer [LGeGeL] respectively. With the base-stabilized germanium(I) dimers in hand, they were used to investigate C-C bond formation reactions through the polymerization of various α,β -unsaturated carbonyl compounds to form corresponding polymers with low molecular weight and low dispersity. The successful polymerization led us to investigate and propose the mechanism of polymerization in a traditional initiation-propagation-termination manner. In chapter 3, we showed the synthesis of the base-stabilized unsymmetric silagermyne [LGeSiR]. The in-situ generation of LGeK was when the 2-imino-5,6-methylenedioxyphenyl chlorogermylene was treated with excess potassium graphite. The silagermyne was afforded from the reaction of LGeK with the amidinato chlorosilylene [RSiCl]. We then investigated the reactivity of LGeSiR with various Lewis acids, chalcogens and transition metal carbonyls, of which the successful isolation of the [LGe-Te-Si(Te)R] complex was reported by X-ray crystallography. Additionally, we attempted to mimic a push-pull NHC-disilyne -ZnCl₂ with LGeSiR but instead of forming the push-pull complex, we formed a [LH]-GeCl₂ dimer isolable by X-ray crystallography.

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List of Abbreviations and Symbols

Abbreviations/Symbols	Representation
δ	NMR chemical shift in Hz
$^{\circ}$	Degree(s)
$^{\circ}\text{C}$	Degrees Celsius
$\text{\AA}$	Angstrom(s)
ACN	Acetonitrille
Ar	Aryl
Bbt	2,6-bis[bis-(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl
BMA	Butyl methacrylate
Bu	Butyl
cat.	Catalyst
Cp	Cyclopentadienyl
DCM	Dichloromethane
DCTB	Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile
DEE	Diethyl ether
DFT	Density function theory
E+	Electrophile
EA	Ethyl acetate
EMA	Ethyl methacrylate
Eqv.	Equivalent(s)
Et	Ethyl
eV	Electronvolt(s)
GC-MS	Gas chromatography-mass spectrometry
GPC	Gel permeation chromatography
h	Hour(s)
Hex	Hexane
HOMO	Highest occupied molecular orbital
HRMS	High-resolution mass spectrometry
iPr	Isopropyl
K	Kelvin

Kcal	Kilocalorie(s)
LC-MS	Liquid chromatography-mass spectrometry
LUMO	Lowest unoccupied molecular orbital
m/z	Mass-to-charge ratio
m	Milli
MALDI-TOF-MS	Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry
MBO	3-methyl-3-buten-2-one
Me	Methyl
Mes	Mesityl (2,4,6-trimethylphenyl)
MMA	Methyl methacrylate
mol	Mole(s)
MPO	3-methyl-3-penten-2-one
MS	Mass spectrometry
nBu	n-Butyl
NHC	N-heterocyclic carbene
nm	Nanometer(s)
NMR	Nuclear magnetic resonance
Nu ⁻	Nucleophile
Ph	Phenyl
ppm	Parts per million
RT	Room temperature
Sol	Solvent
Tbt	2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl
^t Bu	<i>Tert</i> butyl
TFA	Trifluoroacetate
THF	Tetrahydrofuran
TMS	Trimethylsilyl
Tol	Toluene
TS	Transition state

Chapter 1: Introduction

1.1 Introduction to main-group compounds

Main-group element compounds are able to exhibit reactivity similar to that of transition-metal complexes.¹ This discovery was uncovered from the desire to synthesize the then-unknown main-group compounds as stable species. Past examples have shown that heavier main-group elements cannot form multiple bonds due to the weak $p\pi$ - $p\pi$ overlap. However, in recent years, with the aid of sterically hindered substituents for kinetic stabilization, several stable multiply-bonded heavier main-group element compounds were able to be isolated. They were considered as the heavier element congeners of alkynes and possess frontier orbitals with small energy gaps (≤ 4 eV) – a property associated with transition-metal complexes.¹ As such, these species can mimic the transition metal reactivity towards small molecules like H_2 , N_2O , NH_3 and CO_2 (Figure 1.1).

Figure 1.1. Examples of TM reactivity towards small molecules

In addition, there has been remarkable growth in the studies of low oxidation state main-group chemistry. Elements in the s-block can typically access the +1

(Group I) and +2 (Group II) oxidation states, and the lighter elements in the *p*-block follow a similar pattern related to the number of valence electrons they possess. The key deviation from the single-oxidation state trend in main-group elements arises upon the descent of the *p*-block. Going down the *p*-block, the main-group elements are subjected to the inert pair effect. The existence of low-valent main-group elements, essentially with an oxidation state between zero and their common oxidation states, usually involves the impartation of addition stability. This is generally through complexation or from kinetic stabilization by ligand scaffolds with a substantial steric bulk. The additional stabilization hinders or greatly suppresses the disproportionation reaction to both the elemental state and the common oxidation state.¹ When these species possess filled and empty orbitals with small energy gaps (≤ 4 eV), they will show transition metal-like reactivity.

1.2 Inert Pair Effect

The term ‘inert pair effect’ describes the phenomenon when the heavier main-group elements exhibit a valence less by 2 than expected from their classic electronic configuration corresponding to the group that they belong to.⁶ Pitzer⁷, as well as Pykko and Descalux⁸, generally explained the inert pair effect as a relativistic effect that causes the *s*-electrons to be more strongly attracted to the nucleus than expected. The presence of non-bonding valence electrons on sub-valent metal atoms of the *p*-block elements commonly results in stereochemical distortion of the coordination environment around the metal atom.⁹ When the energy difference between filled and empty orbitals of a heavier main-group element is small (≤ 4 eV), it resembles the small energy gap among *d*-orbitals in a transition metal. In this context, it is possible for heavier main-group elements to exhibit transition-metal-like reactivity.

1.3 Heavier group 14 alkene analogues

The first heavier group 14 element compound with multiple bonding were the alkene analogues, synthesized by Lappert¹⁰, West¹¹ and Brook¹² respectively (Figure 1.2a-c). Their structures illustrate the differential bonding whereby *trans*-pyramidal geometries (C_{2h}) were observed instead of the typical planar

D_{2h} geometry in alkenes and the bond shortenings (with respect to a single bond) are decreasing down the group.¹³⁻¹⁶ Going down the group, the M=M double bond is due to the overlapping of two non-bonding lone pairs of electrons. In the tin, lead and several of the germanium alkene analogues, monomeric :MR₂ molecules (M = Ge, Sn or Pb, R = hydrocarbyl group) are produced via dissociation in solution at room temperature. Conversely, in the case of silicon, dissociation is not observed for disilenes at room temperature because there is only slight deviation from planarity while the bond length of Si-Si remains largely consistent with double bonds.¹³⁻¹⁵

Figure 1.2. The first synthesized heavier group 14 alkene analogues

Very recently, Inoue and co-workers reported the isolation of the first tetradisilene that displays the reactivity of a bis(silyl)silylene and its subsequent activation of small molecules namely H₂ and NH₃ via oxidative addition (Figure 1.3).¹⁷ Both were carried out at low temperatures of -40 °C and -80 °C respectively and reached completion in 30 and 5 minutes respectively, showing the thermal stability and further proving to be a favourable breakthrough in small molecules activation. This study, along with other examples of silylenes, show transition-metal-like reactivity in the activation of small molecules.¹⁸⁻²¹

Transition-metal-like reactivity in heavier group 14 elements namely embodies the inert pair effect (section 1.2 above) and the second-order Jahn-Teller (SOJT) distortion (section 1.4 below). When a heavier main-group element has a small energy gap (≤ 4 eV), it resembles the small energy gap among d-orbitals in a transition metal. This reduced HOMO-LUMO gap enhances the accessibility to both orbitals and the compound can exhibit many uses, one of which being the ability to activate small molecules.

Figure 1.3. Synthesis and Reactivity of bis(silyl)silylene **II** and its more stable isomer tetrasilyldisilyne **II'**

1.4 Heavier group 14 alkyne analogues

Similar bonding pattern is observed in the heavier group 14 alkyne analogues, as represented in table 1.1.²²⁻²⁵ Figure 1.4 illustrates the first of heavier group 14 alkyne analogues - synthesized by Power and co-workers, beginning with the lead analogue²⁵, followed by the tin²⁴ and germanium²³ analogues. The silicon analogue was synthesized by Sekiguchi and co-workers in 2004.²²

Figure 1.4. The first synthesized heavier group 14 alkyne analogues

Table 1.1. Structural data for heavier group 14 element alkyne analogues¹

Compound	M≡M (Å)	M≡M-R bending angle (degrees)	Shortening (%)
2.0622(9) ²²	137.44(4)	11.87
2.285(6) ²³	128.67(8)	6.35
2.6675(4) ²⁴	125.1(2)	5.07
3.1811 ²⁵	94.26(4)	-9.69
Ar' = C ₆ H ₃ -2,6(C ₆ H ₃ -2,6- <i>i</i> Pr ₂) ₂ Ar* = C ₆ H ₃ -2,6(C ₆ H ₂ -2,4,6- <i>i</i> Pr ₃) ₂			

The key to successful synthesis of heavier group 14 alkyne analogues is dependent on the choice of the ligands acting as the steric protection group.²⁶ Prompted by the theoretical calculations of Nagase et al. that the digermynes TbtGe≡GeTbt (Tbt = 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl) can be isolated without dimerization, Tokito and co-workers synthesized a digermine compound using Bbt (Bbt = 2,6-bis[bis-(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) by easy reduction with potassium graphite (Figure 1.5a).²⁶ To add on, the same group more recently reported the reversible addition of terminal alkenes to both digermynes BbtGe≡GeBbt (Figure 1.5b and TbtGe≡GeTbt (Figure 1.5c).²⁷

Figure 1.5. a) Synthesis of a digermynes with Bbt ligand; b) Reaction of digermynes **Ia** with alkenes **II** and **III**; c) Reaction of digermynes **Ib** with alkene **II**

Just as with the heavier group 14 element analogues of alkenes, the triple bond in linear acetylene slowly becomes a single bond in the lead congener and the two original π -bonds are converted into two non-bonding electron pairs. Essentially, going down the group, the degree of non-bonding electron localization at the heavier group 14 element increases and the reactivity of the molecule is enhanced. The tetrel element possesses an electron-deficient, unsaturated character leading to the availability of both donor and acceptor sites within the molecule, enhancing their reactivity down the group. The bonding angle was noted to decrease from silicon to lead.

