Simple synthetic methods towards reactive low valent germanium compounds

Muhammad Luthfi Ismail

2019

Muhammad Luthfi Ismail. (2019). Simple synthetic methods towards reactive low valent germanium compounds. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/106680>

<https://doi.org/10.32657/10220/48969>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SIMPLE SYNTHETIC METHODS TOWARDS REACTIVE
LOW VALENT GERMANIUM COMPOUNDS**

MUHAMMAD LUTHFI BIN ISMAIL

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

**SIMPLE SYNTHETIC METHODS TOWARDS REACTIVE
LOW VALENT GERMANIUM COMPOUNDS**

MUHAMMAD LUTHFI BIN ISMAIL

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

27th June 2019

.....
Date

.....
Muhammad Luthfi Bin Ismail

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

27th June 2019

.....
Date

.....
Assoc. Professor Cheuk-Wai So

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals where I was the first and/or corresponding author.

Chapter 1 is published as M.L.B. Ismail and C.-W. So. Synthesis of a Dimeric Phosphine-Stabilized Phosphidogermanium(I)-Amidogermanium(II) Derivative. *Chemical Communications*, Advance Article (2019). DOI: 10.1039/C8CC09454C

The contributions of the co-authors are as follows:

- Associate Professor So provided the initial project direction and edited the manuscript drafts.
- I co-designed the study with Associate Professor Cheuk-Wai So and performed all the laboratory work at the Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences. I also analyzed the data.
- All laboratory work including Nuclear Magnetic Resonance (NMR) Spectroscopy measurements and experiments were conducted by me.

Chapter 2 is published as M.L.B. Ismail, F.-Q. Liu, W.-L. Yim, R. Ganguly, Y. Li, and C.-W. So. Reactivity of Base-Stabilized Germanium(I) Dimer toward Group 9 Metal(I) Chloride and Manganese Decacarbonyl. *Inorganic Chemistry* **56**, 5402-5410 (2017). DOI: 10.1021/acs.inorgchem.7b00503

The contributions of the co-authors are as follows:

- Associate Professor Cheuk-Wai So provided the initial project direction and edited the manuscript drafts.
- I co-designed the study with Fu-Quan Liu and Associate Professor Cheuk-Wai So. Both Fu-Quan Liu and I performed all the laboratory work and analyzed the data at the Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences.
- Dr Rakesh Ganguly and Dr Li Yongxin analyzed X-ray crystallographic data.
- Dr Yim Wai-Leung performed DFT calculations

27th June 2019

.....
Date

.....
Muhammad Luthfi Bin Ismail

Abstract

This thesis describes the unique synthetic strategy towards a variety of low oxidation state germanium compounds without the use of harsh reagents.

Chapter 1 describes the synthesis of a phosphine-stabilized phosphidogermanium(I) dimeric derivative, $[\text{Ge}(\text{Cl})\{\text{N}(\text{Ar})\text{PPh}_2\}(\text{Ph}_2\text{P})\text{Ge:}]_2$ (**1.3**) isolated from a reaction of $[\text{L}\{(\text{Ar})(\text{Ph}_2\text{P})\text{N}\}\text{Si:}]$ (**1.1**) and GeCl_2 .dioxane. Compound **1.3** was isolated alongside the amidinato amidosilylene – germylene adduct, $[\text{L}\{(\text{Ar})(\text{Ph}_2\text{P})\text{N}\}\text{Si:}\rightarrow\text{GeCl}_2]$ (**1.2**). A crude ^{29}Si NMR spectrum of the mother liquor revealed the presence of silaamine $[\text{LSi}(=\text{NAr})\text{Cl}]$ (**1.4**) and trichlorosilane derivative (LSiCl_3) (**1.5**). The thermal conversion of **1.1** to its constitutional isomer, together with the isolated products, and detected intermediates hints at a possible mechanism which involves several redox processes. Additionally, the preliminary reactivity of compound **1.3** with $\text{B}(\text{C}_6\text{F}_5)_3$ resulted in the formation of its oxidised product $[\{\text{Ph}_2\text{PN}(\text{Ar})\text{GeCl}\}\{\text{Ph}_2\text{PGeCl}\}]$ (**1.7**).

Chapter 2 describes the isolation of a variety of transition metallogermylene complexes by a reaction of base – stabilized germanium(I) dimer $[\text{LGe}]_2$ (**2.1**, L = 2-imino-5,6-methylenedioxyphenyl) with various transition metal complexes. These reactions represent a rare example of metallogermylene synthesis without the use of harsh transition metallate complexes in salt metathesis reactions.

Chapter 3 describes the simple synthesis of the first germylenysilylene (**3.3**) starting from the 2-imino-5,6-methylenedioxyphenylchlorogermylene (**3.1**). Suitable crystals of compound **3.3** for X-ray crystallography could not be isolated due to its inherent instability. Compound **3.3** decomposes into unidentified products within days in solution. However, it is sufficiently stable to be characterized by multinuclear NMR spectroscopy.

An in-situ generated **3.3** can undergo a clean reaction with 2 equivalents of 2,6-diisopropylphenylazide at low temperature to form compound **3.4**. Compound **3.4** represents a rare example of a silaamidinato germylene. The proposed structure of compound **3.3** can be inferred from the molecular structure of **3.4**.

Acknowledgements

Firstly, I wish to convey my sincere appreciation to my supervisor, Associate Professor Cheuk-Wai So for his support, unending guidance and limitless patience over my whole PhD candidature. I am proud to have worked with him and in retrospect, I would not have considered any other supervisor for my PhD journey. This thesis would not have been possible without his advice and input.

I would also like to express my gratitude to my seniors and mentors throughout my 4 years in the laboratory namely Dr Chia Siew Peng, Dr Chan Yuk Chi, Dr Li Yan, Dr Rahul Kumar Siwatch, Dr Ho Ying Fu Samuel, Dr. Seow Su Yi Celestine, Dr Shan Yuliang for inspiring confidence and their constant encouragements throughout my PhD studies. Special mention goes to Dr Chia Siew Peng for her guidance when I first started out as an undergraduate student in the laboratory. Her teaching methods inspired me to pursue research as a PhD student.

I would like to show my appreciation to all my present colleagues namely Khoo Yee Teng Sabrina, Chia Cher Chiek, Leong Bi Xiang, Fan Jun, Ong Xin Yi Melissa and Lee Jiawen, Smith Samuel Gordan Fitzgerald and Wee Yi Shuo Meldon for the terrible but ultimately funny jokes, the small talks and the numerous times they have given encouragements. The vibrant atmosphere that we, as a group, have cultivated in the very toxic laboratory have made the final year of my PhD studies more bearable.

I am deeply appreciative of the assistance rendered over the years by the technical and administrative staff. Without their support, the submission of this thesis would not be completed on time. My deep respect and heartfelt appreciation goes to the X-ray crystallographers in CBC namely Dr Rakesh Ganguly and Dr. Yong-Xin Li for performing X-ray crystallography for the crystals that I have isolated throughout my 4 years in NTU CBC.

I appreciate the financial support received by means of the NTU research scholarship, from Nanyang Technological University.

I am grateful for my parents and siblings who have stood by my decision to pursue PhD. For the most part, they have been an excellent source of emotional support and have been very understanding of the insane work hours.

Last but not least, I cannot even begin to say how thankful I am for my wife, Nurseha Binti Ishak and my son, Muhammad Uzayr Bin Muhammad Luthfi. They have both been a constant source of motivation for me to complete my PhD studies when times appeared the bleakest. I am sure that without them I would not be this close to finishing and for that, I am forever in debt.

27th June 2019

Muhammad Luthfi Bin Ismail

Division of Chemistry and Biological Chemistry
School of Physical and Mathematical Sciences
Nanyang Technological University

Table of Contents

Abstract	7
Acknowledgements	10
Table of Contents	12
Abbreviations.....	14
List of Synthesized Compounds	16
Chapter 1	19
1.1 Introduction	19
1.2 Results and Discussion	23
1.3 Conclusion	35
1.4 Experimental Section	36
1.5 References	40
Chapter 2	42
2.1 Introduction	42
2.2 Results and Discussion	45
2.3 Conclusion	63
2.4 Experimental Section	64
2.5 References	70
Chapter 3	73
3.1 Introduction	73
3.2 Results and Discussion	77

3.3	Conclusion	81
3.4	Experimental Section	82
3.5	References	85
	Appendix	86

Abbreviations

THF	tetrahydrofuran
<i>t</i> Bu	Tert-butyl
t	Triplet
s	Singlet
ppm	Parts per million
Ph	Phenyl
NMR	Nuclear magnetic resonance
M.p.	Melting point
mmol	millimole
Mes	2,4,6-trimethylphenyl (Mesityl)
Me	Methyl
m	Multiplet
LUMO	Lowest occupied molecular orbital
IR	Infrared
<i>i</i> Pr	Isopropyl
HOMO	Highest occupied molecular orbital
h	Hour(s)
g	Gram(s)
equiv	Equivalent
Dec.	Decomposed
d	Doublet
Cp*	Pentamethylcyclopentadienyl
Cp	Cyclopentadienyl

calcd	Calculated
br	Broad
Ar	2,6-diisopropylphenyl
μ	Mu
$^{\circ}\text{C}$	Degree Celsius
$^{\circ}$	Degree
δ	Chemical shift
$\text{\AA}$	Angstrom

List of Synthesized Compounds

Formula	Numbering Scheme	Page	Structure
$C_{39}H_{51}Cl_2GeN_3PSi$	1.2	21
$C_{72}H_{74}Cl_2Ge_4N_2P_4$	1.3	21
$C_{39}H_{51}N_3PSi$	1.6	24
$C_{36}H_{37}Cl_2Ge_2NP_2$	1.7	26
$C_{39}H_{51}Cl_2N_3PSiSn$	1.8	30
$C_{48}H_{54}Cl_4N_2P_2Sn_3$	1.9	31
$C_{37}H_{48}ClGeNO_2Rh_2$	2.2	43

$C_{29}H_{36}Cl_2GeNO_2Rh$	2.3	43
$C_{37}H_{48}ClGeIr_2NO_2$	2.4	43
$C_{29}H_{36}Cl_2GeIrNO_2$	2.5	43
$C_{50}H_{48}Ge_2Mn_2N_2O_{12}$	2.7	51
$C_{48}H_{48}Co_2Ge_2N_2O_{10}$	2.9	55
$C_{53}H_{48}Fe_3Ge_2N_2O_{15}$	2.10	57
$C_{50}H_{48}Fe_2Ge_2N_2O_{12}$	2.11	60

Chapter 1.

Synthesis of a Phosphine-Stabilized Phosphidogermanium(I) – Amidogermanium(II) Derivative[†]

1.1 Introduction

Tetrylenes of composition $[L_2E:]$ ($E = \text{Si, Ge, Sn, Pb}$; $L = \text{supporting ligand}$) comprise vacant p orbital and a lone pair of electrons on the group 14 atoms in the oxidation of +II.¹ These electronic structures enable them being both donors and acceptors. In this context, they are highly reactive and readily undergo oligomerization. In the 1970s, Lappert et al. reported that these compounds can be stabilized kinetically and/or thermodynamically by a variety of anionic ligands, especially steric hindered amido ligands ($-\text{NR}_2$) due to effective $p\pi$ - $p\pi$ interaction between the vacant p orbital at heavier group 14 atoms and the lone pair electrons on N atoms.² Subsequently, the chemistry of heavier carbene analogues has been explosively explored.³ In contrast to ubiquitous amido ligands, it is surprising that phosphide-based ligands ($-\text{PR}_2$) in di-substituted tetrylenes are rather less well established.⁴ This disparity may be attributed to weak $\text{P}_{\text{phosphido}}\text{-E}$ σ -bonds in comparison with the corresponding $\text{N}_{\text{amido}}\text{-E}$ bonds. In addition, the lone pair electrons on P atoms in diphosphatetrylenes remain stereochemically active due to the high energetic barrier to achieve a planar geometry at the P atoms.⁵ These result in diphosphidotetrylenes always existing in dimeric form.⁶

[†] Portions of this chapter are adapted with permission from Ismail, M. L. B.; So, C. W. *Chem. Commun.* **2019**, 55, 2074–2077. Copyright (2019) The Royal Society of Chemistry

Scheme 1-1: Examples of dimeric diphosphidotetrylenes featuring pyramidal phosphorus geometry

The first isolable diphosphido tetrylene $[(t\text{Bu}_2\text{P})_2\text{Pb}]_2$ (**1A**), was isolated by Cowley and co-workers in 1988.⁶ Compound **1A** was isolated by a reaction of PbCl_2 and 2 equivalents of $\text{Li}(\text{PrBu}_2)$. X-ray crystallographic analysis revealed that the Pb_2P_2 four-membered ring in **1A** is planar with the terminal phosphide groups located trans to each other. Buhro and co-workers isolated the diphosphido tin(II) and lead(II) dimer (**1B**) by reacting $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{E}$ ($\text{E} = \text{Sn}, \text{Pb}$) with $(\text{Me}_3\text{Si})_2\text{PH}$.^{7a} Westerhausen and co-workers independently synthesized $[\text{Sn}\{\text{P}(\text{SiMe}_3)_2\}_2]_2$ by reacting $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ and $[(\text{Me}_3\text{Si})_2\text{P}]_2\text{Mg}$.^{7b} The germanium analogue **1C** was synthesized by du Mont and coworkers by reacting the $\text{Ph}_3\text{P}-\text{GeCl}_2$ adduct and 2 equivalents of $(i\text{Pr})_2\text{P}(\text{SiMe}_3)$. Similarly, Izod and co-workers synthesized the diphosphido germanium(II) featuring 2 chiral terminal phosphine groups (**1D**).⁸ It is noteworthy that the terminal phosphine groups adopt a cis configuration with respect to the P_2Ge_2 ring, unlike the example in **1A**.

Scheme 1-2: Examples of monomeric diphosphidotetraylenes and tetraphosphidodisilene

There are only a handful examples of stable and monomeric diphosphidotetraylenes such as $[(\text{Ar}_2\text{P})_2\text{E}]$ ($\text{E} = \text{Ge, Sn}$) (**1E**)⁹, and $[\{(\text{Tripp})_2\text{FSi}\}(i\text{Pr}_3\text{Si})\text{P}]_2\text{E}$ ($\text{E} = \text{Ge, Sn, Pb}$; $\text{Tripp} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$) (**1F**)¹⁰ which were synthesized and structurally characterized. Similarly, tetraphosphidoditetrarelenes $[(\text{R}_2\text{P})_2\text{E}=\text{E}(\text{PR}_2)_2]$, in which the $\text{E}=\text{E}$ double bond are stabilized by four phosphido ligands, is scarce. Only one example of the tetraphosphidodisilene $[\{(\text{Mes})_2\text{P}\}_2\text{Si}=\text{Si}\{\text{P}(\text{Mes})_2\}_2]$ (**1G**) was isolated by the reaction of SiBr_4 and $[\{(\text{Mes})_2\text{P}\}\text{Li}]$.¹¹ Moreover, diphosphidotetraylenes $[(\text{R}_2\text{P})\text{E}\equiv\text{E}(\text{PR}_2)]$ and the corresponding base-stabilized derivatives $[(\text{R}_2\text{P})(\text{LB})\ddot{\text{E}}-\ddot{\text{E}}(\text{LB})(\text{PR}_2)]$ ($\text{LB} = \text{Lewis base}$) are still unknown, although a stable diamidodigermine and diamidodistannyne $[\{(\text{Ar}^*)(i\text{Pr}_3\text{Si})\text{N}\}\text{E}]_2$ ($\text{E} = \text{Ge, Sn}$; $\text{Ar}^* = 2,4,6\text{-}i\text{Pr}\{\text{C}(\text{H})\text{Ph}_2\}_2\text{C}_6\text{H}_2$) were recently synthesized.¹²

Considering that stable ditetrelynes and their base-stabilized derivatives are capable of undergoing transition-metal-like reactivity,¹³ diphosphidoditetrelynes should be worthwhile synthetic targets both for fundamental reasons and their potential application in small molecules activation. Herein, we report the use of a redox-active phosphinoamido silylene to synthesize a mixed-valent germanium (I,II) complex containing a phosphine-stabilized phosphidogermanium(I) dimer moiety.

1.2 Results and Discussion

Scheme 1-3: Synthesis of **1.2** – **1.5**

The reaction of $[L\{(Ar)(Ph_2P)N\}Si:]$ (**1.1**, $L = PhC(NtBu)_2$)¹⁴ with $GeCl_2$.dioxane in toluene for 16 hours afforded an orange coloured mixture. The reaction mixture was filtered and concentrated to afford the amidinato amidosilylene-germylene adduct $t[L\{(Ar)(Ph_2P)N\}Si:\rightarrow GeCl_2]$ (**1.2**· C_7H_8) as colourless crystalline solid (Yield: 31.6 %). To account for the peculiar orange colour of the solution, the mother liquor was decanted into another flask, and concentrated further to afford the phosphine-stabilized phosphidogermanium(I) dimer $[Ge(Cl)\{N(Ar)PPh_2\}(Ph_2P)Ge:]_2$ (**1.3**· C_7H_8) as an orange crystalline solid (Yield: 4.9 %). The following mother liquor was then analyzed by ^{29}Si NMR spectroscopy, which showed the presence of silaimine $[LSi(=NAr)Cl]$ (**1.4**) and $[LSiCl_3]$ (**1.5**).¹⁹ It is noteworthy that compound **1.3**· C_7H_8 is a rare example containing 2 different low-valent germanium centres (I & II), which was prepared without the use of harsh reducing agents, such as potassium graphite or sodium naphthalenide. Driess et al. also reported the synthesis of a germanium(I) dimer from the N-heterocyclic germanium(II) nucleophile $[L'GeK(Et_2O)_2]$

[L' = C(Me)CHC(Me)NAr] with the β -diketiminato germanium(II) chloride [HC{C(Me)N(Ar)}₂GeCl] without harsh reducing agents.^{15a}

Figure 1-1: Molecular structure of **1.2**·C₇H₈ with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are excluded for clarity. Selected bond lengths (Å) and angles (deg): Si1- Ge1 2.4863(5), Si1- N1 1.8572(17), Si1- N2 1.8051(17) N3-Si1 1.7509(15), N3-P1 1.7329(16) Ge1-Cl1 2.2997(6) Cl2-Ge1 2.3162(6); Cl2-Ge1-Si1 91.686(19), Cl1-Ge1-Si1 92.174(19), Cl1-Ge1-Cl2 98.18(2), N2-Si1-N1 72.01(7), P1-N3-Si1 102.07(8), N3-Si1-Ge1 116.23(6), N2-Si1-Ge1 118.87(5), N1-Si1-Ge1 107.74(5)

Compound **1.2**·C₇H₈ was characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **1.2**·C₇H₈ displays characteristic resonances for the Ar, PPh₂ substituents and the amidinate ligand. The ³¹P NMR signal of **1.2**·C₇H₈ (δ 44.9 ppm) is upfield shifted compared to **1.1** (δ 54.1 ppm). The ²⁹Si NMR resonance displays a doublet (δ -12.9 ppm, ²J_{Si-P} = 43.1 Hz) showing an unexpected upfield shift in compared to **1.1** (δ 10.7 ppm) despite the lone pair electrons on the Si(II) centres donating to the vacant orbitals on the Ge(II) atom. The molecular structure of compound **1.2**·C₇H₈ (Figure 1-1) shows that the Si1 atom adopts a distorted tetrahedral geometry, while the Ge1 atom displays a distorted trigonal

pyramidal geometry (the sum of bond angles: 282.04°). This indicates that the Ge1 atom comprises a lone pair of electrons. The Si1-Ge1 bond (2.4863(5) Å) is slightly shorter than that of another silylene-germylene adduct [L{(Me₃Si)₂N}Si:→GeCl₂] (2.5259(13) Å).^{15b} The N3-Si1 bond (1.7509(15) Å) is shorter than in **1.1** (1.796(2) Å) while the N3 atom possesses a trigonal planar geometry. The geometry about the N3 atom indicates some degree of delocalization of the lone pair on N3 across the N3-Si1 bond which leads to the upfield shift for the ²⁹Si NMR signal of **1.2**·C₇H₈.

