Studies towards the Synthesis of a Heterobimetallic Zirconium Germanium Complex from Imidozirconocenes, Germanimines and Germylenes

By

Peter Chapple

A thesis

Submitted to Victoria University of Wellington

In partial fulfilment of the requirements for the degree of

Masters of Science

In Chemistry

Victoria University of Wellington

2018

Abstract

Early-late transition metal heterobimetallic complexes with direct metal to metal interactions are desirable synthetic targets due to the complementary reactivity of the two different metals present in these compounds. The electron-rich late transition metal (often Rh, Ir, Fe, or Mo), and electron-poor early transition metal create an ideal environment for heterolytic bond cleavage in what is often termed ‘cooperative reactivity’. This project aimed to synthesise a zirconium-germanium heterobimetallic complex based on a known heterobimetallic ligand scaffold; **1**.

The synthesis of the desired heterobimetallic **1** was attempted using two different synthetic approaches. The first involved the investigating the reactivity between an unsaturated zirconium nitrogen bond (an imidozirconocene) and a germanium(II) source with a lone pair of electrons (known as a germylene). The second approach investigated the reactivity between an unsaturated germanium nitrogen bond (a germinimine) and a zirconium(II) source. In order to have the highest chance of success, a wide range of germanium and zirconium complexes were synthesised.

The novel germylenes include [Ge(NAPH^{TMS})] (NAPH^{TMS} = [1,8-((CH₃)₃Si)N)₂C₁₀H₆]) and [Ge(BIAN^{Mes})] (BIAN^{Mes} = [(2,4,6-Me(C₆H₂)N)₂C₁₂H₆])). These proved to be unreactive towards the imidozirconium species [Cp₂Zr(NAr*)(THF)] and [Cp₂Zr(NDipp)(THF)] (Ar* = (2,6-(C₆H₅)₂CH)-4-(^tBu)C₆H₂), Dipp = (2,6-((CH₃)₂CH)C₆H₃)) as well as other amidozirconocenes. However, within these studies, the mixed coordination germanium species [[Ge(NAPH^{TMS})Ge(Bu)(NAPH^{TMS})]⁻[Li(THF₄)]⁺ and [[Ge(NAPH^{TMS})Ge(Me)(NAPH^{TMS})]⁻[Li(THF₄)]⁺] were synthesised. Density functional theory (DFT) molecular orbital calculations were used to help explain the observed reactivity.

With regards to the second approach, routes to new germinimine complexes such as [(HMDS)₂Ge(NMes)] ((HMDS) = ((CH₃)₃Si)₂N), Mes = (2,4,6-CH₃(C₆H₃))), were explored, and several methods for generating “Cp₂Zr” were examined. Although these conditions proved unsuccessful for generating **1**, the reaction between dialkyl zirconocene with azides to form novel zirconocene triazenido complexes was discovered and the sterics affecting the synthesis of new germinimine complexes was investigated.

Acknowledgements

Primarily I would like to thank my research supervisor Dr. Robin Fulton, for her direction and support over the last two years. Without her guidance and patience, I would certainly not have been able to complete this thesis. Robin's flexibility and openness towards suggestions always made me feel like I had real influence and ownership of my research and made the lab work much more enjoyable.

Thank you to Assoc. Prof. Martyn Coles for his help with crystallography and for always making group meetings a pleasant experience, even when they were scheduled first thing in the morning. I would also like to thank the rest of the inorganic synthesis group, Mat, Cara, Putri, Loc, Dylan, Ryan, Struan and Amanda for making the lab an enjoyable place to work every day. Ryan deserves a special mention, as he taught me most of the practical synthetic chemistry I know and was always a useful sounding board for new ideas. To Dr. Matthias Lein, your assistance with the computational work was invaluable.

I would also like to acknowledge VUW and the Curtis-Gordon scholarship for providing me with funding over the two years.

Thanks to all my flatmates over the two years, who have had to put up with my constant facts about both chemistry and science in general, without your support writing this thesis would have been a lot more difficult. I must also thank my parents, both for their backing and for not forcing me into getting a real job when I finished my undergraduate studies. Finally, I must pay thanks to my wife Emily. Without your love (and constant reminders to keep working) this thesis would not have been possible.

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Glossary

δ	Chemical shift (ppm)
λ	Wavelength
λ_{Max}	Wavelength of maximum absorption
NMR	Nuclear magnetic resonance
^1H NMR	Proton nuclear magnetic resonance
^{13}C NMR	Carbon nuclear magnetic resonance
α	Alpha-position (adjacent atom)
$\text{\AA}$	Angstrom
Ad	Adamantyl
Ar	Some form of aryl substituent
Ar (characterisation)	Aryl or aromatic region
Approx.	Approximately
β	Beta-position (1 atom removed from adjacent atom)
Bn	Benzyl group
br	Broad signal
Bu	<i>n</i> -butyl substituent
C₆D₆	Deuterated benzene
Cp	Cyclopentadienyl ring
Cp*	Pentamethylcyclopentadienyl ring
Cy	Cyclohexyl
d	Doublet
dd	Doublet of doublets
DHA	Dihedral angle
Dipp	2,6-Diisopropylphenyl
DMP	2,6-Dimethylphenyl
eq	Equation
Eq.	Equivalence
Et	Ethyl
Et₂O	Diethyl ether
<i>i</i>Pr	Iso-propyl substituent

HMDS	Hexamethyldisilazide
HOMO	Highest occupied molecular orbital
IR	Infra-red spectroscopy
J	Scalar coupling constant (Hz)
LUMO	Lowest unoccupied molecular orbital
m	Multiplet
<i>meta</i>	Meta- position
Me	Methyl
Methine	A CH group
Mes	Mesityl group
Methylene	A CH ₂ group
<i>ortho</i>	Ortho- position
<i>para</i>	Para- position
Ph	Phenyl
ppm	Parts per million
R	An unspecified substituent
s	Singlet
t	Triplet
q	Quartet
quin	Quintet
tol	Toluene
THF	Tetrahydrofuran
^tBu	<i>Tert</i> -butyl substituent
TMS	Trimethylsilyl
UV/vis	Ultraviolet-visible spectroscopy
v	Wavenumbers (cm ⁻¹)
NCCCN	Refers to the plane defined by N ₁ -C ₁ -C ₂ -C ₃ -N ₂

List of newly synthesised compounds

Abbreviated Name	Complex Number	Structure
$[\text{Ge}(\text{BIAN}^{\text{Mes}})]$	2
$[\text{Ge}(\text{NAPH}^{\text{TMS}})]$	3
$[(\text{Ge}(\text{NAPH}^{\text{TMS}})\text{Bu})(\text{Ge}(\text{NAPH}^{\text{TMS}}))][\text{Li}(\text{THF})_4]$	4
$[(\text{Ge}(\text{NAPH}^{\text{TMS}})\text{Me})(\text{Ge}(\text{NAPH}^{\text{TMS}}))][\text{Li}(\text{THF})_4]$	5
$[\text{Ge}(\mu\text{-NAr}^*)_2]$	6
$[(\text{Cl})\text{Ge}(\text{N}(\text{Cy})\text{CNCy})\text{NAr}^*)]$	7

$[\text{Ge}(\text{NAPH}^{\text{TMS}})(\text{N}_4\text{Mes}_2)]$	8	The structure shows a central Germanium (Ge) atom bonded to a 1,2-bis(trimethylsilyl)phenyl group (NAPH ^{TMS}) and a 1,2,3,4-tetramethyl-1,2,3,4-tetraazapentalene ligand (N ₄ Mes ₂).
$[(\text{HMDS})_2\text{Ge}(\text{NMes})]$	9	The structure shows a central Germanium (Ge) atom bonded to two hexamethyldisilazide (HMDS) ligands and an N-methyl-1,2,3,4-tetraazapentalene ligand (NMes).
$[(\text{HMDS})_2\text{Ge}(\text{N}_4\text{Ph}_2)]$	10	The structure shows a central Germanium (Ge) atom bonded to two HMDS ligands and a 1,2,3,4-tetraphenyl-1,2,3,4-tetraazapentalene ligand (N ₄ Ph ₂).
$[(\text{HMDS})\text{Ge}(\text{NTMS})(\text{N}(\text{TMS})\text{Ar}^*)]$	11	The structure shows a central Germanium (Ge) atom bonded to one HMDS ligand, one trimethylsilyl (TMS) ligand, and a chiral 1,2,3,4-tetraazapentalene ligand with phenyl (Ph) and tert-butyl (tBu) substituents.
$[(\text{HMDS})_2\text{Ge}(\text{CCPh})(\text{NHMe})]$	12	The structure shows a central Germanium (Ge) atom bonded to two HMDS ligands, a 1-phenyl-2-propynyl ligand (CCPh), and an N-methyl-1,2,3,4-tetraazapentalene ligand (NHMe).
$[(\text{HMDS})_2\text{Ge}(\text{N}_2\text{OPhNC}(\text{O})\text{NMes})]$	13	The structure shows a central Germanium (Ge) atom bonded to two HMDS ligands and a 1,2,3,4-tetraazapentalene ligand with a 4-nitrophenyl (NO ₂) substituent and a carbonyl group (C=O).
$[\text{Cp}_2\text{Zr}(\text{NHDipp})(\text{Me})]$	14	The structure shows a central Zirconium (Zr) atom bonded to two cyclopentadienyl (Cp) ligands, an NHDipp ligand (where H is a hydride and Dipp is a diphenylpropyl group), and a methyl (Me) ligand.

$[\text{Cp}_2\text{Zr}(\text{Me})(\text{NHAr}^*)]$	15
$[\text{Cp}_2\text{Zr}(\text{Me})(\text{NH}(\text{DMP}))]$	16
$[\text{Cp}_2\text{Zr}(\text{NPh})(\text{Bn})]$	17
$[\text{Cp}_2\text{Zr}(\mu\text{-NPh})_2]$	18
$[\text{Cp}_2\text{Zr}(\text{NHDMP})(\text{Bn})]$	19
$[\text{Cp}_2\text{Zr}(\text{NAr}^*)(\text{THF})]$	20
$[\text{Cp}_2\text{Zr}(\text{Bu})(\text{N}_3(\text{Bu})(\text{Mes}))]$	21
$\text{Cp}_2\text{Zr}(\text{Me})(\text{N}_3(\text{Me})(\text{Mes}))$	22
$[\text{Cp}_2\text{Zr}(\text{Me})\text{N}_3(\text{Me})(\text{C}_6\text{H}_5)]$	23
$[\text{Cp}_2\text{Zr}(\text{Bn})(\text{N}_3(\text{Bn})(\text{Mes}))]$	24

<p>[Ar*N3]</p>	<p>25</p>
<p>[Ar*Cl]</p>	<p>26</p>

1 Introduction

1.1 Project Aims

The aim of this project was to synthesise an amide supported germanium – zirconium heterobimetallic complex **1**, similar to known transition metal heterobimetallic complexes.¹

Figure 1: Synthetic target heterobimetallic complex 1.

The desired complex was targeted due to its possible unique reactivity with small molecules due to having a highly polarised zirconium germanium bond. The activation of small molecules by metal complexes has traditionally been an area of research almost exclusively reserved for transition metals. However, the development of sterically demanding ligand systems that can kinetically stabilise reactive low valent main group complexes has increased the number of oxidation states commonly accessible to main group compounds. This kinetic stabilisation has led to an increase in the known chemistry of main group compounds including the synthesis of complexes with multiple bonds between the heavier main group elements, synthesis of stable low valent compounds with open coordination sites, complexes with stable paramagnetic electron configurations (radicals) with unpaired electrons centred on heavier main group elements and the development of main group complexes with frustrated Lewis pairs.²⁻⁵ Many of these main group compounds have been shown to activate a range of both polar and non-polar bonds of small molecules including H-H, N-H, C-H, B-H and Si-H bonds.⁶⁻⁸

Scheme 1: Proposed synthetic routes to the desired heterobimetallic complex 1.

Two approaches were proposed for the synthesis of **1**. The first was from the reaction of a germylene with an imidozirconocene, the second was from the reaction of a Zr(II) species (the Negishi reagent 'Cp₂Zr') with a germanimine (Scheme 1).⁹ This thesis contains the theory, synthesis and characterisation of a range of germanium and zirconium compounds used in the attempted synthesis of **1**. All compounds and precursors synthesised in this project (with the exception of zirconocene dichloride, phenylazide, meistylazide, **25** and **26**) were air and moisture sensitive, as such, all manipulations were performed under a dry and oxygen free N₂ environment using Schlenk-line and cannula techniques, or in a nitrogen filled glovebox.

1.2 Group 14 Chemistry

1.2.1 Metallene multiplicity and electronic stabilisation

Group 14 metallenes are main group MX₂ (M = Si, Ge, Sn, Pb) species with M in the +2 oxidation state and a lone pair of electrons. They are the heavier analogues of carbenes and can undergo similar chemistry to their carbon analogues.¹⁰ The lighter metallenes (M = Si, Ge) possess a nucleophilic sp²-hybrid σ-orbital, and an empty electrophilic p orbital (the p_π orbital). Heavier group 14 metallenes (M = Sn, Pb) display different reactivity to the lighter analogues due to an increasing inert pair effect. This results in the valence electrons being held more tightly to the nucleus (due to ineffective shielding by d and f orbitals) and therefore do not participate in σ bonding interactions.¹¹⁻¹² Due to this difference in reactivity, the heavier metallenes were not investigated in this project. In addition, as silylenes are less stable than germylenes, the main focus on creating a group 4-group 14 heterobimetallic complex was using germylenes.¹³ These complexes can exist as GeX₂ species (X = anionic ligand), however will readily dimerise if not kinetically stabilised using significant steric bulk on the anionic X ligand.

Group 14 metallenes can exist in either a singlet or triplet multiplicity state. The singlet state occurs when both electrons of the lone pair occupy the σ symmetry orbital (the highest occupied molecular orbital

Figure 2: Electron occupation of singlet and triplet metallene.

(HOMO)), leaving an empty p_π orbital (the lowest unoccupied molecular orbital (LUMO)), while the triplet state occurs when one electron is located in each of these orbitals (Figure 2).

The energy splitting of these orbitals generally dictates the ground state of the metallene, with high σ - p_π orbital gaps favouring the singlet ground state, and small σ - p_π energy splitting favouring the triplet ground state. The ground state of the metallene can have a large effect on the reactivity of the species, as singlet metallenes will have greater amphiphilic reactivity (acting as a Lewis acid or Lewis base), while triplet ground state metallenes react with greater radical character. The singlet state becomes more dominant moving down the group 14 metallenes, due to the increased σ - p_π orbital energy splitting, as the σ orbital increases in s-character down the group.¹⁴

The reactivity of carbenes and their group 14 metallene analogues ($X_2M:$) towards bond activation has been known to be highly dependent on the nature of the X substituent due to its effect on the HOMO-LUMO gap of the molecule. A smaller HOMO-LUMO energy gap increases the carbene's reactivity towards bond activation. For instance, it has been shown that a narrower bond angle at the group 14 centre (X-M-X) is associated with a greater s-character of the HOMO orbital, a lower HOMO energy and hence a larger HOMO-LUMO energy gap (Figure 3).¹⁵⁻¹⁶ This increased s-character is usually found in molecules with a cyclic backbone or with extremely electron withdrawing α atoms of the X substituents.

The LUMO energy can also be altered through the use of other substituents. For instance, π -donor substituents have been shown to make the LUMO molecular orbital to take on M-X π^* character, increasing the relative energy of the orbital, thus increasing the HOMO-LUMO energy gap. This occurs because the donation of electron density into the p_π^* orbital through increases its antibonding character, increasing the orbitals relative energy, resulting in carbene analogues with more π -donating ability usually existing in a singlet state due to the relative increase in the energy of the LUMO orbital.¹⁷ These strong π -donor substituents, for instance nitrogen, also normally decrease the X-M-X bond angle. DFT (density

functional theory) calculations have provided data that indicates germylenes with α substituents with weak π donor properties and high electropositivity have smaller HOMO-LUMO gaps and are therefore more kinetically labile to oxidative bond activation.¹⁶ As such germylenes with silyl and boryl α substituents generally exhibit higher reactivity than germylenes with nitrogen or phosphorus α substituents.

Figure 3: Orbital energy diagram showing relative stabilisation and destabilisation of HOMO through changes in the electronegativity of the α substituents.

The X-M-X bond angle plays an important role in the formation of singlet and triplet metallenes, with smaller bond angles ($<90^\circ$) favouring singlet species while larger angles favour triplet species, as at angles below 90° the energy of the singlet species drops below that of the triplet state.¹⁸ Bulky substituents that favour wide X-M-X bond angles therefore are more likely to adopt triplet multiplicity

1.2.2 The Synthesis of Germylenes Supported with Acyclic Nitrogen based ligands and *N*-Heterocyclic based ligands

Germylenes that have nitrogen α substituents are synthesised through two standard routes, a salt metathesis reaction with a suitably lithiated pre-ligand or transamination to give the desired compound and a free amine. A lot of early work on stable monomeric germylenes was carried out by Lappert et al.,

who synthesised the monomeric bivalent germylene using the bulky $[(\text{N}(\text{Si}(\text{Me}_3))_2)]^-$ (HMDS) ligand system by treatment of $\text{GeCl}_2 \cdot \text{dioxane}$ with $\text{LiN}(\text{SiMe}_3)_2$ to give $[\text{Ge}(\text{N}(\text{Si}(\text{Me}_3))_2)_2]$, **I** (eq. 1).¹⁹

Compound **I** was a dimer in the solid state, but as a monomeric germylene species in solution as determined by absorption data indicating the presence of a lone pair on the germanium. The monomeric unit was shown to be a singlet $:\text{MR}_2$ species.²⁰ Compound **I** has proven to be a useful precursor in the synthesis of *N*-heterocyclic germylenes (NHGe's) by transamination due to the high proton affinity of (HMDS).