The bonding of the heavier group 14 element alkyne analogues has also been studied widely. The deviation from linear to trans-bent structures is best explained by the basis of the mixing of the σ^* -level and the in-plane π -level – resulting in increased non-bonding electron density at the central atoms. This mixing is a second-order Jahn-Teller (SOJT) effect. The SOJT effect arises from the intramolecular mixing of the filled highest occupied molecular orbital (HOMO) and an unoccupied orbital (LUMO+1).²⁸ The molecular orbital diagram is represented in Figure 1.6. In the molecular orbital description of

bonding in group 14 alkyne analogues, SOJT effect mixing of σ^* and π – as well as σ and π^* levels (n_+ and n_- signify a non-bonding orbital which is symmetric or unsymmetric with respect to inversion) – leads to the presence of nonbonded electron pair character (as in the $b_u(n_-)$ orbital) at the heavier group 14 elements. This mixing induces the non-bonding, lone pair character in the HOMO (generally a π -orbital), which can significantly affect the molecular shape, resulting in geometrical distortion through interelectronic repulsion.²⁸ The mixing occurs to a more significant extent in the heavier elements, where separation of the bonding orbital and the antibonding orbital is half or less than half that of carbon analogues. This, in turn, leads to weaker bonding between the heavier elements due to the increased inter-electronic repulsion between the central tetrel atoms.²⁹

SOJT mixing of a σ^* - and an in-plane p-orbital in the heavier group 14 alkyne analogues occurs upon the bending since both orbitals have b_u symmetry in the C_{2h} point group.¹ Such occurrence results in the conversion of the original in-plane π -orbital into an approximately non-bonded lone pair n_- combination (slipped p-bond). The mixing of the σ - and π^* -orbitals (both a_g symmetry) also occurs and weakens the σ -bond. In the trans-bent (C_{2h}) structure, the HOMO (π -orbital, a_u) can act as a Lewis base electron donor, while the virtual lone pair combination $a_g(n_+)$ acts as a lone-pair acceptor orbital. The MO explanation is consistent with the analogous valence bond drawings (Figure 1.6).

Figure 1.6. Molecular orbital representing the SOJT mixing effect of the trans-bent heavier group 14 alkynes

Huo et al. carried out an extensive study on the nature of the E-E bonds in heavier ditetrel alkyne analogues $\text{ArE}\equiv\text{EAr}$ ($\text{Ar} = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2$; $\text{E} = \text{Si, Ge, Sn, Pb}$) through calculations and comparisons using a combination of the “atoms in molecules” (AIM) theory, the electron localization function (ELF) method and molecular orbital analysis. The following conclusions were drawn from the study – the nature of the $\text{E}\equiv\text{E}$ bond differs from the classical covalent triple bond in acetylene or diphenylacetylene since the $\text{E}\equiv\text{E}$ bonds display charge-shift character, the strength of the $\text{E}\equiv\text{E}$ bonds were found to decrease down the group, and that the ELF valence basin centroids of the $\text{E}\equiv\text{E}$ bond was away from the two central atoms insinuating that more bonding components are coming from the donor-acceptor interactions involving the lone pair orbitals. The conclusions drawn from the ELF analysis are in agreement with the trans-bent E_2H_2 .³⁰

Due to the presence of transition metal-like filled and empty orbital with small energy gap, heavier alkyne analogues show transition-metal like reactivity. Jones and co-workers synthesized the first example of a digermynes comprising a Ge-Ge single bond, while each Ge center comprises a lone pair orbital and vacant p-orbital as shown in Figure 1.7a.³¹ The digermynes was then investigated for its ability to activate dihydrogen in the solid state (Figure 1.7b), in reference to the study by Power and co-workers in 2005, demonstrating the first example that H_2 was activated by a main-group metal complex.³² The activation of dihydrogen both in solution and in the solid state was found to be successful at atmospheric pressures.³¹ However, the mechanism is still as-yet-unknown.

Figure 1.7. Synthesis of a digermine with a Ge-Ge single bond and the activation of dihydrogen

1.5 Reaction with Small Molecules

The HOMO and LUMO in both are energetically accessible and this property allows for activation of small molecules like H_2 , CO , NH_3 to state a few. The trans-bent dimetallene systems are the only isolable form of heavier group 14 compounds taking on the E_2R_2 composition and they are found to be capable for small molecules activation.³³

1.6 Aims of the Thesis

The study of heavier group 14 elements and their complexes is much more extensive than this introduction can cover. It is evident that within the realm of low-valent tetrel elements, there is much to be explored. There is vast potential in this class of compounds to undergo greater development in both the area of catalysis as well as discovery into the synthesis of novel molecules. In this thesis, I will cover my exploration in two areas – namely the catalysis by a base-stabilized digermine and the synthesis of an unsymmetrical dimetallene. A more detailed explanation can be found in the next two chapters.

Chapter 2: Catalytic C-C bond Formation by a Frustrated Lewis Pair (FLP) system consisting of a Base-Stabilized Germanium (I) Dimer

2.1: Introduction

Carbon-carbon (C-C) bond formation is the basis for nature's essential molecules and the C-C bond forms the 'backbone' of almost every organic molecule.³⁴ The C-C bond formation is one of the most fundamental and useful reactions in organic chemistry and there has been an explosive growth in methods for the development of the formation of C-C bonds over the years.¹

Among these methods, frustrated Lewis pair (FLP) chemistry have attracted much attention because it is a more sustainable option compared to precious metal catalytic system. The FLP arises when the combination of a Lewis acid and a Lewis base are sterically hindered from forming a classic Lewis acid-base adduct.³⁵ The different forms of FLPs are shown in Figure 2.1. FLP systems typically involve 3 components: The FLP (a Lewis acid and a Lewis base) coming together and acting on a substrate. FLPs resemble transition metal complexes in small-molecule activation. For example, Stephan et al. reported the first reversible, metal-free hydrogen activation by a phosphonium-borate FLP.³⁶ In this reaction, the first step is either the initial proton migration or hydride migration, followed by a 1,2-hydride elimination by the FLP, *p*-(Mes₂PH)C₆F₄(BH(C₆F₅)₂) to cleanly lose the hydrogen atom as shown in Figure 2.2 below.³⁶

Figure 2.1. A typical FLP system

Figure 2.2. FLP system losing a H_2 molecule through 1,2-hydride elimination

The scope of substrates has since been expanded, including that of enamines, silyl-enol-ethers³⁷, enones³⁸, oximes³⁹, olefins⁴⁰ and polyaromatics⁴¹ (Figure 2.3).

Figure 2.3. Catalytic and stoichiometric hydrogenation by FLPs

Beyond H_2 activation, many other small molecules are captured by different kinds of FLPs. Figure 2.4 shows the ability of FLPs to activate small molecules like CO_2 , SO_2 , N_2O , NO and CO .³⁷

Figure 2.4. Examples of small molecules activation with FLP³⁷

While CO₂ and SO₂ bind in an analogous fashion, the N₂O activation results in a linear PN₂OB linkage.⁴² The FLP adduct of NO forms an oxygen radical. FLPs also aid in the stoichiometric reduction of CO with HB(C₆F₅)₂⁴³ or H₂.⁴⁴

Polymerization reactions can also be mediated by FLPs as shown by Chen and co-workers.⁴⁵⁻⁴⁷ Their FLP system consists of the Lewis acid Al(C₆F₅)₃ and Lewis bases phosphines or carbenes to polymerize a list of monomers – methyl methacrylate (MMA), methylene butyrolactones, α-methylene-γ-butyrolactone and γ-methyl-α-methylene-γ-butyrolactone. These polymerization reactions proceeded via the zwitterionic (Figure 2.5) intermediate. In the case of MMA polymerization, it is found to be a zero-order reaction after an induction period, indicating a bimolecular, activated-monomer propagation mechanism.⁴⁶

Figure 2.5. $\text{Al}(\text{C}_6\text{F}_5)_3$ -based classical Lewis pair (CLP) and frustrated Lewis pair (FLP) examples and their formation of a zwitterionic species upon reaction with MMA, that is active for polymerization

More examples of polymerization by FLPs were demonstrated by Chen and co-workers, where they synthesized pyridine- and 2-oxazoline-functionalized vinyl polymers via alane-based FLPs (Figure 2.6a).⁴⁸ In addition, Würthwein and co-workers reported the oligomerization of cyanamides via the use of an Al/N FLP (Figure 2.6b).⁴⁹ FLP radicals derived from NO for the polymerization of acrylates and vinyl monomers were also developed by Erker and co-workers.⁵⁰

Figure 2.6. a) N-functionalized monomers as well as LAs and LBs, which construct the FLPs used in the polymerization; b) an Al/N FLP system in the oligomerization of cyanamides⁴⁹

As mentioned above, carbenes can act as Lewis bases in a FLP system. It is therefore anticipated that its heavier analogues, germylenes, can catalyze C-C bond formation reactions since they possess Lewis basic characteristics, having comparable σ -donating ability as their lighter analogues.

In 2018, Sugahara et al. reported the use of a digermynes to catalyze the regioselective cyclotrimerization of terminal alkynes⁵¹, whereby the mechanism proceeds through an oxidative addition step between the terminal alkyne and the digermynes forming a Ge(III)-Ge(I) complex (Figure 2.7). This aroused our interest in whether a base-stabilized germanium(I) dimer, also known as bis(germylene), can form a FLP with strong Lewis acid to catalyze C-C bond formation.

Figure 2.7. a) Oxidative addition between a terminal alkyne and a digermine; b) Reaction mechanism for the cyclotrimerization by the digermine

In this chapter, we seek to investigate the FLP system between germanium(I) dimers and the strongly Lewis acidic tris(pentafluorophenyl)borane (B(C₆F₅)₃)

on C-C bond formation reactions, leading to polymerization of α,β -unsaturated carbonyl compounds.

2.2 Results and Discussion

To begin with, the amidinato germanium(I) dimer⁵² **2** and the 2-imino-5,6-methylenedioxyphenyl germanium(I) dimer⁵³ **4** were synthesized according to literature.