Figure 1-2: Molecular structure of **1.3**·C₇H₈ with thermal ellipsoids set at 50% probability level. Solvent molecules and hydrogen atoms are excluded for clarity. Selected bond lengths (Å) and angles (deg): Ge1-N1 1.954(3), Cl1-Ge1 (2.3158(11), P1-Ge1 (2.4632(11), Ge2-P1 (2.4141(12), Ge2-P2 2.4709(11), N1-P2 1.675(4), Ge2-Ge2A 2.5574(9); N1-Ge1-Cl1 100.35(10), N1-Ge1-P1 90.16(10), Cl1-Ge1-P1 93.12(4), P1-Ge2-P2 85.91(4), P1-Ge2-Ge2A 98.89(4), P2-Ge2-Ge2A 96.82(3), P2-N1-Ge1 129.31(19), Ge2-P1-Ge1 114.15(4), N1-P2-Ge2 115.41(13)

Compound **1.3**·C₇H₈ (orange crystals) is unstable in solution at room temperature, which afforded the phosphamine [Ph₂PN(H)Ar]. Its presence was detected (43.2 ppm) by ³¹P NMR spectroscopy. It is relatively stable, in an inert argon atmosphere, in the solid state. In this context, it was characterized by X-ray crystallography and solid-state ³¹P NMR spectroscopy. The ³¹P CPMAS NMR spectrum depicts two signals at δ 103.63 and -14.03 ppm corresponding to the Ge-P(Ph)₂-N(Ar) and GeP(Ph)₂Ge moieties, respectively. The X-ray crystal structure of compound **1.3**·C₇H₈ shows that it has a trans bent geometry, while the Ge₂P₂N rings are puckered. The germanium atoms possess a trigonal pyramidal geometry (sum of bond angles, Ge1: 283.64°; Ge2: 281.59°). The Ge2-Ge2A bond (2.5575(7) Å) is shorter than that of the Ge^I-Ge^I bond in the amidinato germanium(I) dimer [LGe:]₂ (2.57(5) Å).¹⁶ The Ge2-P2 (2.471(1) Å) and Ge1-P1 (2.463(1) Å) bonds are slightly longer than the Ge2-P1 bond (2.414(1) Å). They are intermediate values between the P→Ge donor acceptor interaction (2.525(3), 2.612(3) Å) in the dimeric phosphinoamido chlorogermylene [Ph₂PN(Ar)GeCl]₂¹⁷ and the Ge-P electron sharing bond (2.3823(12) Å) in the diphosphidogermylene [(Ar₂P)₂Ge:].⁹ The P2-N1 (1.674(4) Å) and N1-Ge1 (1.954(3) Å) bond length are comparable with those of [Ph₂PN(Ar)GeCl]₂ (P-N: av. 1.683; N-Ge: av. 1.933 Å).

Scheme 1-4. Synthesis of compound **1.6**

To gain an insight into the reaction mechanism, an attempt to understand the stability of compound **1.1** was performed. When left to stand at room temperature, a solution of

compound **1.1** slowly undergoes a 1,2-rearrangement of the phosphido functional group to form the constitutional isomer **1.6**. This process can be accelerated to completion by heating a deuterated-benzene solution of **1.1** at 80°C overnight. The conversion was confirmed by both NMR spectroscopy (^{31}P NMR: δ - 54 ppm) and X-ray crystallography (Figure 1-3). Since the isomerization requires heating for completion, it is anticipated that the reaction mechanism may not proceed through the formation of **1.6**. However, these results indicate that the PPh_2 substituent is labile.

Figure 1-3. Molecular structure of **1.6** with thermal ellipsoids set at 50% probability level. Hydrogen atoms are excluded for clarity. Selected bond lengths (Å) and angles (deg): N1-Si1 1.8172(12), Si1-N2 1.8458(12), N3-Si1 1.5842(12), P1-Si1 2.2738(5), C5-N2 1.3373(18), C5-N1 1.3435(17); N2-Si1-N1 71.76(5), N3-Si1-P1 118.77(5), N1-Si1-P1 106.07(4), N2-Si1-P1 111.22(4)

The reaction mechanism is further indicated by the following reaction. The reaction of compound **1.3**·C₇H₈ with two equivalents of B(C₆F₅)₃ in toluene for 16 hours afforded a mixture of unidentified products containing four-coordinate boron centres (see ¹¹B NMR spectrum, appendix) and the phosphinamido- and phosphido-substituted chlorogermylene complex [{Ph₂PN(Ar)GeCl} {Ph₂PGeCl}] (**1.7**, Scheme 1-5). The reaction mechanism is unknown, but it seems that compound **1.3**·C₇H₈ easily undergoes oxidation to form compound **1.7**. In other words, compound **1.7** could be an intermediate in the reaction of **1.1** and GeCl₂.dioxane, which could then be reduced to form compound **1.3**·C₇H₈.

Scheme 1-5: Synthesis of **1.7**

Compound **1.7** exists as a mixture of cis- and trans-isomers in solution at room temperature, which was confirmed by two sets of two doublets in the ³¹P NMR (first set: δ 88.6 ppm, ³J_{PP} = 34.7 Hz (Ph₂PGeCl), -19.3 ppm, ³J_{PP} = 34.7 Hz (Ph₂PN(Ar)GeCl); second set: δ 96.7 ppm, ³J_{PP} = 30.3 Hz (Ph₂PGeCl), -27.1 ppm, ³J_{PP} = 30.3 Hz (Ph₂PN(Ar)GeCl). Compound **1.7** decomposes in solution above 80°C. The molecular structure of the cis-**1.7** isomer (Figure 1-4) shows that the Ge1 (sum of bond angles: 282.77°) and Ge2 (sum of bond angles: 272.45°) atoms adopt a distorted trigonal pyramidal geometry, which implies the presence of a stereochemically active lone pair. The P1-Ge2 bond (2.4039(11) Å) is slightly shorter than the

P1-Ge1 (2.4604(11) Å) and P2-Ge2 bonds (2.4861(11) Å). All three bonds are comparable to those found in compound **1.3**·C₇H₈.

Figure 1-4. Molecular structure of compound **1.7** with thermal ellipsoids set at 50% probability level. Hydrogen atoms are excluded for clarity. There are two separate molecules with slightly different bond angles and bond lengths in the asymmetric unit of **1.7**. Only one of the structures is shown for clarity. Selected bond lengths (Å) and angles (deg): Cl1-Ge1 2.2929(12), Cl2-Ge2 2.2468(12), Ge1-N1 1.965(3), Ge1-P1 2.4604(11), Ge2-P1 2.4039 (11), Ge2-P2 2.4861(11), N1-P2 1.668(3); N1-Ge1-Cl1 98.52(10), N1-Ge1-P1 88.83 (10), Cl1-Ge1-P1 95.42(4), Cl2-Ge2-P1 90.37 (4), Cl2-Ge2-P2 96.92(4), P1-Ge2-P2 85.22(4), C1-N1-P2 121.0(3), C1-N1-Ge1 109.5(2), P2-N1-Ge1 129.36(19), Ge2-P1-Ge1 113.67(4), N1-P2-Ge2 114.84(12)

With the spectroscopic data of compounds **1.2**·C₇H₈ and **1.4** - **1.7** in hand, the reaction mechanism for the formation of **1.3**·C₇H₈ was studied, whereby the reaction of **1.1** and GeCl₂.dioxane was monitored by ³¹P NMR spectroscopy. In the first 10 minutes, the ³¹P NMR spectrum showed that compound **1.2**·C₇H₈ was the major product. This illustrates that the formation of **1.2**·C₇H₈ is faster than the isomerization of **1.1** (Scheme 1-4). After 30 minutes,

the ^{31}P NMR spectrum shows the formation of **1.7**, while the signal for compound **1.2**·C₇H₈ diminished. After 16 hours, compound **1.3**·C₇H₈ was observed in the ^{31}P NMR spectrum.

Scheme 1-6: Synthesis of compound **1.7**.

On the basis of the above experimental results, the reaction mechanism is proposed (Scheme 1-6). It is suggested that compound **1.1** reacts with GeCl_2 to form compound **1.2**·C₇H₈ first. Subsequently, compound **1.2**·C₇H₈ rearranges to form a chlorosilylene “ LSiCl ” **A** intermediate and a phosphinamido chlorogermylene “ $\text{Ph}_2\text{PN}(\text{Ar})\text{GeCl}$ ” **B** intermediate, whereby the amido group substitutes the Cl atom in the GeCl_2 moiety (Scheme 1-7).

Scheme 1-7: The proposed mechanism of **A** and **B**

In addition, compound **1.2**·C₇H₈ undergoes an alternative rearrangement, whereby the lone pair electrons on the Ge^{II} centre attack on the P atom to form compound **1.4** and a phosphide chlorogermylene “Ph₂PGeCl” **C** (Scheme 1-8). A similar mechanism was reported in the reaction of the amidinato amidosilylene [LSiN(SiMe₃)₂] with SiI₄ in which the I atom of SiI₄ attacks the vacant p orbital on the Si^{II} centre, followed by the elimination of SiMe₃I to form “LSi(I)=NSiMe₃” intermediate.¹⁸ Finally, intermediates **B** and **C** coordinate with each other to form compound **1.7**, which is then reduced by the intermediate **A** to afford **1.3**·C₇H₈ and **1.5** (Scheme 1-6). In support of this hypothesis, the amidinato chlorosilylene **A** was reacted with compound **1.7** in C₆D₆ at room temperature for 16h (Scheme 1-5),¹⁹ which afforded a mixture of compounds **1.3**·C₇H₈ and **1.5**.

Scheme 1-8: The proposed mechanism for the formation of **1.4** and **C**

Scheme 1-9: Synthesis of **1.8**·C₇H₈

Figure 1-5: Molecular structure of compound **1.8**·C₇H₈ with thermal ellipsoids set at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. . Selected bond lengths (Å) and angles (deg): Si1-Sn1 2.707(3), Cl2-Sn1 2.463(3), N1-Si1 1.814(9), Cl1-Sn1 2.479(3), Si1-N2 1.868(9), N3-Si1 1.738(9); N3-Si1-Sn1 118.0(3), N2-Si1-Sn1 106.0(3), N1-Si1-Sn1 117.1(3), C16-N3-P1 124.7(7), C16-N3-Si1 129.3(7), Si1-N3-P1 104.3(5), Cl2-Sn1-Cl1 93.20(12), Cl1-Sn1-Si1 89.68(10), Cl2-Sn1-Si1 93.30(9)

Following complete characterization of **1.3**·C₇H₈, the reactivity **1.1** toward SnCl₂ was also studied. The reaction of **1.1** with SnCl₂ afforded the amidinato amidosilylene-stannylene adduct [L{(Ar)(Ph₂P)N}Si:→SnCl₂] (**1.8**·C₇H₈), which was obtained as colorless crystalline solid. The ¹H NMR spectrum of **1.8**·C₇H₈ depicts one set of resonances for the amidinate ligand,

Ar and PPh₂ substituents. The ³¹P NMR signal (δ 45.1 ppm) is slightly downfield with the signal with that of **1.2**·C₇H₈ (δ 44.8 ppm). The ¹¹⁹Sn NMR spectrum features a doublet (δ 58.1 ppm, ³J_{Sn-P} = 358.4 Hz) which is shielded compared with that of the amidinato amidosilylene- [L{(Me₃Si)₂N}SiSnCl₂] (δ 77.2 ppm)²⁰, which indicates that the Si-Sn bond in **1.8**·C₇H₈ is donor-acceptor interaction. However, compound **1.8**·C₇H₈ is unstable in solution (C₆D₆) overnight, which afforded a mixture of **1.5** and tin metal, confirmed by NMR spectroscopy. In this context, ²⁹Si NMR signal cannot be obtained. The molecular structure of **1.8**·C₇H₈ is comparable with that of **1.2**·C₇H₈ and the Si-Sn bond (2.707(3) Å) is comparable with that of [L{(Me₃Si)₂N}SiSnCl₂] (2.7325(18) Å)²⁰.

Scheme 1-8: Synthesis of compound **1.9**

To further understand the mechanism for the formation of **1.3**·C₇H₈, compound **1.8**·C₇H₈ was reacted with GeCl₂·dioxane in toluene for 16 hours to form the phosphinamido chlorostannylene-dichlorostannylene adduct [{Ph₂PN(Ar)}SnCl]₂SnCl₂ (**1.9**). The presence of the [Ph₂PN(Ar)SnCl] fragment in compound **1.9** which is the Sn analogue of intermediate **B** [Ph₂PN(Ar)GeCl] indicates that the formation of intermediate **B** is feasible and further corroborates the mechanism (Scheme 1-7). The ¹H NMR analysis of compound **1.9** displays characteristic signals for Ar and PPh₂ substituents.

Figure 1-6: Molecular structure of compound **1.9** with thermal ellipsoids set at 50% probability level. Hydrogen atoms and solvent molecules are excluded for clarity. Selected bond lengths (Å) and angles (deg): Sn1-Cl1 2.442(2), Sn1-Cl2 2.5412(19), Sn2-Cl3 2.7647(19), Sn2-Cl2 2.7505(19), N1-Sn1 2.176(6), N1-P1 1.653(6), P1-Sn2 2.7260(19); C1-N1-Sn1 108.5(4), C1-N1-P1 120.4(5), P1-N1-Sn1 131.1(3), N1-Sn1-Cl2 88.82(17), Cl1-Sn1-Cl2 89.08(7), N1-Sn1-Cl1 97.20(17)

The molecular structure of **1.9** shows that two PNSn_2Cl five-membered rings are puckered, along with $\text{Cl}_2\text{-Sn}_2\text{-Cl}_3$ moiety bridged between two $\text{Ph}_2\text{PN}(\text{Ar})\text{SnCl}$ units. The Sn1/3 and Sn2 atoms possess a trigonal and square pyramidal geometry respectively, which indicates the presence of a lone pair of electrons on these atoms. The Sn-N bonds (Sn1-N1: 2.176(6) Å; Sn3-N2: 2.160(6) Å) are comparable with that of amidostannylene $[\text{HC}\{(\text{PPh}_2=\text{NSiMe}_3)(\text{PPh}_2=\text{S})\}\text{SnN}(\text{SiMe}_3)_2]$ (2.152(4) Å).²¹ The Sn-P bond (average 2.726 Å) are longer than the P-Sn coordinate covalent bond in $[\text{SnCl}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}]$ (2.6481(17) Å).²²

1.3 Conclusion

In conclusion, the reaction of **1.1** with GeCl_2 .dioxane afforded a phosphine-stabilized phosphidogermanium(I) dimer moiety in a dimeric phosphine-stabilized phosphidogermanium(I)–amidogermanium(II) derivative **1.3**· C_7H_8 . Mechanistic studies show that the reaction proceeds through the formation of an amidinato amidosilylene–germylene adduct **1.2**· C_7H_8 , which then rearranges to afford a mixture of the phosphinoamido- and phosphido-substituted chlorogermylene complex **1.7**, amidinato chlorosilylene intermediate **A** and amidinato silaimine **1.4**. Complex **1.7** is then reduced by the amidinato chlorosilylene intermediate **A** to give **1.3**· C_7H_8 and amidinato trichlorosilane **1.5**. Lastly, the formation of **1.8**· C_7H_8 and its conversion to **1.9** confirms the plausible formation of intermediate **B** ($\text{Ph}_2\text{PN}(\text{Ar})\text{GeCl}$).

1.4 Experimental Section

General 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. $\text{GeCl}_2 \cdot \text{dioxane}$ and SnCl_2 were purchased from Sigma Aldrich and used as received. Compound **1.1** was prepared by methods outlined in the literature.¹⁴ The ^1H , ^{13}C , ^{29}Si and ^{31}P NMR spectra were recorded in deuterated benzene (C_6D_6) on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe_4 for ^1H , ^{13}C and ^{29}Si and 85% H_3PO_4 for ^{31}P . Elemental analyses were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

X-ray Data Collection and Structural Refinement. Intensity data for compounds **1.2**· C_7H_8 , **1.3**· C_7H_8 , **1.6**, **1.7**, **1.8**· C_7H_8 and **1.9** were collected using a Bruker APEX II diffractometer using graphite monochromated Mo- $\text{K}\alpha$ radiation (0.71073 Å). 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 F^2 .²³ 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.