Bidentate ligands that form *N*-heterocycles upon coordination have also been used to stabilise monomeric germylenes. Ligands that coordinate through nitrogen atoms offer high stability as the nitrogen can act as both a σ -acceptor and π -donor and can hence electronically stabilise many compounds. The cyclisation of these ligands provides a chelating effect, which leads to them having increased stability relative to acyclic diaminogermylenes through more favourable entropy of formation. The bis(amido)silyl ligand $[\text{iPr}_2\text{Si}(\text{NR})_2]$ ($\text{R} = \text{Dipp}$ (2,6-diisopropylphenyl), SiPh_3) has been used to synthesise 2 stable germylenes (eq.2).⁵ Compound **II(a)** and **II(b)** were generated from the lithiated ligand and $\text{GeCl}_2 \cdot \text{dioxane}$ and shown to be thermally stable up to 300 °C

Interesting solid-state data from the crystal structures of **II(a)** and **II(b)** reveal N-Ge-N bite angles of 81.26° and 83.31° respectively, as well as Ge-N bond lengths of 1.863 Å for (a) and 1.883 Å for (b). This is a relatively wide bite angle for an NHGe with a four-membered ring, indicating that the germanium atom is sitting deep into the bonding pocket of the ligand. The relatively short N-Ge bond distances of 1.863 Å for

II(a), relative to the normal range of Ge-N bond distance for nitrogen based ligands of 1.819-1.999 Å also indicates that the germanium atom sits further into the bonding pocket.^{13, 21}

The addition of 1,2 diaminobenzenes with one equivalent of the germylene **I** gives the benzannulated N-heterocyclic germylenes with various bulky substituents on the amine (equation 3).²²⁻²³ The solid state structure of **III(d)** shows shorter Ge-N bond lengths of 1.866 and 1.862 Å and a N-Ge-N bite angle of 87.17°.

Germylenes with ligand systems bearing unsaturated backbones and ring fused annulated systems have aromatic resonance structures available to them. This aromaticity plays an important role in their electronic stability with both theoretical and experimental results showing that cyclic delocalisation of electrons promotes thermodynamic stabilisation.²⁴

The BIAN^{Dipp} ligand **IV(a)** (1,2-[(2,6-*i*Pr₂C₆H₃)N]₂C₁₂H₆), **IV(b)** BIAN^{bph} (1,2-[(2-PhC₆H₄)N]₂C₁₂H₆) and **IV(c)** BIAN^{dtb} (1,2-[(2,5-*t*Bu₂C₆H₃)N]₂C₁₂H₆) have also been shown to stabilise monomeric germylene complexes using the σ acceptor and π donor properties associated with their nitrogen atoms (eq. 4).²⁵

The reduction of 1,2-bis[2,5-di-*tert*-butylphenyl]imido]acenaphthalene or other substituted acenaphthalene ligand with activated magnesium gives the monomeric magnesium complex. This compound can then undergo transmetallation with GeCl₂.dioxane to give the complexes **IV(a)**, **IV(b)** and **IV(c)**. Complex **IV(a)** can also be synthesised from the reduction of GeCl₄ with (BIAN^{Dipp})Na₄. The solid-state crystal structures show average Ge-N bond lengths of 1.891 Å for **IV(a)**, 1.878 for **IV(b)** and 1.910 Å for **IV(c)**. The N-Ge-N bond angles of 85.20°, 85.03° and 84.01° for **IV(a)**, **(b)** and **(c)** respectively, indicate

the steric bulk around the *N*-aryl ring of the ligand, with the more sterically constraining *N*-aryl groups resulting in a longer Ge-N bond length (**IV(a)** and **IV(c)**).

A similar ligand to the BIAN ligand that has also been used to synthesise monomeric germylenes is the (Z)-*N*2,*N*3-dimesityl-but-2-ene-2,3-diamine ligand (mesityl = Mes = 2,4,6 trimethylphenyl). Transamination of the preligand with **I** has led to compound **V** in a 41% yield (eq. 5). The Ge-N bond distance is 1.864 Å, and the N-Ge-N bond angle of **V** is 82.64°.

The ligand system 1,8-di(isopropylamino)naphthalene ($\text{NAPH}^{i\text{Pr}}$) has also been used to synthesise monomeric germylene compounds.²⁶ The reaction of the lithiated ligand with GeCl_2 .dioxane gives **VI**. The same compound can also be afforded by the reaction of the preligand with the germylene **I** (Scheme 2). The Ge-N bond lengths of **VI** are 1.841 and 1.842 Å and the N-Ge-N bite angle is 97.32°. The increased bite angle of the ligand is due to the larger chelate of **VI**; creating a 6-membered ring upon coordination of germanium, opposed to 5 or 4 membered rings in the previous examples. The solid-state structure of **VI** has the orientation of with both isopropyl groups sitting below the plane of the naphthalene-based backbone, with the germanium atom sitting slightly above the NCN plane (determined as the plane of the nitrogen atoms with the carbon atom in the β -position to both nitrogens).

Scheme 2: Synthesis of N-heterocyclic germylene **VI from $\text{NAPH}^{i\text{Pr}}$.**

1.2.3 The synthesis of germylenes supported other ligands

Germylenes supported by non-nitrogen based ligands have also been synthesised. Carbon, oxygen and silicon based ligands are most common; however, others are known including phosphorus and boron

based-ligands.^{16, 27-30} To limit the scope of this project due to time constraints, only nitrogen based ligands were used in the attempted synthesis of **1**. A full literature review is therefore outside the scope of this work, however other significant ligand systems used for the stabilisation of germylenes such as the terphenyl ligand will be discussed. Also included is an example highlighting the importance of sufficient steric bulk to kinetically stabilise monomeric germylene. For further information, the reader is directed to excellent reviews by Roesky et al. and Polo et al.³¹⁻³²

The importance of steric bulk in kinetically stabilising germylenes is evident from the comparison of known monomeric germylenes to their digermene dimers. The bulky terphenyl^{Mes} based ligand has been shown to kinetically stabilise monomeric germanium(II) in both the solid and liquid state.³³ The germylene [Ge(C₆H₃-2,5-Mes₂)₂]; **VII**, was synthesised from the addition of 2 equivalents of the lithiated ligand [Li(C₆H₃-2,5-Mes₂)] to GeCl₂.dioxane (eq. 6). The monoaryl derivative [Ge(C₆H₃-2,5-Mes₂)Cl] was also synthesised in the same manner using one equivalent of the lithiated ligand at -78°C.

The vital role of steric bulk in kinetic stabilisation of germylenes is highlighted by the compound tetrakis(2,6-diethylphenyl)digermene, **IX(a)**.³⁴ This species is formed from the photolysis of hexakis(2,6-diethylphenyl)cyclotrigermane, **VIII** (eq. 7). The ligand 2,6-had insufficient steric bulk to kinetically stabilise the monomeric germylene, instead the digermene is formed.

The isolation of tetramesityldigermene, **IX(b)**, also synthesised in the photolysis reaction from hexamesitylcyclogermane **VIII**, indicates that the mesityl ligand (2,4,6-trimethylphenyl) is also not bulky enough to kinetically stabilise a monomeric germylene (eq. 7)³⁵.

The bulkier 2,4,6-triisopropylphenyl ligand has also been shown to be incapable of kinetically stabilising the germylene through steric bulk, instead giving the digermene **XI**.³⁶ However the 2,4,6-*tert*-butylphenyl ligand has been shown to kinetically stabilise the germylene in solution (Scheme 3) to give the monomeric germylene **X**.

Scheme 3: Synthesis of digermene and germylene by salt metathesis.

1.2.4 Germylene Reactivity

The reactivity of germylenes has been studied for their potential use in the activation of small molecules. Variation of the HOMO-LUMO energy difference can have a large effect on the reactivity of the germylene towards a range of small molecules.

Aldridge et al. have showed that kinetically stabilised germylenes can undergo intramolecular C-H activation at room temperature.¹⁶ Compound **XII** undergoes intramolecular activation through cleavage of the C-H bond on one of the *ortho* CH₃ positions of the mesityl substituents, resulting in oxidation of the Ge(II) to Ge(IV) to give **XIII** (eq. 8).

This C-H bond activation can be rationalised by the extremely low HOMO-LUMO gap present in the germylene of 180 kJ mol⁻¹ or 1.87 eV. Other metallene systems have also shown intramolecular C-H activation. The acyclic silylene $[(\text{Me}_3\text{Si})(\text{Dipp})\text{N})\text{Si}(\text{B}(\text{NDippCH}_2)_2)]$ undergoes insertion into one of the C-H bonds of the boryl-Dipp group to give **XIV** (eq. 9).⁸

Germynes can also activate a range of small molecules, as shown by the reaction of the germylene **XV** with ammonia and dihydrogen to give **XVI** and **XVII** respectively (Scheme 4).

Scheme 4: Intermolecular N-H and H-H activation by germylene compound.

Compounds **XVI** and **XVII** were confirmed by single crystal X-ray diffraction studies. Widening of the C-Ge-Si bond angle from 112.47° to 125.16° for **XVII** and 125.79° for **XVI** is observed. Similar widening of the X-Ge-X angle has also been observed in the formation of other Si(IV) and Ge(IV) compounds in oxidative addition reactions of the respective silylene or germylene.^{8, 33} This widening due to the reduced size of Ge(IV) relative to Ge(II) and Si(II). The Ge-Si and Ge-C bond lengths of **XVI** and **XVII** also contract relative to **XV** due to the increased electrostatic attraction between the atoms.

Germynes with *N*-heterocyclic ligand systems have also been shown to be reactive towards small molecules. The germylene $[\text{CH}((\text{C}=\text{CH}_2)(\text{CMe})(2,6\text{-}^i\text{PrC}_6\text{H}_3\text{N}))_2\text{Ge}]$ has been shown to cleave an N-H bond of ammonia at room temperature to give **XVIII** (eq. 10).³⁷

Unlike the previous example the reaction does not oxidise the germanium atom, instead the protonation of the terminal methylene results in electron delocalisation across the ring of the ligand. This results in a lengthening of the Ge-N bonds of the ligand in the solid-state structure from 1.865 Å and 1.866 Å to 2.030 Å, also resulting in a narrowing of the N-Ge-N bite angle of the ligand from 95.04° to 88.60°.

1.2.5 Imido-Chemistry

Imido functional groups (RN^{2-}) are present in both organic and inorganic chemistry. Imido complexes have been shown to exhibit several different binding modes, with each having a unique reactivity. Commonly seen binding modes include the terminal bent binding mode, where the nitrogen atom has a formal double bond to another element (imido if the other element is not carbon, imine if the formal double bond is to a carbon) or symmetrically bridging, where the ligand coordinates to two other elements. Terminal linear imido complexes are extremely short and almost triple bond like in character. They occur primarily with transition metals.³⁸⁻³⁹ In this project germanium imides will be referred to as germanimines to distinguish them from the group 4 compounds, which will be referred to as imido compounds.

Figure 4: Common imido coordination modes.

Transition metal imido complexes have been synthesised through a variety of different routes. The first common synthetic method is through the deprotonation of an amido complex. Another well documented

synthesis is the reaction of halogenated compounds with an amidolithium salt. Alpha abstraction processes have also been used to synthesise imido complexes from diamido metal complexes.

1.2.6 Germanimine Synthesis and Reactivity

Germanimine complexes ($R_2Ge=NR'$) were first synthesised in the early 1990s from the reaction of sterically protected germynes with bulky azides. Despite being synthesised over twenty years ago, there are still only 12 examples of germanimines; as such they remain a rarity.⁴⁰⁻⁴¹ The first germanimine **XIX**, was synthesised by the treatment of the bulky germylene $[Ge(N(SiMe_3)(Dipp))_2]$ with $[N_3(Dipp)]$ in THF at room temperature.

The single crystal X-ray diffraction study showed the solid state structure had a trigonal planar geometry around the germanium atom (Σ internal angles = 359.97°), and a $Ge=N$ double bond length of $1.703(2)$ Å.⁴² $Ge-N$ single bond distances were shown to be $1.819(3)$ Å and $1.826(3)$ Å, making the $Ge-N$ bonds approximately 0.12 Å longer than the $Ge=N$ bond. This 0.12 Å contraction was considered a relatively small bond contraction for a double bond, with the authors commenting that most double bond contractions occur more in the order of 0.20 Å.

Bis(germanimines) have also been synthesised from the addition of a diazidosilane to bis(bis(trimethylsilyl)methyl)germylene to give the bis(germanimine) **XX** with the evolution of a colourless gas (eq. 12).⁴¹

Wesemann et al. have also synthesised a germanimine **XXII** using a bulky azide to oxidise the terphenyl stabilised germylene as the kinetic product.⁴³ Upon heating the germanimine to 45 °C for 5 days the germanimine underwent an intramolecular rearrangement to give a phosphinimide **XXII** as the thermodynamic product.

Scheme 5: Synthesis of Wesemann's tetrylene complex using adamantyl azide.

When there is insufficient steric bulk to kinetically stabilise the germanimine, the imine undergoes an [3+2] cycloaddition with an equivalent of azide to form an extremely stable tetrazene product (eq. 13).

Two such germanes are the *N*-heterocyclic supported compound **XXIII** and the bis-amide supported germane **XXIV**.^{23, 44} These reactions highlight the importance of the use of sufficient steric bulk in both the azide and the germylene to sufficiently kinetically stabilise the desired germanimine.

Figure 5: Germanes **XXIII** and **XXIV**, products of azide insertion into germanimine bond.

1.2.7 Low oxidation state germanium donor interactions

Mixed geometry bimetallic germanium amide species have previously been synthesised from reactions of germanium(II) sources with bulky amide ligands.⁴⁵⁻⁴⁶ These compounds have been shown to exhibit different geometrical orientations at each germanium atom, and hence have interesting and unique bonding properties that highlight the multiple coordination modes of germanium. Two of these compounds are that of Leung et al.'s germanium-iron heterobimetallic compound **XXV** and Jones's bulky germanium dimer **XXVI** after activation of hydrogen in the solid state (Figure 6).

Figure 6: Leung's complex (**XXV**) and Jones's germanium dimer after hydrogen addition (**XXVI**).

XXV is a unique heterobimetallic that has germanium atoms present in both a tetrahedral and trigonal pyramidal geometry. The germanium atoms are in the +1 oxidation state, but are both kinetically

stabilised through the use of steric bulk and electronically stabilised by the donation of nitrogen atom from the pyridyl ring. The lone pair on the one of the germanium atoms acts as a donor to the iron atom of the $[\text{Fe}(\text{CO})_4]$ moiety, while the lone pair on the other germanium atom is acting as a stereochemically active lone pair. In Jones's molecule **XXVI**, a kinetically stabilised germanium compound, the two germanium atoms are also in different geometries, with the 4-coordinate geometry having a tetrahedral geometry while the 2-coordinate germanium has a bent geometry. The two germanium atoms are in different oxidation states, with the 4-coordinate geometry being in the formal +3 oxidation state while the 2-coordinate geometry is formally in the +1 oxidation state. These complexes show the high number of oxidation states and coordination numbers available to kinetically stabilised germanium, and highlight its possible potential use in catalytic heterobimetallic complexes.

Figure 7: Resonance structures of XXVII and XXVIII.

Alcarazo et al. and Rivard et al. have also described interesting germanium compounds displaying unique donor properties allowing oligerimisation (**XXVII** and **XXVIII**).⁴⁷⁻⁴⁸ Compound **XXVII** shows a molecule germanium dichloride supported with a donor carbodiphosphorone ligand. The effect this has on the germanium dichloride molecule is that the lone pair of electrons on the germylene can then donate into an empty p orbital of another equivalent of germanium dichloride, giving a negative charge on the germanium atom, depending on how the structure is drawn due to its resonance forms (Figure 7). The donation of the lone pair of electrons into the empty p orbital of the second equivalent of germanium dichloride is highlighted by the almost 90° bond angles between the to Ge-Ge-Cl bonds. The NHC donor stabilised compound **XXVIII** exhibits the exact same donor-acceptor interaction between germanium dichloride units. These compounds show the ability for germanium(II) to be used as a σ donor for suitable acceptor compounds.

1.3 Group 4 Chemistry

1.3.1 Zirconium Imides – Imidozirconocenes

Donor stabilised imidozirconocene complexes $[\text{Cp}_2\text{Zr}=\text{NR}(\text{THF})]$ could also provide an intermediate towards synthesis of the desired imido bridged zirconium germanium product. The first zirconium bearing a terminal imide ($\text{Zr}=\text{NR}$) was reported in 1988 as the THF adduct $[\text{Cp}_2\text{Zr}=\text{N}(\text{tBu})(\text{THF})]$.⁴⁹ The compound was formed from $[\text{Cp}_2\text{Zr}(\text{Me})(\text{N}(\text{H})(\text{tBu}))]$, **XXIX**, which is synthesised either from the reaction of $[\text{Cp}_2\text{Zr}(\text{Me})_2]$ with $[\text{NH}_2\text{tBu}]$ in benzene at 80°C , or from the reaction of $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ with the lithium salt $[\text{Li}][\text{NHtBu}]$ at 25°C in THF. Heating of $[\text{Cp}_2\text{Zr}(\text{Me})(\text{N}(\text{H})(\text{tBu}))]$ in THF for 3 days at 85°C led to the elimination of methane, giving $[\text{Cp}_2\text{Zr}=\text{N}(\text{tBu})(\text{THF})]$, **XXX** in a 71% yield (Scheme 6).

Scheme 6: Synthesis of imidozirconocene **XXX through thermolysis to eliminate methane.**

More recently, imidozirconocenes have been shown to be synthesised from the readily available starting material $[\text{Cp}_2\text{ZrCl}_2]$.⁵⁰ When the lithium amine salt $[\text{Li}][\text{NHR}]$ ($\text{R} = 4\text{-CMe}_3\text{-C}_6\text{H}_4$, $2,6\text{-Me}_2\text{-C}_6\text{H}_3$) is added to $[\text{Cp}_2\text{ZrCl}_2]$ in THF at room temperature the alkyl amide $[\text{Cp}_2\text{Zr}(\text{N}(\text{H})(\text{R}))_2]$ is formed ($\text{R} = 4\text{-CMe}_3\text{-C}_6\text{H}_4$, $2,6\text{-Me}_2\text{-C}_6\text{H}_3$). Thermolysis of this bisamidozirconocene generated the imidozirconocene through the extrusion of an amine, however; due to the reversible nature of this reaction the imidozirconocene was not isolable.

The choice of amide is important in the synthesis of the imidozirconocene. Amines without sufficient steric bulk will readily undergo [2+2] cycloadditions upon generation of the imidozirconocene to give the imido bridged dimer (Figure 8). An example of this is the bis(μ -imido) dimer $[\text{Cp}_2\text{Zr}(\mu\text{-N}(4\text{-Me}_3\text{CC}_6\text{H}_4)_2)_2]$, **XXXI(d)** which indicates that the *para-tert-butyl-phenyl* is functionally too small to prevent dimerisation.