2.2.1 Synthesis of amidinato germanium(I) dimer, **2**

Phenyllithium was added to N,N'-di-*tert*-butylcarbodiimide in diethyl ether (DEE) and the reaction was allowed to proceed to completion over the course of 4 hours. Next, GeCl₂-dioxane (1:1) was added to the reaction mixture at -78 °C and allowed to stir overnight. The amidinate-stabilized chlorogermylene, [RGeCl], (**1**, R = PhC(N^{*t*}Bu)₂) was obtained (Figure 2.8a). Treatment of compound **1** with potassium graphite (KC₈) afforded the amidinato germanium(I) dimer [RGeGeR], (**2**, R = PhC(N^{*t*}Bu)₂) (Figure 2.8b). Compound **1** was isolated as air- and moisture- sensitive colourless crystals while compound **2** was isolated as air- and moisture- sensitive dark orange crystals.

The ¹H NMR spectra obtained for both compounds **1** and **2** are good matches to the previously published examples⁵²; the ^{*t*}Bu protons in **1** are represented by a singlet at 1.01 ppm while the ^{*t*}Bu protons in **2** are downfield shifted in comparison and show a singlet resonance at 1.32 ppm.

Figure 2.8. a) Synthesis of the amidinate-stabilized chlorogermylene **1**; b) Synthesis of the amidinato germanium(I) dimer **2**

2.2.2 Synthesis of 2-imino-5,6-methylenedioxyphenyl germanium(I) dimer, **4**
 One equivalent of LLi (L = C₆H₂-5,6-OCH₂O-2-(C=NAr)) was treated with GeCl₂·dioxane (1:1) and allowed to stir overnight to yield LGeCl (**3**). The mixture was filtered and concentrated to obtain air- and moisture- sensitive colourless crystals of **3** (Figure 2.9a). Subsequent reduction of **3** with potassium graphite in THF afforded the germanium(I) dimer, LGeGeL (**4**, Figure 2.9b), which was isolated as air- and moisture- sensitive dark red crystals of **4**.

Likewise, the ¹H NMR data corresponds to previously reported literature – for compound **3**, the -OCH₂O- protons are non-equivalent and show two singlets at 5.18 and 5.27 ppm, the signal for the MeC=N protons is at 1.68 ppm. In comparison, the signal for the MeC=N protons in compound **4** is downfield shifted at 1.97 ppm.

Figure 2.9. a) Synthesis of the 2-imino-5,6-methylenedioxyphenyl chlorogermylene **3**; b) Synthesis of the 2-imino-5,6-methylenedioxyphenyl germanium(I) dimer **4**

2.2.3 Catalytic attempts using **1** and **3**

Even though we had already planned to use **2** and **4** to investigate C-C bond formation, we were interested in the catalytic abilities of compounds **1** and **3** as well. However, we found that even when the catalyst loading was increased to 5 mol%, no sign of catalytic ability took place at high temperatures for extended durations. We therefore conclude that compounds **1** and **3** are not catalytically suitable for C-C bond formation.

2.2.4. Polymerization using **2** and **4**

Following the successful syntheses, the germanium(I) dimers **2** and **4** were employed in the investigation of their C-C bond-forming abilities. They were used catalytically in the polymerization of various α,β -unsaturated carbonyl compounds (Figure 2.10).

Figure 2.10. Monomers used for polymerization by **2** and **4**

To begin, the FLP of **2** and $\text{B}(\text{C}_6\text{F}_5)_3$ was used in the investigation of C-C bond formation. Optimization was first carried out.

To find out the time required for the reaction to proceed to completion, 3 identical reactions with varying durations were carried out – 0.5 mol% of **2** and 1.0 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ was added to **a**, MMA (methyl methacrylate), in toluene at room temperature and their results are represented in table 2.1 below. Upon a 2 hour reaction (entry 3), full conversion was observed via NMR whereby poly(MMA) with low dispersity and low molecular weight was yielded. ($M_n = 2.582 \times 10^3 \text{ g mol}^{-1}$, repeating unit, $n = 25$, polydispersity index, Đ : 2.75).

The NMR analysis of poly(MMA) and the subsequent examples was performed with the crude resulting mixture of the reaction to compare the integration between the product and monomer peaks.

GPC analysis was performed on the purified polymer to obtain the M_n and Đ . The repeating unit was obtained with a formula: M_n / M_r of monomer.

Table 2.1: Polymerization of the various monomers with **2**/ $B(C_6F_5)_3$ FLP

Entry	Substrate	Time (h)	Temperature (°C)	Conversion (%)
1	a	0.5	25	15
2		1	25	54
3		2	25	100
4	b	2	25	100
5	c	2	25	27
6		5	25	100
7	d	2	25	0
8		5	25	0
9		16	25	0
10		2	110	0
11		5	110	0
12		16	110	0
13	e	2	25	0
14		5	25	0
15		16	25	0
16		2	110	0
17		5	110	0
18		16	110	0
19	f	2	25	15
20		5	25	26
21		16	25	100
22	g	2	25	0
23		5	25	0
24		16	25	0
25		2	110	22
26		5	110	50
27		16	110	100
28	h	2	25	0
29		5	25	0
30		16	25	0

31		2	110	15
32		5	110	44
33		16	110	100
34	i	2	25	0
35		5	25	0
36		16	25	0
37		2	110	0
38		5	110	0
39		16	110	0
40	j	2	25	0
41		5	25	0
42		16	25	0
43		2	110	0
44		5	110	0
45		16	110	0

The scope was then extended on the remaining substrates and the results are represented in Table 2.1 as well. In these reactions, likewise, 0.5 mol% of **2** and 1.0 mol% of B(C₆F₅)₃ were added respectively to the substrates in toluene at room temperature and was left to stir for a varying amount of time depending on the completion of the reactions.

From Table 2.1, only **b**, **c** and **f** were able to reach full conversion at room temperature. For the case of **b** (EMA), poly(EMA) ($M_n = 3.115 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 27$; polydispersity index, $\bar{D}$: 2.62) was formed (entry 4). For **c** (BMA), poly(BMA) ($M_n = 3.042 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 21$; polydispersity index, $\bar{D}$: 2.54) with low molecular weight and dispersity were formed (entry 6). Additionally, for **f** (met.tig.), poly(met.tig.) ($M_n = 4.337 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 38$; polydispersity index, $\bar{D}$: 1.98) with high molecular weight and low dispersity was formed (entry 21).

Further tests were carried out on substrates **e**, **g-j** to find out the C-C bond formation ability at high temperatures (110 °C). The results are also represented in Table 2.1 below.

At increased temperatures, the polymerization of substrates **g** (MBO) and **h** (MPO) took place to completion when left to stir for 16 hours overnight. Poly(MBO) ($M_n = 3.028 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 36$; polydispersity index, $\bar{D}$: 2.11) with low molecular weight and dispersity (entry 27) as well as poly(MPO) ($M_n = 3.710 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 39$; polydispersity index, $\bar{D}$: 3.62) with low molecular weight and high dispersity (entry 33) were obtained. The polymers that were formed from substrates **a-c** and **f-h** are shown in Figure 2.11 below. Substrates **d**, **e**, **i** and **j** were found to be unable to polymerize even at high temperatures for extended durations (entries 12, 18, 39 and 45).

Figure 2.11. *Polymers of **a-c** and **f-h***

Next, the FLP of **4** and $\text{B}(\text{C}_6\text{F}_5)_3$ was used to investigate the C-C bond formation in the same set of substrates. The results were mostly identical to that of the FLP system of **2** and $\text{B}(\text{C}_6\text{F}_5)_3$.

Similarly, we began with the investigation of the duration required for the polymerization of **a** to proceed to completion, in 3 separate reaction vials. 0.5 mol% of **4** and 1.0 mol% of $\text{B}(\text{C}_6\text{F}_5)_3$ was added to **a** in toluene at room temperature and their results are represented in Table 2.4 below. Upon a 2 hour reaction (entry 3), full conversion was observed via NMR, whereby poly(MMA) with low

molecular weight and low dispersity was yielded. ($M_n = 3.872 \times 10^3 \text{ g mol}^{-1}$, repeating unit, $n = 38$, polydispersity index, $\bar{D}$: 2.94).

Table 2.2. Polymerization of MMA with 4/B(C₆F₅)₃ FLP

Entry	Substrate	Time (h)	Temperature (°C)	Conversion (%)
1	a	0.5	25	19
2		1	25	66
3		2	25	100
4	b	2	25	100
5	c	2	25	36
6		5	25	100
7	d	2	25	0
8		5	25	0
9		16	25	0
10		2	110	0
11		5	110	0
12		16	110	0
13	e	2	25	0
14		5	25	0
15		16	25	0
16		2	110	0
17		5	110	0
18		16	110	0
19	f	2	25	27
20		5	25	43
21		16	25	100
22	g	2	25	0
23		5	25	0
24		16	25	0
25		2	110	14
26		5	110	33

27		16	110	100
28	h	2	25	0
29		5	25	0
30		16	25	0
31		2	110	20
32		5	110	47
33		16	110	100
34	i	2	25	0
35		5	25	0
36		16	25	0
37		2	110	0
38		5	110	0
39		16	110	0
40	j	2	25	0
41		5	25	0
42		16	25	0
43		2	110	0
44		5	110	0
45		16	110	0

We proceeded to perform a substrate scope as with **2**, checking the completion of the reaction at the 2- and 5-hour mark, before leaving the reaction mixture to stir overnight for 16 hours.

Likewise, only **b**, **c**, and **f** were able to reach full conversion at room temperature. For the case of **b**, poly(EMA) with high molecular weight and low dispersity ($M_n = 7.266 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 63$; polydispersity index, $\mathcal{D}$: 2.18) was afforded (entry 4). In contrast, in the case of **c**, poly(BMA) with low molecular weight and low dispersity ($M_n = 5.092 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 35$; polydispersity index, $\mathcal{D}$: 3.14) was formed (entry 6). Additionally, for **f**, poly(met.tig.) ($M_n = 3.538 \times 10^3 \text{ g mol}^{-1}$; repeating unit, $n = 31$; polydispersity index, $\mathcal{D}$: 2.33) with low molecular weight and low dispersity was formed (entry 21).

Lastly, we raised the temperature to 110 °C and performed the reaction on substrates **d**, **e**, **g-j**.