Synthesis of $[\text{L}\{(\text{Ar})(\text{Ph}_2\text{P})\text{N}\}\text{Si} \rightarrow \text{GeCl}_2]$ (1.2**· C_7H_8).** Toluene (20 mL) was added to a mixture of $[\text{L}\{(\text{Ar})(\text{Ph}_2\text{P})\text{N}\}\text{Si}]$ (**1.1**) (0.62 g, 1.00 mmol) and $\text{GeCl}_2 \cdot \text{dioxane}$ (0.23 g, 1.00 mmol) and stirred for 16 hours at ambient temperature. The reaction mixture was filtered and concentrated to ca. 10 mL to afford compound **1.2**· C_7H_8 as colourless crystalline solid. Single

crystals of **1.2**·C₇H₈ suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.27 g (31.7 %). Mp. 213.7 °C (dec.). Elemental analysis calcd for C₄₆H₅₈Cl₂GeN₃PSi: C, 64.58; H, 6.83; N, 4.91. Found: C, 63.54; H, 6.55; N, 5.11. ¹H NMR (399.5 MHz, C₆D₆, 24.9 °C): δ 0.23 (d, ²J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 1.24 (s, 18H, *t*Bu), 1.29 (d, ²J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 3.52 (br, 2H, CH(CH₃)₂), 6.83 – 7.01 (m, 8H, Ph), 7.03 – 7.12 (m, 4H, Ph), 7.29 (d, 1H, ³J_{HH} = 7.7 Hz, Ph), 7.50 (m, 4H, Ph), 8.54 (d, 1H, ³J_{HH} = 7.7 Hz, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 23.92, 24.05 (CH(CH₃)₂), 28.41 (CH(CH₃)₂), 31.95, 55.62 (*t*Bu), 125.11, 126.60, 127.24, 128.38, 128.45, 129.91, 130.30, 130.59, 133.70, 135.34 (d, ²J_{C-P} = 21.9 Hz), 104.59, 147.33. ³¹P{¹H} NMR (160.2 MHz, C₆D₆, 24.9 °C): δ 44.90. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 24.9 °C): δ -12.85 (d, ²J_{SiP} = 34.7 Hz)

Synthesis of [Ge(Cl){N(Ar)PPh₂}(Ph₂P)Ge:]₂ (1.3**·C₇H₈).** The mother liquor from the synthesis of **1.2**·C₇H₈ was decanted into another flask and concentrated to ca. 5mL to afford **1.3**·C₇H₈ as orange crystalline solid. Single crystals of **1.3**·C₇H₈ suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution Yield: 0.07 g (4.9 %). Mp. 183.5 °C (dec.). Elemental analysis calcd for C₇₂H₇₂Cl₂Ge₄N₂P₄: C, 59.53; H, 5.13; N, 1.93. Found: C, 59.37; H, 5.02; N, 1.87. ³¹P{¹H} CP-MAS NMR: δ -14.03, 103.63

Synthesis of [L(PPh₂)Si=NAr] (1.6**).** C₆D₆ (0.4 mL) was added to **1.1** (31 mg) in an NMR tube. The resulting solution was heated to 80 °C for 16 hours and monitored periodically by ³¹P{¹H} NMR. All volatiles were removed and hexane (1.0 mL) was charged to the NMR tube. It was then filtered and concentrated to give **1.6** as yellow crystalline solid. Single crystals of **1.6** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the hexane solution. Yield: 29 mg (93.5 %). Mp. 212.9 °C (dec.). Elemental analysis calcd

for C₃₉H₅₀N₃PSi: C, 75.56; H, 8.13; N, 6.78. Found: C, 76.24; H, 8.01; N, 6.64. ¹H NMR (399.5 MHz, C₆D₆, 23.3 °C): δ 1.01 (s, 18H, *t*Bu), 1.45 (d, ³J_{HH} = 7.30 Hz, 12H, CH(CH₃)₂), 4.23 (sept, ³J_{HH} = 7.30 Hz, 2H, CH(CH₃)₂), 6.84 – 6.90 (m, 4H, Ph), 7.01 – 7.11 (m, 8H, Ph), 7.37 (d, ³J_{HH} = 7.75 Hz, 2H, Ph), 7.96 – 8.00 (m, 4H, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 28.40, 23.30 (CH(CH₃)₂), 31.25, 41.52 (*t*Bu), 123.33, 128.11, 128.71, 131.08, 131.29, 148.22, 150.67 (Ph). ³¹P{¹H} NMR (160.2 MHz, C₆D₆, 24.9 °C): δ -53.56. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 24.9 °C): -77.70 (d, ¹J_{SiP} = 10.6 Hz)

Synthesis of [{Ph₂PN(Ar)GeCl}{Ph₂PGeCl}] (1.7). Toluene (20mL) was added to a mixture of **1.3**·C₇H₈ (0.58 g, 0.40 mmol) and B(C₆F₅)₃ (0.41 g, 0.80 mmol) at room temperature and stirred for 16 hours. The reaction mixture was filtered to remove insoluble solids, and the solution concentrated to obtain **1.7** as colourless crystalline solid. Single crystals of **1.7** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.03g (9.7 %) Mp. 192.5 °C. Elemental analysis calcd for C₃₆H₃₇Cl₂Ge₂NP₂: C, 56.76; H, 4.90; N, 1.84. Found: C, 55.87; H, 4.78; N, 1.76. ¹H NMR (399.5 MHz, C₆D₆, 24.9 °C): δ 0.51 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 0.63 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 1.43 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 1.47 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 4.10 (sept, ³J_{HH} = 6.8 Hz, 1H, CH(CH₃)₂), 4.18 (sept, ³J_{HH} = 6.8 Hz, 1H, CH(CH₃)₂), 6.78 – 6.93 (m, 7H, Ph), 6.98 – 7.13 (m, 8H, Ph), 7.44 – 7.50 (m, 3H, Ph), 7.63 – 7.68 (m, 2H, Ph), 7.73 – 7.81 (m, 3H, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 23.31, 28.45 (CH(CH₃)₂), 118.06, 124.12, 126.28, 133.67, 135.09, 136.05, 142.38 (Ph). ³¹P{¹H} NMR (160.2 MHz, C₆D₆, 24.9 °C): δ -19.31 (d, ²J_{PP} = 34.7 Hz), 88.64 (d, ²J_{PP} = 34.7 Hz).

Synthesis of [L{(Ar)(Ph₂P)N}Si:→SnCl₂] (1.8·C₇H₈). Toluene (20 mL) was added to a mixture of [L{(Ar)(Ph₂P)N}Si:] (**1.1**) (0.62 g, 1.00 mmol) and SnCl₂ (0.19 g, 1.00 mmol) and

stirred for 16 hours at ambient temperature. The resulting mixture was filtered and concentrated to ca. 10 mL to give compound **1.8**·C₇H₈ as colourless crystalline solid. Single crystals of **1.8**·C₇H₈ suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.12g (14.8 %). Mp. 204.9 °C (dec.). Elemental analysis calcd for C₃₉H₅₀Cl₂N₃PSiSn: C, 57.87; H, 6.23; N, 5.19. Found: C, 58.26; H, 6.12; N, 5.28. ¹H NMR (399.5 MHz, C₆D₆, 23.3 °C): δ 0.22 (d, ³J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 0.30 (s, 18H, *t*Bu), 1.27 (d, ³J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 3.48 (br, 2H, CH(CH₃)₂), 6.82 – 6.86 (m, 1H, Ph), 6.90 – 6.98 (m, 2H, Ph), 7.00 – 7.10 (m, 9H, Ph), 7.26–7.28 (m, 1H, Ph), 7.47 – 7.49 (m, 4H, Ph), 8.66 – 8.69 (m, 1H, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 28.41, 30.62 (CH(CH₃)₂), 32.09, 55.41 (*t*Bu), 125.15, 126.61, 127.23, 128.28, 129.47, 129.97, 130.57, 134.10, 134.80, 135.07, 140.64, 147.32, 173.85 (Ph). ³¹P{¹H} NMR (160.2 MHz, C₆D₆, 24.9 °C): δ 45.04. ¹¹⁹Sn{¹H} NMR (147.6 MHz, C₆D₆, 24.9 °C): δ 58.14 (d, ³J_{SnP} = 358.4 Hz)

Synthesis of {[Ar](PPh₂)NSnCl]₂-SnCl₂} (1.9) Toluene (20mL) was added to a mixture of **1.8**·C₇H₈ (0.81 g, 1.00 mmol) and GeCl₂.dioxane (0.23 g, 1.00 mmol) at ambient temperature and stirred for 16 hours. The resulting pale red solution was filtered and concentrated to give **1.9** as colourless crystalline solid. Yield: 0.11g (27.1%, based on the amount of Sn atoms in **1.8**·C₇H₈). Mp. 182.4 °C (dec.). Elemental analysis calcd for C₄₈H₅₄Cl₄N₂P₂Sn₃: C, 47.30; H, 4.47; N, 2.30. Found: C, 46.45; H, 4.29; N, 2.15. ¹H NMR (399.5 MHz, C₆D₆, 24.9 °C): δ 0.41 (br, 12H, CH(CH₃)₂), 1.17 (br, 12H, CH(CH₃)₂), 3.60 (sept, ³J_{HH} = 6.83 Hz, 4H, CH(CH₃)₂), 6.93 – 7.09 (m, 16H, Ph), 7.47 – 7.49 (m, 2H, Ph), 7.82 (br, 8H, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 116.34, 118.06, 122.48, 130.49, 133.67, 135.01, 146.72 (Ph). ³¹P{¹H} NMR (160.2 MHz, C₆D₆, 24.9 °C): δ 67.19. ¹¹⁹Sn{¹H} NMR (147.6 MHz, C₆D₆, 24.9 °C): δ -110.03 (d, ²J_{SnP} = 156.1 Hz, Ph₂PN(Ar)SnCl), -102.00 (t, ¹J_{SnP} = 69.4 Hz, Ph₂P→SnCl₂←PPh₂)

1.5 References

1. Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, Wiley, Chichester, U.K., **2010**.
2. Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 21, 895-896
3. For recent reviews see: (a) Mizuhata, Y.; Sasamori, T.; Tokito, N. *Chem. Rev.* **2009**, 109, 3479; (b) Lappert, M. F.; Power, P. P.; Protchenko, A.; Seeber, A.; *Metal Amide Chemistry*, Wiley, Chichester, UK, **2009**; (c) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, 33, 5165–5179.
4. For a review see: Izod, K. *Coord. Chem. Rev.* **2012**, 256, 2972–2997 and references therein
5. Rivard, E.; Sutton, A. D.; Fetting, J. C.; Power, P. P. *Inorg. Chim. Acta.* **2007**, 360, 1278 - 1286.
6. Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *Polyhedron.* **1988**, 7, 1909 – 1910
7. (a) Goel, S. C.; Chiang, M. Y.; Rauscher, D. J.; W.E. Buhro, *J. Am. Chem. Soc.* **1993**, 115, 160-169 (b) Westerhausen, M.; Enzelberger, M. M.; Schwarz, W. *J. Organomet. Chem.* **1995**, 491, 83-90
8. Izod, K.; Stewart, J.; Clark, E. R.; Clegg, W.; Harrington, R. W. *Inorg. Chem.* **2010**, 49, 4698 -4707
9. a) Izod, K.; Evans, P.; Waddell, P. G.; Probert, M. R. *Inorg. Chem.* **2016**, 55, 10510-10522; b) Izod, K.; Rayner, D. G.; El-Hamrini, S. M.; Harrington, R. W.; Baisch, U. *Angew. Chem., Int. Ed.* **2014**, 53, 3636-3640
10. Driess, M.; Janoschek, R.; Pritzkow, H.; Rell, S.; Winkler, U. *Angew. Chem., Int. Ed.* **1995**, 34, 1614–1616
11. Izod, K.; Evans, P.; Waddell, P. G. *Angew. Chem., Int. Ed.* **2017**, 56, 5593-5597.

12. Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2011**, 133, 18622-18625
13. Power, P. P. *Organometallics*, **2007**, 26, 4362 – 4372
14. Khan, S.; Pal, S.; Kathewad, N.; Purushothaman, I.; De, S.; Parameswaran, P. *Chem. Commun.* **2016**, 52, 3880 - 3882
15. a) Wang, W.; Inoue, S.; Yao, S.; Driess, S. *Chem. Commun.* **2009**, 2661 - 2663 b) Shan, Y.-L.; Leong, B.-X.; Xi, H.-W. Ganguly, R.; Li, Y.; Lim, K. H.; So, C.-W. *Dalton. Trans.* **2017**, 46, 3642-3648
16. Sen, S. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2010**, 49, 5786 - 5788
17. Pal, S.; Dasgupta, R.; Khan, S. *Organometallics*. **2016**, 35, 3635-3640
18. Shan, Y.-L.; Leong, B.-X. Li, Y. Ganguly, R.; So, C.-W. *Inorg. Chem.* **2017**, 56, 1609 – 1615
19. So, C.-W. ; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, 45, 3948-3950; b) Khan, S.; Sen, S. S.; Kratzert, D.; Tavcar, G.; Roesky H. W.; Stalke, D. *Chem. - Eur. J.*, **2011**, 17, 4283-4290.
20. Shan, Y.-L.; Leong, B.-X.; Xi, H.-W. Ganguly, R.; Li, Y.; Lim, K. H.; So, C.-W. *Dalton. Trans.* **2017**, 46, 3642-3648
21. Guo, J.; Lau, K.-C.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Chem. Commun.* **2010**, 46, 1929-1931
22. Davis, M. F.; Clarke, M.; Levason, W.; Reid, G.; Webster, M. *Eur. J. Inorg. Chem.* **2006**, 2773-2782.
23. Sheldrick, G. M. SHELXL-97; Universitat Göttingen: Göttingen, Germany, 1997.

Chapter 2.

Metallogermylene: Reactivity of a Base-Stabilized Germanium(I) Dimer toward Group 9 Metal(I) Chloride and Various Transition Metal Carbonyl[‡]

2.1 Introduction

Germynes of composition $[R_2Ge:]$ (R = supporting ligand) have attracted much attention owing to their unique carbene like electronic properties.¹ Usually, they are highly reactive and tend to easily undergo oligomerization. However, they can be stabilized by incorporating steric hindered substituents and/or by coordinating with Lewis base ligands. The resulting germynes have been shown to have a very rich chemistry² and that includes transition-metal-like reactivity to activate small molecules at ambient temperature.³

Scheme 2-1: Typical synthetic route of metallogermynes (**1A**)

Another spectacular type of germynes is metallo-substituted germylene complexes, which comprise a direct $M-Ge^{II}$ σ bond. However, they have received less attention due to limited synthetic strategies. Usually, they are synthesized by the metathesis reaction of anionic transition metalate complexes with halogermynes $[RGeX]$ (X = halide). For example, the

[‡] Portions of this chapter are adapted with permission from Ismail, M. L. B.; Liu, F.-Q.; Yim, W.-L.; Ganguly, R.; Li, Y.; So, C. W. *Inorg. Chem.* **2017**, 56, 5402–5410. Copyright (2017) American Chemical Society

(supermesityl)ferriogermylene $[\text{Mes}^*\text{GeFe}(\text{CO})_2\text{Cp}]$ ($\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$) (**2A**) was prepared by reacting the supermesityl chlorogermylene with $[\text{K}\{\text{Fe}(\text{CO})_2\text{Cp}\}]$.⁴

Scheme 2-2: Examples of other known metallogermylene

In addition, the transition metallogermylenes $[\text{ArMesGeM}(\eta^5\text{-Cp})(\text{CO})_3]$ ($\text{M} = \text{Cr, Mo, W}$; $\text{Ar}^{\text{Mes}} = \text{C}_6\text{H}_3\text{-2,6-Mes}_2$; $\text{Mes} = \text{C}_6\text{H}_2\text{-2,4,6-Me}_3$) (**2B**) were synthesized by the reactions of $\text{Na}[\text{M}(\eta^5\text{-Cp})(\text{CO})_3]$ ($\text{M} = \text{Cr, Mo, W}$) with the m-terphenyl chlorogermylene $[\text{ArMesGeCl}]$.⁵ Other base-stabilized transition metallogermylenes were synthesized in similar ways (**2C-2F**).⁶⁻¹⁰ In addition, their electronic properties were elucidated by DFT calculations.¹¹

Scheme 2-3: Reversible activation of Si-H and B-H bond on a cationic metallogermylene

Moreover, recent studies show that the cationic metallogermylene $[\text{Cp}^*(\text{CO})_3\text{WGe}(\text{I}_{\text{Ar}})](\text{BAr}^{\text{F}}_4)$ ($\text{I}_{\text{Ar}} = \text{:C}\{\text{N}(\text{Ar})\text{CH}\}_2$; $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$; $\text{Cp}^* = \text{C}_5\text{Me}_5$) (**2G**) was found to exhibit transition-metal-like reactivity, which reversibly activated the Si-H bond of ethyldimethylsilane and the B-H bond of pinacolborane at ambient temperature.¹² In this context, new strategies for synthesizing metallogermynes should be explored. Our group showed that the amidinato silicon(I) dimer $[\{\text{PhC}(\text{NtBu})_2\}\text{Si:}]_2$ reacted with $[\text{Rh}(\text{cod})\text{Cl}]_2$ to give the base-stabilized rhodosilylene dimer $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}\mu\text{-}\{\text{Rh}(\mu\text{Cl})_2\text{Rh}(\text{cod})\}]_2$ comprising $\text{Si}^{\text{II}}\text{-Rh}^{\text{II}}$ bonds.¹³ It is anticipated that such tactics can be applied in the synthesis of transition metallogermynes. In this chapter, we outline the reactivity of a base-stabilized germanium(I) dimer toward group 9 metal(I) chloride $[\text{M}(\text{cod})\text{Cl}]_2$ ($\text{M} = \text{Ir, Rh}$) and various transition metal carbonyl complexes $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{Co}_2(\text{CO})_8]$ and $[\text{Fe}_2(\text{CO})_9]$.

2.2 Results and Discussion

Scheme 2-4: Synthesis of **2.2** – **2.5**

The reaction of the 2-imino-5,6-methylenedioxyphenylgermanium(I) dimer $[LGe:]_2$ (**2.1**, $L = 2\text{-imino-5,6-methylenedioxyphenyl}$)¹⁴ with 1.5 molar equivalents of $[RhCl(cod)]_2$ in toluene at ambient temperature afforded a mixture of the rhodogermylene-chlororhodium(I) complex $[LGe\mu\text{-}\{Rh(cod)\}_2Cl]$ (**2.2**, Scheme 2-4) and chlorogermylene-chlororhodium(I) complex $[L(Cl)GeRh(cod)Cl]$ (**2.3**). The reaction mixture was filtered and then further concentrated to afford **2.2** as a highly air- and moisture-sensitive dark purple crystalline solid (Yield: 40.8%). It comprises a rhodogermylene $[LGeRh(cod)]$ moiety, which has a $Ge^{II}\text{-}Rh^I$ bond, coordinating with a $[Rh(cod)Cl]$ fragment (see below). The mother liquor is filtered and then further concentrated to afford a mixture of **2.2** and orange crystals of **2.3**. An attempt to isolate pure compound **2.3** by recrystallization failed. However, compound **2.3** can be synthesized by another way. The reaction of the chlorogermylene $[LGeCl]$ (**2.6**) with 0.5 molar equivalents of $[RhCl(cod)]_2$ in toluene gave compound **2.3** in good yield (85.7%, Scheme 2-5).