Figure 8: Imido bridged zirconocene dimer XXXI(d).

However, *tert*-butyl and Dipp groups have been shown to be bulky enough to suppress dimerisation of the imidozirconocene, allowing isolation of the imidozirconocenes **XXX** and **XXXI(a)** respectively. Similarly, when the zirconocene used has one pentamethylcyclopentadienyl ligand (Cp^*) instead of a Cp ligand, the imido complex **XXXI(b)** can also be isolated.⁵¹ Hence the steric bulk of the Cp ligands also plays a role on the stability of the imidozirconocene. Figure 9 provides a range of crystallographic data for THF adduct monomer imidozirconocene complexes.⁵²

Table 1: Relevant bond distances and angles for a range of imidozirconocene complexes.

	Zr=N (Å)	Zr-N-C (°)	Zr-Cp (Å)
$\text{Cp}_2\text{Zr}=\text{N-}^t\text{Bu}(\text{THF})$, XXX	1.826(4)	174.4(3)°	2.325
$\text{Cp}_2\text{Zr}=\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{THF})$, XXXI(a)	1.888(2)	159.1(2)°	2.312(1), 2.277(1)
$\text{CpCp}^*\text{Zr}=\text{N-}p\text{-tol}(\text{THF})$, XXXI(b)	1.881(3)	168.4(2)°	2.2799(3), 2.2725(3)
$\text{CpCp}^*\text{Zr}=\text{N-}^t\text{Bu}(\text{THF})$, XXXI(c)	1.846(2)	169.5(2)°	2.3268(3), 2.2835(2)

XXX

XXXI(a)

XXXI(b)

XXXI(c)

Figure 9: Complexes shown in Table 1.

The data in Table 1 shows a more obtuse Zr-N-C bond angle in the Dipp substituted imide (**XXXI(a)**) relative to the other three complexes, reflecting the increased steric bulk at the 2,6 positions of the phenyl ring. Comparing **XXX** to **XXXI(c)** reveals a decrease in the Zr-N-C bond angle from 174.4(3)° to 169.5(2)°, indicating that the Cp* ligand results in a more obtuse bond angle than the Cp ligand. The Zr-N bond length is also longer in **XXXI(c)** 1.881(3) Å than in **XXX** 1.826(4) Å. These structural changes between **XXX** and **XXXI(c)** are likely a result of the increased electron donating ability and increased steric bulk of the Cp* ligand. The data in Table 1 also indicates that the alkyl-imido complexes have shorter Zr=N distances than the aryl-imido complexes. An example of this is the comparison of CpCp*Zr=N-*p*-tol(THF) and CpCp*Zr=N-*t*Bu(THF). The increased steric bulk of the *tert*-butyl over the *p*-toluidine would lead to the assumption that the Zr=N distance in Zr=N-*t*Bu would be longer than in the less sterically hindered Zr=N-*p*-tol. However, from the data obtained by the authors this was not the case. Investigating the orbital arrangement of the systems lead to the explanation for the observed lengthening and shortening of the Zr=N bond. The Zr-N σ bond is primarily made up of the interaction between an imide orbital of a_1 symmetry and an orbital from the Cp₂Zr fragment with $2a_1$ symmetry. The π component of the Zr-N bond is formed through the interaction between the matching b_2 orbital of the imide and zirconium respectively. The third nitrogen based orbital of b_1 symmetry cannot interact with the vacant a_1 orbital on the zirconium fragment, as the only orbital on the zirconium fragment with b_1 symmetry is a high energy orbital Zr-Cp antibonding character. The poor energetic overlap between the imide and zirconium based b_1 orbitals is probably a weak interaction due to this significant energy difference. As such the Zr-N interaction can best be thought of as a double bond with a large, filled nonbonding orbital present on the nitrogen atom.⁵³ However, the disparity in bond lengths between the aryl and alkyl substituted imidozirconocenes indicate that the imide b_1 symmetry orbital is probably not entirely dissociated from the Zr-N bonding. The lengthening of the Zr-N bond in the arylimido species indicates that the nitrogen based b_1 orbital of the *N*-arylimido complex is stabilized by the π system of the *N*-aryl substituent. This separates the Zr fragment and imide based b_1 orbitals further, reducing the impact on the Zr-N bonding. This stabilisation is not present in the alkylimide substituents, and as such, the energy matching between the b_1 orbitals of the nitrogen and zirconium fragment is slightly improved, resulting in a stronger interaction (a shorter bond).

As the molecular orbital arising from the interaction of the two aforementioned b_1 orbitals has antibonding character, the Zr-Cp distance observed would be expected to decrease for the alkyl imidozirconocene complexes over the aryl imidozirconocene complexes. This is observed in the data in Table 1, in which there is a 0.05-0.06 Å increase in the Zr-Cp bond lengths.

Figure 10: Relative orbital energy diagram of alkyl and aryl imidozirconocenes.

Imidozirconocenes have also been shown to undergo a range of reactions with various substrates. One such reaction is the [2+2] cycloaddition between imidozirconocenes and small unsaturated molecules such as heterocumulenes.⁵⁴ When the THF adducts of the imidozirconocenes $\text{Cp}_2\text{Zr}=\text{N}(\text{R})$ were treated with various symmetrical carbodiimides, diazametallacycles were formed in high yields (Scheme 7).

Scheme 7: Reactions of imidozirconocenes with various heterocumulenes.

Increasing the steric bulk of the imidozirconocene resulted the [2+2] cycloaddition reaction occurring only in the case of less bulky carbodiimides such as $i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$. Although there were two possible regioisomers as potential products of the cycloaddition, one in which a zirconium carbon bond would be formed and one in which a zirconium nitrogen bond would be formed, only one of the products (the zirconium nitrogen bond) was formed.

As imidozirconocenes readily undergo [2+2] cycloadditions they have also been investigated for their potential use as catalysts in imine metathesis and in the hydroamination of alkynes.⁵¹ When $\text{CpCp}^*\text{Zr}=\text{N}^t\text{Bu}(\text{THF})$ is used as a catalyst for the olefin metathesis of $p\text{-TolCH}=\text{CH-}p\text{-Tol}$ with $\text{PhCH}=\text{CHPh}$ a 1:1:1:1 equilibrium mixture of the imines $p\text{-TolCH}=\text{NPh}$ and $\text{PhCH}=\text{N-}p\text{-Tol}$ were generated along with the alkene starting materials. (Scheme 8).

Scheme 8: Catalytic cycle of imidozirconocenes mediated imide metathesis.

The use of imidozirconocenes as catalysts for the hydroamination of alkynes has also been achieved (Scheme 9).

Scheme 9: Catalytic cycle of imidozirconocene mediated alkyne hydroamination.

Imidozirconocenes have also had their reactivity towards azides investigated.⁵⁵⁻⁵⁷ The imidozirconocene have been shown to undergo [3+2] cycloadditions with azides to form tetrazene products (Scheme 10). Compound **XXXIV(a)** was characterised by a single crystal X-ray diffraction study. The Zr-N bond lengths were 1.380 Å, longer than the the N=N bond length of 1.281 Å. The tetrazene ligand had a N-Zr-N bond angle of 75.2°, smaller to that of **XXIII** (82.62°) and **XXIV** (82.21°).

Scheme 10: Synthesis and reactivity of tetrazene zirconium complexes from an imidozirconocene.

These tetrazene compounds have also been shown to react with methylacetylene, with the methylacetylene inserting into the N-N bond to synthesise the insertion products **XXXIV(b)** and **XXXV**. Of these products, only **XXXV** has been characterised by X-ray diffraction, and provides an interesting comparison to the triazenido ligand due to the lack of resonance structures and structural rigidity provided by the NC=CN=N bonding motif.⁵⁸

1.3.2 Zirconium-Germanium compounds

Zirconium germanium compounds are rare, but there have been two examples of a Zr-Ge bond being characterised by X-ray diffraction. The transmetalation reaction of 1,2-dipotassiotetrakis(trimethylsilyl)digermene with magnesium bromide followed treatment with zirconocene dichloride results in the zirconocenedigermene complex **XXXVI** (Scheme 11).⁵⁹ The only characterisation of this compound was by ¹H NMR spectroscopy. When the compound **XXXVI** was treated with trimethylphosphine, the phosphine adduct **XXXVII** was isolated in the solid state and characterised by an X-ray diffraction study. The ²⁹Si NMR spectrum suggested partial germylene character of the coordinated digermene.

Scheme 11: Synthesis of XXXVII from XXXI.

More recently the reaction of a disilylated five membered cyclic germylene with a range of group IV metallocene dichlorides has been reported.⁶⁰ The reduction of the group IV metallocene dichlorides with

magnesium in the presence of the germylene triethylphosphine adduct in THF gave the metallocene germylene compounds as triethylphosphine adducts (eq. 14).

The products were isolated and characterised using single crystal X-ray diffraction. For all three products the germanium atom sits in the metallocenes equatorial plane, with the bidentate silicon chelating ligand near orthogonal to this plane. This is also observed in the equivalent stannylene and plumbylene compounds, as well as known titanocene and hafnocene silylene complexes isolated as either trimethylphosphine, THF or isonitrile adducts.⁶¹⁻⁶³ The authors propose that this orientation leads to favourable orbital overlap between transition metals filled d orbitals and the empty germylene p_{π} orbital. For complex **XXXVIII**, the Ge-Zr bond distance was found to be 2.63 Å in the solid state, significantly shorter than the 2.87 Å and 2.89 Å Ge-Zr bond previously reported for the aforementioned zirconocene germane species. This shortening of the bond reflects the double bond character associated with the heterobimetallic complex **XXXVIII**. The bonding in the complex is described by a σ -bonding, π -backbonding Scheme shown in Figure 11.⁶⁰

Figure 11: Orbital energy diagram showing bonding interaction of the heterobimetallic complex XXVII and relative stabilisation and destabilisation of the π and π^* orbitals.

1.4 Imido-Bridged Bimetallic Compounds Synthesis and Reactivity

Early-late transition metal heterobimetallics have been studied in the past due to the complementary reactivity of the two different transition metals present in the compounds. The electron-rich late transition metal (often Rh, Ir, Fe, or Mo), and electron-poor early transition metal create an ideal environment for heterolytic bond cleavage in what is often termed 'cooperative reactivity'.⁶⁴⁻⁶⁵

A heterobimetallic compound is any compound that contains in its structure two different metal atoms. These compounds often have unique chemistry that is significantly different from the properties of the individual metals, are hence are of interest due to the unique and unpredictable properties these compounds contain.

The synthesis of the early-late imido bridged heterobimetallic $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{-IrCp}^*]$ has previously been reported.⁶⁵ The addition of 2 equivalents of $n\text{-BuLi}$ to $[\text{Cp}_2\text{ZrCl}_2]$ at $-30\text{ }^\circ\text{C}$ in THF followed by addition of $[\text{Cp}^*\text{Ir}\equiv\text{N}^t\text{Bu}]$ led to compound **XXXIX** (Scheme 12).

Scheme 12: Synthesis of heterobimetallic XXXIX via the Negishi reagent.

Compound **XXXIX** was subjected to a wide reactivity study with H_2 , PhMeSiH_2 , H_2NAr , $t\text{BuOH}$, $p\text{-tolylOH}$, $(\text{CH}_3)_2\text{CO}$, H_2S and HPeEt_2 . The resulting compounds from addition of these compounds is shown in Scheme 13. Compound **XXXIX** reacts with both polar and non-polar substrates. Most reactions occur as addition reactions across the Ir-Zr bond, as these centers are both electron deficient regarding the 18 electron rule (both Zr and Ir have 16 electron configurations). In this reactivity, zirconium acts as a Lewis acid while iridium acts as a Lewis base.

The complex **XXXIX** was shown to react with X-H bonds ($\text{X} = \text{H}$, $\text{SiPh}(\text{H})\text{Me}$, NHAr , $\text{O-}p\text{-tolyl}$, $\text{O-}t\text{Bu}$, $\text{CH}_2\text{C}(\text{O})\text{CH}_3$) to form a new metallacycle with a bridging hydride ligand coordinated to the iridium and zirconium centres, and the X functionality bound to the zirconium centre (Scheme 13). The proposed mechanism for these reactions involves the complexation of the hard heteroatom to the zirconium center, followed by a proton transfer to the iridium center.

Scheme 13: Reactivity of complex XXXIX with a range of polar small molecules.

However, complex **XXXIX** also showed different reactivity towards other substrates. The reaction with H_2S produced a new metallacycle with a bridging sulfur ligand and the evolution of hydrogen gas. The addition of the more sterically demanding *p*-thiocresol resulted in two products in equilibrium; the product shown in Scheme 14, as well as the hydrogen bridged complex with the thiol on the zirconium atom. The reaction of complex **XXXIX** with the phosphine HPeEt_2 also produced a new metallacycle, with a bridging phosphine. However, the insertion of the phosphine into the complex was not between the Ir-Zr bond, but the Ir-N bond.

Scheme 14: X-H Addition to complex XXXIX.

2 Results and Discussion: Group 14 Chemistry

This chapter discusses the synthesis and reactivity of some novel germanium compounds including germynes, mixed coordination germanium compounds and germanimines. The germynes and germanimines were synthesised for their use in the synthesis of **1**, while the mixed coordination compounds are discussed due to their unique bonding interactions. Density functional theory (DFT) molecular orbital calculations were also used to investigate the reactivity and bonding in the germynes and mixed coordination germanium compounds. Finally, DFT was also used to investigate the change in structure and bonding of the heavier group 14 complexes (M = Ge, Sn, Pb) for the [(1E)-N1,N2-dimesitylacenaphthylene-1,2-diimine]; [BIAN^{Mes}] and [N1,N8-bis(trimethylsilyl)naphthalene-1,8-diamine]; [NAPH^{TMS}] ligands.

2.1 Germylene Synthesis

N-heterocyclic germynes were synthesised due to their ease of synthesis and the ready availability of the required starting materials. As previously mentioned, the properties of NHGes over other germenylene varieties is limited, however due to the advantages discussed earlier a mix of known and previously unknown NHGe species were synthesised.

2.1.1 [Ge(BIAN^{Mes})] synthesis **2**

[Ge(BIAN^{Mes})], **2** was synthesised in a two-step process. Addition of [(1E)-N1,N2-dimesitylacenaphthylene-1,2-diimine]; [BIAN^{Mes}-H] to magnesium turnings in THF resulted in the formation of a green solution after 3 days at 100 °C, from which dark violet [(BIAN^{Mes})Mg(THF₃)] was isolated. Compound **2** was then formed by addition of a THF solution of this compound to GeCl₂.dioxane at -30 °C.

Scheme 15: Synthesis of **2 from [BIAN^{Mes}] preligand.**

The ^1H NMR spectrum of **2** revealed two singlets at δ 2.29 and 2.26 ppm integrating to 12 and 6 protons respectively, corresponding to the methyl groups on the *N*-mesityl functional group. The resonance at δ 6.92 ppm integrating for 4H is assigned to the *meta*-protons of the *N*-mesityl group. Three additional resonances were found corresponding to the *ortho*, *meta* and *para* position of the naphthalene backbone at δ 6.59 (doublet), 6.90 (triplet), and 7.20 (doublet), respectively. The ^1H NMR spectrum is indicative of a complex with a plane of symmetry.

Figure 12: *Ortho*, *meta* and *para* positions of **2.**

Dark brown crystals suitable for an X-ray diffraction study were grown after layering a concentrated toluene solution of **2** with hexane and letting stand at room temperature for 5 days. The solid-state crystal structure of [Ge(BIAN^{Mes})] reveals two molecules in the asymmetric unit (molecule A and B) with similar bond lengths and angles, as such, only one molecule A will be described. The angle between the mesityl group and BIAN backbone in molecule A is 86.19° and 87.61°. This angle is similar to that of other BIAN-germanium complexes. For instance, in compound **IV(a)** the angle between the *N*-aryl plane and the BIAN backbone is 86.15° and 88.98°. The planes of the phenyl rings in each of the mesityl groups do not sit in plane with each other and instead have an angle between planes of 8.36°. The Ge-N bond length of molecule A is 1.891 and 1.880 Å, similar to **IV(a)** (1.885 and 1.897 Å) but shorter than **IV(c)** (1.904 and 1.915 Å) and longer than **IV(b)** (1.878 Å). These are also longer than the Ge-N bond lengths of **V** of 1.864 Å. The N(3)-Ge(2)-N(4) bite angle of 84.39° is similar to **IV(a)**, **IV(b)** and **IV(c)** (85.20°, 85.03° and 84.01°), but larger than **V** (82.84°), indicating that the different backbone of **2** has the germanium atom sitting further in the binding pocket of the ligand.²⁵

Figure 13: ORTEP representation of 2. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 2: Selected bond lengths and angles of 12.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.894(2)	N(1)-Ge(1)-N(2)	84.39(9)
Ge(1)-N(2)	1.893(2)	Ge(1)-N(1)-C(13)	129.08(16)
N(1)-C(13)	1.369(3)	Ge(1)-N(2)-C(22)	127.31(15)
N(2)-C(22)	1.370(3)	N(1)-C(1)-C(3)	135.2(2)
C(1)-C(2)	1.379(4)	N(1)-C(1)-C(2)	115.0(2)
N(1)-C(1)	1.435(3)	N(2)-C(2)-C(11)	135.3(2)
N(2)-C(2)	1.429(3)	N(2)-C(2)-C(1)	115.3(4)

2.1.2 [Ge(NAPH^{TMS})] synthesis 3

[Ge(NAPH^{TMS})] **3** was synthesised from the *N*1,*N*8-bis(trimethylsilyl)naphthalene-1,8-diamine preligand [NAPH^{TMS}-H] *via* lithiation and salt methathesis. Lithiation with 2 equivalents of *n*-BuLi afforded the lithiated intermediate salt of the ligand which underwent salt metathesis with GeCl₂.dioxane in THF to give the germylene [Ge(NAPH^{TMS})] as orange crystals. [Ge(NAPH^{TMS})] was characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, UV-Vis spectroscopy and single crystal X-ray diffraction.

Scheme 16: Synthesis of 3 using [NAPH^{TMS}] ligand.

The ¹H NMR spectrum of **3** has a downfield shift in resonance attributed to the *N*-TMS functional group from [NAPH^{TMS}-H] to δ 0.34 ppm from 0.18 ppm. The three aromatic peaks in the naphthalene backbone are seen as a doublet of doublets at δ 7.21 ppm for the *para* protons, a triplet at δ 7.13 ppm for the *meta* protons and a doublet of doublets at δ 6.71 ppm for the *ortho* protons.