The results obtained from the tests at 110 °C were akin to that with the FLP of **2** and B(C₆F₅)₃. Only **g** and **h** were able to polymerize at higher temperatures, poly(MBO) ($M_n = 2.103 \times 10^3$ g mol⁻¹; repeating unit, $n = 25$; polydispersity index, $\bar{D}$: 2.56) with low molecular weight and dispersity (entry 27) as well as poly(MPO) ($M_n = 3.995 \times 10^3$ g mol⁻¹; repeating unit, $n = 42$; polydispersity index, $\bar{D}$: 2.44) with low molecular weight and low dispersity (entry 33) was obtained. On the other hand, substrates **d**, **e**, **i** and **j** remained unreacted even when we increased both the duration and the temperature of the reaction (entries 12, 18, 39 and 45).

2.2.4a MALDI-TOF-MS

Figures 2.12a and 2.12b shows the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra of these polymer-iodides. For the sample preparation, we used trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix and CF₃COONa as an additive salt. The studied polymers can possess ¹²C and ¹³C atoms. For simplicity, the theoretical masses discussed below and the experimental masses given in the figures (MALDI-TOF-MS spectra) are those without ¹³C atom (i.e. with only ¹²C atoms); unless otherwise specified, those masses are compared.

With the use of MALDI-TOF-MS, the pattern of repeating units of the polymers formed can be observed. Figure 2.12a presents the poly(MMA), poly(EMA) and poly(BMA) spectra for catalysis with **2** and figure 2.12b presents the poly(MMA), poly(EMA) and poly(BMA) spectra for catalysis with **4**. 2.12ai and 2.12bi show the poly(MMA) spectra and proves the formation of a polymer with the repeating of unit ranging from 100.04 to 100.08 for MMA with the molecular mass of 100.12 g/mol. 2.12aai and 2.12bii show the poly(EMA) spectra and proves the formation of a polymer with the repeating of unit ranging from 114.06 to 114.12 for EMA with the molecular mass of 114.14 g/mol. 2.12aiii and 2.12biii show the poly(BMA) spectra and proves the formation of a polymer with the repeating of unit ranging from 142.11 to 142.16 for BMA with the molecular mass of 142.20 g/mol. Poly(met.tig.), poly(MPO) and poly(MBO) are still not able to be

characterized by MALDI-TOF-MS but further studies are in progress to investigate how to best isolate the polymers formed for this analysis.

Figure 2.12a. MALDI-TOF-MS spectra for polymers catalyzed by **2**

Figure 2.12b. MALDI-TOF-MS spectra for polymers catalyzed by **4**

2.2.5 Mechanism of polymerization reaction

The mechanism of the C-C bond formation mediated by the FLP of **2** and $\text{B}(\text{C}_6\text{F}_5)_3$ was studied, whereby it was investigated according to initiation, propagation and termination of a polymerization reaction.

2.2.5a Initiation

To start off, the mixture of 2 equivalents of MMA (0.02 mmol) and 1 equivalent of **2** (0.01 mmol) was added to benzene- d_6 in a J-Young NMR tube. Upon sonicating for 30 minutes, the ^1H NMR spectrum shows 4 characteristic ^tBu groups at 1.12, 1.16, 1.19 and 1.23 ppm. Excess MMA was also detected in the spectrum. These observations indicate that only 1 equivalent of MMA was involved in the reaction.

Hence, we repeated the reaction with 1 equivalent of MMA (0.01 mmol) added to 1 equivalent of **2** (0.01 mmol) in benzene- d_6 in a J-Young NMR tube. The ^1H NMR spectrum shows closely similar characteristic peaks at 1.13, 1.16, 1.20 and 1.24 ppm. However, excess MMA was not detected, leading us to suggest that only one Ge-center from **2** reacts with the MMA molecule to form a 5-membered ring at a single Ge-center **2a** (Figure 2.12).

Figure 2.13. 5-membered ring forming at a single Ge-center

2.2.5b Propagation

Based on our observations in the initiation, the following structures (Figure 2.13) are proposed as the intermediates in the polymerization reaction. 1 equivalent of MMA added to 1 equivalent of **2** forms a 5-membered ring at a single Ge-center, leading to the propagation step.

Figure 2.14. Proposed intermediate of catalysis

2.2.5c Termination

In order to determine the termination step, we need to find out the end-group of the polymer. LC-MS and MALDI-TOF-MS were performed to obtain the molecular weight of the polymers. Based on the MS results, the end-group from both chain ends of the poly(MMA) has a mass of 100 gmol^{-1} – corresponding to the molecular weight of a single monomer molecule of MMA (section 2.2.3a). From this, we can deduce that the poly(MMA) formed is ended by a proton on one side; and a $\text{CH}_2\text{CO}_2\text{Me}$ on the other side (Figure 2.14). We further confirmed this through ^1H NMR where the peaks at 5.47ppm and, 6.20ppm were present indicating the presence of 1 alkene end group.

Figure 2.15. Short-chain poly(MMA)

To form the above-mentioned end-groups, the mechanism of the termination step is proposed as follows (Figure 2.15).

Figure 2.16. Mechanism for termination step

2.2.5d Catalytic Cycle

Based on the steps proposed above, the catalytic cycle is proposed as in Figure 2.16 below.

The cycle begins with the initiation step where a [1+4] cycloaddition takes place between a single MMA molecule with one Ge-center in **2** to form **5**. The reaction continues with another molecule of MMA reacting with **5**, forming the zwitterionic **Int 1**. A chain of poly(MMA) is formed in **Int 2** when continuous C-C bond formation takes place. $\text{B}(\text{C}_6\text{F}_5)_3$ then extracted a hydride from the methyl group at the chain-end, forming the end-group. The $\text{H-B}(\text{C}_6\text{F}_5)_3$ anion performed a hydride attack on the carbon center attached to the Ge-center, allowing the release of the poly(MMA) and regeneration of **2** and $\text{B}(\text{C}_6\text{F}_5)_3$ for use again in the catalysis.

Figure 2.17. Overall catalytic cycle

2.3 Conclusion

In conclusion, the germanium(I) dimers **2** and **4** have been found to be capable of forming a FLP with the Lewis acidic $\text{B}(\text{C}_6\text{F}_5)_3$ to catalyze C-C bond formation towards a variety of α,β -unsaturated carbonyl compounds, resulting in polymerization with low molecular weight and low dispersity. We have also derived a catalytic cycle for the FLP system of **2** and $\text{B}(\text{C}_6\text{F}_5)_3$ through the classic initiation-propagation-termination steps – where a 5-membered ring with a Ge

center is first formed followed by the poly(MMA) chain where C-C bond formation continues. The reaction reaches termination when the $\text{B}(\text{C}_6\text{F}_5)_3$ extracts a hydride from the end of the chain and the $\text{H-B}(\text{C}_6\text{F}_5)_3$ anion does a hydride attack on the Ge center, releasing both poly(MMA) and **2**. We predict that the catalytic cycle for the FLP system of **4** and $\text{B}(\text{C}_6\text{F}_5)_3$ will likely be identical to the one we proposed.

Chapter 3: Synthesis and Reactivity of a Base-Stabilized Silagermyne

3.1 Introduction

Many examples of complexes exhibiting multiple-bonding between silicon and germanium atoms have been reported in the homo-bimetallic forms. The synthesis and isolation of a hetero-bimetallic species between the two atoms have been challenging due to the differential behaviour of both atoms in multiple-bonding environments.

In disilynes, mixing of the σ^* and π level is incomplete such that in-plane π -level is found to be not fully converted to a σ -level but retains more than half of the bonding character, resembling a skewed π -orbital. On the contrary, the conversion seems almost complete in digermynes and the bond order is approximately 2.²⁹

The previously reported heavier group 14 element alkene analogues $R_2E=ER_2$ were found to possess trans-bent geometries in the solid state (Figure 3.1) but have the tendencies to dissociate into the monomeric, singlet $R_2E:$ forms in solution.⁵⁴

Figure 3.1. Trans-bent geometries of heavier group 14 element alkene analogue

Rivard and co-workers reported the experimental verification of the first inorganic analogues of ethylene, $H_2Si=EH_2$ ($E = Ge, Sn$), which are stable at room temperature.⁵⁵ The synthetic pathway towards the $H_2Si=GeH_2$ and $H_2Si=SnH_2$ complexes are illustrated in Figure 3.2. As shown in Figure 3.2, compound **III** exists as a coordinated H_2SiGeH_2 silagermyne unit within the $C_{IPr}-Si-Ge-W$ array and the Si-Ge bond length is similar to the Si-Ge single bond in H_3SiGeH_3 .⁵⁵ Compound **III** also exhibited considerable thermal stability in the solid state and is stable for extended periods of time in refluxing toluene.⁵⁵

On the other hand, compound **IV** is significantly less stable and was found to decompose in Et₂O even at low temperatures of -30°C.⁵⁵

Figure 3.2. Rivard's synthesis of the heavier group 14 analogues of ethylene⁵⁵

The isolation of the first stable unsymmetric ditetrelene was reported by Sekiguchi and co-workers and the step-by-step reaction scheme is shown in Figure 3.3. To begin, DsINpSiSiH₂Cl was reacted with Ph(R₂N)₂SiLi (R₂N = pyrrolidino) and deaminative chlorination using gaseous HCl and reduction by LiAlH₄. The tetradihydrosilane was then formed, following the triflation of the phenyl group and reaction with silyl potassium. Finally, the final disilyne was afforded by first chlorinating the tetradihydrosilane and subjecting the chlorinated product to reductive dechlorination.⁵⁶

$\text{Dsi} = \text{CH}(\text{SiMe}_3)_2$
 $\text{Np} = \text{CH}_2^t\text{Bu}$

- (a) = (1) $\text{Ph}(\text{R}_2\text{N})_2\text{SiLi}$ ($\text{R}_2\text{N} = (\text{CH}_2\text{CH}_2)_2\text{N}$), THF, 0 deg.cel.
 (2) dry HCl, Et_2O , RT
 (3) LiAlH_4 , Et_2O , RT
 (b) = (1) $\text{CF}_3\text{SO}_3\text{H}$, toluene, RT
 (2) $\text{Dsi}_2^i\text{PrK/HMPA/THF/DME}$
 (c) = Cl_2 , CH_2Cl_2 , -78 deg.cel.
 (d) = KC_8 , THF, -78 deg.cel.