Scheme 2-5: Synthesis of **2.3** and **2.5** from compound **2.6**

A similar reaction of **2.1** with 1.5 molar equivalents of $[\text{IrCl}(\text{cod})]_2$ gave a mixture of the iridogermylene-chloroiridium(I) complex $[\text{LGe}\mu\text{-}\{\text{Ir}(\text{cod})\}_2\text{Cl}]$ (**2.4**, Scheme 2-4 and chlorogermylene-chloroiridium(I) complex $[\text{L}(\text{Cl})\text{GeIr}(\text{cod})\text{Cl}]$ (**2.5**), which were isolated as black (Yield: 38.7%) and orange crystals by recrystallization, respectively. Compound **2.5** can also be synthesized by the reaction of $[\text{LGeCl}]$ (**2.6**) with 0.5 molar equivalents of $[\text{IrCl}(\text{cod})]_2$ in toluene (Scheme 2-5).

Compounds **2.2** and **2.4** were characterized by NMR spectroscopy. Their ^1H NMR spectra show one set of resonances due to the cod moieties and ligand backbone, in which two doublets (**2.2**: δ 1.00, 1.91 ppm; **2.4**: δ 0.96, 1.76 ppm) and a septet (**2.2**: δ 3.27 ppm; **2.4**: δ 3.09 ppm) correspond to the *i*Pr substituents. The spectra also show one singlet (**2.2**: δ 5.35 ppm; **2.4**: δ 5.36 ppm) being attributable to the OCH_2O protons.

Figure 2-1. Molecular structure of **2.2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-Rh1 2.3993(8), Rh1-Cl1 2.4304(19), Ge1-C1 1.948(8), C1-C7 1.414(13), C7-C8 1.447(13), N1-C8 1.315(11), Ge1-N1 1.972(8); Rh1-Ge1-Rh1A 79.84(4), Rh1-Cl1-Rh1A 78.62(7), N1-Ge1-C1 83.0(4), Ge1-C1-C7 112.3(7), C1-C7-C8 114.4(8), C7-C8-N1 115.5(8), C8-N1-Ge1 114.8(6).

Compounds **2.2** and **2.4** were characterized by X-ray crystallography. Each molecular structure (**2.2**: Figure 2-1, **2.4**: Figure 2-2) shows a puckered GeM_2Cl ring. The germanium atom adopts a tetrahedral geometry being coordinated to the bidentate 2-imino-5,6-methylenedioxyphenyl ligand and the metal (**2.2**: Rh; **2.4**: Ir) centres. The latter also coordinate to a bridging Cl atom and cod molecules.

Figure 2-2: X-ray crystal structure of **2.4** (30% probability level). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-Ir1 2.4270(5), Ir-Cl1 2.4228(11), Ge1-C1 1.926(6), C1-C2 1.419(8), C2-C8 1.456(8), N1-C8 1.307(7), Ge1-N1 1.970(5); Ir1-Ge1-Ir1A 78.066(19), Ge1-Ir1-Cl1 81.48(3), Ir1-Cl1-Ir1A 78.23(4), C1-Ge1-N1 83.7(2), Ge1-C1-C2 111.9(4), C1-C2-C8 114.7(5), C2-C8-N1 114.8(5), C8-N1-Ge1 114.9(4)

The N1-C8 (**2.2**: 1.315(11); **2.4**: 1.307(7) Å), Ge1-N1 (**2.2**: 1.972(8); **2.4**: 1.970(5) Å) and Ge1-C1 (**2.2**: 1.948(8); **2.4**: 1.926(6) Å) bonds are comparable with those in **2.1** (N-C: 1.310(5); Ge-N: 2.022(3); Ge-C: 1.968(4) Å). The Ge-Rh bond lengths (2.3993(8) Å) in **2.2** are slightly shorter than the Ge^{II}-Rh^I donor-acceptor single bond length in the base-stabilized germylene-rhodium(I) complexes (**2H**: 2.445(1) - 2.4499(8); **2I**: 2.4153(2) Å; Scheme 3).^{15, 16a} Moreover, the Ge-Ir bond lengths (2.4270(5) Å) in **2.4** are intermediate values between the Ge^{II}-Ir^{III} donor-acceptor single bond length in the base-stabilized germylene-iridium(III) complex **2J** (2.4203(3) Å) and the Ge^{IV}-Ir^I bond length in the germyliridium complex **2K** (2.4716(4) Å).¹⁶ Although Ge^{II}-Ir^I adducts are known,^{16a, 17} no X-ray crystallographic data, along with the Ge^{II}-Ir^I bond lengths, were reported as yet.

Scheme 2-6: The base-stabilized germylene-rhodium(I) **2H** – **2I**, base-stabilized germylene-iridium(III) **2J** and germyliridium(I) **2K** complexes.

To understand the bonding situation in compounds **2.2** and **2.4**, compound **2.2** was investigated by DFT calculations.¹⁸ The HOMO-5 (Figure 2-3) illustrates the lone pair orbital on the Ge1 atom donating to the d_{xy} orbitals on the Rh1/1A atoms. The HOMO shows the Ge-Rh σ orbitals. The large difference in NPA charges of the Rh and Ge atoms (Rh: -0.27 e, Ge: + 1.04 e), along with the small Wiberg bond indices of Ge-Rh bonds (WBI: 0.628), imply the Ge-Rh bonds being single bonds with significant ionic nature. Similar bonding situation can be found in other metallogermylenes.¹¹ There is no indication of a significant Rh-Rh bonding contribution, as all Rh-Rh bonding orbitals across the rhomboid Rh_2GeCl core are fully offset by their antibonding counterpart.

On the basis of experimental and theoretical results, compounds **2.2** and **2.4** comprise a Group 9 metallogermylene moiety being coordinated to a chlorometal(I) moiety. Their Lewis structures are illustrated in Figure 2-3.

Figure 2-3: (a) The HOMO and (b) HOMO-5 of **2** and (c) the Lewis structures of **2.2** and **2.4**

Compounds **2.3** and **2.5** were characterized by NMR spectroscopy. Their ^1H NMR spectra show one set of resonances due to the cod moieties and ligand backbone, in which four doublets (**2.3**: δ 0.86, 0.94, 1.36, 1.90 ppm; **2.5**: δ 0.87, 0.89, 1.37, 1.76 ppm) and two septets (**2.3**: δ 3.10–3.90 ppm; **2.5**: 3.10, 3.66 ppm) correspond to the *i*Pr substituents. In addition, two doublets (**2.3**: δ 5.11, 5.16 ppm; **2.5**: δ 5.08, 5.13 ppm) are attributable to the OCH_2O protons. Although compounds **2.3** and **2.5** were isolated as orange crystalline solids, crystals of **3** were too small, which cannot be analysed by X-ray crystallography. As a result, only X-ray structural data of compound **2.5** is discussed herein (Figure 2-4). The Ge centre in **2.5** adopts a tetrahedral geometry, which coordinates with the bidentate ligand and Cl and Ir atoms. The Ge1–Ir1 bond length is 2.4019(13) Å, which is slightly shorter than the Ge^{II} – Ir^{III} donor-acceptor bond length in **C**. It is also anticipated that compound **2.3** could exhibit a similar structure.

Figure 2-4: X-ray crystal structure of **2.5** with thermal ellipsoids at the 30% probability level. Ge1-Ir1 2.4019(13), Ir1-Cl2 2.358(3), Ge1-N1 2.022(9), Ge1-C1 1.943(11), C1-C2 1.407(15), C2-C8 1.467(16), C8-N1 1.311(14); N1-Ge1-C1 82.9(4), N1-Ge1-Ir1 117.6(3), C1-Ge1-Ir 134.5(3).

Scheme 2-7: Proposed mechanism for the formation of **2.2 – 2.5**

The reactions of the chlorogermylene **2.6** with $[\text{MCl}(\text{cod})]_2$ provide insights into the mechanism for the formation of **2.2** and **2.4**. It is anticipated that in the presence of $[\text{MCl}(\text{cod})]_2$, compound **2.1** underwent a disproportionation reaction to form the “ LGe^+ ” and “ LGe^- ” intermediates. Each of the “ LGe^+ ” and “ LGe^- ” intermediate reacts with $[\text{MCl}(\text{cod})]_2$ ($\text{M} = \text{Rh}$, Ir) to form the “ $\text{LGeM}(\text{cod})$ ” and “ LGeCl ” intermediates, respectively. Subsequently, they react with another molecule of $[\text{MCl}(\text{cod})]_2$ to form $[\text{LGe}\mu\text{-}\{\text{M}(\text{cod})\}_2\text{Cl}]$ ($\text{M} = \text{Rh}$ (**2.2**), Ir (**2.4**)) and $[\text{L}(\text{Cl})\text{GeM}(\text{cod})\text{Cl}]$ ($\text{M} = \text{Rh}$ (**2.3**), Ir (**2.5**)), respectively. Such a mechanism is different from the reaction of the amidinato silicon(I) dimer $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Si:}]_2$ with two equivalents of $[\text{Rh}(\text{cod})\text{Cl}]_2$, which proceeded through the homolytic cleavage of the $\text{Si}^{\text{I}}\text{-Si}^{\text{I}}$ bond and the displacement of two cod molecules, to give the base-stabilized rhodosilylene dimer $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Si}\mu\text{-}\{\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{cod})\}]_2$ comprising $\text{Si}^{\text{II}}\text{-Rh}^{\text{II}}$ bonds.¹³ Attempts to isolate the monomeric metallogermylene intermediate “ $\text{LGeM}(\text{cod})$ ” by reducing the molar equivalent of $[\text{MCl}(\text{cod})]_2$ and controlling the reaction temperature only yielded the same compound **2.2** and **2.4** which was confirmed by X-ray crystallography. This indicates that the intermediate “ $\text{LGeM}(\text{cod})$ ” is very reactive and once formed, it continues to react to form **2.2** and **2.4** respectively.

Scheme 2-8: Synthesis of **2.7** and **2.8**

Scheme 2-9: Mechanism for the formation of **2.7**

The mechanism is verified by the reaction of **2.1** with 0.5 molar equivalents of $\text{Mn}_2(\text{CO})_{10}$ in refluxing toluene to afford a mixture of the base-stabilized manganogermylene dimer $[(\text{LGe})\mu\text{-}\{\text{Mn}(\text{CO})_4\}]_2$ (**2.7**, Scheme 2-8), the free ligand [LH] (**2.8**) and germanium. The presence of **2.8** suggests that compound **2.1** underwent a disproportionation with $\text{Mn}_2(\text{CO})_{10}$. The reaction mixture was filtered and further concentrated to afford **2.7** as a highly air- and moisture-sensitive dark-red crystalline solid (Yield: 46.3 %). Compound **2.7** was characterized by NMR spectroscopy and X-ray crystallography. Its ^1H NMR spectrum displays resonances attributable to the ligand backbone in which two doublets (δ 0.87 and 1.53 ppm) and a septet (δ 3.29 ppm) correspond to the *i*Pr substituents and a singlet (δ 5.54 ppm) attributes to the OCH_2O protons. The molecular structure of **2.7** (Figure 2-5) shows that the Mn_2Ge_2 ring is planar and rhombic. Similar Ge_2M_2 rings can be found in the reaction of the germyne

$[\text{Ar}^{\text{Pri4}}\text{Ge}]_2$ ($\text{Ar}^{\text{Pri4}} = 2,6\text{-Ar}_2\text{C}_6\text{H}_3$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_5$) with $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) under UV irradiation to form $[\text{Ar}^{\text{Pri4}}\text{GeM}(\text{CO})_4]_2$, but the reaction mechanisms are unknown as yet.¹⁹

Figure 2-5: Molecular structure of **2.7** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-Mn1 2.4991(4), Ge1-Mn1A 2.4936(4), Ge1-N1 2.116(2), Ge1-C5 1.983(2), N1-C12 1.309(3), C11-C12 1.461(3), C5-C11 1.417(3); Mn1-Ge-Mn1A 102.373(12), Ge1-Mn1-Ge1A 77.626(12), N1-Ge1-C5 81.27(8), Ge1-C5-C11 113.59(16), C5-C11-C12 115.5(2), C11-C12-N1 117.2(2), C12-N1-Ge1 112.44(15).

The Ge1 and Ge1A atoms, which adopt a distorted tetrahedral geometry, are coordinated with the bidentate 2-imino-5,6-methylenedioxyphenyl ligand and two manganese (Mn1 and Mn1A) atoms. The latter are also bonded to four CO moieties to adopt an octahedral geometry. The N1-C12 (1.309(3) Å), Ge1-N1 (2.116(2) Å) and Ge1-C5 (1.983(2) Å) bonds are comparable with those in **2.1** (N-C: 1.310(5); Ge-N: 2.022(3); Ge-C: 1.968(4) Å). The Ge1-Mn1 (2.4991(4) Å) and Ge1-Mn1A (2.4936(4) Å) bond lengths are almost identical. They are comparable with the bridging (2.480(2) Å) and terminal Mn-Ge bond lengths (2.502(2) Å) in

the manganogermanium(IV) complex $[\text{Mn}_2(\text{CO})_8\{\mu\text{-Ge}(\text{Br})\text{Mn}(\text{CO})_5\}]_2$ (**2L**, Scheme 2-10).²⁰ They are also comparable with those in the germanium cluster containing $\text{Mn}(\text{CO})_5$ ligands $[\text{Ge}_4\text{Br}_4\{\text{Mn}(\text{CO})_5\}_4]$ (2.4795(16), 2.4811(16) Å).²¹ However, they are longer than the $\text{Ge}^{\text{II}}\text{-Mn}^{\text{I}}$ donor acceptor interaction in the terminal germylene-manganese adducts, such as $[\{\text{HC}(\text{CMeNAr})_2\text{Ge}(\text{OH})\{\text{Mn}(\text{Cp})(\text{CO})_2\}\}]$ (**2M**, 2.345(1) Å)²² and $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CGe}\{\text{Mn}(\text{CO})_2\text{Cp}\}]$ (**2N**, 2.236(1) Å).²³ The $\text{Mn1}\cdots\text{Mn1A}$ distance (3.890 Å) is significantly longer than that in the germylenes-bridged dimanganese complex $[\{\text{Me}_2\text{Si}(\text{N}t\text{Bu})_2\text{Ge}\}\mu\text{-}\{\text{Mn}(\text{CO})_4\}]_2$ (**2P**) comprising two bridging germylenes and a Mn-Mn bond (3.024(2) Å).²⁴ This indicates that there is no interaction between two Mn centres in **2.7**.

Scheme 2-10. The manganogermanium(IV) complex **2L**, germylene-manganese adducts **2M** – **2N**, and germylenes-bridged dimanganese complex **2P**

Compound **2.7** was investigated by DFT calculations.¹⁸ The HOMO-9 (Figure 2-6) shows the lone pair orbitals on the Ge1/1A atoms donating to the d_{xz} orbitals on the Mn1/1A

atoms. The HOMO-1 and HOMO demonstrate the Mn-Ge σ orbitals due to the overlapping of the d_{yz} and d_z^2 orbitals on the Mn centres with the p orbitals of the Ge centres, respectively. The large difference in NPA charges of the Mn1/1A and Ge1/1A atoms (Mn: -1.35, -1.34 e, Ge: +1.15 e), along with small Wiberg bond indices of Mn-Ge bonds (WBI: 0.659, 0.669, 0.715, 0.725), imply the Ge-Mn bonds being single bonds with significant ionic nature.

Figure 2-6. (a) The HOMO, (b) HOMO-1, (c) HOMO-9 and (d) Lewis structure of **2.7**

On the basis of experimental and theoretical studies, compound **2.1** undergoes a disproportionation with $\text{Mn}_2(\text{CO})_{10}$ to form **2.8**, germanium and the manganogermylene intermediate “ $\text{LGeM}(\text{CO})_5$ ”. Subsequent elimination of CO and dimerization result in forming compound **2.7**. The mechanism is supported by recent results that the ferriostannylene $[\text{Ar}^{\text{Pri}4}\text{SnFe}(\text{CO})_2\text{Cp}]$ underwent the elimination of CO under UV irradiation to form the Sn_2Fe_2

dimer $[\text{Ar}^{\text{Pri}4}\text{SnFe}(\text{CO})\text{Cp}]_2$.²⁵ Modifying the amount of $\text{Mn}_2(\text{CO})_{10}$ still led to the formation of compound **2.7** which was confirmed by X-ray crystallography.

Scheme 2-11: Synthesis of **2.9**·C₇H₈.

The reaction of the germanium(I) dimer $[\text{L}'\text{Ge}]_2$ (**2.1**, $\text{L}' = 2\text{-imino-5,6-methylenedioxyphenyl}$) with $\text{Co}_2(\text{CO})_8$ in refluxing toluene for 16 hours, which proceeded through the insertion of the $\text{Ge}^{\text{I}}\text{-Ge}^{\text{I}}$ bond in **2.1** with $\text{Co}_2(\text{CO})_8$ and the subsequent displacement of two CO molecules to afford the base-stabilized cobaltogermylene dimer $[(\text{L}'\text{Ge})\mu\text{-}\{\text{Co}(\text{CO})_3\}]_2$ (**2.9**·C₇H₈). The reaction mixture was filtered and further concentrated to afford a highly air- and moisture-sensitive dark red crystalline solid (Yield: 35.2 %). The dark red crystalline solid is diamagnetic, which is consistent with DFT calculation that the singlet state is more stable by 26.7 kcal/mol than the triplet state. However, it was highly unstable in solution, which became paramagnetic with $\mu_{\text{eff}} = 1.82 \mu_{\text{B}}$, indicating one unpaired electron at a cobalt atom. These results suggest that compound **2.9**·C₇H₈ may dissociate to form monomeric form in solution .

Figure 2-7: Molecular structure of **2.9**·C₇H₈ with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are excluded for clarity. Selected bond lengths (Å) and bond angles (°): Ge1–Co1 2.3449(3), Ge1–Co1A 2.3450(3), Ge1–C1 1.9457(18), Ge1–N1 2.0442(15), Ge1–C1 1.9457(18), C1–C6 1.410(3), C6–C7 1.461(3), C7–N1 1.310(2); Co1–Ge1–Co1A 109.884(10), Ge1–Co1–Ge1A 70.116(10), C1–Ge1–N1 82.18(7), C6–C1–Ge1 112.90(13), C7–N1–Ge1 113.04(12), C6–C7–N1 116.02(16)

The molecular structure of **2.9**·C₇H₈ (Figure 2-7) shows that the Co₂Ge₂ ring is planar and rhombic. Similar Ge₂M₂ rings can be found in the base-stabilized manganogermylene dimer [(L'Ge) μ -{Mn(CO)₄}]₂ being isolated by the reaction of **2.1** with Mn₂(CO)₁₀ in refluxing toluene. The Ge1 atom, which adopts a distorted tetrahedral geometry, are coordinated with the bidentate 2-imino-5,6-methylenedioxyphenyl ligand and two cobalt (Co1 and Co1A) atoms. The latter are also bonded to three CO moieties to adopt a trigonal pyramidal geometry. The Ge1–Co1 (2.3450(5) Å) and Ge1–Co1A (2.3687(4) Å) bonds are almost identical. They are longer than the terminal Ge^{II}–Co⁰ and Ge^{II}–Co^I donor-acceptor interaction in the base-stabilized germylene-cobalt complexes such as [L{(Me₃Si)₂N}GeCo(CO)₃]₂ (2.2959(7) Å)²⁶ and [Fc{(L)Ge}]₂CoCp (2.1967(6) and 2.1979(6) Å).²⁷ In contrast, they are comparable with the bridging Ge–Co bonds in the amidinato germylene-cobalt carbonyl complex [Co₂{ μ -

$\kappa^2\text{Ge}, N\text{-Ge}\{(\text{NiPr})_2\text{CPh}\}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-CO})(\text{CO})_5]$ (2.2983(4), 2.3633(4) Å).²⁶ The long Co1...Co1A distance (3.8585(5) Å) indicates that there is no interaction between two Co centres. Modifying the amount of $\text{Co}_2(\text{CO})_8$ still led to the formation of compound **2.9**·C₇H₈ which was confirmed by X-ray crystallography.