Figure 14: *Ortho*, *meta* and *para* positions of **3.**

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **3** in hexane. The solid-state crystal structure data of **3** shows one molecule in the asymmetric unit. The molecule shows a twisted naphthalene backbone with one of each of the nitrogen atoms sitting above or below the plane of the naphthalene ring. The *N*-TMS groups also sit above Si(2) and below Si(1) the naphthalene plane respectively. The twist in the naphthalene backbone is quite pronounced, and is exhibited by the angle between the C(1)-C(5) and C(6)-C(10) planes of 5.77(6)°. This is a significantly twisted structure compared to complexes **VI** and other diaminonaphthalene based ligands, in which the naphthalene ring is normally completely planar as would be expected of an sp^2 hybridised system.⁶⁶⁻⁶⁸ Complex **III(d)** has similar Ge-N bond distances of 1.866 and 1.862 Å, indicating the size of the carbon backbone has little influence on the ligands coordination to germanium.²³ **3** has longer N-Si bond lengths than **VI** of 1.842 and 1.841 Å. The change in Ge-N bond length when comparing *N*-*i*Pr to *N*-TMS likely results from the increased steric bulk associated with the TMS group over the *i*Pr group, as well as the difference in electronics due to the lower electronegativity of Si over C resulting in more electron density on the nitrogen atoms and shorter Ge-N bond distance. The solid-state structure of **3** differs significantly to the compound [Sn(NAPH^{TMS})] (**XL**), in which the tin atom sits above the plane of the naphthalene ring with the *N*-TMS groups sitting below the plane.⁶⁶

Figure 15: ORTEP representation of **XL, showing out of the NCCCN plane tin atom.**

This indicates that the tin(II) cannot fit into the bonding pocket of the ligand plane, presumably due to the larger ionic radii on Sn(II) over Ge(II). However, it is interesting that in the solid-state structure of **3** the

naphthalene backbone twists to accommodate the germanium atom, opposed to being isostructural with **XL** with the metal atom sitting above the plane of the naphthalene backbone, as the large extended π system of the [NAPH^{TMS}] would be expected to result in a linear naphthalene backbone, with a high energy barrier to the conformational twisting required to fit Ge(II) in plane.

Figure 16: ORTEP representation of **3**. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 3: Selected bond lengths and angles of **3**.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.8641(16)	N(1)-Ge(1)-N(2)	98.11(7)
Ge(1)-N(2)	1.8577(16)	Ge(1)-N(1)-Si(1)	114.67(10)
N(1)-C(1)	1.413(2)	Ge(1)-N(2)-Si(2)	116.34(10)
N(2)-C(9)	1.405(2)	Ge(1)-N(2)-C(9)	123.34(12)
		Ge(1)-N(1)-C(1)	124.31(12)
		N(1)-C(1)-C(10)	121.80(15)
		N(2)-C(9)-C(10)	121.51(15)

2.1.3 Attempted synthesis of [Pb(NAPH^{TMS})]

The synthesis of [Pb(NAPH^{TMS})] was also attempted from using the same synthetic route that was successful for **3**. After workup, a yellow solution was observed to change over a number of days to give a vibrant dark green solution, identified as **XLI** by single crystal X-ray diffraction and ¹H NMR spectroscopy. **XLI** has been previously synthesised from the decomposition of the thallium compound [Tl₂(NAPH^{TMS})] at 90 °C.⁶⁹ It is presumed that, like the thallium compound, the lead complex [Pb(NAPH^{TMS})] also undergoes demetallation to give **XLI** and a black solid assumed to be elemental lead. Our results suggest that the lead complex is a better synthetic route to **XLI**, as, unlike the thallium complex, the solution gave **XLI** at -30 °C (Scheme 17).

Scheme 17: Synthesis of **XLI** from attempted synthesis of [Pb(NAPH^{TMS})].

2.2 DFT Analysis of Group 14 Structures

To further investigate the structure, bonding and potential reactivity of the synthesised germylenes relative to their heavier group 14 analogues (Sn, Pb) geometry optimisations and molecular orbital (MO) density functional theory (DFT) calculations were carried out. Structures were optimized in the PBE1PBE/def2SVP level of theory for geometry optimisations and PBE1PBE/def2TZVP level of theory for molecular orbital calculations.

2.2.1 [Ge(NAPH^{TMS})]

The geometry optimisation of **2** gave bond lengths that agree well with the bond lengths of the solid-state crystal structure data. Other calculated computational information such as stretching frequencies, partial

charges and molecular orbitals can provide useful insight about the structure, bonding and reactivity of inorganic complexes and will therefore be discussed.

Table 4: Crystal structure bond lengths. Computational bond lengths in brackets. The NCN plane is defined as the plane of the nitrogen atom with the carbon atom β to both nitrogen atoms.

	[Ge(NAPH ^{TMS})]	[Ge(NAPH ^{TMS})]	[Sn(NAPH ^{TMS}) (XL)]	[Sn(NAPH ^{TMS})]	[Pb(NAPH ^{TMS})]
M-N (Å)	1.864	[1.863]	2.100	[2.078]	[2.186]
	1.858	[1.863]	2.100	[2.078]	[2.186]
N-C (Å)	1.413	[1.404]	1.383	[1.402]	[1.398]
	1.405	[1.404]	1.390	[1.402]	[1.398]
N-Si (Å)	1.772	[1.797]	1.735	[1.782]	[1.766]
	1.770	[1.979]	1.746	[1.782]	[1.766]
C-C average (Å)	1.405	[1.408]	1.405	[1.409]	[1.411]
M-NCN Plane	4.31°	[0.01°]	35.26°	[0.01°]	[29.35°]

Table 4 compares bond lengths for gas phase optimised structures and the crystal structure data (either obtained or literature values). The solid-state bond distances agree well with the theoretical gas-phase bond distances. Also included is the angle between the metal atom and the plane of the two nitrogen atoms and the β carbon atom to these nitrogen atoms (the NCN plane). This was included as in the crystal structure data it was noted that as progresses down group 14 the metal atom sits further out of plane with the NCN atoms. This is likely due to the increasing ionic radii of the metal ions (Ge²⁺ 87 < Sn²⁺ 118 < Pb²⁺ 133 pm) resulting in the binding pocket being too small. Interestingly, the DFT calculations only expect this out of plane conformation for the lead atom, but the crystal structure data clearly shows that in the solid-state structure of the tin complex **XL**, this out of plane effect is pronounced.

Figure 17: Frontier molecular orbitals of [Ge(NAPH^{TM_S})].

To gain more insight into the trend of potential reactivity for the heavier group 14 structures molecular orbital (MO) calculations were carried out to compare the energy gap of the frontier molecular orbitals. The molecular orbital calculations were completed using the PBE1PBE/def2TZVP level of theory on the geometry optimized gas-phase structures. The MOs for [Ge(NAPH^{TM_S})] are depicted in Figure 17. The HOMO of the complex appears to be strongly located on the π system of the naphthalene ring with density delocalized onto the nitrogen atoms. The LUMO has a major contribution from the empty p orbital, while the LUMO+1 has the electron density located both on the π system of the naphthalene ring and as a node on the germanium atom. The HOMO-LUMO energy gap, used commonly as an indicator for potential reactivity of inorganic complexes was calculated to be 354 kJ mol⁻¹ (3.67 eV). This is a relatively large energy gap for a germylene and would indicate that the complex is likely unreactive towards a range of small molecules.

2.2.2 [Sn(NAPH^{TMS})]

The frontier molecular orbitals for [Sn(NAPH^{TMS})] (**XL**) show similar areas of electron density as the [Ge(NAPH^{TMS})], with the HOMO electron density being located on the π system of the naphthalene ring, while the LUMO electron density is mainly located on the empty p orbital of the tin atom, with a small amount of electron density on the p orbitals of the nitrogen atoms.

Figure 18: Frontier molecular orbitals of [Sn(NAPH^{TMS})].

The orbital size the empty p orbital electron density of the LUMO has increased relative to **3**, though this effect was not quantified using NBO calculations due to time constraints. The HOMO-LUMO energy gap was calculated to be 294 kJmol⁻¹ (3.05 eV), 60 kJ mol⁻¹ lower than for the germylene complex, indicating [Sn(NAPH^{TMS})] would be more reactive towards a range of small molecules.

2.2.3 [Pb(NAPH^{TMS})]

For completeness, the frontier molecular orbitals were also calculated for the complex [Pb(NAPH^{TMS})]. The results showed the continued trend as group 14 is descended; the molecular orbitals have the electron density located on the π naphthalene ring and the nitrogen atoms in the HOMO, while the LUMO has the majority of the electron density located in the empty p orbital on the lead atom.

Figure 19: Frontier molecular orbitals of [Pb(NAPH^{TMS})].

The summary of the MO calculations is summarised in Table 5 and Figure 19. The data shows that as group 14 descends the energy of the LUMO decreases while the HOMO increases in energy, decreasing the HOMO-LUMO energy gap. This would be expected to result in a higher reactivity for the heavier [NAPH^{TMS}] compounds.

Table 5: Relative orbital energies calculated for **3**, XL and [Pb(NAPH^{TMS})].

	[Ge(NAPH ^{TMS})]	[Sn(NAPH ^{TMS})]	[Pb(NAPH ^{TMS})]
HOMO-1 (kJ mol ⁻¹)	-656.36	-624.85	-588.10
HOMO(kJ mol ⁻¹)	-496.21	-483.08	-467.33
LUMO(kJ mol ⁻¹)	-141.77	-189.03	-212.66
LUMO+1 (kJ mol ⁻¹)	-76.14	-68.26	-76.14
HOMO-LUMO (kJ mol ⁻¹)	354.43	294.05	254.67
HOMO-LUMO (eV)	3.67	3.05	2.64

Figure 20: Diagram showing energy of frontier MO's for [NAPH^{TMS}] compounds.

For a comparison, the [BIAN^{Mes}] heavier group 14 compounds (Ge, Sn, Pb) were also investigated computationally to gain insight into their bonding and reactivity. A comparison with the crystal structure data can only be made for [(GeBIAN^{Mes})], as the other two complexes ([Sn(BIAN^{Mes})] and [Pb(BIAN^{Mes})] were not able to be synthesised. Unlike the group 14 compounds supported with the [NAPH^{TMS}] ligand, all three of the optimised structures for the [BIAN^{Mes}] ligand predict that the metal atom will sit in the plane of the N-C=C-N ligand backbone. This is surprising when comparing the results to the [NAPH^{TMS}] optimisations, as [BIAN^{Mes}] would be expected to have a smaller binding pocket. The data suggests that as the metal atom ionic radii increases the metal to nitrogen bond length increases, the lengthening of this bond paired with the decreasing electronegativity as group 14 descends results in a shortening of the N-C bond lengths to both the carbon backbone of the ligand and to the mesityl groups. This could be due to the significant increase in negative charge located on the nitrogen atoms for the tin and lead complexes, likely due to the significantly lower electronegativity for these metals compared to germanium.⁷⁰

Table 6: Crystal structure of selected bond lengths compared to computationally derived optimized bond lengths.

	[Ge(BIAN ^{Mes})] (2)	[Ge(BIAN ^{Mes})]	[Sn(BIAN ^{Mes})]	[Pb(BIAN ^{Mes})]
M-N (Å)	1.891	[1.905]	[2.130]	[2.240]
	1.889	[1.905]	[2.130]	[2.240]
N-C (Å)	1.375	[1.365]	[1.359]	[1.352]
	1.371	[1.365]	[1.359]	[1.352]
N-C(Mes) (Å)	1.429	[1.422]	[1.419]	[1.415]
	1.431	[1.422]	[1.419]	[1.415]
C=C (Å)	1.379	[1.386]	[1.398]	[1.406]
M-NC=CN Plane (°)	0.32	[0.01]	[0.01]	[0.00]
Partial Charge on Metal		[0.145]	[0.405]	[0.408]
Partial Charge on N		[0.060]	[-0.279]	[-0.278]

2.2.4 [Ge(BIAN^{Mes})]

The calculated frontier molecular orbitals of [Ge(BIAN^{Mes})] show the electron density of the HOMO sits in the π system of the 5-membered heterocyclic ring, with a slightly larger coefficient of electron density on the germanium atom relative to the rest of the heterocyclic ring. The LUMO has the electron density calculated as occupying the π system of the naphthalene based carbon backbone of the ligand, with no electron density on either the germanium atom or the mesityl groups. The LUMO+1 orbitals almost exclusively have the electron density on an empty p orbital of the germanium atom. The calculated HOMO-LUMO gap for [(Ge(BIAN^{Mes})] is 304.55 kJmol⁻¹, 3.16 eV) which indicates that the energy barrier to reactivity is smaller for [(Ge(BIAN^{Mes})] than [Ge(NAPH^{TMS})]. This, however, does not consider any steric activity on reaction rate, so cannot be thought of as a definitive indication of reactivity.

Figure 21: Frontier molecular orbitals for [Ge(BIAN^{Mes})].

2.2.5 [Sn(BIAN^{Mes})]

The gas phase geometry optimisation shows the mesityl groups on the nitrogen atoms sit orthogonal to the plane of the sp^2 hybridised carbon backbone of the ligand. This compound probably exists in this conformation to minimise steric repulsion between the methyls in the 2,6 positions of the mesityl group

with the tin atom and with the carbons of the sp^2 hybridised carbon backbone of the ligand. The frontier molecular orbitals of $[\text{Sn}(\text{BIAN}^{\text{Mes}})]$ show the electron density of the HOMO located on the π system of the tin, nitrogen and α -carbon atoms, while the LUMO orbital electron density is located on the π system of the sp^2 hybridised carbon backbone. The HOMO energy of $[\text{Sn}(\text{BIAN}^{\text{Mes}})]$ is $-446.33 \text{ kJ mol}^{-1}$, slightly higher energy than the complex $[\text{Sn}(\text{NAPH}^{\text{TMS}})]$ ($-483.08 \text{ kJ mol}^{-1}$). The LUMO energy of $-162.78 \text{ kJ mol}^{-1}$ is also higher energy than $[\text{Sn}(\text{NAPH}^{\text{TMS}})]$, but the actual HOMO-LUMO energy gap ($283.55 \text{ kJ mol}^{-1}$) is less than the $[\text{Sn}(\text{NAPH}^{\text{TMS}})]$ ($294.05 \text{ kJ mol}^{-1}$). This indicates that the $[\text{Sn}(\text{BIAN}^{\text{Mes}})]$ complex would likely be more reactive towards small molecules than the complex $[\text{Sn}(\text{NAPH}^{\text{TMS}})]$. The LUMO orbital electron density is located on the π system of the naphthalene ring and the α carbons bonded to the nitrogen atoms. The electron density of the LUMO+1 is located on a p orbital of the tin atom, the same as the germanium analogue.

Figure 22: Frontier molecular orbitals for $[\text{Sn}(\text{BIAN}^{\text{Mes}})]$.

2.2.6 $[\text{Pb}(\text{BIAN}^{\text{Mes}})]$

The gas phase geometry optimisation of $[\text{Pb}(\text{BIAN}^{\text{Mes}})]$ showed the same conformation as the germanium and tin analogues with the mesityl plane orthogonal to the plane of the sp^2 hybridised backbone. The metal to nitrogen bond lengths lengthen, as would be expected due to the increased ionic radii of Pb(II) meaning it will sit further outside the binding pocket relative to the Ge(II) and Sn(II) . The length of the N-C of the sp^2 hybridized system shortens from 1.359 to 1.352 Å from Sn to Pb, while the C-C(Mes) bond

also shortens from 1.419 to 1.415 Å. This could be due to the decreased electron density on nitrogen as group 14 is descended, as is evident from the partial charges on the nitrogen atom going from Ge to Pb (Table 7).

The frontier molecular orbitals for $[\text{Pb}(\text{BIAN}^{\text{Mes}})]$ show a significant difference in the LUMO electron density from the lighter two group 14 analogues. For the Ge and Sn complexes the LUMO electron density was located almost entirely on the π system of the carbon backbone of the ligand, with the LUMO+1 having its electron density located on the metal π orbital of the metal. For Pb these molecular orbitals are reversed, with the LUMO of the Pb complex being lower in energy than the increasing energy of the MO relating to the π system of the carbon backbone of the ligand (Table 7). This implies that as group 14 descends, this orbital becomes a more energetically favourable state. The partial positive charge on the metal atom of the complexes can also be seen to increase as group 14 descends. This could be a function of either the decreasing electron density of the metal ions, although due to the increasing inert pair effect as the group descends it would be expected that the partial charge on the metal might decrease as more electron density is located on the metal (and therefore not in bonding MO bonding combinations).

Figure 23: Frontier Molecular orbitals for $[\text{Pb}(\text{BIAN}^{\text{Mes}})]$.

The summary of the MO calculations for the $[\text{BIAN}^{\text{Mes}}]$ complexes is summarised in Table 7 and Figure 24. The data shows that as group 14 descends the energy of the LUMO does not significantly change while the HOMO increases in energy, decreasing the HOMO-LUMO energy gap. This would be expected to result in a higher reactivity for the heavier $[\text{BIAN}^{\text{Mes}}]$ compounds.

Table 7: Crystal structure of selected bond lengths compared to computationally derived optimised bond lengths.

	$[\text{Ge}(\text{BIAN}^{\text{Mes}})]$	$[\text{Sn}(\text{BIAN}^{\text{Mes}})]$	$[\text{Pb}(\text{BIAN}^{\text{Mes}})]$
HOMO-1 (kJ mol^{-1})	-614.35	-603.85	-595.97
HOMO(kJ mol^{-1})	-475.20	-446.32	-425.32
LUMO(kJ mol^{-1})	-170.65	-162.78	-168.03
LUMO+1 (kJ mol^{-1})	-118.14	-160.15	-154.90
HOMO-LUMO (kJ mol^{-1})	304.55	283.55	257.29
HOMO-LUMO (eV)	3.16	2.94	2.67

Figure 24: Diagram showing energy of frontier MO's for $[\text{BIAN}^{\text{Mes}}]$ compounds.