Figure 3.3. Sekiguchi's synthetic route to the first unsymmetrical disilyne

Since the discovery and development of heavier group 14 alkyne analogues began, extensive studies regarding the reactivity of these compounds were also carried out. In 2005, Power and co-workers examined the reactivity of the germanium and tin analogue of ethyne towards various unsaturated molecules.⁵⁷ The digermynes (Figure 1.2) was found to react with $^t\text{BuNC}$ and PhCN to form the isonitrile adduct and the cyclic product which features a $\text{C}_2\text{N}_2\text{Ge}_2$ 6-membered ring as shown in Figure 3.4.⁵⁷ Additionally, the reaction of the digermynes with diphenylacetylene (PhCCPh) yielded a stable Ge-C-C-Ge 4-membered 1,2-digermacyclobutadiene ring⁵⁸ (Figure 3.4).

Figure 3.4. Power's study on the reactivity of germanium and tin analogue of ethyne⁵⁷

Sekiguchi and co-workers examined the nature of the π -bond in the disilyne (Figure 1.2) by studying the reactivity of the disilyne with alkenes and alkynes.⁵⁹ The disilyne was treated with both the cis- and trans- isomer of 2-butene as well as phenylacetylene. It was found that the reactions with the disilyne formed 4- and 6- membered ring-structures respectively (Figure 3.5). Theoretical studies have been done to show that the first step to the formation of the disilacyclobutadiene complexes was through a [1+2] cycloaddition from the interaction between the in-plane LUMO (π_{in}^*) of the disilyne and the HOMO of 2-butene to produce the silacyclopropylsilylene intermediate. While in the case of the formation of 1,2-disilabenzene, the first step is to generate the 1,2-disilacyclobutadiene-like intermediate which will then undergo a [2+4] cycloaddition reaction with a second acetylene molecule. Both the determined mechanisms did not agree with literature reports on the π -bond of disilenes undergoing [2+2] cycloadditions towards both alkenes and alkynes to give disilacyclobutane and disilacyclobutene derivatives respectively.^{16, 60}

Figure 3.5. Sekiguchi's study of the reactivity of the disilyne towards unsaturated molecules²²

Thus far, there have been no reports of the synthesis of unsymmetrical dimetallynes ($\text{E}\equiv\text{E}'$) ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$, $\text{E}' = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$, $\text{E}\neq\text{E}'$); both their isolation and reactivity remain as areas for exploration.

In this chapter, we present our synthesis of an unsymmetrical heavier group 14 dimetallayne and investigate its reactivity towards various Lewis acids, chalcogens and transition metal carbonyls.

3.2 Results and Discussion

To begin with, the 2-imino-5,6-methylenedioxyphenyl chlorogermylene **3** and the amidinate-stabilized chlorosilylene **7** were synthesized according to literature.^{53, 61} They were then used to prepare a base-stabilized silagermyne.

3.2.1 Synthesis of 2-imino-5,6-methylenedioxyphenyl chlorogermylene, **3**

3 was synthesized as described in chapter 2. One equivalent of LLi (L = C₆H₂-5,6-OCH₂O-2-(C=NAr)) was treated with GeCl₂-dioxane and allowed to stir overnight to yield, LGeCl (**3**). The mixture was filtered and concentrated to obtain air- and moisture- sensitive colourless crystals of **3**.

3.2.2 Synthesis of amidinate-stabilized chlorosilylene, **7**

Phenyllithium was added to N,N'-di-*tert*-butylcarbodiimide in DEE and the reaction was allowed to proceed to completion over the course of 4 hours. Next, trichlorosilane (HSiCl₃) was added to the reaction mixture at -78 °C, warmed to 0 °C and allowed to stir overnight to obtain RSiHCl₂, **6** (R = PhC(N^{*t*}Bu)₂) (Figure 3.6a). **6** was treated with LiN(TMS)₂ in toluene at -78 °C to yield the amidinate-stabilized chlorosilylene, [RSiCl], (**7**, R = PhC(N^{*t*}Bu)₂) (Figure 3.6b). Compound **7** was isolated as air- and moisture- sensitive colourless crystals.

Figure 3.6. a) Synthetic route to obtain the RSiHCl₂ **6**; b) Synthesis of the amidinate-stabilized chlorosilylene **7**

3.2.3 Synthesis of the unsymmetrical silyagermyne (LGeSiR), **9**

The synthetic route to obtain compound **9** is as shown in Figure 3.7 below.

Figure 3.7. Synthesis of the LGeSiR (**9**) through LGeK (**8**)

Compound **3** was reacted with excess KC_8 in THF, generating a deep red solution of compound **8** within an hour. **8** is generated in-situ as with literature⁵³ and used immediately in the subsequent step. 1 equivalent of **7** was first diluted in THF and added dropwise to **8** at $-78\text{ }^\circ\text{C}$, warmed to $0\text{ }^\circ\text{C}$ and stirred for another 1 hour. Upon dropwise addition, there is a significant colour change in the solution, from the initial deep red to dark blue almost instantaneously, indicating the occurrence of a reaction. At the end of the hour, filtration was carried out to remove the KCl as the by-product.

Multiple attempts were made to crystallize compound **9** for X-ray crystallography. A variety of solvents were employed – DEE, toluene, benzene, fluorobenzene, THF, hexane, pentane, and 1,2-difluorobenzene – for crystallization both at room temperature and at ice-point ($0\text{ }^\circ\text{C}$) but were all unsuccessful. This can be attributed to the instability of **9** in solution – **9** was found to decompose in solution, into unidentified products, over the course of 2 weeks at room temperature.

However, **9** was still sufficiently stable to be characterized by means of NMR spectroscopy. The ^1H NMR spectrum of **9** shows a septet at 3.07 ppm and two doublets at 1.00 and 1.55 ppm that are representative of the 2,6-diisopropylphenyl group on the iminophenyl ligand. Additionally, the $-\text{OCH}_2\text{O}-$ protons displayed a singlet at 5.67 ppm and the $t\text{Bu}$ protons on the amidinato ligand displayed a singlet 1.07 ppm. The ^{29}Si NMR of **9** has a single signal at 70.9 ppm. This signal lies very close to the literature value for the amidinato silicon(I) dimer which has a signal at 75.71 ppm⁶² on the ^{29}Si NMR. This closeness brings us to the deduction that the silicon atom in **9** is possibly bonded to a low-valent germanium atom, giving us the proposed structure of **9** in Figure 3.6.

Due to the inability to successfully isolate **9**, in the following sections 3.2.5-3.2.7, the trapping of **9** with Lewis acids, chalcogens and metal carbonyls will be discussed. Attempts to isolate the derivatives of **9** in order to show the presence of the $\text{Si}\equiv\text{Ge}$ triple bond will also be presented.

3.2.4 Reactivity of **8**

We investigated the reactivity of **8** with two germanium(II) complexes and in both cases (Figure 3.8), the 2-imino-5,6-methylenedioxyphenyl germanium(I) dimer, **4** was formed instead.

Figure 3.8. Reactivity of **8**

3.2.5 Reactivity of **9** with Lewis acids

Due to the dual-Lewis-basic Si and Ge sites on compound **9**, we sought the use of Lewis acids to stabilize in the hopes to isolate a derivative of **9**. After the synthesis of compound **9** in the reaction, volatiles were removed after the filtration step and a re-dilution was taken place with the respective solvent used for each trapping reaction. It should be noted that the following trapping reactions were done at -78°C and warmed to room temperature while leaving to stir overnight for 16 hours.

Treatment of **9** with 1 equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene (Figure 3.9a) resulted in an almost instant colour change from dark blue to dark green. We were not able to obtain a single crystal for X-ray crystallography, rather, a greenish-yellow oil was afforded upon concentration of the solution. The spectroscopic data of this reaction indicate a mixture of unidentified products.

Treatment of **9** with 1 and 2 equivalents of borane dimethylsulfide ($\text{BH}_3 \cdot \text{SMe}_2$) (Figure 3.9b) gave rise to differential colour changes, forming a dark green and a brown solution respectively. The brown solution was concentrated to 5 mL and we observed an orange oil in a yellow solution. Light yellow crystals were obtained for but were too thin and brittle for X-ray crystallography. The ^{11}B NMR of the brown solution displayed two prominent peaks – a large signal in

the region of -20.5 ppm which corresponds to BH_3SMe_2 , indicating a large excess of the reactant, as well as a slightly smaller peak at 38 ppm indicating the formation of a new product. On the basis of ^{11}B NMR and ^1H NMR, we are unable to predict the structure of the product.

Treatment of **9** with gallium trichloride (GaCl_3) (Figure 3.9c) also afforded a dark green solution. Upon concentration in toluene to 5 mL, there was a significant colour change from dark green to orange and the formation of an orange oil. The solution was then completely dried out under vacuum and in the ^{29}Si NMR of the crude dried product, the signal at 70.9 ppm was no longer present. The reaction was then attempted in THF and had similar observations. However, the spectroscopic data indicate that a mixture of unidentified products was formed.

Treatment of **9** with 1 and 2 equivalents of trimethylaluminium (AlMe_3) (Figure 3.9d) turned the solution dark green immediately upon addition of AlMe_3 . The significant peaks were not present in the ^1H NMR spectrum of the crude mixture. The disappearance of the septet at 3.07 ppm, the doublets at 1.00 and 1.55 ppm, as well as the singlet at 5.67 ppm, could indicate the decomposition of the product. Even though the relevant Schlenk techniques were employed, white fumes were observed when the reaction mixture was exposed to even a minuscule amount of air, further confirming our suspicions that the product had decomposed during the reaction.

Figure 3.9. Reactivity of **9** with Lewis acids

3.2.6 Reactivity of **9** with chalcogens

Chalcogens (heavier group 16 elements) possess the ns^2np^4 electronic configuration (represented in table 3.1) and as such, they are 2 electrons short of a filled valence shell. In reactions with metals, chalcogens typically acquire 2 additional electrons and form compounds in the -2 oxidation state.

*Table 3.1. Reactivity of **9** with chalcogens*

Chalcogen	Symbol	Atomic No.	Electronic Configuration
Sulfur	S	16	[Ne] $3s^2 3p^4$
Selenium	Se	34	[Ar] $3d^{10} 4s^2 4p^4$
Tellurium	Te	52	[Kr] $4d^{10} 5s^2 5p^4$

Compound **9** was treated with 1 to 3 equivalents of sulfur (S), selenium (Se) and tellurium (Te) respectively and the colour change for each reaction is as described in table 3.2 below. It should be noted that the following reactions were done in THF and in the absence of light, at $-78\text{ }^{\circ}\text{C}$ and warmed to room temperature while leaving to stir overnight for 16 hours.