Scheme 2-12: Synthesis of compound **2.10**·3C₇H₈.

Having demonstrated the reaction of **2.1** with $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ to generate metallogermylene dimers, we were keen to expand the study to iron carbonyl derivatives. The reaction between **2.1** and 2 equivalents of $\text{Fe}_2(\text{CO})_9$ in toluene at room temperature for 16 hours led to the isolation of $[\text{Fe}(\text{CO})_3]\mu\text{-}\{(\text{LGe})\rightarrow\text{Fe}(\text{CO})_4\}_2$ (**2.10**·3C₇H₈), which can be interpreted as a bis-ferrogermylene coordinated to 2 $\text{Fe}(\text{CO})_4$ fragments. The isolation of **2.10**·3C₇H₈ contrasts with the result reported by Roesky and coworkers, where the reaction between amidinato germanium(I) dimer and 2 equivalents of $\text{Fe}_2(\text{CO})_9$ did not cleave the Ge-Ge bond.²⁸ All volatiles were removed, and the resulting solids were extracted with toluene, filtered and concentrated to afford **2.10**·3C₇H₈ as black crystalline solids (37.9 %). The paramagnetic character of **2.10**·3C₇H₈ leads to weak and broad ¹H NMR signals. The mother liquor was decanted and concentrated to afford a mixture of **2.10**·3C₇H₈, and $[(\text{LGe})\rightarrow\text{Fe}(\text{CO})_4]_2$ (**2.11**·C₇H₈) as a minor product. The presence of **2.11**·C₇H₈ hints at a possible mechanism.

However, our attempts to isolate compound **2.11**·C₇H₈ in a sufficiently pure manner by reacting compound **2.1** with one equivalent of Fe₂(CO)₉ led to a mixture of unidentifiable products. Further attempts to replicate the formation of **2.10**·3C₇H₈ and **2.11**·C₇H₈ by reacting Fe(CO)₅ with **2.1** in refluxing toluene led only to the formation of an iron mirror and unidentified products.

Figure 2-8: Molecular structure of **2.10** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are excluded for clarity. Selected bond lengths (Å) and bond angles (°): Fe1-Ge1 2.3242(7), Fe1-Ge2 2.4248(7), Fe1-Fe2 2.8486(8), Fe2-Ge1 2.3628(7), Fe3-Ge2 2.3710(6), Ge1-N1 2.028(3), C1-Ge1 1.938(4), C1-C7 1.412 (5), C7-C8 1.462(5), C8-N1 1.303(5); Ge1-Fe1-Fe2 53.190(19), Ge1-Fe2-Fe1 51.959(19), Fe1-Ge1-Fe2 74.85(2), Fe1-Ge1-Fe2 74.85(2), Fe3-Ge2-Fe1 127.45(3)

The molecular structure of **2.10**·3C₇H₈ features 2 germanium atoms (Ge1, Ge2) adopting a distorted tetrahedral geometry with different coordination environments. One Ge

atom (Ge1) lies in a planar GeFe₂ three membered ring. The Ge1-Fe1 (2.3242(7) Å) and Ge1-Fe2 (2.3628(7) Å) is comparable to the Ge^I→Fe(CO)₄ dative bond (2.3402(4) Å).²⁸ The Fe2-Fe1 distance (2.8485(8) Å) is slightly longer than the covalent radii for low spin iron (2.64 Å) and slightly shorter than for high spin iron (3.04 Å)²⁹ indicative of some interaction between the two Fe centres. The environment around the Ge2 atom is markedly different. The Fe1-Ge2-Fe3 bond angle (127.45(3) °) is much wider than the Fe1-Ge1-Fe2 bond angle (74.85(2) °). The Ge2-Fe3 bond length (2.3710(6) Å) is comparable to Ge1-Fe1 and Ge1-Fe2 which suggests that it is a dative bond. The Ge2-Fe1 bond length (2.4248(7) Å) is longer than Ge2-Fe3 but is comparable to Ge-Fe σ bond (2.4415(11) Å) in the amidinato ferroggermylene⁸ which suggests that Ge2-Fe2 is a polarized covalent bond.

Figure 2-9: Molecular structure of **2.11**·C₇H₈ with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are excluded for clarity. Selected bond lengths (Å) and bond angles (°): Fe1-Ge1 2.3436(9), Fe2-Ge2 2.3497(9), Ge1-N1 2.060(4), Ge1-Ge2 2.5916(7), C8-N1 1.314(6), C7-C8 1.457(7), C1-Ge1 1.957(5), C1-C7 1.418(7); C7-C1-Ge1 112.0(3), C1-C7-C8 114.8(4), N1-C8-C7 116.6(4), C8-N1-Ge1 112.1(3), C1-Ge1-N1

82.24(18), Fe1-Ge1-Ge2 130.19(3), Fe2-Ge2-Ge1 128.98(3), C1-Ge1-Fe1 119.77(14), N1-Ge1-Fe1 115.15(11), C1-Ge1-Ge2 91.25(14), N1-Ge1-Ge2 106.30(11)

The molecular structure of **2.11**·C₇H₈ features 2 germanium atoms with distorted tetrahedral geometry. Each Fe atom adopts a trigonal bipyramidal geometry. The Ge1-Ge2 bond length (2.5916(7) Å) is slightly longer than in **2.1** (2.5685(5) Å) and in {PhC(NtBu₂)Ge→Fe(CO)₄}₂ (2.5512(5) Å).²⁸ The Fe1-Ge1 (2.3436(9) Å) and Fe2-Ge2 (2.3497(9) Å) bond lengths are comparable to the Ge^I→Fe(CO)₄ dative bond (2.3402(4) Å)²⁸ which indicates that they are coordinate covalent bonds.

Scheme 2-13: Proposed mechanism for the formation of **2.10**·3C₇H₈ and **2.11**·C₇H₈

On the basis of experimental results, the mechanism for the formation of **2.10**·3C₇H₈ and **2.11**·C₇H₈ is proposed. In an analogous reaction to the one proposed by Roesky and coworkers²⁸, **2.1** reacts with 2 equivalents of Fe₂(CO)₉ to form **2.11**·C₇H₈ transiently and Fe(CO)₅. **2.11**·C₇H₈ reacts with Fe(CO)₅ in solution to form compound **2.10**·3C₇H₈ with the elimination of 2 equivalents of CO gas.

2.3 Conclusion

The Group 9 metallogermylene-chlorometal(I) complexes $[\text{LGe}\mu\text{-}\{\text{M}(\text{cod})\}_2\text{Cl}]$ ($\text{M} = \text{Rh}$ (**2.2**), Ir (**2.4**)), dimeric manganogermylene $[(\text{LGe})\mu\text{-}\{\text{Mn}(\text{CO})_4\}]_2$ (**2.7**), dimeric cobaltogermylene $[(\text{LGe})\mu\text{-}\{\text{Co}(\text{CO})_3\}]_2$ (**2.9**· C_7H_8) were afforded by the reaction of the 2-imino-5,6-methylenedioxyphenylgermanium(I) dimer **2.1** with $[\text{MCl}(\text{cod})]_2$ ($\text{M} = \text{Rh}, \text{Ir}$), $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$, respectively. Experimental and theoretical studies conclusively show that **2.1** can undergo disproportionation reaction with suitable substrates to form transition metallogermylene moieties. Additionally, the reaction between **2.1** and 2 equivalents of $\text{Fe}_2(\text{CO})_9$ with the concomitant elimination of $\text{Fe}(\text{CO})_5$ led to the formation of a bis-ferrogermylene coordinated to 2 $\text{Fe}(\text{CO})_4$ fragments $[\text{Fe}(\text{CO})_3]\mu\text{-}\{(\text{LGe})\rightarrow\text{Fe}(\text{CO})_4\}_2$ (**2.10**· $3\text{C}_7\text{H}_8$). It is believed that the reaction proceeds first through the coordination of **2.1** to 2 $\text{Fe}(\text{CO})_4$ fragments followed by the cleavage of the $\text{Ge}(\text{I})\text{-Ge}(\text{I})$ bond by the generated $\text{Fe}(\text{CO})_5$ by-product. This hypothesis is corroborated by the isolation of minor product $\{(\text{LGe})\rightarrow\text{Fe}(\text{CO})_4\}_2$ (**2.11**· C_7H_8).

2.4 Experimental Section

General Procedure. All starting materials were obtained commercially and used as received. All manipulations involving air sensitive compounds were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were purified by the MBRAUN MB SPS-5 solvent purification system. $[\text{RhCl}(\text{cod})]_2$, $[\text{IrCl}(\text{cod})]_2$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ were purchased from Sigma Aldrich and used as received. Compound **2.1** was prepared as described in the literature.¹⁴ ^1H and ^{13}C NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are referenced to SiMe_4 for ^1H and ^{13}C NMR. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2.2**, **2.4**, **2.5**, **2.7**, **2.9**· C_7H_8 , **2.10**· $3\text{C}_7\text{H}_8$ and **2.11**· C_7H_8 were collected using a Bruker APEX II diffractometer using graphite monochromated Mo- $\text{K}\alpha$ radiation (0.71073 Å). 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 F^2 .³⁰ 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.

Synthesis of $[(\text{LGe})\mu\text{-}\{\text{Rh}(\text{cod})\}_2\text{Cl}]$ (2.2**).** A solution of $[\text{RhCl}(\text{cod})]_2$ (0.38 g, 0.75 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **2.1** (0.39 g, 0.49 mmol) in Toluene

(12 mL) at room temperature. The reaction mixture was stirred for 16 h and then filtered. The filtrate was concentrated to afford compound **2.2** as dark purple crystalline solid. Single crystals of **2.2** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.17 g (40.8%). Mp: 194 °C. Elemental analysis calcd for $C_{37}H_{48}ClGeNO_2Rh_2$: C, 52.12; H, 5.67; N, 1.64. Found: C, 51.90; H, 5.51; N, 1.61. 1H NMR (399.5 MHz, C_6D_6 , 23.9 °C): δ 1.00 (d, $^3J_{HH} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.64 (s, 3H, CH_3), 1.69-1.74 (m, 3H, CH_2 of cod), 1.91 (d, $^3J_{HH} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.98-2.05 (m, 4H, CH_2 of cod), 2.14-2.19 (m, 3H, CH_2 of cod), 2.36-2.57 (m, 6H, CH_2 of cod), 3.27 (sept, $^3J_{HH} = 6.9$ Hz, 2H, $CH(CH_3)_2$), 4.27-4.31 (m, 2H, C=CH of cod), 4.71-4.76 (m, 2H, C=CH of cod), 4.95-5.00 (m, 2H, C=CH of cod), 5.28-5.34 (m, 2H, C=CH of cod), 5.35 (s, 2H, OCH_2O), 6.68 (s, 1H, Ph), 6.70 (s, 1H, Ph), 7.13-7.21 (m, 3H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6 , 25.1 °C): δ 17.57, 24.79 ($CH(CH_3)_2$), 26.52, 28.64 ($CH(CH_3)_2$), 29.15, 29.82, 34.40, 35.38 (CH_2 of cod), 62.77 (d, $J_{Rh-C} = 12.5$ Hz, C=C of cod), 62.32 (d, $J_{Rh-C} = 10.5$ Hz, C=C of cod), 93.30 (d, $J_{Rh-C} = 6.8$ Hz, C=C of cod), 94.66 (d, $J_{Rh-C} = 6.8$ Hz, C=C of cod), 100.95, 107.80, 123.92, 125.36, 134.21, 139.66, 142.85 (Ar), 145.12 (CH_3), 150.61 (OCH_2O), 162.17 (C=NAr). The mother liquor was decanted and further concentrated to afford a mixture of **2.2** and orange crystalline solids of compound **2.3**. In this context, the yield of compound **2.3** cannot be calculated.

Synthesis of $[L(Cl)GeRh(cod)Cl]$ (2.3**).** Compound **2.3** was prepared by another method. A solution of $[RhCl(cod)]_2$ (0.13 g, 0.26 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **2.6** (0.22 g, 0.51 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 h and then filtered. The filtrate was concentrated to afford **2.3** as an orange crystalline solid. Yield: 0.29 g (85.7%). Mp: 225 °C. Elemental analysis calcd for $C_{29}H_{36}Cl_2GeNO_2Rh$: C, 51.44; H, 5.36; N, 2.07. Found: C, 50.58; H, 5.51; N, 2.21.

^1H NMR (399.5 MHz, C_6D_6 , 23.9 °C): δ 0.86 (d, $^3J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.94 (d, $^3J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.36 (d, $^3J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.41-1.50 (m, 2H, CH_2 of cod), 1.69-1.78 (m, 2H, CH_2 of cod), 1.72 (s, 3H, CH_3), 1.85-1.93 (m, 1H, CH_2 of cod), 1.90 (d, $^3J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.95-2.05 (m, 2H, CH_2 of cod), 2.16-2.24 (m, 1H, CH_2 of cod), 3.10 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.65-3.71 (m, 1H, C=CH of cod), 3.90 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 4.47-4.51 (m, 1H, C=CH of cod), 5.11 (d, $^2J_{\text{HH}} = 0.9$ Hz, 1H, OCH_2O), 5.16 (d, $^2J_{\text{HH}} = 0.9$ Hz, 1H, OCH_2O), 5.32-5.38 (m, 1H, C=CH of cod), 5.75-5.81 (m, 1H, C=CH of cod), 6.39 (d, 1H, Ph), 7.12-7.14 (m, 2H, Ph), 7.18-7.22 (m, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 25.1 °C): δ 17.59, 24.47, 24.98, 25.37 ($\text{CH}(\text{CH}_3)_2$), 25.65, 27.13 ($\text{CH}(\text{CH}_3)_2$), 28.30, 29.57, 29.81, 35.21 (CH_2 of cod), 66.38 (d, $J_{\text{Rh-C}} = 12.5$ Hz, C=C of cod), 70.71 (d, $J_{\text{Rh-C}} = 12.5$ Hz, C=C of cod), 100.51 (d, $J_{\text{Rh-C}} = 7.7$ Hz, C=C of cod), 102.17 (Ph), 102.55 (d, $J_{\text{Rh-C}} = 7.7$ Hz, C=C of cod), 108.29, 124.74, 124.82, 128.77, 132.49, 136.96, 143.25, 143.83 (Ph), 150.86 (CH_3), 153.39 (OCH_2O), 180.55 (C=NAr).

Synthesis of $[(\text{LGe})\mu\text{-}\{\text{Ir}(\text{cod})\}_2\text{Cl}]$ (2.4**).** A solution of $[\text{IrCl}(\text{cod})]_2$ (0.50 g, 0.75 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **2.1** (0.39 g, 0.49 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 h and then filtered. The filtrate was concentrated to afford compound **2.4** as black crystalline solid. Single crystals of **2.4** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.20 g (38.7%). Mp: 202 °C. Elemental analysis calcd for $\text{C}_{37}\text{H}_{48}\text{ClGeIr}_2\text{NO}_2$: C, 43.09; H, 4.69; N, 1.36. Found: C, 42.91; H, 4.55; N, 1.31. ^1H NMR (399.5 MHz, C_6D_6 , 23.9 °C): δ 0.96 (d, $^3J_{\text{HH}} = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.43-1.52 (m, 6H, CH_2 of cod), 1.76 (d, $^3J_{\text{HH}} = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.82 (s, 3H, CH_3), 1.91-2.08 (m, 4H, CH_2 of cod), 2.18-2.32 (m, 6H, CH_2 of cod), 3.09 (sept, $^3J_{\text{HH}} = 6.4$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 4.25-4.29 (m, 2H, C=CH of cod), 4.42-4.47 (m, 2H, C=CH of cod), 4.77-4.81 (m, 2H, C=CH of cod), 4.89-

4.94 (m, 2H, C=CH of cod), 5.36 (s, 2H, OCH₂O), 6.71 (d, 1H, Ph), 7.08-7.10 (m, 2H, Ph), 7.17-7.21 (m, 2H, Ph). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25.1 °C): δ 16.66, 24.55 (CH(CH₃)₂), 26.11, 29.06 (CH(CH₃)₂), 29.28, 30.60, 34.21, 36.54 (CH₂ of cod), 48.33, 49.73, 75.89, 76.99 (C=C of cod), 100.74, 107.43, 123.65, 125.00, 132.20, 138.97, 142.41, 142.91 (Ph), 145.41 (CH₃), 150.35 (OCH₂O), 162.38 (C=NAr). The mother liquor was decanted and further concentrated to afford a mixture of **2.4** and an orange crystalline solid of compound **2.5**. In this context, the yield of compound **2.5** cannot be calculated.