2.3 Mixed Coordination Germanium Species:

The anionic species $[\text{Ge}(\text{NAPH}^{\text{TMS}})\text{Ge}(\text{Bu})(\text{NAPH}^{\text{TMS}})]^-$ **4** and $[\text{Ge}(\text{NAPH}^{\text{TMS}})\text{Ge}(\text{Me})(\text{NAPH}^{\text{TMS}})]^-$ **5** have been synthesised by the addition of *n*-BuLi or MeLi to **3** in THF. In both **4** and **5** the overall negative charge of the species appears to be located on the three-coordinate germanium in an interesting donor-acceptor type relationship. The complexes were originally synthesised accidentally during the synthesis of **3**, when the $[\text{NAPH}^{\text{TMS}}\text{-H}]$ preligand was lithiated *in situ* before its addition to GeCl_2 . Residual *n*-BuLi in the reaction reacted with **3**, resulting in the formation of **4**. Complex **4** and **5** were more easily synthesised from the addition of half a molar equivalent of either *n*-BuLi or MeLi to clean samples of **3**. Although the complexes are not relevant to the synthesis of the desired heterobimetallic **1**, the complexes are reported here as they have unique structure and bonding properties, as well as giving some insight into the reactivity of germylene **3**.

2.3.1 $[\text{Ge}(\text{NAPH}^{\text{TMS}})\text{Ge}(\text{Bu})(\text{NAPH}^{\text{TMS}})]^- [\text{Li}(\text{THF}_4)]^+$ **4**

The ^1H NMR spectrum for **4** displayed many new resonances compared to the free germylene **3**. The most significant of these resonances are the high field signals attributed to the incoming alkyl fragment (δ 1.19-1.14, 0.75, 0.50 ppm), which would be expected to show four resonances; however, the signal at δ 0.50 ppm appears to be two overlapping signals, as is evident from its integration (four protons). The ^1H NMR spectrum also has two new resonances attributed to the two different TMS environments in the high field (δ 0.54, 0.44 ppm), both of which integrate to 18 protons. The resonances at δ 3.29 and 1.23 ppm are attributed to the four THF molecules solvating the lithium ion (also confirmed by the solid-state crystal structure), but it should be noted that these shifts are upfield shifted from free THF in C_6D_6 resonances (δ 3.57 and 1.40 ppm respectively) which would be expected due to the electronic influence of the lithium ion.⁷¹

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **4** in THF. The solid-state crystal structure data of **3** shows the Ge(1) in a distorted trigonal pyramidal arrangement with three coordinating atoms while Ge(2) is in a distorted tetrahedral arrangement (Figure 25). The Ge(1)-Ge(2) bond length of 2.6222 Å is longer than that of **XXV** (Ge-Ge 2.611 Å), shorter than **XXVII** (Ge-Ge 2.881 Å), and significantly longer than the sum of two Ge covalent radii (2.44 Å).^{45-46, 72} The asymmetric unit cell of **4** shows 1 molecule with a 4 coordinate tetrahedral germanium (Ge(2)) supported by the N-heterocyclic [NAPH^{TMS}] ligand and an alkyl chain, and a second 3 coordinate germanium (Ge(1)) atom supported with the same N-heterocyclic [NAPH^{TMS}] ligand. A THF solvated lithium ion balances the charge of the negatively charged germanium to make the unit cell a neutral species.

Figure 25: Diagram of potential bonding interaction of **4 and **5**.**

The different coordination numbers at each of the germanium atoms means that the bite angles of the two N-heterocyclic ligands are different, as can be seen by the N(1)-Ge(1)-N(2) bond angle being 91.70(6)^o while the N(3)-Ge(2)-N(4) bond angle is 92.53(7)^o. The angle the germanium sits out of the nitrogen-naphthalene plane is also significantly different for the two germanium atoms, with Ge(2) sitting further out of this plane than Ge(1). The complex appears to be best described as a mixed coordination germanium complex, where the tetrahedral geometry Ge(2) and trigonal pyramidal Ge(1) are in the Ge(II) oxidation state. As can be seen from Table 8 the Ge(2)-N bond lengths of 1.9162(12) and 1.9189(12) Å are shorter longer than the Ge(1)-N bond lengths of 1.9433(12) and 1.9295(12) Å, and are at the top range of Ge(IV)-N bond distances seen in the literature, which tend to range from 1.80-1.91 Å, indicating a Ge(II) oxidation state on Ge(2).⁷³⁻⁷⁸ The Ge(1) atom sits significantly out of the NCN plane (the plane defined by the nitrogen atoms and the naphthalene backbone) of the ligand relative to the free germylene unlike the free germylene **3**, in which the germanium atom sits almost exactly in plane. The Ge(1)-N bond lengths are also significantly longer than in the free germylene. Both of these effects are attributed to the donation of electron density into the empty p orbital of Ge(1) from Ge(2), resulting in a change to the idealised sp² hybridisation present in the free germylene.

Figure 26: ORTEP representation of 4. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 8: Selected bond lengths and angles of 4.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-Ge(2)	2.6222(2)	Ge(2)-Ge(1)-N(2)	102.63(5)
Ge(1)-N(1)	1.9433(12)	Ge(2)-Ge(1)-N(1)	95.32(4)
Ge(1)-N(2)	1.9295(12)	Ge(1)-Ge(2)-N(3)	129.47(4)
Ge(2)-N(3)	1.9162(12)	Ge(1)-Ge(2)-N(4)	107.04(4)
Ge(2)-N(4)	1.9189(12)	Ge(1)-Ge(2)-C(33)	117.93(7)
Ge(2)-C(33)	1.9901(14)	N(3)-Ge(2)-C(33)	102.07(7)
		N(4)-Ge(2)-C(33)	101.76(6)
		Ge(2)-N(3)-Si(3)	124.51(8)
		Ge(2)-N(4)-Si(4)	124.13(7)
		Ge(1)-N(2)-Si(2)	116.52(6)
		Ge(1)-N(1)-Si(1)	117.27(6)
		N(1)-Ge(1)-N(2)	91.70(6)
		N(3)-Ge(2)-N(4)	92.53(7)

2.3.2 [Ge(NAPH^{TMS})Ge(Me)(NAPH^{TMS})]⁻[Li(THF₄)]⁺ **5**

The ¹H NMR spectrum of compound **5** has two new resonances from the TMS environments (δ 0.38, 0.37 ppm), which have a small chemical shift downfield from the free germylene (δ 0.34 ppm). There are two peaks at δ 3.11 and 1.09 ppm integrating for 8 protons each which are assigned to the four THF atoms solvating the lithium ion. These signals are shifted significantly upfield from the free THF in C₆D₆ shift, and are also significantly higher field than the solvating THF signals present in the ¹H NMR spectrum of **5**, indicating the THF molecules are somehow more shielded in the methyl complex than in the butyl complex **4**. The aromatic protons are attributed to 5 signals at δ 7.27 (doublet, 2H), 7.22 (doublet, 2H), 7.15-7.12 (multiplet, 4H), 6.93 (doublet, 2H) and 6.84 (doublet, 2H).

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **5** in THF. The solid-state data for **5** shows that the asymmetric unit contains one molecule of the Ge anion and one THF solvated Li⁺ counterion. The geometry around the germanium atoms is similar to **4** with Ge(1) having distorted trigonal pyramidal geometry while Ge(2) has distorted tetrahedral geometry. The Ge(1)-Ge(2) bond length of 2.632 Å is longer than is the analogous butyl complex **4** (2.622 Å). The bite angle of the naphthalene based ligands are 91.16° and 92.68° for N(1)-Ge(1)-N(2) and N(3)-Ge(2)-N(4) respectively,

which are similar to the butyl complex (91.70° and 92.53°), implying that the steric effect of the alkyl fragment has little effect of the bonding of the naphthalene moieties to the germanium atoms. The Ge(1)-N bond distances of 1.954 and 1.947 Å are slightly longer in the methyl complex than the butyl complex (1.943 and 1.930 Å). The Ge(2)-N bond distances (1.915 and 1.925 Å) are slightly shorter than Ge(1)-N bond distance. The trigonal pyramidal geometry at Ge(1) indicates that the lone pair is stereochemically active, and that therefore the germanium is analogous to 3-coordinate germanium anions [GeR₃]⁻. Although this anionic germanium is common, it is more frequently seen in cluster compounds or chalcogen and halogen stabilised phosphonium salts.⁷⁹⁻⁸⁴ Interestingly, the germanium atom Ge(1) sits significantly out of the NCCCN plane relative to the free germylene as in **4**. This also aligns with the significant lengthening of the 3 coordinate Ge(1)-N bond lengths from 1.85-1.86 Å in **3** to 1.94-1.95 Å in **5**. This would be expected if Ge(2) was donating its lone pair of electron density into the empty p orbital of Ge(1) in the proposed dative bond.

Table 9: Selected bond lengths and angles of 5.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-Ge(2)	2.6323(6)	Ge(2)-Ge(1)-N(2)	96.30(9)
Ge(1)-N(1)	1.954(3)	Ge(2)-Ge(1)-N(1)	96.44(9)
Ge(1)-N(2)	1.947(3)	Ge(1)-Ge(2)-N(3)	115.45(9)
Ge(2)-N(3)	1.915(3)	Ge(1)-Ge(2)-N(4)	121.09(11)
Ge(2)-N(4)	1.925(3)	Ge(1)-Ge(2)-C(33)	119.59(11)
Ge(2)-C(33)	1.980(4)	N(3)-Ge(2)-C(33)	101.31(16)
		N(4)-Ge(2)-C(33)	101.97 (16)
		Ge(2)-N(3)-Si(4)	121.29(18)
		Ge(2)-N(4)-Si(3)	124.97(19)
		Ge(1)-N(2)-Si(2)	120.59(17)
		Ge(1)-N(1)-Si(1)	118.29(16)
		N(1)-Ge(1)-N(2)	91.16(13)
		N(3)-Ge(2)-N(4)	92.68(14)

Figure 27: ORTEP representation of 5. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

To gain further insight into the bonding of the anionic germanium species DFT calculations were run using the PBE1PBE/def2SVP level of theory for geometry optimisations and PBE1PBE/def2TZVP level of theory for molecular orbital calculations. To simplify the calculations the solvated lithium ion was excluded from calculations and the molecules were instead run with an overall negative charge. For compound **4**, the partial charge calculations showed the charge on the two germanium atoms differed, with Ge(1) having a partial charge of (- 0.08) while Ge(2) had a positive charge of (+ 0.164) (appendix 5.5). These values are both lower than the charge on Ge on the free germylene **3**, which was calculated on the same basis set to be (+ 0.219). The negative charge of the molecule is primarily located on the carbons of the TMS groups, as well as on the nitrogen atoms in the *N*-heterocyclic ring. The positive charges are primarily located on the silicon atoms of the TMS groups and on Ge(2). The carbons present in the naphthalene rings appear to have both positive and negative partial charges, while the butyl group bonded to Ge(2) has partial negative charges on the carbon atoms, as would be expected of a alkyl fragment.

For comparison to **4**, partial charges of the anionic species **5** were also calculated. Once again for simplicity the solvated lithium counterion was omitted from the calculations. After a geometry optimisation the molecular orbitals and partial charges were calculated for the compound as a singlet anion. Comparing the data to the butyl species **4**, the methyl ligand in **5** carries a much higher negative charge (-0.419 compared to -0.223 at the α -carbon) than the butyl fragment, but the butyl fragment overall carries more of the fraction of relative negative charge compared to the methyl fragment. It can also be seen that Ge(2) carries a reduced partial positive charge (0.127) relative to Ge(2) in the butyl complex **4** (0.164). This reduced charge on Ge(2) together with the increased charge on Ge(1) (0.029 compared to -0.008) gives some insight into the electronic state of the Ge complexes, and offers some explanation for why the Ge(1)-Ge(2) bond distance in the methyl complex is longer than in that of the butyl complex (2.632 Å compared to 2.622 Å).

Table 10: Selected bond lengths and angles of **4 and **5**, calculated quantities shown in brackets.**

	Complex 5	Complex 4	Complex [5]	Complex [4]
N-Ge-N angle (°)	91.16	91.7	[90.17]	[90.29]
N-Ge[R]-N (°)	92.68	92.53	[92.21]	[92.30]
Ge-N (Å)	1.954, 1.947	1.943, 1.930	[1.936], [1.960]	[1.944], [1.966]
Ge[R]-N (Å)	1.915, 1.925	1.916, 1.919	[1.918], [1.913]	[1.913], [1.917]
Ge-R (Å)	1.9801	1.9901	[1.972]	[1.985]
N-Ge(1)-Ge(2)* angle (°)	99.13	102.9	[100.76]	[100.74]
N-Ge(2)-Ge(1)* angle (°)	133.22	132.18	[135.12]	[133.26]
Ge-Ge (Å)	2.6323	2.6222	[2.613]	[2.609]
NGeN-NGeN Torsion angle (°)	172.74	158.17	[159.18]	[158.64]

Interestingly the NGeN-NGeN torsion angle for the two species is significantly different for the two compounds (172.74° and 158.17° for the methyl and butyl species respectively). The data would suggest that the steric profile of the butyl substituent plays a much greater role than the methyl group. As shown in Table 10, the computational data agrees well with the the experimental solid-state data, except that there is a discrepancy between the torsion angle for the methyl compound **5**. The most stable conformation for complexes **4** and **5** from both the computational optimisation appears to be an eclipsed conformation (as viewed down the Ge-Ge bond) (Figure 28). However, the experimental crystal structure evidence of **5** suggests that when the methyl substituent is used the lowest energy conformation is instead an staggered arrangement in which the lone pair on Ge(1) is staggered between the two Ge(2)-N bonds (Figure 28).

Figure 28: Conformations of **4 and **5** as viewed down the Ge(1) Ge(2) bond for solid-state data of **4** (eclipsed), and **5** (staggered).**

The best description of the bonding present in the compounds **4** and **5** appears to be an interaction similar to the Ge(II) $\rightarrow$ Ge(II) dative bonds of (**XXVII**) and (**XXVIII**).⁴⁷⁻⁴⁸ Though while **XXVII** is zwitterionic, **4** and **5** instead have a lithium counterion. For **XXVII** the authors reasoning for the dative germanium-germanium bond was that due to the strong donor capacity of the carbodiphosphorane, making the germanium that the diphosphorane donates its lone pair to is rendered basic enough then react with a second equivalent on GeCl_2 . The suggested evidence for this is the shortening of the Ge-Cl bonds on the 'donor' germanium atom shortening from 2.063 to 1.960 Å.

DFT studies conducted on species **4** and **5** also offer an insight into their structure and bonding. For compound **4** the HOMO has electron density mostly on the Ge(1) lone pair, as well as a smaller electron density on the Ge(2) lone pair. The HOMO also shows a small amount of electron density present in the π system of the naphthalene backbone on Ge(1). The LUMO shows electron density almost exclusively located on the π system of the naphthalene ring on the Ge(2) naphthalene fragment. To gain an indication of the possible reactivity of complex **4** towards small molecules the energy gap of the frontier molecular orbitals was calculated. The HOMO of **4** was stabilised relative to **5** with an energy of $-231.04 \text{ kJ mol}^{-1}$. The LUMO was also lower in energy in **4** than in complex **5**, with an energy calculated to be $157.53 \text{ kJ mol}^{-1}$. This gave a HOMO-LUMO gap of 0.403 eV or $388.57 \text{ kJ mol}^{-1}$. This data is tabulated in Table 11. This large energy barrier to reactivity was also observed in experimental result, in which stoichiometric reactions with a range of unsaturated small molecules (DIC, PhNCNPh, PhCOPh, MesN_3) gave no observable products by ^1H NMR spectroscopy.

HOMO

HOMO-1

LUMO

LUMO+1

Figure 29: Frontier molecular orbitals of 4.

HOMO

HOMO-1

LUMO

LUMO+1

Figure 30: Frontier molecular orbitals of 5.

The structure of **5** shows that the electron density of the HOMO is primarily a σ -lone pair orbital with a significant coefficient on the germylene acceptor atom and the π orbitals of the nitrogen atom bonded to this germanium, with a small amount of electron density on the π orbitals of the naphthalene ring of the acceptor fragment to the species. The LUMO electron density is a π orbital on the donor germylene naphthalene backbone, with no electron density shown on either of the germanium atoms.

The HOMO-LUMO energy gap was calculated to give an indication of the possible reactivity of the species towards small molecules. The energy of the HOMO was calculated to be $-225.79 \text{ kJ mol}^{-1}$ while the LUMO was calculated to be $162.78 \text{ kJ mol}^{-1}$. This gives a frontier molecular orbital energy gap of 4.03 eV or 388 kJ mol^{-1} . This energy gap is relatively large (larger than the HOMO-LUMO gaps of **2** and **3**), and may indicate that the germanium species is relatively stable, indeed the physical properties of the species indicated this, with the dimer being stable in the solid state for 6 months and not decomposing when heated in benzene up to 80°C .

Table 11: Calculated frontier molecular orbital energy gaps for 4 and 5.

	Compound 4	Compound 5
HOMO-1 (kJ mol^{-1})	-244.17	-238.92
HOMO(kJ mol^{-1})	-231.04	-225.79
LUMO(kJ mol^{-1})	157.53	162.78
LUMO+1 (kJ mol^{-1})	165.40	173.28
HOMO-LUMO (kJ mol^{-1})	388.57	388.57
Energy (eV)	4.03	4.03

2.4 Bulky germanium amides.

2.4.1 Attempted Synthesis of $[\text{Ge}(\text{NAr}^*)_2]$

Due to the low reactivity of the NHGe molecules **2** and **3** it was decided that a more reactive germylene species should be synthesised. Bis-amide germylenes have been shown to be more reactive than NHGe s, hence it was decided that a new germylene would be synthesised using the bulky primary amine $[\text{NH}_2\text{Ar}^*]$ ($\text{Ar}^* = 2,6\text{-dibenzhydryl-4-}(tert\text{-butyl})\text{phenyl}$). The free amine was lithiated using $n\text{-BuLi}$ in situ before being added to half an equivalent of $\text{GeCl}_2\cdot\text{dioxane}$ (Scheme 18). Although it was expected that this reaction would lead to the bis-amide, the product that was obtained was instead the cyclic amido bridged dimer **6** $[(\text{Ge}(\mu\text{-NAr}^*))_2]$.

Scheme 18: Reaction of bulky lithiated amines with germanium dichloride.