*Table 3.2. Colour change observation for reactivity of **9** with chalcogens*

Chalcogen	Equivalents	Colour change	Time taken
S	1	Blue solution $\rightarrow$ yellow solution	Over 3h
	2	Blue solution $\rightarrow$ dark orange solution	Immediately
	3	Blue solution $\rightarrow$ dark orange solution	Immediately
Se	1	Blue solution $\rightarrow$ yellow solution	Over 3h
	2	Blue solution $\rightarrow$ dark orange solution	Immediately
	3	Blue solution $\rightarrow$ dark orange solution	Immediately
Te	1	Blue solution $\rightarrow$ yellow solution	Over 3h

	2	Blue solution → dark orange solution	Immediately
	3	Blue solution → dark orange solution	Immediately

Isolation of crystals for X-ray crystallography was only successful for the reaction of compound **9** with 2 equivalents of Te; after stirring for 16 hours, the reaction mixture was filtered in the dark and left to stand in the dark. Dark orange crystals of **10** (Figure 3.10) were observed after 2 days. The X-ray crystal structure obtained is as shown in Figure 3.11. The dark orange crystals were insoluble in C₆D₆, CD₃CN and THF-d₈. We obtained the ²⁹Si and ¹²⁵Te NMR with a concentrated crude reaction mixture. ²⁹Si NMR shows a single signal at -85.6 ppm and the ¹²⁵Te NMR shows two signals at -0.18 and -0.74 ppt. The Si=Te bond had a bond length of 2.3638(12) Å which is longer than the recently reported shortest yet Si=Te bond length of 2.246(7) Å⁶³, longer than 3-coordinate Si=Te (2.3210(6) Å)⁶⁴ but shorter than 4-coordinate Si=Te (2.3720(15) – 2.383(2) Å)⁶⁵. The Ge-Te bond length is reported to be 2.6604(5) Å that in a GeTe monolayer with the Ge-Te bond length being 2.77 Å.⁶⁶

Figure 3.10. Synthesis of **10**

Figure 3.11. Molecular structure of **10** (thermal ellipsoids set at 30% probability). Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: O1-C17 1.378(5), O1-C18 1.418(5), O2-C18 1.435(6), O2-C19 1.371(5), Ge1-N3 2.057(3), Ge1-Te1 2.6604(5), Te1-Si1 2.4701(13), Si1-Te2 2.3638(12), Si1-N1 1.825(4), Si1-N2 1.820(4), C5-N1 1.340(5), C5-N2 1.331(5); C19-O2-C18 105.5(3), O2-C18-O1 108.6(4), C18-O1-C17 105.6(3), C16-Ge1-N3 80.43(15), C16-Ge1-Te1 93.59(12), Ge1-Te1-Si1 92.02(3), Te1-Si1-Te2 117.14(5), Te1-Si1-N1 110.85(12), Te1-Si1-N2 110.35(12), N1-Si1-N2 71.61(16), N1-C5-N2 106.0(4), N1-Si1-Te2 118.94(12), N2-Si1-Te2 119.71(12)

3.2.7 Reactivity of **9** with transition-metal carbonyls

Compounds in which heavier low-valent group 14 elements are bonded to a transition metal (TM) are being described in ever-increasing numbers in recent years.⁶⁷ We expect that upon treatment of **9** with TM carbonyls, the lone pair of electrons on either the Si or the Ge atom will attack the TM center and a π -backdonation will occur to the carbonyls, causing the TM to lose 1 or more CO units. This may enhance the stability of compound **9**. It should be noted that the following reactions were done at -78 °C and warmed to room temperature while leaving to stir overnight for 16 hours.

Treatment of **9** with diiron nonacarbonyl ($\text{Fe}_2(\text{CO})_9$) gave a dark red solution (Figure 3.12a). Crystallization attempts in both toluene and THF were

unsuccessful. The crude ^1H NMR of the resulting mixture found that the septet has shifted upfield to 2.90 ppm, but the **9-Fe** complex cannot be isolated.

Treatment of **9** in dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) gave a dark red solution as well (Figure 3.12b). Upon concentration in THF, a light red oil was observed in the dark red solution. No crystals were obtained for X-ray crystallography.

Both tungsten pentacarbonyl complexes, $\text{W}(\text{CO})_5\cdot\text{THF}$ and $\text{W}(\text{CO})_5\cdot\text{MeCN}$, were pre-formed according to literature.⁶⁸⁻⁶⁹ Treatment of **9** in $\text{W}(\text{CO})_5\cdot\text{THF}$ (Figure 3.12c) gave a green solution and colourless crystals were observed upon concentrating to 10 mL. X-ray crystallography confirmed the identity of these crystals to be tungsten hexacarbonyl ($\text{W}(\text{CO})_6$). Colourless crystals of $\text{W}(\text{CO})_6$ were also obtained from the dark yellow solution formed when **9** was treated with $\text{W}(\text{CO})_5\cdot\text{MeCN}$ in THF (Figure 3.12d). Given these observations, we have sufficient grounds to believe that there is successful coordination of **9** to the $\text{W}(\text{CO})_5$ complexes resulting in the liberation of a CO unit that attacks another W atom, forming $\text{W}(\text{CO})_6$. However, isolation and characterization of the predicted coordination product are still impossible.

Figure 3.12. Reactivity of **9** with TM-carbonyls

3.2.8 Attempt to imitate a “push-pull” NHC-disilyne-ZnCl₂ complex

We attempted to mimic Sekiguchi's and Driess' “push-pull” complex by replacing the disilyne with compound **9**.⁷⁰ The reaction was allowed to proceed in the following pathway as described in the literature (Figure 3.13).

Figure 3.13. Synthesis of Sekiguchi's and Driess' “Push-pull” NHC-disilyne-ZnCl₂ complex⁷⁰

Treatment of **9** with the NHC 1,3,4,5-tetramethylimidazol-2-ylidene turns the mixture red, after leaving to stir overnight and work-up, a dark orange solution is obtained. Hexane was removed by vacuum and the solids were re-diluted in toluene before addition of zinc chloride (ZnCl₂). Upon adding ZnCl₂, there is no observable colour change, the colour change happened gradually over the course of 2 days into a dark green mixture. The work-up is done to obtain a greenish-yellow solution which separates into 2 clear layers upon concentration. The reaction pathway is illustrated in Figure 3.14. Instead of the desired push-pull dimetallyne complex, a GeCl₂ dimer as colourless crystals (Figure 3.15) was yielded. Isolation of the other products is still in progress.

Figure 3.14. Reaction pathway of **9** with ZnCl₂

Figure 3.15. Molecular structure of **11** (thermal ellipsoids set at 30% probability). Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Cl1 2.2181(15), Ge1-Cl2 2.3762(14), C5-N1 1.313(6), C5-N2 1.346(6), Ge1-N1 2.004(5); N1-C5-N2 118.3(5), N1-Ge1-Cl1 112.33(13), Cl1-Ge1-Cl2 111.32(6), Cl1-N1-Ge1 117.3(4), Ge1-Cl2-Ge1 88.16(5), N1-Ge1-Cl2 123.04(12)

3.3 Conclusion

In conclusion, the unsymmetrical silyagermyne **9** (LGeSiR , $\text{L} = \text{C}_6\text{H}_2\text{-5,6-OCH}_2\text{O-2-(C=NAr)}$, $\text{R} = \text{R} = \text{PhC(N}^t\text{Bu)}_2$) was synthesized through simple procedures and characterized by NMR. Attempts at characterization by X-ray crystallography is still in progress. The various reactivities of **9** were investigated. Two notable reactivities are that of **9** with 3 equivalents of Te, affording a product (**10**) with the unique Te=Si-Te-Ge bond and **9** with 1,3,4,5-tetramethylimidazol-2-ylidene which yielded a product (**11**) with a unique Ge-Cl-Ge-Cl 4 membered ring. There has, however, been no success in isolating a compound that clearly demonstrates the presence of the $\text{Si}\equiv\text{Ge}$ triple bond. At the moment, we are attempting to isolate crystals for X-ray crystallography and further characterization.

Experimental Procedures

All chemical reactions were carried out using conventional Schlenk techniques, under an atmosphere of argon gas. The solvents used were purified by the MBRAUN MB SPS-5 solvent purification system. Tetrahydrofuran was distilled from sodium- benzophenone.

GeCl_2 .dioxane, monomers **a-i**, $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{LiN}[\text{Si}(\text{CH}_3)_3]$, HSiCl_3 , $\text{BH}_3\cdot\text{SMe}_2$, GaCl_3 , AlMe_3 , sulfur powder, selenium powder, tellurium powder, $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$ were purchased from Sigma Aldrich, monomer **j** was purchased from Tokyo Chemical Industry Co. Ltd. and used as received.

The ^1H , ^{13}C and ^{29}Si NMR spectra were recorded in deuterated benzene (C_6D_6) unless otherwise stated, on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe_4 for ^1H , ^{13}C and ^{29}Si . Multiplicities are given as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet). The number of protons (n) for a given resonance is given by nH and coupling constants are given as a J value in Hz.

All reagents were degassed and handled under an inert argon atmosphere using syringe and cannula techniques. Unless otherwise noted, all reactions were prepared in oven-dried glassware in an argon-filled inert atmosphere box and performed in sealed vessels.

Mass spectrometry was performed with a ThermoFinnigan LCQ Fleet MS. The sample was dissolved in and diluted with ACN for analysis.

The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300×8.0 mm; bead size = $7\ \mu\text{m}$; pore size = $20\text{--}200\ \text{\AA}$). The eluent was THF at a flow rate of $1.0\ \text{mL/min}$ ($40\ ^\circ\text{C}$). Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The monomer conversion was determined from the peak area. The column system was calibrated with standard polystyrenes and poly(methyl methacrylate)s. GPC samples were prepared in the following way: all volatiles were removed with the rotary

evaporator. THF was added to redilute the remnants and reprecipitation was done by adding hexane into the diluted solution. The mixture was filtered to obtain white solids as the residue and the white solids were dried into powder. The powder was then dissolved in THF and the solution was used for GPC.