Synthesis of [LGe(Cl)Ir(cod)Cl] (2.5). Compound **2.5** was prepared by another method. A solution of [IrCl(cod)]₂ (0.17 g, 0.25 mmol) in toluene (12mL) was added dropwise to a stirred solution of **6** (0.22 g, 0.51 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 h and then filtered. The filtrate was concentrated to afford **5** as orange crystalline solids. Single crystals of **2.5** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.17 g (32.9%). Mp: 229°C. Elemental analysis calcd for C₂₉H₃₆Cl₂GeIrNO₂: C, 45.45; H, 4.73; N, 1.82. Found: C, 44.97; H, 4.68; N, 1.76. ¹H NMR (399.5 MHz, C₆D₆, 23.9 °C): δ 0.87 (d, ³J_{HH} = 5.0 Hz, 3H, CH(CH₃)₂), 0.89 (d, ³J_{HH} = 5.0 Hz, 3H, CH(CH₃)₂), 1.11-1.25 (m, 2H, CH₂ of cod), 1.37 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.51-1.60 (m, 2H, CH₂ of cod), 1.71 (s, 3H, CH₃), 1.76 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.81-1.95 (m, 2H, CH₂ of cod), 2.05-2.18 (m, 2H, CH₂ of cod), 3.10 (sept, ³J_{HH} = 6.9 Hz, 1H, CH(CH₃)₂), 3.39-3.44 (m, 1H, C=CH of cod), 3.66 (sept, ³J_{HH} = 6.9 Hz, 1H, CH(CH₃)₂), 4.15-4.20 (m, 1H, C=CH of cod) 4.91-4.97 (m, 1H, C=CH of cod), 5.08 (d, ²J_{HH} = 0.9Hz, 1H, OCH₂O), 5.13 (d, ²J_{HH} = 0.9 Hz, 1H, OCH₂O), 5.40-5.46 (m, 1H, C=CH of cod), 6.39 (d, 1H, Ph), 6.72 (d, 1H, Ph), 7.00-7.08 (m, 1H, Ph), 7.11-7.15 (m, 1H, Ph), 7.18-7.20 (m, 1H, Ph). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25.1 °C): δ 17.60,

24.49, 25.01, 25.35 (CH(CH₃)₂), 25.48, 27.44 (CH(CH₃)₂), 28.35, 29.82, 31.45, 36.40 (CH₂ of cod), 49.88, 52.98, 87.63, 90.37 (C=C of cod), 102.26, 108.48, 124.71, 124.82, 125.37, 125.63, 128.25, 128.46, 128.87, 129.02, 132.36, 136.70, 143.16, 143.68 (Ph), 151.03 (CH₃), 153.56 (OCH₂O), 181.08 (C=NAr).

Synthesis of [(LGe) μ -{Mn(CO)₄}]₂ (2.7). A solution of **2.1** (0.39 g, 0.49 mmol) in toluene (12 mL) was added dropwise to a stirred suspension of Mn₂(CO)₁₀ (0.20 g, 0.51 mmol) in toluene (12 mL) at room temperature. The reaction mixture was refluxed overnight and then filtered. The filtrate was concentrated to afford compound **2.7** as dark red crystalline solid. Single crystals of **2.7** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.13 g (46.3%). Mp: 261 °C. Elemental analysis calcd for C₅₀H₄₈Ge₂Mn₂N₂O₁₂: C, 53.43; H, 4.30; N, 2.49. Found: C, 53.39; H, 4.23; N, 2.25. ¹H NMR (399.5 MHz, C₆D₆, 23.3 °C): δ 0.87 (d, ³J_{HH} = 6.4 Hz, 12H, CH(CH₃)₂), 1.53 (d, ³J_{HH} = 6.4 Hz, 12H, CH(CH₃)₂), 1.84 (s, 6H, CH₃), 3.29 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 5.54 (s, 4H, OCH₂O), 6.60 (s, 2H, Ph), 6.62 (s, 2H, Ph), 7.04-7.16 (m, 6H, Ph). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25.1 °C): δ 21.65, 24.44 (CH(CH₃)₂), 25.40, 28.91 (CH(CH₃)₂), 101.62, 102.28, 108.28, 124.90, 126.69, 130.45, 130.87, 132.36, (Ph), 143.21 (CH₃), 149.95 (OCH₂O), 178.12 (C=NAr), 232.41, 234.42 (CO). IR (Nujol, cm⁻¹): 2951s, 2920s, 2851s, 2004w, 1954w, 1938w, 1913w, 1454s, 1377s, 1259m, 1092m, 1020m, 800s, 721s.

Synthesis of [(LGe) μ -{Co(CO)₃}]₂ (2.9·C₇H₈): Toluene (20 mL) was added to a mixture of **2.1** (0.39 g, 0.50 mmol, 1.0 equiv.) and Co₂(CO)₈ (0.17 g, 0.50 mmol, 1.0 equiv.) and refluxed overnight. After filtration, the filtrate was concentrated to obtain **2.9·C₇H₈** dark red crystalline solid. Single crystals of **2.9·C₇H₈** suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. The dimeric structure of **2.9·C₇H₈** appears

to convert into its monomer in solution to yield a paramagnetic species with 1 unpaired electron ($\mu_{\text{eff}} = 1.82 \mu_{\text{B}}$). As such, no NMR data is available. Yield: 0.19 g (35.2 %). M.p. 165 °C (dec). NMR data for **2.9**·C₇H₈ is not available Elemental analysis calcd for C₆₂H₆₄Co₂Ge₂N₂O₁₀: C 59.09, H 5.12, N 2.22; Found: C 57.52 H 5.85 N 2.01

Synthesis of [Fe(CO)₃]μ-{(LGe)→Fe(CO)₄}₂ (2.10**·3C₇H₈):** Toluene (20 mL) was added to a mixture of **2.1** (0.3950 g, 0.500 mmol, 1.0 equiv.) and Fe₂(CO)₉ (0.3640 g, 1.000 mmol, 2 equiv) and stirred overnight. All volatiles were removed by vacuum and the resulting solids were extracted with toluene (20 mL). After filtration, the filtrate was concentrated to afford **2.10**·3C₇H₈ as black crystalline solid. Single crystals of **2.10**·3C₇H₈ suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. No NMR data or evans method data is available as compound **2.10**·3C₇H₈ is insoluble in common hydrocarbon solvents and visibly decomposes in THF. The use of other solvents for characterization is underway. Yield: 0.24 g (37.9 %). M.p. 180 °C (dec.). Elemental analysis calcd for C₅₃H₄₈Fe₃Ge₂N₂O₁₅ C 50.29, H 3.82, N 2.21; Found C 51.16, H 3.57, N 2.28. The mother liquor was concentrated to afford a mixture of **2.10**·3C₇H₈ and red crystals [(LGe)→Fe(CO)₄]₂ (**2.11**·C₇H₈) as a minor product. As a pure sample of **2.11**·C₇H₈ cannot be isolated, no spectroscopic data is available.

2.5 References

1. Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*; Wiley: Chichester, U.K., **2010**.
2. (a) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, 109, 3479–3511. (b) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, 111, 354–396. (c) Marschner, C. *Eur. J. Inorg. Chem.* **2015**, 2015, 3805–3820.
3. For recent reviews, see: (a) Bourissou, D.; Guerret, O.; Gabbaie, F. P.; Bertrand, G. *Chem. Rev.* **2000**, 100, 39–92. (b) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, 2, 389–399. For recent articles, see: (c) Pu, L.; Hardman, N. J.; Power, P. P. *Organometallics* **2001**, 20, 5105–5109. (d) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, 48, 798–800. (e) Wang, X.; Zhu, Z.; Peng, Y.; Lei, H.; Fetting, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2009**, 131, 6912–6913. (f) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fetting, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, 131, 16272–16282. (g) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Organometallics* **2011**, 30, 6490–6494. (h) Brown, Z. D.; Guo, J.-D.; Nagase, S.; Power, P. P. *Organometallics* **2012**, 31, 3768–3772. (i) Brown, Z. D.; Erickson, J. D.; Fetting, J. C.; Power, P. P. *Organometallics* **2013**, 32, 617–622. (j) Dube, J. W.; Brown, Z. D.; Caputo, C. A.; Power, P. P.; Ragogna, P. J. *Chem. Commun.* **2014**, 50, 1944–1946. (k) Dube, J. W.; Graham, C. M. E.; Macdonald, C. L. B.; Brown, Z. D.; Power, P. P.; Ragogna, P. J. *Chem. - Eur. J.* **2014**, 20, 6739–6744. (l) Erickson, J. D.; Fetting, J. C.; Power, P. P. *Inorg. Chem.* **2015**, 54, 1940–1948. (m) Usher, M.; Protchenko, A. V.; Rit, A.; Campos, J.; Kolychev, E. L.; Tirfoin, R.; Aldridge, S. *Chem. - Eur. J.* **2016**, 22, 11685–11698. (n) Del Rio, N.; Lopez-Reyes, M.; Baceiredo, A.; Saffon-Merceron, N.; Lutters, D.; Müller, T.; Kato, T. *Angew. Chem., Int. Ed.* **2017**, 56, 1365–1370.
4. Jutzi, P.; Leue, C. *Organometallics* **1994**, 13, 2898–2899.

5. Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **2000**, 122, 650–656.
6. Inoue, S.; Driess, M. *Organometallics*. **2009**, 28, 5032– 5035.
7. Filippou, A. C.; Stumpf, K. W.; Chernov, O.; Schnakenburg, G. *Organometallics*. **2012**, 31, 748–755.
8. Jones, C.; Rose, R. P.; Stasch, A. *Dalton. Trans.* **2008**, 2871–2878.
9. Leung, W.-P.; Chiu, W.-K.; Mak, T. C. W. *Organometallics*. **2012**, 31, 6966– 6971.
10. Inomata, K.; Watanabe, T.; Tobita, H. *J. Am. Chem. Soc.* **2014**, 136, 14341–14344.
11. (a) Pandey, K. K.; Power, P. P. *Organometallics*. **2011**, 30, 3353–3361. (b) Pandey, K. K.; Jones, C. *Organometallics*, **2013**, 32, 3395–3403. (c) Pandey, K. K.; Patidar, P.; Vishwakarma, R. *Eur. J. Inorg. Chem.* **2014**, 2014, 2916–2923. (d) Pandey, K. K. *J. Organomet. Chem.* **2014**, 761, 134–141.
12. Inomata, K.; Watanabe, T.; Miyazaki, Y.; Tobita, H. *J. Am. Chem. Soc.* **2015**, 137, 11935–11937.
13. Khoo, S.; Yeong, H.-X.; Li, Y.; Ganguly, R.; So, C.-W. *Inorg. Chem.* **2015**, 54, 9968–9975.
14. Chia, S.-P.; Yeong, H.-X.; So, C.-W. *Inorg. Chem.* **2012**, 51, 1002–1010.
15. Garcia, J. M.; Ocando-Mavarez, E.; Kato, T.; Coll, D. S.; Briceno, A.; Saffon-Merceron, N.; Baceiredo, A. *Inorg. Chem.* **2012**, 51, 8187–8193.
16. (a) Alvarez-Rodriguez, L.; Cabeza, J. A.; Fernandez-Colinas, J. M.; Garcia-Alvarez, P.; Polo, D. *Organometallics*. **2016**, 35, 2516–2523. (b) Kameo, H.; Ishii, S.; Nakazawa, H. *Dalton. Trans.* **2012**, 41, 11386–11392.
17. Walz, F.; Moos, E.; Garnier, D.; Koeppe, R.; Anson, C. E.; Breher, F. *Chem. - Eur. J.* **2017**, 23, 1173–1186.
18. For the details of DFT calculations, see the Appendices.

19. McCrea-Hendrick, M. L.; Caputo, C. A.; Linnera, J.; Vasko, P.; Weinstein, C. M.; Fetting, J. C.; Tuononen, H. M.; Power, P. P. *Organometallics*. **2016**, 35, 2759–2767.
20. Preut, H.; Haupt, H. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, 35, 729–730.
21. Schenk, C.; Schnepf, A. *Dalton. Trans.* **2007**, 5400–5404.
22. Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. *Organometallics*. **2006**, 25, 2381–2383.
23. Leung, W.-P.; So, C.-W.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Inorg. Chem.* **2005**, 44, 7286–7288.
24. Veith, M. In *Metal Clusters in Chemistry, Vol. 1: Molecular Metal Clusters*, Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, 1999; p 76.
25. Lei, H.; Guo, J.-D.; Fetting, J. C.; Nagase, S.; Power, P. P. *Organometallics*. **2011**, 30, 6316–6322.
26. Cabeza, J. A.; Garcia-Alvarez, P.; Perez-Carreno, E.; Polo, D. *Chem. Eur. J.* **2014**, 20, 8654–8663.
27. A. Brueck, D. Gallego, W. Wang, E. Irran, M. Driess, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2012**, 51, 11478–11482.
28. Sen, S. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D.; *Inorg. Chem.* **2010**, 49, 5786 – 5788
29. Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832 – 2838 .
30. Sheldrick, G. M. SHELXL-97; Universitat Göttingen: Göttingen, Germany, 1997.

Chapter 3.

Synthesis and Reactivity of a Base-Stabilized Germenylenysilylene: a Base-Stabilized Heterodinuclear Group 14 Alkyne Analogue

3.1 Introduction

The isolation of heavier group 14 alkyne analogues has been a subject of great interest in recent years. Due to the poor overlap of p orbitals for heavier elements ($E = \text{Pb} - \text{Si}$), it was not possible to synthesize the heavier congeners of alkyne until recent advances in ligand design. By utilizing extremely bulky aryl ligands, Power and coworkers isolated the first diplumbyne (**3A**) (RPbPbR , $\text{R} = 2,6\text{-(2,4,6-}i\text{Pr}_3\text{C}_6\text{H}_2)\text{C}_6\text{H}_3$) in 2000. ⁴ This was followed closely by the isolation of the first digermynes (**3C**) (RGeGeR , $\text{R} = 2,6\text{-(2,4,6-}i\text{Pr}_3\text{C}_6\text{H}_2)\text{C}_6\text{H}_3$) ³ and the first distannyne (**3B**) (RSnSnR , $\text{R} = 2,6\text{-(2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{C}_6\text{H}_3$). ² The complete set of heavier group 14 alkyne analogues was finished upon the isolation of the first disilyne (**3D**) (RSiSiR , $\text{R} = \text{Si}(i\text{Pr})\{\text{CH}(\text{SiMe}_3)_2\}_2$) by Sekiguchi and coworkers by utilizing bulky silyl substituents. ¹ The rich chemistry of these highly reactive species is reflected by the number of reviews dedicated to the subject. ⁵

Scheme 3-1: Examples of heavier alkyne analogues

Consequently, interest in the isolation of group 14 element(I) dimer started gaining momentum. Often considered the base-stabilized analogues of heavier alkyne analogues, these reactive compounds share a striking similarity in structure to the diplumbyne with a single tetrylene-tetrylene σ -bond and a lone pair on each tetrylene atom. Since the isolation of the first Ge(I) dimer by Jones and coworkers in 2006 ⁶, numerous other groups have attempted and succeeded in isolating group 14 element(I) dimers featuring a variety of ligands including amidinato, guanidinato, 2,6-diiminophenyl, amido, pyridyl-1-azaallyl and NHC. ⁷

Scheme 3-2: Activation of H_2 by a germanium(I) dimeric derivative

Group 14 element(I) dimers have a wide range of different reactivity patterns. For instance, Jones and coworkers reported that the germanium(I) dimer with the bulky Ar^* amido ligands (**3E**) mimic the reactivity of digermynes by activating H_2 . ⁸ Furthermore, our group has had success in recent years, synthesizing a wide range of 4 – membered rings containing heavier group 14 elements by using the amidinato silicon(I) dimer as a starting material. ⁹ Even more fascinating are our recent efforts in using the NHC-stabilized iodosilicon(I) dimer as a synthon for the isolation of extremely reactive species. ¹⁰

Scheme 3-3: Synthesis of parent silyliumylidene cation from NHC-stabilized silicon(I) dimer

The reaction of 4 equivalents of I_{Me} [$\{\text{MeC}(\text{Me})\text{N}\}_2\text{C:}$] with the I_{Ar} stabilized iodosilicon(I) dimer led to the formation of the first NHC-stabilized silyliumylidene cation. The reaction seems to begin by the displacement of iodide ions and the larger I_{Ar} by I_{Me} followed by the homolytic cleavage of the Si-Si single bond to generate a silicon(I) radical intermediate. The radical intermediate then abstracts a H• radical from toluene to form the parent silyliumylidene cation.

Scheme 3-4: Synthesis of unsymmetrical Ge(I) dimer and germylene-stannylene

With the wide variety of heavier group 14 element(I) dimers available, it is only logical that the next step would be to isolate heterobimetallic group 14 complexes bearing a formal σ metal-metal bond. The only example of such an attempt was reported by Driess and coworkers where the isolated potassium germylenide salt¹¹ was reacted with the β -diketiminato chlorogermylene and β -diketiminato chlorostannylene to form the first heteroleptic germanium(I) dimer and germylene-stannylene with a formal Ge-Sn σ bond.¹² Interestingly, no additional reactivity for these compounds have been reported. It is anticipated that such unsymmetrical heterobimetallic main group complexes will be much more reactive and could give rise to hitherto unknown structures. In this chapter, we report a simple synthetic procedure towards the first base-stabilized germylenylsilylene, which was characterized by multinuclear NMR spectroscopy and its preliminary reactivity towards aryl azides.

3.2 Results and Discussion

Scheme 3-5: Synthesis of **3.1-3.3**, Ar = 2,6-diisopropylphenyl

Compound **3.1** and **3.2** were prepared by methods outlined in the literature.¹³ Compound **3.1** was reacted with excess KC_8 in the presence of THF to generate a deep red solution of compound **3.2** within 1 hour and used immediately for the next step. 1 equivalent of amidinato-chlorosilylene diluted in THF was added dropwise to the in-situ generated **3.2** at -78°C and warmed to 0°C and stirred for another 1 hour. The colour changed from dark red to dark blue within minutes indicating that a reaction occurred. The volatiles were removed to obtain compound **3.3** as a dark blue solid.

Initial attempts at the crystallization of compound **3.3** for X-ray crystallography in a variety of solvents have not been successful due to its inherent instability in solution. Compound **3.3** decomposes into unidentified products within days in solution according to ^1H NMR. However, compound **3.3** is sufficiently stable to be characterized by ^1H , ^{13}C and ^{29}Si NMR spectroscopy. ^1H NMR spectrum displays a septet at δ 3.12ppm and two doublets δ 1.61 and 1.03 ppm corresponding to the Ar group on the iminophenyl ligand. In the ^1H NMR spectrum, there is a singlet corresponding to the OCH_2O protons, as well as a singlet at 1.08ppm corresponding to the tert-butyl protons on the amidinato ligand. The ^{29}Si NMR spectrum shows a signal at δ 70.91ppm. This value is very close to the reported ^{29}Si NMR signal for amidinato silicon(I) dimer (δ 75.71ppm)⁷ⁱ and implies that the silicon atom in **3.3** is directly bonded to a low valent germanium atom. As such, the structure of **3.3** proposed in scheme 3-5 is plausible.

Scheme 3-2: Synthesis of **3.4**·0.5C₇H₈, Ar = 2,6-diisopropylphenyl

Compound **3.4**·0.5C₇H₈ was synthesized by reacting compound **3.3** and 2,6-diisopropylphenylazide. 2,6-diisopropylphenylazide diluted in toluene was added dropwise to a stirring solution of **3.3** in toluene at low temperature and stirred for an hour. Within 5 minutes, effervescences were observed in the reaction mixture indicating the elimination of dinitrogen from the aryl azide in the reaction. The colour gradually changed over the first 10 minutes at low temperature from blue to orange indicative of a successful reaction. The reaction mixture was allowed warm to room temperature and stirred for another 2 hours. The mixture was then filtered and concentrated to afford **3.4**·0.5C₇H₈ as orange crystals in 68% yield.