2.4.2 Synthesis of $[(\text{Ge}(\mu\text{-NAr}^*))_2]$ **6**

6 was originally synthesised from the attempt to generate germanium bis-amide $[\text{Ge}(\text{NAr}^*)_2]$ and was characterized by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, elemental analysis and single crystal X-ray diffraction. The ^1H NMR of the crystalline product shows the downfield shift of the *tert*-butyl ($t\text{Bu}$) peak to δ 1.13 ppm from δ 1.11 ppm (for the free amine) in deuterated benzene. The singlet at δ 5.47 ppm from the methine (CH) environment is shifted downfield to δ 6.43 ppm, which would be expected due to the deshielding effect of the germanium atom. The ^1H NMR spectrum also shows a strong new doublet in the aromatic region at 7.27 ppm, while the remainder of the aromatic protons are seen as multiplets overlapping with residual toluene in the sample.

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **6** in toluene. However, due to incomplete collection of the data resulting in obscurities in the X-ray crystal structure data, analysis of the compound was not possible, however, connectivity was able to be confirmed.

Figure 31: ORTEP representation showing connectivity of 6. Hydrogens omitted for clarity.

The use of bulky amines such as 2,4,6 tributylaniline, terphenyl^{Mes}amine and 2,4,6 trifluoroaniline in the synthesis of bulky amide germanium dimers previously been reported, although the manuscripts only offer speculation as to the reaction mechanism for the formation of the dimer.⁸⁵⁻⁸⁷

Figure 32: Amido-bridged germanium compounds XLIII and XLIV.

Three different synthetic pathways were proposed by Lappert et al. in the synthesis of **XLIII**. Firstly, it was proposed that after the formation of the mono-lithiated amine salt the subsequent addition of

GeCl₂.dioxane could react at the mono-amide chloride bridged dimer **XLV(a)** (Scheme 19). This would then react further to either go to the bis-amide and onto the imine **XLV(b)**. Secondly, after formation of the chloride bridged dimer, it was proposed that elimination of HCl could also generate the germanimine directly (**XLV(b)**). Thirdly, the germanium tetracycle could also be formed from the amide bridged complex **XLV(c)**, with the elimination of an equivalent of free amine. To further investigate the possible reaction pathway, it was decided that we would try to trap Lappert's proposed germanimine intermediate species **XLV(b)** with a carbodiimide, to see whether the [2+2] cycloaddition product could be synthesised and characterised.

Scheme 19: Lappert's different proposed synthetic pathways to XLIII.

2.4.3 Synthesis of [(Cl)Ge(N(Cy)C(NHCy)NAr*)] **7**

In order to trap out the possible intermediate germanimine in a [2+2] or [2+3] cycloaddition, the reaction to synthesise **6** was carried out again, but in the presence of dicyclohexylcarbodiimide (DCC). However, instead of the a germylene being synthesised through a cycloaddition with DCC, the product **7** was synthesised in good yields (eq. 16). Compound **7** was synthesised using equal molar amounts of the lithiated amine [NH₂Ar*], dicyclohexylcarbodiimide (DCC) and GeCl₂.dioxane. After stirring in THF overnight and extraction into toluene the sample was purified by crystallisation at -30 °C. The crystalline product was characterised by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, elemental analysis and single crystal X-ray diffraction.

Unfortunately, the synthesis of **7** doesn't assist in determining the reaction mechanism for the synthesis of **6**, as the DCC is appears to be reacting with the chloride bridged monoamide germylene similar to **XLV(a)**, before the generation of the germanimine **XLV(b)**. The ¹H NMR spectrum of complex **7** shows a range of new high field signals from the phenyl rings, though interestingly the compound has more than the 4 expected resonances in this region. Integration of the peaks indicates that while two of the phenyl rings are still equivalent in solution, the other two phenyl rings are in different chemical environments. The ¹H NMR spectrum also indicates that the meta protons on the NAr* phenyl backbone are no longer equivalent, which further indicates that the molecule is asymmetric in solution. The *tert*-butyl chemical shift is upfield from the free amine (δ 1.11 ppm) at δ 1.08 ppm. There are a range of weak signals from the cyclohexyl group from δ 1.45 to 0.10 ppm; however, due to the relatively low intensity of these signals they have been assigned as multiplets since J_{HH} coupling constants could not be determined.

Figure 33: Structure of compound XLVI.

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **7** in toluene. The solid-state crystal structure data has one molecule of **7** present in the asymmetric unit, along with two disordered toluene molecules modelled as rigid bodies at half occupancy. The solid -state data reveals that the complex is a germanium-guanidinate compound, with the bulky *N*-Ar* located α to the germanium atom, with delocalised electron density across the N(1)-C(1)-N(2) atoms. The molecule is trigonal pyramidal at Ge, with the lone pair being stereochemically active. **7** has a Ge-Cl bond distance of 2.3148(9) Å, longer than the Ge-Cl bond distance of GeCl₂.dioxane of 2.250 Å. The Ge-N bond distances of **7** are 2.024(3) and 1.998(3). The Ar* and cyclohexyl (Cy) group bonded to the α nitrogens are located above and below the Ge(1)-N(1)-N(2) plane. The structure indicates a possible electronic interaction between one of the flanking phenyl rings of the Ar* group and the germanium atom, though it is also possible that this is just a crystal packing effect. The distance of the centroid of this phenyl ring to the germanium atom is 3.3639(15) Å. The bite angle of the guanidinate ligand is 65.73(2)°. The most similar compound to **7** is the aluminium guanidinate **XLVI** (Figure 33).⁸⁸ The guanidinate ligand has a bite angle of 67.35°, larger than that of **7**, although this would be expected due to the smaller radii of Al(III) compared to Ge(II). The Al-N bond distances of 2.027 and 1.922 Å are slightly shorter than in **7**, though because the ligand is coordinating to another metal the comparison is not a great one. Other complexes with guanidinate ligands were deemed structurally to different for useful comparisons to be made.⁸⁹⁻⁹⁰

Table 12: Selected bond lengths and angles of 7.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-Cl(1)	2.3148(9)	Cl(1)-Ge(1)-N(1)	98.43(8)
Ge(1)-N(1)	2.024(3)	Cl(1)-Ge(1)-N(2)	98.03(10)
Ge(1)-N(2)	1.998(3)	N(1)-Ge(1)-N(2)	65.73(11)
C(1)-N(3)	1.349(4)	Ge(1)-N(1)-C(1)	91.75(19)
N(1)-C(1)	2.023(3)	Ge(1)-N(2)-C(1)	93.33(19)
N(2)-C(1)	1.995(3)	N(1)-C(1)-N(3)	122.4(3)
		N(2)-C(1)-N(3)	128.7(3)
		Ge(1)-N(1)-C(2)	136.0(2)
		Ge(1)-N(2)-C(3)	135.5(2)

Figure 34: ORTEP representation of **7**. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

2.4.4 Attempted Synthesis of $[\text{Ge}(\text{N}(\text{Cy})(\text{CNCy})\text{NAr}^*)]$

To investigate whether **7** could be used as a precursor to the germylene $[\text{Ge}(\text{N}(\text{Cy})(\text{CNCy})\text{NAr}^*)]$ the reaction of **7** with *n*-BuLi was attempted. The rationale is that the Bu[−] nucleophile could abstract the amido proton on N(3) of **7**, elimination of LiCl could result in the dianionic guanidinate ligand on germanium, and a new synthetic route to a range of new germylene compounds would be generated. To a stirred and cooled solution of **7** in diethyl ether was added one equivalent of *n*-BuLi. The reaction then had another equivalent of *n*-BuLi added and the solution rapidly went vibrant orange. After workup and purification *via* recrystallisation a number of lithium salts of the ligand were obtained as crystals. ¹H NMR spectroscopy of the reaction mixture identified several resonances for ^tBu environments indicating a range of products that could not be accurately identified. Although the initial equivalent of *n*-BuLi may have deprotonated the β carbon of the ligand the likely second equivalent likely generated unstable germanium alkyl species that quickly decomposed to a range of products.

2.5 Synthesis of Germanimines

One of the synthetic routes proposed to generate zirconium germanium compounds was through the formation of a highly reactive germanimine species ($R_2Ge=NR'$) followed by addition of a Zr(II) species. Germanimines have been synthesised in the literature previously from the oxidative addition of an azide to an $NHGe$, however, little to no further reactivity studies have been completed and hence the suitability of the species for use in inorganic synthesis remains unknown.^{41, 43, 91-92}

2.5.1 Attempted Synthesis of $[(NAPH^{TMS})Ge(NMes)]$

Our first attempted synthesis of a germanimine was through the treatment of **3** with one equivalent of $[MesN_3]$. The rationale behind using this germylene was its reduced steric bulk on the nitrogen atoms compared to **2** and its relatively easy synthesis. The two compounds were dissolved in deuterated benzene and transferred into an NMR tube fitted with a Young's tap. The reaction was monitored by 1H NMR spectroscopy. No evidence of the germanimine was ever detected, however a new series of resonances indicated the presence of a new product in a 1:1 ratio with **3**. Following workup and purification by crystallisation, the product was determined to be the tetrazene **8**.

Scheme 20: Synthesis of **8** from the treatment of **3** with $[MesN_3]$.

2.5.2 [Ge(NAPH^{TMS})(N₄Mes₂)] Synthesis **8**

Compound **8** was synthesised through the addition of two equivalents of mesitylazide to **2** at room temperature. The proposed synthetic Scheme for the reaction is shown in Scheme 20. Compound **8** is likely the addition product of the germanimine species with an extra equivalent of azide to give the thermodynamically stable tetrazene product. The reaction appears to happen extremely quickly at RT, as even when the reaction was carried out in the presence of the trapping agent 4-nitrophenylisocyanate the tetrazene **8** was observed as the only product by ¹H NMR spectroscopy. The ¹H NMR spectrum for **8** has an upfield shift of the TMS resonance to δ 0.09 ppm, while the two methyl resonances of the azide shift significantly downfield from the free azide to δ 2.58 (*ortho* methyls) and 2.09 ppm (*para* methyl) respectively. Four aromatic resonances are also observed in the low field as would be expected for the three naphthalene environments as well as the two meta protons of the phenyl ring of the azide moiety. The integration of these resonances indicates a 2:1 ratio of the mesityl to naphthalene environments.

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **8** in hexane. The solid-state X-ray crystal structure shows one molecule in the asymmetric unit. The structure has a severely distorted tetrahedral geometry at the germanium atom, likely a result of the conformational constraint from the [NAPH^{TMS}] ligand. Like the free germylene the germanium atom lies in plane with the slightly twisted naphthalene ring, with one of each of the coordinating nitrogen atom lying above and below this plane and the TMS groups sitting further above or below the nitrogen atom (in respect of the naphthalene germanium plane). The plane of the mesityl groups lie almost perpendicular to each (the angle between the planes is 104.94°) other but are twisted away from the TMS groups presumably to reduce steric interactions. Comparing the structure to the most similar compound in the literature; **XXIII** the increased steric interaction between the TMS groups and the mesityl groups can be seen.⁴⁴ While in **XXIII** the phenyl rings sit almost in plane with each other, and this plane is perpendicular to the N(^tBu)-Ge-N(^tBu) plane, **8** has the N(1)-N(2)=N(2i)-N(1i) plane twisted away from being perpendicular, presumably to minimise the steric interaction between the mesityl groups and the TMS groups on the [NAPH^{TMS}] ligand. The Ge(1)-N(1) bond length of 1.846 Å is similar to the Ge-N bond distance in **XXIII**, as is the N(1)-N(2) and N(2)-N(2i) distances of 1.391 and 1.269 Å (1.414 and 1.252 Å respectively in **XXIII**). The similar, though more conformationally free tetrazagermole **XXIV** has similar Ge-N bond lengths for the tetrazene ligand 1.850 and 1.852 Å **XXIV** also has the N-N distances in the tetrazene of 1.394 and 1.360 Å, similar to **8**. The Ge(1)-N(3) bond distance of 1.816 Å in **8** is longer than that of **XXIII** (1.808 and 1.812

Å) and shorter than **XXIV** (1.822 and 1.834 Å). A summary of the relevant crystallographic bond lengths and distances is summarized in Table 12.

Figure 35: ORTEP representation of **8**. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 12: Selected bond lengths and angles of **8**.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.8458(12)	N(3)-Ge(1)-N(3i)	106.19(9)
N(1)-C(1)	1.4336(18)	N(1)-Ge(1)-N(1i)	84.28(7)
N(1)-N(2)	1.3913(17)	N(3)-Ge(1)-N(1)	127.73(5)
N(2)-N(2i)	1.269(3)	Ge(1)-N(1)-C(1)	132.3(1)
Ge(1)-N(3)	1.8155(13)	Ge(1)-N(3)-Si(1)	121.01(7)
N(3)-Si(1)	1.7789(14)	Ge(1)-N(1)-N(2)	112.12(9)
		N(1)-N(2)-N(2i)	115.73(7)

2.5.3 Synthesis of [(HMDS)₂Ge(NMes)] **9**

After the synthesis of **8** indicated that **3** was too reactive to successfully synthesise the desired germanimine it was decided that a similar reaction would be attempted with the germylene **I**, since it had been shown to be bulky enough to kinetically stabilise other germanimines such as **XXI**.

Addition of one equivalent of [MesN₃] to **I** in hexane at -30 °C resulted in bubbles in the reaction mixture and changed the colour of the solution from orange to pale orange. After concentration of the solution, single, X-ray quality crystals were grown at -30 °C, which were determined to be the germanimine complex **9**.

The ¹H NMR spectrum of **9** shows 4 singlets. There is one peak at δ 0.29 ppm (36H), upfield shifted from the free germylene (δ 0.34 ppm). The 3 mesityl singlet resonances at δ 6.99 (2H), 2.47 (6H) and 2.28 (3H) are all downfield shifted from the free azide, as would be expected due to the deshielding of the germylene. The integrals indicate the presence of only one equivalent of azide in the crystals as opposed to two in the germanium-tetrazene compound **8**.

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **9** in hexane. The solid-state X-ray crystal structure of **9** is consistent with the presence of a germanium nitrogen double bond. The crystal packs with two molecules asymmetric unit, though as the compounds have similar bond lengths and angles only one molecule will be discussed here. Compound **9** has a distorted trigonal planar geometry around Ge(1), with the N(1) atom sitting 9.25° above the N-Ge-N plane of the HMDS ligands (Σ internal angles in 359.91 around the Ge(1) atom). This trigonal planar arrangement is strong evidence for the Ge(1)-N(1) double bond. The Ge(1)-N(1) bond length of 1.713(3) Å is slightly longer than the known germanium nitrogen double bonds in the literature compounds **XIX** (1.703 Å), **XXI** (1.705 Å) and **XXIII** (1.682 Å), and may indicate the Ge(1)-N(1) bond is more labile towards a range of reactive small molecules.^{40-41, 43} The length of this bond is surprising, as the relative steric bulk of the ligand scaffold seems to be less for **9** than **XXI**, and the imine steric bulk is larger in **XIX** than complex **9**. The Ge(1)-N(2)

and Ge(1)-N(3) distances are 1.813(3) and 1.826(3) Å respectively, which is short for Ge(IV)-HMDS bond lengths, which usually range between 1.80-1.91 Å.⁹³⁻⁹⁷ The short length is probably due to a complex range of factors, though [Ge^{IV}(HMDS)₂X₂] compounds with other strongly σ -accepting α atoms such as nitrogen or oxygen tend to have shorter Ge-N(HMDS) bond lengths.^{75, 93, 98-99} The N(1)-C(1) bond distance of 1.394(5) Å is slightly shorter than literature germanimines **XXI** and **XIX** and there are no unexpected or especially surprising bond angles present in the structure.

Figure 36: ORTEP representation of 9 (one molecule shown). 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 13: Selected bond lengths and angles of 9.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.713(3)	N(1)-Ge(1)-N(2)	112.38(15)
Ge(1)-N(2)	1.813(3)	N(1)-Ge(1)-N(3)	130.72(14)
Ge(1)-N(3)	1.826(3)	N(2)-Ge(1)-N(3)	116.81(14)
N(2)-Si(1)	1.754(3)	Ge(1)-N(2)-C(1)	130.2(3)
N(2)-Si(2)	1.780(3)	Ge(1)-N(2)-Si(1)	119.54(18)
N(3)-Si(3)	1.769(3)	Ge(1)-N(2)-Si(2)	114.99(17)
N(3)-Si(4)	1.764(3)	Ge(1)-N(3)-Si(3)	117.37(17)
N(1)-C(1)	1.394(5)	Ge(1)-N(3)-Si(4)	120.57(5)
		Si(1)-N(2)-Si(2)	121.56(19)
		Si(3)-N(3)-Si(4)	121.75(18)

2.5.4 Synthesis of [(HMDS)₂Ge(N₄Ph₂)] **10**

To investigate the effect of using a less bulky azide for the synthesis of germanimines, **1** was treated with the less bulky azide [PhN₃]. Addition of 1 equivalent of phenylazide to **1** at room temperature gave the 1:1 ratio of compound **10** to **1**.

The ¹H NMR spectrum of the crude reaction mixture indicates that the desired germanimine [(HMDS)₂Ge(=NPh)] was formed but then undergoes an additional [3+2] cycloaddition with additional azide to form **10**.

The ¹H NMR spectrum of purified **10** shows 4 resonances. The TMS resonance has shifted upfield to δ 0.24 ppm from δ 0.32 ppm in **1**. There are three resonances for the aromatic protons, a signal at δ 7.62 ppm (2H), a multiplet from δ 7.00-6.93 ppm (4H) and a multiplet from δ 6.89-6.80 ppm (4H). The 2:1 relative integrals

of the aromatic resonances to the TMS resonance indicate two equivalents of phenylazide has reacted for one equivalent of **1**.

Crystals suitable for an X-ray diffraction study were grown from a concentrated solution of **10** in hexane. The solid-state crystal structure data of **10** has two molecules in the asymmetric unit (A and B), however as there two molecules have similar bond lengths and angles only one (A) will be discussed here. There is a distorted tetrahedral geometry around the germanium atoms, with a bite angle of the tetrazene ligand for N(1)-Ge(1)-N(4) of 82.3(3). Comparing **10** to **8**, the HMDS ligands are spaced further apart with a N(5)-Ge(1)-N(6) angle of 120.3°, compared to 106.19° for the N-Ge-N angle of the [NAPH^{TMS}] ligand, though this is likely also effected by the constraint of [NAPH^{TMS}] being a bidentate ligand. The germanium nitrogen bond distances to the coordinating tetrazene nitrogens are longer in **10** (1.863(7) and 1.877(7) Å) than **8** (1.8458(12) Å). The N=N bond is 0.026 Å longer in **10** than **8**, which also could be due to the decreased steric bulk of the azide or of the ancillary ligand. The intermediate germanimine species was never observed in the ¹H NMR in the synthesis of **10**, indicating that the steric bulk of the azide is essential in the synthesis and kinetic stabilisation of germanimines.