The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL Ltd., Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared the polymer solution to 10 g/L in THF in all cases), matrix solution (DCTB: 10 g/L in THF), and cationization agent solution (NaTFA: 10 g/L in THF). The MALDI-TOF-MS samples were prepared by the dried droplet method. The polymer, matrix, and cationization agent solutions (all in THF) were mixed together in ratios of 1/2/1 (v/v/v). Then, 5 μ L of the mixed solution was deposited on the target plate and dried in the air at room temperature.

Intensity data for compounds **10** and **11** were collected using a Bruker APEX II diffractometer. All measurements were performed at 103(2) K. The structures were solved by direct phase determination (SHELXS- 97) and refined for all data by full-matrix least-squares methods on F2.18 Data were corrected for absorption effects using the Multi-Scan method (SADABS). All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

Chapter 2

1: To a 250 mL Schlenk flask was added a solution of N,N'-di-*tert*-butylcarbodiimide (3.8 mL, 20 mmol) in DEE (100 mL) and phenyllithium (19.8 mL, 20 mmol) at -78 °C. The solution was left stirring for 4 hours. The prepared solution of was added dropwise to a second Schlenk flask with GeCl₂.dioxane (5.10 g, 22 mmol) at -78 °C. The solution was left to stir overnight, filtered and concentrated to obtain air- and moisture-sensitive colourless crystals. Mp: 145-150 °C. Elemental analysis (%) calcd for C₁₅H₂₃ClGeN₂ (339.45): C 53.18; H 6.77; N 8.27; found, C, 52.66; H, 6.63; N, 8.06. ¹H NMR (200 MHz, THF-d₈, 25 °C): δ = 1.08 ppm (s, 18H, *t*Bu), 7.41-7.48 ppm (m, 5H, Ph); ¹³C{¹H}NMR (500 MHz, THF-d₈, 25 °C): δ = 31.8 (CMe₃), 54.2 (CMe₃), 128.6, 128.9, 129.1, 129.9, 130.6, 135.6 (Ph), 173.3 ppm (NCN); EI-MS: m/z(%): 338.5[M⁺], (100).

2: To another Schlenk flask, **1** (1.02 g, 3 mmol) and KC₈ (0.406 g, 3 mmol) were added to THF (50 mL) and left to stir overnight. The resultant mixture was filtered and concentrated to afford air- and moisture- sensitive dark orange crystals. Mp: 220-225 °C. Elemental analysis (%) calcd for C₃₀H₄₆Ge₂N₄ (607.99): C 59.26; H 7.63; N 9.22; found, C, 57.52; H, 7.47; N, 8.54. Due to the sensitivity of the crystals the analytical values show some deviation from the calcd one. ¹H NMR (200 MHz, THF-d₈, 25 °C): δ = 1.16 ppm (s, 36H, *t*Bu), 7.34-7.39 ppm (m, 10H, Ph); ¹³C{¹H}NMR (500 MHz, THF-d₈, 25 °C): δ = 31.9 (CMe₃), 32.1 (CMe₃), 53.5 (CMe₃), 55.0 (CMe₃), 123.0, 126.9, 127.8, 128.1, 128.3,

128.9, 129.1, 129.4, 129.9, 130.5, 131.5, 138.0 (Ph), 154.5 (NCN), 164.3 ppm (NCN); EI-MS: $m/z(\%)$: 608.5 $[M^+]$ (100).

3: To a 250 mL Schlenk flask was added LLi (L = C₆H₂-5,6-OCH₂O-2-(C=NAr)) (5.76 g, 20 mmol) and diethyl ether (100 mL). The reaction mixture was left to stir for 4 hours before being added dropwise a second Schlenk flask with GeCl₂.dioxane (5.10 g, 22 mmol) at -78 °C and left to stir overnight. The resulting mixture is then filtered and concentrated to obtain air- and moisture-sensitive colourless crystals. Mp: 207 °C. Elem anal. Calcd for C₂₁H₂₄ClGeNO₂: C, 58.59; H, 5.62; N, 3.25. Found: C, 58.21; H, 5.43; N, 3.19. ¹H NMR (395.9 MHz, [D₆]benzene, 23.3 °C): δ 0.84 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 0.91 (d, ³J_{HH} = 7.2 Hz, 3H, CH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 1.43 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂), 1.68 (s, 3H, CH₃), 2.64 (sept, ³J_{HH} = 6.8 Hz, 1H, CH(CH₃)₂), 3.21 (sept, ³J_{HH} = 6.8 Hz, 1H, CH(CH₃)₂), 5.18 (s, 1H, OCH₂O), 5.27 (s, 1H, OCH₂O), 6.53 (d, ³J_{HH} = 8.2 Hz, 1H, Ph), 6.83 (d, ³J_{HH} = 8.2 Hz, 1H, Ph), 6.99–7.01 (m, 1H, Ph), 7.10–7.13 (m, 2H, Ph). ¹³C{¹H} NMR (100.6 MHz, [D₆]benzene, 24.0 °C): δ 17.18, 24.08, 24.22, 25.23 (CH(CH₃)₂), 28.24, 29.15 (CH(CH₃)₂), 101.33, 107.48, 124.03, 124.81, 125.23, 135.36, 138.08, 141.12, 143.15, 145.22 (Ar/Ph), 150.73 (CH₃), 151.11 (OCH₂O), 178.88 (C=NAr).

4

4: To another Schlenk flask, **3** (1.17 g, 3 mmol) and KC_8 (0.406 g, 3 mmol) were added to THF (50 mL) at -78°C and left to stir for 16 hours. The resultant mixture was filtered and concentrated to afford air- and moisture- sensitive deep red crystals. Mp: 243°C . Elem anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{Ge}_2\text{N}_2\text{O}_4$: C, 63.83; H, 6.13; N, 3.55. Found: C, 63.67; H, 5.92; N, 3.31. ^1H NMR (395.9 MHz, $[\text{D}_6]\text{benzene}$, 23.3°C): δ 0.89 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.12 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.22 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.47 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.97 (s, 6H, CH_3), 2.60 (br s, 2H, $\text{CH}(\text{CH}_3)_2$), 3.41 (br s, 2H, $\text{CH}(\text{CH}_3)_2$), 5.17 (br s, 2H, OCH_2O), 5.28 (br s, 2H, OCH_2O), 6.67 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H, Ph), 7.09 (br s, 3H, Ph), 7.18–7.21 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, $[\text{D}_6]\text{benzene}$, 23.0°C): δ 17.55, 23.90, 25.14, 25.48 ($\text{CH}(\text{CH}_3)_2$), 28.31 ($\text{CH}-(\text{CH}_3)_2$), 100.26, 105.47, 123.75, 124.06, 134.09, 140.97, 142.96, 144.61 (Ar/Ph), 148.95 (CH_3), 160.00 (OCH_2O), 166.90 ($\text{C}=\text{NAr}$).

Synthesis of polymers

The synthesis of polymers was done with the same procedure, only varying the amount of monomer added in each reaction.

To a 8 mL glass vial was added the catalyst **2** (0.0060 g, 0.1 mmol) or **4** (0.0079 g, 0.1 mmol), toluene (3 mL) and the respective monomers. The mass of monomer added is represented in the table below. To this mixture was added $\text{B}(\text{C}_6\text{F}_5)_3$ (0.010 g, 0.2 mmol) was added to the vial and the reaction was left to stir. The reaction duration is also represented in the table below. It should be noted that monomers **g** and **h** required a reaction temperature of 110°C while the rest proceeded at room temperature.

Table A.1. Mass of monomer used in the reaction and the duration taken for completion

Monomer Used	Mass (g)	No. of Moles (mmol)	Reaction Duration (h)
a	0.200	2	2
b	0.228	2	2
c	0.284	2	5
f	0.228	2	16
g	0.168	2	16
h	0.196	2	16

poly(**a**)

With **2**: ¹H NMR (399.5 MHz, [D₆]benzene, 25°C): δ 0.90-1.03 (m, 75H, CH₃(chain)), 5.47 (m, 1H, CH₂(end)), 6.20 (m, 1H, CH₂(end)).

With **4**: ¹H NMR (399.5 MHz, [D₆]benzene, 25°C): δ 0.89-1.01 (m, 70H, CH₃(chain)), 5.47 (m, 1H, CH₂(end)), 6.20 (m, 1H, CH₂(end)).

poly(**b**)

With **2**: ¹H NMR (399.5 MHz, [D₆]benzene, 25°C): δ 0.88-0.89 (m, 120H, CH₃(chain)), 5.44 (m, 1H, CH₂(end)), 6.18 (m, 1H, CH₂(end)).

With **4**: ¹H NMR (399.5 MHz, [D₆]benzene, 25°C): δ 0.88 (m, 95H, CH₃(chain)), 5.44 (m, 1H, CH₂(end)), 6.18 (m, 1H, CH₂(end)).

poly(**c**)

With **2**: ¹H NMR (399.5 MHz, [D₆]benzene, 25°C): δ 0.93-0.96 (m, 60H, CH₃(chain)), 5.44m, 1H, CH₂(end)), 6.18 (m, 1H, CH₂(end)).

With **4**: ¹H NMR (399.5 MHz, [D₆]benzene, 25°C): δ 0.92-0.95 (m, 118H, CH₃(chain)), 5.44 (m, 1H, CH₂(end)), 6.17 (m, 1H, CH₂(end))

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6: To a 250 mL Schlenk flask was added a solution of N,N'-di-*tert*-butylcarbodiimide (3.8 mL, 20 mmol) in DEE (100 mL) and phenyllithium (19.8 mL, 20 mmol) at -78 °C. The solution was left stirring for 4 hours. To the prepared solution, trichlorosilane (2.4 mL 22 mmol) was added dropwise at -78 °C. The solution was left to stir overnight, filtered and concentrated to obtain air- and moisture-sensitive colourless crystals. Mp 145-150 °C. Elemental analysis (%) calcd for C₁₅H₂₄Cl₂N₂Si (331.36): C, 54.37; H, 7.30; N, 8.45; found: C, 54.66; H, 7.63; N, 8.06. ¹H NMR (200 MHz, [D6]benzene, 25 °C): δ 1.08 ppm (s, 18H, ^tBu), 6.70 ppm (s, 1H, Si-H), 7.41-7.48 ppm (m, 5H, Ph); ¹³C{¹H}NMR (125.75 MHz, [D6]benzene, 25 °C): δ 31.8 (CMe₃), 54.2 (CMe₃), 128.6, 128.9, 129.1, 129.9, 130.6, 135.6 (Ph), 173.3 ppm (NCN); ²⁹Si{¹H}NMR (99.36 MHz, [D6]benzene, 25 °C): δ -96.834 ppm. EI-MS: m/z(%): 330 [M⁺], (100).