The ¹H NMR spectrum of compound **3.4**·0.5C₇H₈ displays 5 septets (δ 5.11, 4.23, 4.07, 3.39 and 2.11 ppm) corresponding to the 6 isopropyl groups and 2 doublets at δ 5.17 and 5.71 ppm corresponding to 2 inequivalent germinal protons on the OCH₂O groups of the iminophenyl ligand. The spectrum also shows 2 singlets at δ 1.06 and 0.80 ppm corresponding to the tert-butyl groups on the amidinato ligand. The ²⁹Si NMR spectrum displays a signal at δ -75.37 ppm. This upfield shift in NMR signals confirms the oxidation of the silicon atom from +2 in compound **3.3** to +4 in compound **3.4**·0.5C₇H₈.

Figure 3-1: Molecular Structure of **3.4**·0.5C₇H₈ with thermal ellipsoids set at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): N3-Si1 1.6293(14), N2-Si1 1.6750(13), Ge1-N2 2.0133(14), Ge1-N1 2.432(2), N5-Si1 1.8569(13), N4-Si1 1.8435(14), Ge1-C1 2.0192(16), Ge1-N3 2.4005(13); N3-Si1-N4 133.35(7), N3-Si1-N5 111.81(7), N4-Si1-N5 71.08(6), N3-Si1-N2 102.53(7), N2-Si1-N4 115.02(7), N2-Si1-N5 121.89(6), N2-Ge1-C1 109.07(6)

The molecular structure of compound **3.4**·0.5C₇H₈ was confirmed by X-ray crystallographic analysis. The molecular structure of **3.4**·0.5C₇H₈ is shown in figure 3-1. The silicon atom in **3.4**·0.5C₇H₈ adopts a distorted tetrahedral geometry. The Si1-N3 (1.6293(14) Å) bond longer than the Si=N bond (1.568(3) Å) and the Si1-N2 (1.6750(13) Å) bond is marginally shorter than the Si-N single bond (1.695(3) Å) in [tBu₂Si=N-SitBu₃].¹⁴ The germanium atom in **3.4**·0.5C₇H₈ is four-coordinate and has a distorted square pyramidal geometry indicating that there is a stereochemically active lone-pair of electrons. The Ge1-C1 (2.0192(16) Å) bond in **3.4**·0.5C₇H₈ is slightly longer than the Ge-C bond in the 2-imino-5,6-methylenedioxyphenyl-chlorogermylene (1.992(3) Å) and its corresponding germanium(I)

dimer (1.968(4) Å)¹³ The Ge1-Si1 bond (2.7640(7) Å) is longer than the Si→Ge dative bond in the amidinate stabilized Si(II)-Ge(II) adduct, [L{(Me₃Si)₂N}Si→GeCl₂].¹⁵ The Ge1-N1 (2.432(2) Å) and Ge-N3 (2.4005(13) Å) is much longer than the N_{imine}→Ge dative bond in the 2-imino-5,6-methylenedioxyphenyl-chlorogermylene (2.054(2) Å) and its corresponding germanium(I) dimer (2.022(3) Å).¹³ The N1-Ge1-N3 bond angle (172.94(5) °) indicates that each of N1 and N3 lone pair of electrons are donating electron density to the same vacant orbital on the Ge1 atom which leads to much longer bond lengths.

3.3 Conclusion

In conclusion, the first example of a germylenysilylene was synthesized by a simple procedure within hours. It was sufficiently stable in solution to be characterized by multinuclear NMR spectroscopy but decomposes within days into unidentified products. A preliminary reactivity study was conducted on the germylenysilylene (**3.3**) with 2,6-diisopropylphenylazide to generate a silaamidinato germylene (**3.4**·0.5C₇H₈) which was characterized by multinuclear NMR spectroscopy and X-ray crystallography. The molecular structure of **3.4**·0.5C₇H₈ obtained from X-ray crystallographic analysis, confirms the structure of compound **3.3**. Further reactivity and continued attempts to crystallize compound **3.3** are ongoing.

3.4 Experimental Section

General Procedure. All chemical manipulations were performed using standard Schlenk techniques, under an atmosphere of argon gas. The solvents used were purified by the MBRAUN MB SPS-5 solvent purification system. Compound **3.1**, **3.2**,¹⁴ 2,6-diisopropylphenylazide¹⁶ and KC_8 ¹⁷ were prepared by methods outlined in the literature. The ^1H , ^{13}C and ^{29}Si NMR spectra were recorded in deuterated benzene (C_6D_6) on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe_4 for ^1H , ^{13}C and ^{29}Si . Elemental analyses of compound **3.4** $\cdot 0.5\text{C}_7\text{H}_8$ were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

X-ray Data Collection and Structural Refinement. Intensity data for compounds **3.4** $\cdot 0.5\text{C}_7\text{H}_8$ were collected using a Bruker APEX II diffractometer using graphite monochromated Mo-K α radiation (0.71073 Å). 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 F^2 .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.

Synthesis of **3.3**: THF (25mL) was added to a mixture of compound **3.1** (0.43g, 1 mmol) and KC_8 (0.47g, 3.5mmol), at room temperature and stirred for 1 hour. The excess KC_8 was filtered to generate **3.2** in situ without isolation. Amidinato chlorosilylene (0.29g, 1 mmol) diluted in THF (10mL) was added dropwise to **3.2** at -78°C , warmed to 0°C and left to stir for 1 hour at the same temperature. All volatiles were removed to obtain compound **3.3** as a blue powder in quantitative yield (NMR). M.p. 132°C (dec.). 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 (399.5MHz, C_6D_6 , 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, C_6D_6 , 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, C_6D_6 , 24.9°C): δ 70.9.

Synthesis of **3.4**·0.5 C_7H_8 : 2,6-diisopropylphenylazide (0.40g, 2 mmol) diluted in toluene (10mL) was added dropwise to a freshly prepared **3.3** (1 mmol according to the amount **3.1** used) in toluene (30mL) at -78°C and stirred for one hour at that temperature. The reaction mixture was warmed to room temperature and stirred for another 2 hours. The reaction mixture was filtered and concentrated to afford **3.4**·0.5 C_7H_8 as orange crystalline solids. Single crystals of **3.4**·0.5 C_7H_8 suitable for X-ray crystal structure determination, were obtained by slow evaporation of the toluene solution. Yield: 0.68 (67%). M.p. 175°C (dec.). Elemental analysis calcd for $\text{C}_{63.50}\text{H}_{85}\text{GeN}_5\text{O}_2\text{Si}$: C, 72.56; H, 8.15; N, 6.66. Found: C, 72.02; H, 8.19; N, 6.53. ^1H NMR (399.5MHz, C_6D_6 , 24.9°C) δ 0.56 (d, $^3J_{\text{HH}} = 6.81$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.70 (d, $^3J_{\text{HH}} = 6.81$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.79 (s, 9H, tBu), 0.80 – 0.86 (m of overlapping d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.06 (s,

9H, tBu), 1.07 (d overlap with tBu signal, 3H, CH(CH₃)₂), 1.27 – 1.33 (m of overlapping d, 9H, CH(CH₃)₂), 1.41 – 1.46 (m of overlapping d, 9H, CH(CH₃)₂), 1.53 (d, ³J_{HH} = 6.81 Hz, 3H, CH(CH₃)₂), 1.85 (s, 3H, CH₃), 2.11 (sept overlap with toluene signal, 1H, CH(CH₃)₂), 3.39 (sept, ³J_{HH} = 6.81 Hz, 1H, CH(CH₃)₂), 4.08 (sept, ³J_{HH} = 6.81 Hz, 2H, CH(CH₃)₂), 4.24 (sept, ³J_{HH} = 6.81 Hz, 1H, CH(CH₃)₂), 5.12 (sept, ³J_{HH} = 6.81 Hz, 1H, CH(CH₃)₂), 5.17 (d, ²J_{HH} = 0.87 Hz, 1H, OCH₂O), 5.71 (d, ²J_{HH} = 0.87 Hz, 1H, OCH₂O), 6.68 (d, ³J_{HH} = 7.92 Hz, 1H, Ph), 6.74 – 7.01 (m, 6H, Ph), 7.07 – 7.15 (m, 5H, Ph), 7.19 – 7.23 (m, 4H, Ph). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 24.9 °C): δ 18.79, 21.11, 23.19, 23.49, 23.66, 24.13, 24.20, 24.71, 25.51, 25.66, 26.04, 26.49, 26.81, 26.94, 27.62, 27.79, 28.12, 28.30, 28.89, 30.63, 30.88, 54.09, 55.03, 100.41, 106.34, 116.76, 122.33, 122.60, 122.96, 123.84, 124.11, 124.33, 124.47, 124.82, 125.38, 129.01, 130.09, 137.79, 138.93, 139.99, 140.72, 143.08, 145.08, 145.89, 146.91, 147.27, 147.42, 150.69, 164.86, 178.35. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 24.9°C): δ -75.4

3.5 References

1. Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science*. **2004**, *305*, 1755 – 1757
2. Philips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930 – 5931.
3. Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem. Int. Ed.* **2002**, *41*, 1785 – 1787.
4. Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524–3525
5. (a) Wang, W.; Robinson, G. H. *Dalton. Trans.* **2012**, *41*, 337 – 345 (b) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627 – 637 (c) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354 – 396 (d) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016 – 6041 (e) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016 – 6041 (f) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877 – 3923 (g) Mizuhata, Y.; Sasamori, T.; Tokito, N. *Chem. Rev.* **2009**, *109*, 3479 – 3511 (h) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201 – 5213 (i) Nagendran, S.; Roesky, H. W. *Organometallics*. **2008**, *27*, 457 – 492 (j) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047 – 10064 (k) Power, P. P. *Organometallics*. **2007**, *26*, 4362 – 4372 (l) Power, P. P. *Chem. Commun.* **2003**, 2091 – 2101 (m) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463 – 3504
6. Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K. -A.; Stasch, A. *Chem. Commun.* **2006**, 0, 3978-3980
7. (a) Arz, M. I.; Geiß, D.; Straßmann, M.; Schnakenburg, G.; Filippou, A. C. *Chem. Sci.* **2015**, *6*, 6515 – 6524. (b) Chia, S. -P.; Yeong, H. -X.; So, C. -W. *Inorg. Chem.* **2012**, *51*, 1002 – 1010. (c) Chia, S. -P.; Ganguly, R.; Li, Y.; So, C. -W. *Organometallics*, **2012**, *31*, 6415 – 6419. (d) Chia, S. -P.; Xi, H. W.; Li, Y.; Lim, K. H.; So, C. -W. *Angew. Chem. Int. Ed.* **2013**, *52*, 6298 - 6301. (e) Jones, C.; Bonyhady, S. J.; Holzmann, N.;

- Frenking, G.; Stasch, A. *Inorg. Chem.* **2011**, 50, 12315 – 12325. (f) Jambor, R.; Kasna, B.; Kirschner, K. N.; Schurmann, M.; Jurkschat, K. *Angew. Chem. Int. Ed.* **2008**, 47, 1650 – 1653. (g) Khan, S.; Michel, R.; Dieterich, J. M.; Mata, R. A.; Roesky, H. W.; Demers, J. -P.; Lange, A.; Stalke, D. *J. Am. Chem. Soc.* **2011**, 133, 17889 – 17894. (h) Leung, W. -P.; Chiu, W. -K.; Chong, K. -H.; Mak, T. C. W. *Chem. Commun.* **2009**, 44, 6822 – 6824. (i) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C.; *Angew. Chem. Int. Ed.* **2009**, 48, 8536 – 8538. (j) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer III, H. F.; Schleyer, P. von R.; Robinson, G. H. *Science*. **2008**, 321, 1069 – 1071. (k) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmuller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics*. **2008**, 27, 5459 – 5463.
8. Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2011**, 133, 18622 – 18625
9. (a) Zhang, S.-H.; Xi, H.-W.; Lim, K. H.; Meng, Q.; Huang, M.-B.; So, C.-W. *Chem. Eur. J.*, **2012**, 18, 4258 - 4263. (b) Yeong, H.-X.; Zhang, S.-H.;* Xi, H.-W.; Guo, J.-D.; Lim, K. H.; Nagase, S.; So, C.-W. *Chem. Eur. J.*, **2012**, 18, 2685 - 2691. (c) Yeong, H.-X.; Xi, H.-W.; Li, Y.; Kunnappilly, S. B.; Chen, B.; Lau, K.-C.; Hirao, H.; So, C.-W. *Chem. Eur. J.*, **2013**, 19, 14726 - 14731 (d) Zhang, S.-H.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Angew. Chem. Int. Ed.*, **2013**, 52, 12346 – 12349 (e) Zhang, S.-H.; Carter, E.; Xi, H.-W.; Li, Y.; Lim, K. H.; So, C.-W. *Inorg. Chem.*, **2017**, 56, 701-704.
10. Li, Y.; Chan Y. -C.; Leong, B. -X.; Li, Y.; Richards, E.; Purushothaman, I.; De, S.; Parameswaran, P.; So, C. -W. *Angew. Chem. Int. Ed.*, **2017**, 56, 7573 – 7578
11. Wang, W.; Yao, S.; van Wullen, C.; Driess, M. *J. Am. Chem. Soc.* **2008**, 130, 9640 - 9641

12. Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661 – 2663
13. Chia, S. -P.; Yeong, H. -X.; So, C. -W. *Inorg. Chem.* **2012**, 51, 1002 – 1010
14. Wiberg, N.; Schurz, S.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 1053–1054.
15. Shan, Y. -L.; Yim, W. -L.; So, C. -W. *Angew. Chem. Int. Ed.* **2014**, 53, 13155 – 13158
16. Li, Y.; Gao, L.-X.; Han, F.-S. *Chem. Eur. J.* **2010**, 16, 7969 – 7972
17. Ottmers, D. M.; Rase, H. F. *Carbon.* **1966**, 4, 125 – 127
18. Sheldrick, G. M. SHELXL-97; Universitat Göttingen: Göttingen, Germany, 1997.

Appendix

1. Table A1-1: Crystallographic data for compounds 1.2, 1.3 and 1.6

	1.2	1.3	1.6
Formula	C ₄₆ H ₅₈ Cl ₂ GeN ₃ PSi	C ₈₆ H ₉₀ Cl ₂ Ge ₄ N ₂ P ₄	C ₃₉ H ₅₀ N ₃ PSi
M _r	855.50	1636.73	619.88
Color	Colourless	orange	orange
Crystal System	Triclinic	monoclinic	monoclinic
Space Group	P -1	P 1 21/n 1	P 1 21/n 1
a/Å	11.09490(10)	11.7897(2)	17.5974(4)
b/Å	12.63690(10)	16.3455(2)	13.0761(4)
c/Å	17.6502(2)	20.0346(3)	31.5626(8)
α/deg	78.2671(5)	90	90
β/deg	89.0480(5)	103.3601(8)	103.6919(8)
γ/deg	65.4174(5)	90	90
V/ Å ³	2196.90(4)	3756.35(10)	7056.3(3)
Z	2	2	8
d _{calcd} /g cm ⁻³	1.293	1.447	1.167
μ/ mm ⁻¹	2.933	3.668	0.143
F(000)	900	1684	2672
Crystal Size/mm ³	0.120 × 0.220 × 0.300	0.010 × 0.020 × 0.040	0.160 × 0.200 × 0.220
Index Range	-13≤h≤13	-13≤h≤13	-25≤h≤24
	-14≤k≤14	-19≤k≤19	-18≤k≤18
	-21≤l≤20	-23≤l≤23	-45≤l≤45
No. of reflections collected	20072	67727	203092
R1, wR2 [I>2σ(I)]	0.0380, 0.0987	0.0535, 0.1401	0.0495, 0.1077
R1, wR2 (all data)	0.0411, 0.1019	0.0679, 0.1520	0.0763, 0.1237
Goodness Of Fit, F ²	1.025	1.032	1.054
No. of data/ restraints/ param	7569 / 0 / 498	6637 / 0 / 447	22474 / 0 / 813
Largest diff peak, hole/ eÅ ⁻³	0.810, -0.698	2.779, -1.113	1.144, -0.397

2. Table A1-2: Crystallographic data for compounds 1.7 – 1.9

	1.7	1.8	1.9
Formula	C ₃₆ H ₃₇ Cl ₂ Ge ₂ NP ₂	C ₄₆ H ₅₈ Cl ₂ N ₃ PSiSn	C ₄₈ H ₅₄ Cl ₄ N ₂ P ₂ Sn ₃
M _r	761.68	901.60	1218.74
Color	colorless	colorless	colorless
Crystal System	triclinic	orthorhombic	triclinic
Space Group	P -1	P 21 21 21	P -1
a/Å	10.8060(5)	9.1080(2)	10.6912(4)
b/Å	16.9006(7)	17.7299(3)	15.7286(6)
c/Å	20.7677(9)	27.5456(6)	16.7148(6)
α/deg	66.7498(13)	90	109.2748(16)
β/deg	89.8652(15)	90	102.9748(16)
γ/deg	81.2991(16)	90	101.9226(15)
V/ Å ³	3437.8(3)	4448.17(16)	2462.10(16)
Z	4	4	2
d _{calcd} /g cm ⁻³	1.472	1.346	1.644
μ/ mm ⁻¹	2.024	6.531	14.883
F(000)	1552	1872	1208
Crystal Size/mm ³	0.140 × 0.220 × 0.260	0.040 × 0.140 × 0.200	0.060 × 0.100 × 0.300
Index Range		-10≤h≤10	
		-20≤k≤20	
		-32≤l≤32	
No. of reflections collected	22757	49392	8632
R1, wR2 [I>2σ(I)]	0.0707, 0.1694	0.0677, 0.1579	0.0798, 0.2322
R1, wR2 (all data)	0.1224, 0.2075	0.0686, 0.1583	0.0831, 0.2397
Goodness Of Fit, F ²	1.014	1.202	1.147
No. of data/ restraints/ param	22757 / 0 / 783	7737 / 177 / 539	8632 / 0 / 542
Largest diff peak, hole/ eÅ ⁻³	1.880, -1.638	3.158, -1.916	2.639, -1.881

3. NMR spectra of compound 1.2, 1.3 and 1.6-1.9

(a) ^{31}P NMR spectra of compound 1.2

(b) ^{29}Si NMR spectra of compound 1.2

(c) ^{31}P CPMAS NMR spectra of compound **1.3**

(d) Crude ^{29}Si NMR of mother liquor from compound **1.3** showing presence of compound **1.4** and **1.5**