Table 14: Selected bond lengths and angles of 10.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.875(7)	N(1)-Ge(1)-N(4)	82.3(3)
Ge(1)-N(4)	1.868(7)	N(5)-Ge(1)-N(6)	120.3(3)
N(2)-N(3)	1.295(11)	N(1)-Ge(1)-N(5)	108.4(3)
Ge(1)-N(5)	1.842(6)	N(8)-Ge(1)-N(12)	109.4(3)
Ge(1)-N(6)	1.831(6)

Figure 37: ORTEP representation of 10. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

2.5.5 Synthesis of [(HMDS)Ge(NTMS)(N(TMS)Ar*)] **11**

Complex **11** was synthesised from the reaction of **I** with the bulky azide [Ar*N₃] (**25**) at -30 °C in toluene. The solution initially turned orange and a precipitated out an orange solid as the solution warmed up to room temperature. To crystallise the solid for analysis by X-ray diffraction the suspension was heated to supersaturate the solution, resulting in a yellow solution. The solution was cooled to -30 °C to crystallise, resulting in the formation of yellow crystals over 3 days.

An X-ray diffraction study confirmed the synthesis of **11**. This product was presumed to be the rearrangement product of the desired germanimine (Scheme 21). It is likely that the Ge=N bond of the desired product would be long, due to the bulk and electronic properties of the Ar* ligand. It would be expected that this bond would be relatively labile due to the long bond length, and as such may readily undergo rearrangement to a more thermodynamic product at elevated temperatures. The easiest way to prove this theory would be to isolate the original germanimine, however, despite several attempts this was not achieved. The desired germanimine could also be trapped out with unsaturated molecules (carbodiimides, acetylene derivatives) to provide evidence that that the species is being formed even if it cannot be isolated.

Scheme 21: Synthesis of **11 showing assumed intermediate in brackets.**

The ^1H NMR of the crude reaction product identifies three species in solution, assumed to be the desired product $[\text{HMDS}_2\text{GeNAr}^*]$ (identified by the integral ratio 36:9 of the TMS: ^tBu resonances), the crystallised product **11** and the impurity from the azide starting material known to be Ar^*Cl (appendix 5.7). Compound **11** has four high field singlet resonances at δ 1.04 (9H), 0.49 (9H), 0.45 (18H) and -0.15 ppm (9H) attributed to the *tert*-butyl peak of the $[\text{N}(\text{TMS})\text{Ar}^*]$ ligand, the TMS group of the $[\text{N}(\text{TMS})\text{Ar}^*]$ ligand, the $[\text{HMDS}]$ ligand and the imido TMS group respectively. The visible aromatic resonances are a doublet at δ 7.66 ppm (4H), a doublet at 7.51 ppm (4H) and a triplet at δ 7.26 ppm (4H), the other 10 aromatic protons are obstructed by the other signals in the crude NMR. The methine protons have an observable resonance at δ 6.34 ppm (2H), shifted downfield from the free azide (δ 6.06 ppm).

The solid-state X-ray crystal structure has one molecule of **11** and one molecule of toluene present in the asymmetric unit. **11** exhibits a distorted trigonal planar geometry at the germanium atom (Σ angles = 360°) with three coordinated nitrogen atoms. The short Ge(1)-N(1) bond distance (1.683(2) Å) indicates a double bond between Ge(1) and N(1). The double bond is significantly shorter than the imido bond in **9**, but falls within the range of known solid state germanium nitrogen double bonds of 1.669-1.863 Å.^{40-41, 43, 91-92, 100-103} The Ge(1)-N(2) bond distance of 1.825(2) Å for **11** is similar to the Ge(1)-N(2) and Ge(1)-N(3) distances in **9**.

Figure 38: ORTEP representation of 11. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 15: Selected bond lengths and angles of 11.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.683(2)	N(1)-Ge(1)-N(2)	130.31(10)
Ge(1)-N(2)	1.825(2)	N(1)-Ge(1)-N(3)	114.0(1)
Ge(1)-N(3)	1.815(2)	N(2)-Ge(1)-N(3)	115.69(9)
N(2)-Si(1)	1.697(2)	Ge(1)-N(3)-C(1)	113.37(14)
N(2)-Si(2)	1.7659(11)	Ge(1)-N(1)-Si(1)	141.20(14)
N(2)-Si(3)	1.7659(11)	Ge(1)-N(2)-Si(2)	116.65(6)
N(3)-Si(4)	1.782(2)	Ge(1)-N(3)-Si(3)	116.65(6)
N(1)-C(1)	1.459(3)	Ge(1)-N(3)-Si(4)	127.61(11)
		Si(2)-N(2)-Si(3)	122.81(12)

2.5.6 Reactivity of $[(\text{HMDS})_2\text{Ge}(\text{NMe}_3)]$, **9** with unsaturated small molecules

To investigate the reactivity of **9**, reactions with the unsaturated small molecules phenylacetylene and 4-nitrophenylisocyanate were carried out. The small sample of molecules tested indicated the germanimine bond was highly reactive towards unsaturated substrates.

2.5.6.1 Reactivity towards phenylacetylene

Treatment of the *in situ* generated germanimine with 1 equivalent of phenylacetylene led to good yields of the deprotonation product $[(\text{HMDS})_2\text{Ge}(\text{CCPh})(\text{NHMe}_3)]$, **11**, with the phenylacetylene molecule coordinating terminally to the germanium center. The pale-yellow crystals were characterized by ^1H NMR, ^{13}C NMR and single crystal X-ray diffraction.

Scheme 22: Synthesis of **12** from *in situ* generation of **9**.

The ^1H NMR spectrum of **12** shows the downfield shift of the TMS resonance to δ 0.47 ppm (from δ 0.29 ppm in **9**) indicating more deshielding of the TMS methyl groups. The mesityl resonances are also downfield shifted to δ 2.53 and 2.17 ppm for the *ortho* and *para* methyl groups respectively from **9**. A new broad peak at δ 3.11 ppm that integrates to one proton is attributed to the protonation of the imido nitrogen atom to form an amide. There are four aromatic resonances in the ^1H NMR spectrum; a singlet at δ 6.82 ppm attributed to the meta protons of the mesityl group are upfield shifted from **9**, in which the resonance was seen at δ 6.99 ppm. There are three multiplets in the aromatic region (δ 7.62, 7.43 and 6.93 ppm) attributed to the three proton environments of the coordinated phenylacetylene moiety.

Crystals suitable for an X-ray diffraction study were grown from a concentrated hexane solution of **12**. The crystal structure of **12** shows that there is one molecule in the asymmetric unit. There is a distorted tetrahedral arrangement around the germanium centre. Notable bonding features of compound **12** include the short C(22)-C(23) bond distance of 1.199 Å and Ge(1)-C(22)-C(23) bond angle of 174.4°, both of which indicate the presence of a triple bond between C(22) and C(23). This bond distance falls within

the range of known C≡C bond distances (1.194-1.215 Å) in compounds where phenylacetylene terminally coordinates to Ge(IV).¹⁰⁴ The Ge(1)-N(1) bond distance of 1.852 Å is longer than the Ge=N bond distance in complex **9** of 1.713 Å, reflecting the decrease in bond order between the germanium atom and the N(1) atom. The Ge(1)- N(HMDS) bond distances of 1.847 and 1.846 Å are lengthened slightly from **9**, plausibly due to the increase in steric bulk around the germanium atom moving from three to four coordinate. The relatively small steric bulk of phenylacetylene is reflected in the small N(3)-Ge(1)-N(1), N(1)-Ge(1)-C(22) and N(2)-Ge(1)-C(22) bond angles of 107.85°, 108.10° and 106.14°. There is a significant difference in the two N(1)-Ge(1)-N(HMDS) bond angles of 103.90° and 112.79° for N(1)-Ge(1)-N(3) and N(1)-Ge(1)-N(2) respectively which is likely due to the orientation of the mesityl group towards N(2), while the proton on N(1) is orientated towards N(3) when viewed down the Ge(1)-N(1) bond.

Another notable bonding feature of the compound is the migration of the proton from C(22) to N(1), which indicates that the reaction likely proceeds through a deprotonation reaction (Scheme 23). This type of reaction has shown to occur for a variety of main group and transition metal complexes with coordinating nitrogen atoms.¹⁰⁵⁻¹⁰⁸

Scheme 23: Proposed reaction pathway for the synthesis of **12 showing a possible transition state.**

Figure 39: ORTEP representation of 12. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 16: Selected bond lengths and angles of 12.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.8515(19)	N(1)-Ge(1)-N(2)	112.79(8)
Ge(1)-N(2)	1.8472(17)	N(2)-Ge(1)-N(3)	117.52(19)
Ge(1)-N(3)	1.8463(17)	N(3)-Ge(1)-N(1)	103.90(8)
Ge(1)-C(22)	1.917(2)	N(1)-Ge(1)-C(22)	107.85(9)
C(22)-C(23)	1.199(3)	N(2)-Ge(1)-C(22)	108.10(9)
N(1)-C(1)	1.427(3)	N(3)-Ge(1)-C(22)	106.14(9)
		Ge(1)-C(22)-C(23)	174.4(2)
		Ge(1)-N(1)-C(1)	126.16(14)

2.5.6.2 Reactivity towards 4-nitrophenylisocyanate

To investigate if the germanimine **9** was reactive towards the isocyanate functional group a NMR scale reaction with 4-nitrophenylisocyanate was carried out. Nitrophenyl isocyanate was chosen over phenyl isocyanate due to the advantages of weighing a solid opposed to a dense liquid. As per the synthesis of **12** the germanimine was generated *in situ* through the addition of [MesN₃] to a solution of [Ge(HMDS)₂] in deuterated benzene at room temperature. After 10 minutes a solution of 4-nitrophenylisocyanate was added dropwise and the reaction was transferred to an NMR fitted with a young's tap. The reaction was monitored by ¹H NMR spectroscopy. Once the free azide mesityl peaks were no longer observed by ¹H NMR spectroscopy was taken back into the glovebox and recrystallised to obtain compound **13** in a 59% yield. The crystals were characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy and single crystal X-ray diffraction.

Scheme 24: Synthesis of **13** from **9**.

The ¹H NMR spectrum for **13** shows the upfield shifted TMS resonance (δ 0.20 ppm, 36H) from the germanimine, indicating less deshielding around the TMS groups of the HMDS ligands. The characteristic 2:1 ratio singlet for the methyl groups on the mesityl group are shifted to 2.43 and 2.13 respectively, upfield shifted from the germanimine **9** (δ 2.47 and 2.28 ppm), also indicating reduced deshielding, though this may be expected due to the loss of the extended delocalized system of the mesityl group onto the germanium atom. There are two new low field doublets (δ 8.07, 7.64 ppm), attributed to the two hydrogen environments on the 4-nitrophenyl ring. The extremely electron withdrawing nitro group may account for the significant downfield chemical shift of these two proton environments (relative to phenylisocyanate).¹⁰⁹

Crystals suitable for an X-ray diffraction study were grown from a concentrated hexane solution of **13**. The crystal structure for **13** confirms the isocyanate has gone to the cycloaddition product opposed to the insertion product or the imido-group exchange as is known for some other elements in higher oxidation

states.¹¹⁰⁻¹¹¹ The solid-state crystal structure data shows 2 molecules of **13** in the asymmetric unit (molecules A and B). However, as these two molecules have extremely similar bond lengths and angles only one molecule will be discussed (molecule A). The geometry around the germanium atom is a distorted tetrahedral, with the N(1)-Ge(1)-N(2) bite angle averaging 70.91° over the two molecules while the N(HMDS)-Ge-N(HMDS) angle averages 119.13°. The Ge(1)-N(3) and Ge(1)-N(4) bond lengths of 1.809(2) and 1.822(2) Å is over 0.2 Å shorter than is the Ge(IV) complex **12**, possibly due to the increased partial charge on the germanium atom due to the higher number of bonded nitrogen removing more electron density away from the Ge(IV) atom. The N(1)-C(1)-(N(2) angles of 103.2° is similar to the literature values for compounds with ligands of this type.¹¹² A literature comparison for complex **13** is difficult, as the number of 4-coordinate isocyanate cycloaddition products is few, and as far as the author is aware this complex is the first 4-coordinate germanium species with a ligand of this type.

Figure 40: ORTEP representation of 13. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 17: Selected bond lengths and angles of 13.

Bond Lengths (Å)		Bond Angles (°)	
Ge(1)-N(1)	1.894(2)	N(1)-Ge(1)-N(2)	70.94(10)
Ge(1)-N(2)	1.889(2)	N(3)-Ge(1)-N(4)	118.17(11)
Ge(1)-N(3)	1.809(2)	N(1)-C(1)-N(2)	103.2(2)
Ge(1)-N(4)	1.822(2)	N(1)-C(1)-O(1)	128.4(3)
N(1)-C(1)	1.389(4)	N(2)-C(1)-O(1)	128.3(3)
N(2)-C(1)	1.411(4)		
C(1)-O(1)	1.215(4)		

2.6 Summary of Results

The novel germynes **2** and **3** were synthesised and their reactivity was investigated using MO DFT calculations which indicated that **2** would be the more reactive germylene as determined by the calculated HOMO-LUMO energy gap. However, when **2** and **3** were treated with half an equivalent of *n*-BuLi or MeLi compound **2** did not give any reaction products, while compound **3** gave the donor-acceptor complexes **4** and **5**. This indicated that although germylene **2** was theoretically the more reactive germylene the role of steric bulk at the *N* positions of the ligands may have further influenced the germynes reactivity. When germylene **3** was treated with an azide in the attempted synthesis of a germanimine, the tetrazene product **8** was instead formed, indicating that at room temperature the germanimine formed *in situ* is more reactive than towards additional azide than **3**. The germanimine **9** was successfully synthesised from the treatment of [MesN₃] to **I**, however when **I** was treated with the less bulky azide [PhN₃] the tetrazene product **10** was formed under the same conditions, indicating the importance of the steric bulk of the azide. The reactivity of **9** with phenylacetylene and 4-nitrophenylisocyanate to form **12** and **13** showed the Ge=N bond was reactive towards unsaturated small molecules. The treatment of **I** with the more bulky azide [Ar^{*}N₃] gave a range of products, however, the germanimine **11** was isolated and characterised. **11** was presumed to be the thermal rearrangement of the germanimine [(HMDS)₂Ge(NAr^{*})].

3 Results and Discussion: Group 4 Chemistry

3.1 Synthesis of Amides and Imidozirconocene species

3.1.1 Synthetic Strategy

The research in this chapter investigates further the work of Bergman et al. and the use of thermolysis reactions to synthesise imidozirconocenes from cyclopentadienyl supported zirconium amides.^{49, 51, 54, 113-114} (equation 21). These amidozirconocenes and imidozirconocenes were synthesised for their use in the synthesis of **1** (Scheme 1).

Although the literature syntheses generate the zirconium amides *in situ*, in this project the amides were isolated and characterised where possible to gain insight into their structure and bonding. The amides were synthesised in two different methods. The addition of a free amine to $[\text{Cp}_2\text{ZrMe}_2]$ or $[\text{Cp}_2\text{ZrBn}_2]$ at 100 °C was used for the successful synthesis of compounds **17**, **18** and **19** while **14**, **15** and **16** were synthesised from the salt metathesis of $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ with the a lithiated amine. Two different alkyl groups ($\text{Me} = \text{CH}_3$, $\text{Bn} = \text{CH}_2\text{Ph}$) were used due to availability of starting materials, reactivity and atom efficiency. Although the salt metathesis synthetic route was the only successful method to an isolated imidozirconocene (**19**), this route was avoided due to the low overall yields (5.6 – 20.5%) due to the high number of reactions and resulting low atom efficiency required to synthesise imidozirconocenes relative to other pathways (Scheme 25).

Scheme 25: Synthetic route to imidozirconocenes *via* salt metathesis.

Although it has been reported that the species $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ could be synthesised through the addition of 1 equivalent of MeLi at $-30\text{ }^\circ\text{C}$, it was found that the major product under these conditions was actually the bis-methyl species $[\text{Cp}_2\text{ZrMe}_2]$. As such an alternative literature procedure was used to synthesise $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ using trityl chloride in ether to give the monochloride species and triphenylethane, with the two products being easily isolated due to the relative insolubility of $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ in hexane.

3.1.2 Synthesis of $[\text{Cp}_2\text{Zr}(\text{NHDipp})(\text{Me})]$ **14**

The reaction of $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ with one equivalent of the mono-lithiated amine; $[\text{LiNHDipp}]$ in diethyl ether resulted in the formation of the amide $[\text{Cp}_2\text{Zr}(\text{NHDipp})(\text{Me})]$, **14** in a moderate yield (64%). The compound was characterized by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy and by single crystal X-ray diffraction.

The ^1H NMR spectrum shows a chemical shift upfield for the methyl protons to δ 0.23 ppm (from δ 0.45 ppm), likely due to reduced deshielding of the amide relative to the chloride. The isopropyl resonances of the amide are both shifted downfield from the free amine, to δ 3.41 and δ 1.24 ppm for the methine septet and methyl doublet respectively. The cyclopentadienyl resonance is upfield shifted to δ 5.63 ppm and the amide proton is observable as a broad singlet at δ 6.21 ppm, significantly chemical shifted downfield from the free amine likely due to the increased deshielding though proximity to the zirconium atom. The *meta* substituted protons on the phenyl ring are observed as a doublet at 7.16 ppm (the J_{HH} coupling constant could not be determined due to overlap with the solvent signal) and a triplet for the para substituted proton at δ 7.11 ppm.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated toluene solution of **13**. As there are no suitable solid-state comparisons in the literature for **13**, analysis of the solid-state crystal structure data is carried out compared to **14** and **15** later in this chapter.