7: **6** (2.96 g, 10 mmol) and LiN[Si(CH₃)₃] (1.67 g, 10 mmol) were dissolved in Et₂O in 2 separate 100 mL Schlenk flasks. To the flask containing RSiHCl₂ in Et₂O, the flask containing LiN[Si(CH₃)₃] was added dropwise at -78 °C and left to stir for 16 hours. The solution is then filtered and concentrated to obtain air- and moisture-sensitive colourless crystals. M.p. 159 °C; elemental analysis (%) calcd for C₁₅H₂₃ClN₂Si: C 61.10, H 7.87, N 9.51; C 60.95, H 7.64, N 9.35; ¹H NMR (300 MHz, [D6]benzene, 25 °C): δ = 1.08 (s, 18H, ^tBu), 6.78–7.05 ppm (m, 5H, Ph); ¹³C{¹H} NMR (75 MHz, [D6]benzene, 25 °C): δ = 31.4 (CMe₃), 53.7 (CMe₃),

127.4, 127.9, 128.4, 129.8, 133.0 (Ph), 166.7 ppm (NCN); $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz, $[\text{D}_6]\text{benzene}$, 25°C): $\delta = 14.6$; EI-MS: m/z : 295 $[\text{M}^+]$, 231 $[\text{M}^+-\text{Si}-\text{Cl}]$.

8: In a 100 mL Schlenk flask containing a mixture of **3** (0.431 g, 1 mmol) and Kc_8 (0.473 g, 1 mmol), 30 mL of THF was added. The reaction was stirred for 1 hour and filtered to obtain **8** in-situ. Mp: 380°C . ^1H NMR (400.1 MHz, THF-d_8 , 23.3°C): δ 1.03 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.12 (d, $^3J_{\text{HH}} = 7.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 2.12 (s, 3H, CH_3), 2.65 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 5.72 (s, 2H, OCH_2O), 6.31 (d, $^3J_{\text{HH}} = 8.7$ Hz, 1H, Ph), 7.04–7.07 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF-d_8 , 23.3°C): δ 15.71, 23.83 ($\text{CH}(\text{CH}_3)_2$), 27.05, 27.86 ($\text{CH}(\text{CH}_3)_2$), 98.18, 104.07, 119.73, 122.50, 125.25, 128.24, 128.55, 130.18, 145.41 (Ph/Ar), 147.49 (CH_3), 148.06 (OCH_2O), 155.93 ($\text{C}=\text{NAr}$).

9: In the prepared in-situ solution of **8**, **7** (0.295 g, 1 mmol) dissolved in THF was added dropwise at -78°C . The reaction was stirred for 1 hour, filtered and vacuumed dry to obtain the dark-blue crude solids of **9**. Elemental analysis calcd for $\text{C}_{36}\text{H}_{47}\text{GeN}_3\text{O}_2\text{Si}$: C, 66.06; H, 7.24; N, 6.42. Found: C, 65.57; H, 7.18; N, 6.49. ^1H NMR (399.5 MHz, $[\text{D}_6]\text{benzene}$, 24.9°C) δ 1.02 (d, $^3J_{\text{HH}} = 6.81$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.08 (s, 18H, ^tBu), 1.61 (d, $^3J_{\text{HH}} = 6.81$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.12 (sept, $^3J_{\text{HH}} = 6.81$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 5.71 (s, 2H, OCH_2O), 6.86 (s, 1H, Ph), 6.88 (s, 1H, Ph), 7.06 – 7.09 (m, 2H, Ph), 7.20 (br, 3H, Ph), 7.40 (s, 1H, Ph),

7.42 (s, 1H, Ph), 7.55 – 7.58 (m, 1H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_6]\text{benzene}$, 25.1°C): δ 17.41, 24.33, 25.57, 28.26, 28.88, 30.78, 31.73, 32.68, 52.95, 99.59, 105.93, 123.69, 123.90, 129.01, 129.54, 141.56, 142.89, 143.29, 149.30, 153.27, 155.37, 159.40. $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, $[\text{D}_6]\text{benzene}$, 24.9°C): 70.9.

Reaction of **9** with various compounds

The reaction of compound **9** with various compounds is done by dissolving the dried out **9** in a 100 mL Schlenk flask. The other reactant was also dissolved in the respective solvent in another 100 mL Schlenk flask and added dropwise to the flask containing **9** at -78°C . The reactions were left to stir overnight and filtered. The table below shows the amount of reactant that was used with **9**. It should be noted that the experiments involving S, Se and Te were conducted in the absence of light.

Table A.2. Conditions for various experiments to investigate the reactivity of **9**

Reactant	No. of Moles (mmol)	No. of Equivalents	Solvent Used	Mass added (g)
$\text{B}(\text{C}_6\text{F}_5)_3$	1	1	Toluene	0.0512
BH_3SMe_2	1	1	Toluene	0.0760
BH_3SMe_2	2	2	Toluene	0.152
GaCl_3	1	1	Toluene	0.176
AlMe_3	1	1	Toluene	0.144
AlMe_3	2	2	Toluene	0.288
S	1	1	THF	0.0321
S	2	2	THF	0.0642
S	3	3	THF	0.0963
Se	1	1	THF	0.0790
Se	2	2	THF	0.158
Se	3	3	THF	0.237
Te	1	1	THF	0.128
Te	2	2	THF	0.256

Te	3	3	THF	0.384
Fe ₂ (CO) ₉	1	1	THF	0.364
Co ₂ (CO) ₈	1	1	THF	0.342
W(CO) ₅ .THF	1	1	THF	0.396
W(CO) ₅ .MeCN	1	1	THF	0.365

10: The solution of **9** after filtration was added dropwise into another Schlenk flask containing Te (0.256 g, 2 mmol) at -78 °C upon removal of all light sources. The reaction was left to stir overnight and filtered in the absence of light. ²⁹Si{¹H} NMR (79.4 MHz, THF, 24.9 °C): δ -85.6. ¹²⁵Te{¹H} NMR (79.4 MHz, THF, 24.9 °C): -0.738 ppt, -0.180 ppt.

11: The dried out **9** was dissolved in hexane in a 100mL flask and added dropwise to NHC 1,3,4,5-tetramethylimidazol-2-ylidene (0.124 g, 1 mmol). The reaction was left to stir overnight, filtered and volatiles were removed by vacuum and redissolved in toluene and added dropwise to ZnCl₂ (0.136 g, 1 mmol) dissolved in toluene in another Schlenk flask. The reaction was left to stir overnight again and filtered after 16 hours.

Appendix

Chapter 2

i. MALDI-TOF-MS spectrum of poly(MMA) catalyzed by **2**

ii. MALDI-TOF-MS spectrum of poly(EMA) catalyzed by **2**

iii. MALDI-TOF-MS spectrum of poly(BMA) catalyzed by **2**

*a. MALDI-TOF-MS spectra for polymers catalyzed by **2***

i. MALDI-TOF-MS spectrum of poly(MMA) catalyzed by **4**

ii. MALDI-TOF-MS spectrum of poly(EMA) catalyzed by **4**

iii. MALDI-TOF-MS spectrum of poly(BMA) catalyzed by **4**

*b. MALDI-TOF-MS spectra for polymers catalyzed by **4***

c. LC-MS spectrum of poly(MMA) catalyzed by **2**

d. LC-MS spectrum of poly(EMA) catalyzed by **2**

e. LC-MS spectrum of poly(BMA) catalyzed by **2**

f. LC-MS spectrum of poly(MMA) catalyzed by **4**

g. LC-MS spectrum of poly(EMA) catalyzed by 4

h. LC-MS spectrum of poly(BMA) catalyzed by 4

Chapter 3

Table of X-ray Crystallographic Data

Table A.3. Crystal data and structure refinement for **10** and **11**.

	10	11
Empirical Formula	C ₃₆ H ₄₇ GeN ₃ O ₂ SiTe ₂	C ₃₀ H ₄₈ Cl ₄ Ge ₂ N ₄
Formula Weight (g/mol)	909.64	751.70
Crystal System	Orthorhombic	Orthorhombic
Crystal Size (mm)	0.120 x 0.140 x 0.200	0.020 x 0.040 x 0.120
Crystal Habit	Orange block	Colourless needle
Space Group	P 21 21 21	P b c a
a (Å)	11.7824(3)	15.3640(12)
b (Å)	16.6918(3)	10.9280(9)
c (Å)	19.1208(4)	21.3540(13)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å ³)	3760.48(14)	3585.3(5)
Z	4	4
d _{calcd} (mg m ⁻³)	1.607	1.393
μ (mm ⁻¹)	2.402	2.000
F (ooo)	1800	1552
Index Ranges	-19<= <i>h</i> <=19, -20<= <i>k</i> <=27, -31<= <i>l</i> <=23	-19<= <i>h</i> <=19, -13<= <i>k</i> <=14, -27<= <i>l</i> <=25
θ range for data collection (deg)	2.37 to 36.33	2.32-27.10
Reflections Collected	45926	26697
Independent Reflections	18156 [R(int) = 0.0595]	3944 [R(int) = 0.1931]
Coverage of independent reflections (%)	99.7	99.8
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.7610 and 0.6450	0.9610 and 0.7950
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	18156 / 0 / 417	3944 / 0 / 190
Goodness-of-fit on F ²	0.997	1.015
Δ/σ _{max}	0.001	0.001
R ₁ , wR ₂ [I > 2σ(I)]	R ₁ = 0.0464, wR ₂ = 0.0611	R ₁ = 0.0579, wR ₂ = 0.1176
R ₁ , wR ₂ (all data)	R ₁ = 0.0812, wR ₂ = 0.0715	R ₁ = 0.1317, wR ₂ = 0.1485
Largest diff peak/hole (eÅ ⁻³)	1.075 and -0.933	0.473 and -0.607
R.M.S. deviation from mean (eÅ ⁻³)	0.165	0.115

i. ^{29}Si NMR Spectrum of Compound **10**

j. ^{125}Te NMR Spectrum of Compound **10**

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