(e) ^{31}P NMR spectra of compound **1.6**

(f) ^{29}Si NMR spectra of compound **1.6**

(g) ^{31}P NMR spectra of compound **1.7**

(h) Crude ^{11}B NMR spectra from the formation of compound **1.7** showing unknown 4-coordinate boron compounds

(i) ^{31}P NMR spectra of compound **1.8**

(j) ^{119}Sn NMR spectra of compound **1.8**

4. Table A2-1: Crystallographic data for compounds 2.2, 2.4 and 2.5

	2.2	2.4	2.5
Formula	C ₃₇ H ₄₈ ClGeNO ₂ Rh ₂	C ₃₇ H ₄₈ ClGeIr ₂ NO ₂	C ₃₆ H ₄₄ Cl ₂ GeIrNO ₂
M _r	852.62	1031.20	858.41
Color	Purple	black	orange
Crystal System	Orthorhombic	orthorhombic	monoclinic
Space Group	P n m a	P n m a	C 1 2/c 1
a/Å	18.8722(8)	19.0523(8)	31.0583(6)
b/Å	15.9812(7)	15.9424(7)	11.0764(2)
c/Å	11.2988(5)	11.2787(5)	20.1279(4)
α/deg	90	90	90
β/deg	90	90	95.9276(10)
γ/deg	90	90	90
V/ Å ³	3407.7(3)	3425.8(3)	6887.3(2)
Z	4	4	8
d _{calcd} / g cm ⁻³	1.662	1.999	1.656
μ/ mm ⁻¹	1.946	8.734	10.119
F(000)	1728	1984	3408
Crystal Size/ mm	0.05 × 0.04 × 0.02	0.12 × 0.18 ×	0.04 × 0.10 × ×
Index Range	-22 ≤ h ≤ 26	-25 ≤ h ≤ 25	-37 ≤ h ≤ 36
	20 ≤ k ≤ 22	-21 ≤ k ≤ 16	-13 ≤ k ≤ 13
	-16 ≤ l ≤ 14	-14 ≤ l ≤ 14	-23 ≤ l ≤ 23
No. of reflections	25372	45559	23401
R1, wR2 [I>2σ(I)]	0.0527, 0.1202	0.0301, 0.0750	0.0697, 0.1829
R1, wR2 (all data)	0.1396, 0.1924	0.0362, 0.0788	0.0707, 0.1833
Goodness Of Fit, F ²	1.016	1.134	1.506
No. of data/ restraints/ param	5303 / 0 / 225	4246/0/230	6050/705/508
Largest diff peak, hole/	1.226, -2.466	2.680, -1.429	1.523, -2.666

5. Table A2-2: Crystallographic data for compounds 2.7, 2.9

	2.7	2.9
Formula	C ₂₅ H ₂₄ GeMnNO ₆	C ₆₂ H ₆₄ Co ₂ Ge ₂ N ₂ O ₁₀
M _r	561.98	1260.19
Color	red	black
Crystal System	monoclinic	monoclinic
Space Group	P 1 21/c 1	P 1 21/c 1
a/Å	9.6574(11)	11.5881(3)
b/Å	12.1461(14)	12.3248(4)
c/Å	19.850(2)	19.8509(7)
α/deg	90	90
β/deg	90.545(6)	96.2727(12)
γ/deg	90	90
V/ Å ³	2328.3(5)	2818.15(15)
Z	4	2
d _{calcd} / g cm ⁻³	1.603	1.485
μ/ mm ⁻¹	1.876	1.696
F(000)	1144	1296
Crystal Size/ mm	0.100 × 0.120 × 0.320	0.240 × 0.280 × 0.340
Index Range	-12 ≤ h ≤ 12	-9 ≤ h ≤ 16
	-15 ≤ k ≤ 15	-17 ≤ k ≤ 17
	-25 ≤ l ≤ 23	-28 ≤ l ≤ 28
No. of reflections	20410	43291
R1, wR2 [I > 2σ(I)]	0.0553, 0.1083	0.0361, 0.0650
R1, wR2 (all data)	0.1049, 0.1293	0.0663, 0.0731
Goodness Of Fit, F ²	0.976	1.006
No. of data/ restraints/ param	5180/0/312	9004 / 0 / 358
Largest diff peak, hole/	1.268, -0.699	0.541, -0.401

6. Table A2-3: Crystallographic data for compounds 2.10 – 2.11

	2.10	2.11
Formula	C _{70.50} H ₆₈ Fe ₃ Ge ₂ N ₂ O ₁₅	C _{53.50} H ₅₂ Fe ₂ Ge ₂ N ₂ O ₁₂
M _r	1495.99	1171.85
Color	black	Red
Crystal System	triclinic	monoclinic
Space Group	P -1	P 1 21/n 1
a/Å	12.0501(5)	10.6982(3)
b/Å	14.6016(7)	27.2488(6)
c/Å	19.0206(9)	17.3698(4)
α/deg	86.8373(18)	90
β/deg	87.0557(16)	94.5003(8)
γ/deg	85.0601(16)	90
V/ Å ³	3325.5(3)	5047.9(2)
Z	2	4
d _{calcd} / g cm ⁻³	1.494	1.542
μ/ mm ⁻¹	1.600	1.808
F(000)	1534	2396
Crystal Size/ mm	0.040 × 0.200 × 0.340	0.040 × 0.060 × 0.120
Index Range	-17 ≤ h ≤ 17	-13 ≤ h ≤ 13
	-21 ≤ k ≤ 21	-34 ≤ k ≤ 34
	-27 ≤ l ≤ 27	-19 ≤ l ≤ 22
No. of reflections	131060	71522
R1, wR2 [I > 2σ(I)]	0.0610, 0.0942	0.0526, 0.1069
R1, wR2 (all data)	0.1638, 0.1292	0.1121, 0.1429
Goodness Of Fit, F ²	1.024	1.064
No. of data/ restraints/ param	21258 / 57 / 866	11154 / 129 / 675
Largest diff peak, hole/	1.012, -1.231	0.920, -1.228

7. The optimized geometry of compounds **2.2** and **2.7** using PBE-vdW-DF

Compound **2.2**:

Standard orientation:					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
	C	-2.604924	0.417962	0.000000	
	C	-3.673154	-0.459546	0.000000	
	C	-5.002722	-2.311614	0.000000	
	C	-5.000124	-0.034224	0.000000	
	C	-5.342367	1.319006	0.000000	
	C	-4.293790	2.247223	0.000000	
	C	-2.946638	1.815030	0.000000	
	C	-1.819805	2.731003	0.000000	
	C	-2.024168	4.221432	0.000000	
	C	0.609066	2.925770	0.000000	
	C	1.206163	3.254649	1.240900	
	C	1.206163	3.254649	-1.240900	
	C	0.543740	2.893867	2.575700	
	C	0.543740	2.893867	-2.575700	
	C	-0.166910	4.125624	3.194600	
	C	-0.166910	4.125624	-3.194600	
	C	1.538773	2.259583	3.575200	
	C	1.538773	2.259583	-3.575200	
	C	2.427427	3.952069	1.212600	
	C	2.427427	3.952069	-1.212600	
	C	3.029721	4.300183	0.000000	
	C	-0.495291	-1.336192	3.203800	
	C	-0.495291	-1.336192	-3.203800	
	C	-0.680331	-2.305473	2.176300	
	C	-0.680331	-2.305473	-2.176300	
	C	-0.135285	-3.725312	2.178600	
	C	-0.135285	-3.725312	-2.178600	
	C	1.327012	-3.848153	2.684500	
	C	1.327012	-3.848153	-2.684500	
	C	2.193509	-2.668396	2.272400	
	C	2.193509	-2.668396	-2.272400	
	C	2.384957	-1.568788	3.109500	
	C	2.384957	-1.568788	-3.109500	
	C	1.761556	-1.437975	4.493800	
	C	1.761556	-1.437975	-4.493800	
	C	0.209804	-1.620159	4.532800	
	C	0.209804	-1.620159	-4.532800	
	Cl	2.537263	0.070583	0.000000	
	Ge	-0.651039	0.127609	0.000000	
	H	-5.197495	-2.894520	0.911200	
	H	-5.197495	-2.894520	-0.911200	
	H	-6.374358	1.647533	0.000000	
	H	-4.539980	3.308420	0.000000	
	H	-2.610127	4.529910	0.874900	
	H	-2.610127	4.529910	-0.874900	
	H	-1.074473	4.764089	0.000000	
	H	-0.222268	2.131656	2.380600	
	H	-0.222268	2.131656	-2.380600	
	H	-1.016412	4.457796	2.585100	
	H	-1.016412	4.457796	-2.585100	
	H	-0.544977	3.878758	4.196000	
	H	-0.544977	3.878758	-4.196000	
	H	0.526635	4.970117	3.283200	
	H	0.526635	4.970117	-3.283200	
	H	2.323980	2.957956	3.894100	
	H	2.323980	2.957956	-3.894100	
	H	0.996507	1.928241	4.476000	
	H	0.996507	1.928241	-4.476000	
	H	2.020684	1.383951	3.123700	
	H	2.020684	1.383951	-3.123700	
	H	2.914995	4.227125	2.146400	
	H	2.914995	4.227125	-2.146400	
	H	3.960988	4.861531	0.000000	
	H	-1.239228	-0.534981	3.245300	
	H	-1.239228	-0.534981	-3.245300	
	H	-1.568115	-2.193062	1.547400	
	H	-1.568115	-2.193062	-1.547400	
	H	-0.168942	-4.076529	1.139100	
	H	-0.168942	-4.076529	-1.139100	
	H	-0.795563	-4.398846	2.757300	
	H	-0.795563	-4.398846	-2.757300	
	H	1.765122	-4.764726	2.278700	
	H	1.765122	-4.764726	-2.278700	
	H	1.340407	-3.952569	3.777600	
	H	1.340407	-3.952569	-3.777600	
	H	2.869857	-2.821487	1.429900	

H	2.869857	-2.821487	-1.429900
H	3.235603	-0.911382	2.907900
H	3.235603	-0.911382	-2.907900
H	2.235926	-2.151663	5.192800
H	2.235926	-2.151663	-5.192800
H	1.993956	-0.440365	4.875200
H	1.993956	-0.440365	-4.875200
H	-0.195418	-0.937939	5.290300
H	-0.195418	-0.937939	-5.290300
H	-0.044772	-2.636816	4.873400
H	-0.044772	-2.636816	-4.873400
N	-0.618008	2.165330	0.000000
O	-3.621435	-1.857898	0.000000
O	-5.858223	-1.124117	0.000000
Rh	0.863135	-0.948943	1.577200
Rh	0.863135	-0.948943	-1.577200

Compound 2.7:

Standard orientation:					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
	C	-5.522503	-2.647473	1.042135	
	C	-5.966369	-0.238221	2.977888	
	C	-4.028237	-1.727556	3.543228	
	C	-5.715297	-3.331685	-0.155085	
	C	4.713732	-0.141065	3.229014	
	C	3.670415	2.088662	3.815037	
	C	5.189081	2.787002	1.402478	
	C	-4.328381	3.912417	-0.129640	
	C	-3.600310	2.700748	-0.151255	
	C	-4.270360	1.408233	-0.168971	
	C	-5.780395	1.367194	-0.268750	
	C	-4.201909	-0.979356	-0.110087	
	C	-4.375246	-1.669414	-1.341899	
	C	-3.812632	-1.118233	-2.658323	
	C	-1.286529	0.442436	3.341236	
	C	-4.756880	-1.468655	1.103100	
	C	-4.605102	-0.773822	2.462955	
	C	1.046231	1.536940	-1.541855	
	C	-1.008791	0.763462	-3.224425	
	C	0.582493	1.712755	2.031869	
	C	-2.167319	2.678438	-0.144275	
	C	-1.563538	3.924340	-0.149310	
	C	-0.087290	5.655298	-0.128705	
	C	-2.291290	5.125361	-0.117614	
	C	-3.678509	5.151910	-0.105325	
	C	-1.087226	-1.464899	1.472719	
	C	1.005112	-0.834384	3.188863	
	C	1.266493	-0.439346	-3.323476	
	C	-0.537192	-1.718038	-1.988147	
	C	2.150571	-2.671054	0.160754	
	C	1.547607	-3.917874	0.174510	
	C	0.074681	-5.645637	0.055582	
	C	2.274855	-5.116922	0.079591	
	C	3.662288	-5.145185	0.047138	
	C	4.312627	-3.907339	0.085201	
	C	3.584260	-2.695902	0.131202	
	C	4.258191	-1.406470	0.142763	
	C	5.768268	-1.370831	0.228130	
	C	4.198154	0.982239	0.127441	
	C	4.407958	1.620320	1.381924	
	C	3.857586	1.038484	2.690723	
	C	4.744059	1.507532	-1.076037	
	C	4.560488	0.870558	-2.460723	
	C	-4.701856	0.003449	-3.258679	
	C	-3.556838	-2.193062	-3.744838	
	C	-5.131468	-2.852370	-1.329639	
	C	5.758519	3.302330	0.236988	
	C	5.531292	2.668942	-0.982374	
	C	5.896382	0.282135	-2.988814	
	C	4.041344	1.894281	-3.508556	
Ge		-1.400807	0.812913	-0.088965	

Ge	1.401424	-0.796400	0.103294
H	-5.964099	-3.047893	1.955651
H	-5.815343	0.381934	3.869426
H	-6.610345	-1.079208	3.262885
H	-4.699992	-2.579678	3.717202
H	-3.921989	-1.190988	4.494029
H	-6.291669	-4.251254	-0.168853
H	5.780187	0.118311	3.274110
H	4.385339	-0.393503	4.242450
H	3.152352	2.988509	3.458693
H	3.068891	1.649490	4.626343
H	4.630597	2.395402	4.249328
H	5.351206	3.307105	2.343399
H	0.412738	6.003233	-1.038613
H	-4.691044	0.912677	-2.651865
H	-3.924190	0.079542	2.354851
H	-6.497111	0.356875	2.225812
H	0.455788	5.953783	0.776722
H	-3.048789	-2.125544	3.264949
H	-4.228376	6.082549	-0.069022
H	-5.415711	3.909109	-0.122088
H	-6.165903	0.355515	-0.402335
H	-6.123750	1.983604	-1.107560
H	-6.219499	1.786971	0.643444
H	-2.849030	-0.661001	-2.417387
H	-0.481519	-6.098955	0.880730
H	-0.407110	-5.824695	-0.916233
H	4.209750	-6.076202	-0.020938
H	5.399839	-3.903289	0.059459
H	6.160139	-0.359290	0.337761
H	6.113159	-1.971564	1.077877
H	6.199337	-1.814033	-0.676347
H	2.869766	0.629358	2.460493
H	4.602741	-1.043891	2.622982
H	3.834127	0.052259	-2.378738
H	6.375362	-0.387347	-2.266535
H	3.150786	2.427208	-3.163507
H	-4.326938	0.273381	-4.252310
H	-3.034553	-3.072127	-3.347376
H	-2.934917	-1.760259	-4.544152
H	-4.490873	-2.531577	-4.210415
H	-5.265552	-3.416543	-2.248389
H	-5.742709	-0.327839	-3.367742
H	6.347241	4.213521	0.272835
H	5.961818	3.098982	-1.887159
H	5.733464	-0.275408	-3.918940
H	6.593962	1.098992	-3.210374
H	4.810969	2.645276	-3.737328
H	3.796772	1.384222	-4.446821
Mn	0.116922	0.017946	-2.000060
Mn	-0.120726	-0.004327	2.016944
N	-3.521543	0.316236	-0.120812
N	3.512318	-0.310917	0.110883
O	0.951606	2.820603	2.126751
O	-1.983212	0.720788	4.242607
O	-0.210449	4.212678	-0.152024
O	-1.444122	6.208091	-0.078621
O	1.692494	2.462121	-1.238796
O	-1.688125	1.247885	-4.051278
O	-1.752087	-2.341222	1.074330
O	1.697011	-1.401954	3.950778
O	-0.858164	-2.840884	-2.080373
O	1.925072	-0.734813	-4.247546
O	0.196075	-4.218073	0.268376
O	1.429813	-6.198460	0.025109

8. ^1H NMR spectra of compounds **2.2** - **2.7**, **2.9** – **2.11**

(i) ^1H NMR spectrum of compound **2.2**

(ii) ^1H NMR spectrum of compound **2.3**

(iii) Crude ^1H NMR spectrum from the reaction of **2.1** with 1.5 equivalents of $[\text{RhCl}(\text{cod})]_2$

(iv) ¹H NMR spectrum of compound 2.4

(v) ¹H NMR spectrum of compound 2.5

- (vi) Crude ^1H NMR spectrum from the reaction of **2.1** and 1.5 equivalents of $[\text{IrCl}(\text{cod})]_2$

- (vii) Crude ^1H NMR spectrum from the reaction of **2.1** and $\text{Mn}_2(\text{CO})_{10}$ in refluxing toluene

(viii) Solution state Evans NMR method of compound **2.9**

9. **Table 2-4:** $E(S_0)$, $E_u(T_1)$ and ΔE_{st} values^a for the studied complex at B3LYP/6-31G(d)

Complex	$E(S_0)/\text{a.u.}$	$E_u(T_1)/\text{a.u.}$	$\Delta E_{\text{st}}/\text{kcal mol}^{-1}$
Cobaltogermylene (2.9)	-9634.67831679	-9634.63570109	26.7

^a $\Delta E_{\text{st}} = E_u(T_1) - E(S_0)$. A positive value of ΔE_{st} indicates that singlet state is the ground state.

10. Table A3-1: Crystallographic data for compounds 3.4

	3.4
Formula	C _{63.50} H ₈₅ GeN ₅ O ₂ Si
M _r	1051.04
Color	red
Crystal System	triclinic
Space Group	P -1
a/Å	12.0310(4)
b/Å	12.9024(4)
c/Å	21.3468(7)
α/deg	76.2660(10)
β/deg	81.5820(10)
γ/deg	62.9540(10)
V/ Å ³	2864.05(16)
Z	2
d _{calcd} / g cm ⁻³	1.219
μ/ mm ⁻¹	0.603
F(000)	1126
Crystal Size/ mm	0.200 × 0.220 × 0.240
Index Range	-19≤h≤19
	-20≤k≤20
	-34≤l≤33
No. of reflections	63449
R1, wR2 [I>2σ(I)]	0.0546, 0.1220
R1, wR2 (all data)	0.0936, 0.1400
Goodness Of Fit, F ²	1.035
No. of data/ restraints/ param	25000 / 130 / 693
Largest diff peak, hole/	1.094, -0.919

11. Selected NMR spectra of compound **3.3** and **3.4**

(i) Crude ^1H NMR spectra for the formation of compound **3.3**

(ii) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **3.3**

(iii) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **3.4**