Figure 41: ORTEP representation of **14**. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 18: Selected bond lengths and angles of **14**.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	2.080(9)	Zr(1)-N(1)-C(2)	134.7(7)
Zr(1)-C(1)	2.345(18)	N(1)-Zr(1)-C(1)	98.2(7)
Zr(1)-Cp(2)	2.228(8)	Cp(1)-Zr(1)-Cp(2)	136.5(4)
Zr(1)-Cp(1)	2.220(6)	Cp(1)-Zr(1)-C(1)	103.8(6)
		Cp(2)-Zr(1)-C(1)	96.5(8)

3.1.3 Synthesis of [Cp₂Zr(Me)(NHAr*)] 15

The amidozirconocene [Cp₂Zr(Me)(NHAr*)] was synthesised from the addition of the lithiated amine [LiNHAr*] dropwise to [Cp₂Zr(Cl)(Me)] in diethyl ether at -30 °C (equation 23). Following workup the compound was purified by crystallisation from toluene layered with hexane at -30 °C. The crystalline solid was characterised by ¹H NMR, ¹³C NMR and single crystal X-ray spectroscopy.

The ¹H NMR spectrum has a broad singlet at δ 7.24 integrating to 8 protons as well as a broad singlet at δ 6.01 (CHPh₂) integrating for 2 protons, indicating a possible dynamic species in solution at room temperature. The other aromatic protons resonances at δ 7.19 and a multiplet of overlapping signals at δ 7.06-6.99 ppm. The cyclopentadienyl resonance is upfield shifted to δ 5.58 ppm from δ 5.71 ppm, indicating increased shielding of the cyclopentadienyl rings from the starting material. The amide proton peak is observable as a broad singlet at δ 2.79 ppm, while the singlet resonance attributed to the *tert*-butyl environment is shifted to δ 1.09 ppm, upfield from the free amine in deuterated benzene (δ 1.11 ppm). The broad singlet could be due to the inequivalence of some of the phenyl rings on the NHAr* amide ligand, due to the large steric bulk restricting free rotation. If this were the case, heating the compound up would expect to sharpen the peaks up (as the energy related to overcoming the energetic rotation barrier is overcome), while cooling the temperature of the NMR probe down might allow the two dynamic species to be isolated.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated toluene solution of **14**. As discussed earlier analysis of the solid-state crystal structure is carried out later in this chapter.

Figure 42: ORTEP representation of **15**. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 19: Selected bond lengths and angles of **15**.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	2.080(3)	Cp(1)-Zr(1)-N(1)	109.15(10)
N(1)-C(2)	1.412(5)	Cp(2)-Zr(1)-N(1)	105.42(10)
Cp(1)-Zr(1)	2.2316(17)	Cp(1)-Zr(1)-C(2)	104.78(15)
Cp(2)-Zr(1)	2.2251(17)	Cp(2)-Zr(1)-C(2)	103.85(17)
Zr(1)-C(1)	2.303(4)	Zr(1)-N(1)-C(2)	134.9(2)
		C(1)-Zr(1)-N(1)	99.94(15)
		Cp(1)-Zr(1)-Cp(2)	130.51(8)

3.1.4 Synthesis of $[\text{Cp}_2\text{Zr}(\text{Me})(\text{NH}(\text{DMP}))]$ **16**

$[\text{Cp}_2\text{Zr}(\text{Me})\text{NH}(\text{DMP})]$ (DMP = 2,6 dimethylphenyl) was synthesised using two different synthetic routes. The first was the through salt metathesis of the lithiated amine with $[\text{Cp}_2\text{Zr}(\text{Cl})(\text{Me})]$, while the second was the treatment of $[\text{Cp}_2\text{ZrMe}_2]$ with the free amine at 110 °C (Scheme 26). For both reactions, the product was purified after workup by crystallisation. Compound **16** was characterised by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, single crystal X-ray diffraction. Unlike many earlier compounds elemental analysis was able to be obtained accurately for **16**.

Scheme 26: Synthesis of **16 from transamination and salt metathesis reactions.**

The ^1H NMR spectrum of **16** demonstrated one aromatic multiplet resonances for the *meta* and *para* protons on the DMP ring at δ 7.11-7.07 ppm (3H). The cyclopentadienyl resonance at δ 5.34 ppm (10H) has a chemical shift upfield from either starting material, and is also upfield of both **14** and **15**. This could be due to a steric or electronic resulting from the different substitution of the *meta* positions of the phenylamide ring. The 2,6 methyl environments resonate at δ 2.04 ppm (6H) and have a chemical shift downfield compared to the free amine resonance of δ 1.88 ppm. The zirconium-methyl resonance at δ 0.54 also has a chemical shift downfield compared to both $[\text{Cp}_2\text{ZrMe}_2]$ (δ -0.12 ppm) and $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ (δ 0.45 ppm), indicating a change to a more deshielded chemical environment.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated toluene solution of **16**. Analysis of the solid-state crystal structure is carried out later in this chapter (Section 3.1.5).

Figure 43: ORTEP representation of 16. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 20: Selected bond lengths and angles of 16.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	2.078(3)	Zr(1)-N(1)-C(2)	139.6(2)
Zr(1)-C(1)	2.526(5)	N(1)-Zr(1)-C(1)	98.8(2)
Zr(1)-Cp(2)	2.156(2)	Cp(1)-Zr(1)-Cp(2)	141.88(11)
Zr(1)-Cp(1)	2.205(2)	Cp(1)-Zr(1)-C(1)	88.23(15)
		Cp(2)-Zr(1)-C(1)	99.08(14)

3.1.5 Comparison of solid-state crystal structures 14, 15 and 16

The solid-state crystal structures of the amides **13**, **14** and **15** all have a distorted tetrahedral geometry around the Zr(1) atom. The Zr-N bond lengths are extremely similar for all three compounds (2.080(9) Å,

2.078(3) Å and 2.080(3) Å for **14**, **15** and **16** respectively), which would indicate that the steric bulk at the *ortho* positions of the aryl amides has little effect on the length of the Zr-N bond. The data indicates that the Zr(1)-C(1) zirconium-methyl bond distance increases as the steric bulk of the aryl amide is increased. This effect is quite pronounced, with **15** having a Zr(1)-C(1) bond distance over 0.2 Å longer than complex **16**. This effect could be due to a number of different reasons, including solid state crystal packing effects, lengthening due to the increased steric bulk of the amide or a complicated electronic effect due the differing inductive effects of the substituents on the *ortho* positions (and possibly *para* position) of the phenyl ring of the amide. The Zr(1)-N(1)-C(2) bond angle of **15** (139.6(2)°) is significantly more distorted than that in **14** and **16** (134.9(2)° and 134(7)° respectively), indicating that as the steric bulk is increased the angle between these atoms increases, which could be expected to minimise steric interaction between the ligands.

3.1.6 Synthesis of [Cp₂Zr(NHPh)(Bn)] **17**

The amide [Cp₂Zr(NHPh)(Bn)] was synthesised through treatment of bisbenzylzirconocene with aniline at elevated temperatures (eq. 24). This reaction gave a mixture of the products **17** and **18**, although as **18** is an insoluble green solid the ¹H NMR spectrum of the unpurified reaction solution indicated **17** was the only product in solution.

The ¹H NMR spectrum of **17** shows a number of overlapping signals in the aromatic region of the spectrum that are assigned as multiplets δ 7.26-7.19 and 6.90-6.86 ppm. The doublets at δ 7.06 (2H) and 6.76 ppm (2H) are likely the *ortho* substituted protons for each of the phenyl rings. Assignment for each ring resonance was not determined, however, one could speculate that the more downfield shifted resonance would be expected to be from the amide phenyl ring due the expected increased deshielding effect of the nitrogen due to increased electronegativity of carbon over the benzyl. The cyclopentadienyl resonance at δ 5.51 ppm is not shifted from the bis-benzylzirconocene, indicating similar shielding on the cyclopentadienyl ligands. However, the resonance at δ 2.24 ppm (2H) indicates that there has been a

change on the methylene environment on the benzyl fragment, which provides evidence that the amide has been synthesised.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated hexane solution of **17**. The crystal structure reveals a single molecule of **17** in the asymmetric unit. The Zr(1)-N(1) bond distance of 2.112(5) Å is longer than that of the **14** (2.080(9) Å), **15** (2.078(3) Å) and **16** (2.080(3) Å), exhibiting the different electronic and steric profile of the benzyl ligand compared to the methyl ligand. Comparison of the solid-state structure of **17** with [Cp₂Zr(Me)(NHPPh)] would have given more insight into the effect of the benzyl ligand, however, despite several attempts the synthesis and isolation of [Cp₂Zr(Me)(NHPPh)] was not successful. The Zr(1)-C(1) bond length of 2.324(7) Å falls within the range of Zr(1)-C(1) bond distances of **14**, **15** and **16** (2.303(4)-2.526(5) Å), indicating that the Zr-C bond length of arylamidozirconocenes with a benzyl ligand is longer than the equivalent complex with a methyl ligand. The angle between the centroids of the cyclopentadienyl ligands is smaller in **17** (128.82(7)°) than in the methyl complexes **14**, **15** and **16** (136.5(4)°, 141.88(11)° and 134.9(2)° respectively). This is likely due to the increased steric profile of the benzyl ligand compared to the methyl ligand.

Figure 44: ORTEP representation of **17. 30% Thermal ellipsoids. Hydrogens omitted for clarity.**

Table 21: Selected bond lengths and angles of 17.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	2.112(5)	Zr(1)-N(1)-C(8)	140.8(4)
Zr(1)-C(1)	2.324(7)	Zr(1)-C(1)-C(2)	120.6(4)
Zr(1)-Cp(1)	2.229(3)	Cp(1)-Zr(1)-Cp(2)	128.82(12)
Zr(1)-Cp(2)	2.207(3)	N(1)-Zr(1)-C(1)	96.2(2)
N(1)-C(8)	1.394(8)		
C(1)-C(2)	1.498(9)		

3.1.7 Synthesis of [(Cp₂Zr(μ-NPh)₂)] **18**

The amide bridged zirconium dimer **18** was synthesised from the addition of free aniline to bis-benzylzirconocene in deuterated benzene at 100 °C. After heating at for 7 days insoluble green crystals were obtained as the major product. Analysis by ¹H NMR spectroscopy and ¹³C NMR spectroscopy was not possible due to the insolubility of the crystals in all available solvents.

Scheme 27: Synthesis of 16 from transamination and salt metathesis reactions.

The green crystals were submitted for an X-ray diffraction study. However due to inadequate refinement and modelling the crystal structure data is not deemed to be of acceptable quality to be discussed in this thesis (the refinement data and ORTEP diagram are reported in the appendices). The crystal structure data indicates the synthesis of the amido-bridged dimer [(Cp₂Zr(μ-NPh)₂)]. The crystal structure data for **18** shows the zirconium atoms and bridging phenylamide ligand is one plane, with two cyclopentadienyl ligands bonded to each zirconium atom, one located above and one below this plane. The structure of **18** is extremely similar to the literature compound **XXIII** (including significant disorder of the crystal structure) and is also likely formed due to the lack of steric bulk at the *meta* positions of the phenylamide.

3.1.8 Synthesis of [Cp₂Zr(NHDMP)(Bn)] **19**

The amide [Cp₂Zr(NHDMP)(Bn)], **19** was synthesised through treatment of bisbenzylzirconocene with dimethylphenylaniline at elevated temperatures (eq. 25). Compound **19** was characterised by ¹H NMR spectroscopy, ¹³C NMR spectroscopy and single crystal X-ray diffraction.

The ¹H NMR spectrum of **19** revealed 5 aromatic signals, a triplet at δ 7.34 ppm (2H), a doublet at δ 7.22 ppm (2H), a multiplet at δ 7.11 ppm (2H), a triplet at δ 7.05 ppm (1H) and a triplet at δ 6.95 ppm (1H). The aromatic resonances were not assigned to specific hydrogen environments but one would assume the two triplets at δ 7.05 and 6.95 ppm and from the *para* substituted protons of the NHDMP and Bn ligands respectively. The cyclopentadienyl environment is attributed to the resonance at δ 5.44 ppm (10H), chemical shifted upfield from bisbenzylzirconocene (δ 5.51 ppm). The methylene resonance of the benzyl ligand is chemical shifted downfield from δ 1.83 ppm (4H) to δ 2.25 ppm (2H). The *ortho* substituted methyl environments of the NHDMP ligand are observed as a resonance at δ 2.14 ppm, chemical shifted downfield from the free amine (δ 1.88 ppm).

Crystals suitable for an X-ray diffraction study were obtained from a concentrated hexane solution of **19**. The crystal structure reveals a single molecule of **19** in the asymmetric unit as well as a molecule of toluene at half occupancy that was determined not to be interacting with the molecule of **19**. The Zr(1)-N(1) bond distance of 2.087(2) Å is longer than that of the methyl complexes **14** (2.080(9) Å), **15** (2.078(3) Å) and **16** (2.080(3) Å), indicating that the different electronic and steric profile of the benzyl ligand compared to the methyl ligand, however the small difference between the complexes makes doesn't make the differences significant. The Zr(1)-C(9) bond length of 2.355(3) Å falls within the range of Zr(1)-C(1) bond distances of **14**, **15** and **16** (2.303(4)-2.526(5) Å), indicating that the Zr-C bond length of arylamidozirconocenes with a benzyl ligand is longer than the equivalent complex with a methyl ligand. The angle between the centroids of the cyclopentadienyl ligands is much smaller in **17** (130.88(7)°) than in the methyl complexes **14**, **15** and **16** (136.5(4)°, 141.88(11)° and 134.9(2)° respectively), but larger than the benzyl complex **17** (128.82(12)°). The Zr-N(1)-C(1) angle of 137.13° is smaller than that of the Zr(1)-N(1)-C(8) angle of

140.8(4)° in **17**, indicating that as the steric bulk at the *ortho* positions of the phenylamide rings is increased this angle decreases. This is in contrast to the effect observed in the methyl complexes **14**, **15** and **16**.

Table 22: Selected bond lengths and angles of 19.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	2.087(2)	Zr(1)-N(1)-C(1)	137.13(16)
Zr(1)-C(9)	2.355(3)	Zr(1)-C(9)-C(10)	113.21(17)
Zr(1)-Cp(1)	2.212(3)	N(1)-Zr(1)-Cp(1)	106.91(11)
Zr(1)-Cp(2)	2.284(13)	N(1)-Zr(1)-Cp(2)	108.31(7)
		C(9)-Zr(1)-Cp(1)	104.61(11)
		C(9)-Zr(1)-Cp(2)	130.88(7)

Figure 45: ORTEP representation of 19. 30% Thermal ellipsoids. Hydrogens omitted for clarity. Disorder in the Cp2 ring modelled over two positions.

3.1.9 Synthesis of [Cp₂Zr(NAr*)(THF)] **20**

[Cp₂Zr(NAr*)(THF)] (**20**) was synthesised from the thermolysis of **15** at 100 °C in the presence of THF. The orange crystals were characterised by ¹H NMR spectroscopy, ¹³C NMR spectroscopy and single crystal X-ray diffraction.

The ¹H NMR spectrum of **20** indicated all four of the flanking phenyl rings were equivalent, hence were observed as three resonances; a doublet δ 7.39 ppm (8H), a triplet at δ 7.20 ppm (8H) and a triplet of at δ 7.08 ppm (4H) correspond to the *ortho*, *meta* and *para* substituted protons respectively. The singlet at δ 7.05 ppm (2H) was attributed to the *meta* protons on the tetrasubstituted phenyl ring, while the singlet at δ 6.43 ppm (2H) was determined to be the resonance of the equivalent methine (CH) protons. The singlet at δ 5.74 ppm (10H) was attributed to the cyclopentadienyl environment, a chemical shift downfield from the resonance in **15** (δ 5.58 ppm (10H)). The two THF multiplets integrate to 4 protons each, and are shifted from free THF to δ 3.44 ppm and δ 1.08 ppm respectively, indicating increased shielding likely due to coordination to the zirconium atom.⁷¹ There is no observable high field alkyl resonance or broad amide proton in the ¹H NMR spectrum, indicating the loss of the methyl as methane from **15**.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated toluene solution of **20**. The X-ray crystal structure shows one molecule of **20** in the asymmetric unit along with one molecule of toluene and one molecule of THF acting as an electron donor to the zirconium atom. The toluene atom was determined not to be interacting with the solid-state structure **20**. The crystal structure data shows a distorted tetrahedral geometry at the zirconium centre and has the unique almost linear Zr(1)-N(1)-C(1) bond angle of 167.60°, characteristic of the known complexes of this type.^{49, 54-55, 114} This angle is larger than compound (XXXI(a)) (157.17°), but smaller than the known *tert*-butyl imidozirconocene XXX (172.55°, 174.32°). The almost linear bond angle is attributed to the nitrogen acting as a four electron donor, lengthening the Zr-N bond distance and formally making the species a 20 electron complex.⁴⁹ The smaller angle in **20** relative to the literature indicates that the nitrogen may be acting less as a four

electron donor than in **XXX**. The Zr(1)-N(1) bond length of 1.891 Å is longer than that of **XXXI(a)** and **XXX** (1.889 and 1.826 Å respectively), likely due to the increased steric profile of the *N*Ar* ligand over the *N*Dipp and *N*^tBu ligands.¹¹⁵ The Zr(1)-O(1) bond distance of 2.300 Å is longer than in the complexes **XXX** (2.260 Å) and **XXX(a)** (2.240 Å), likely also a reflection of the increased bulkiness of the *N*Ar* ligand, though possibly a function of the ligands increased σ -donor ability relative to other bulky amines due to the increased carbon substitution at the 2,4 and 6 positions of the ligands central phenyl ring. The cyclopentadienyl-zirconium distances (Cp-Zr(1)) are 2.272 Å and 2.289 Å for the two cyclopentadienyl ligands, measured from the centre of the 5 carbon atoms to the zirconium atom. These distances are slightly longer than in that repeated in the literature for the compounds **XXX** and **XXXI(a)**.

Figure 46: ORTEP representation of 20. 30% Thermal ellipsoids. Hydrogens omitted for clarity. Cyclopentadienyl ligands shown with centroids.

Table 23: Selected bond lengths and angles of 20.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	1.891	Zr(1)-N(1)-C(1)	167.60
N(1)-C(1)	1.365	Cp(1)-Zr(1)-Cp(2)	124.89
Zr(1)-Cp(1)	2.289	N(1)-Zr(1)-O(1)	95.91
Zr(1)-Cp(2)	2.272	N(1)-Zr(1)-Cp(1)	113.21
Zr(1)-O(1)	2.300	N(1)-Zr(1)-Cp(2)	110.30

3.2 Insertion Reactions of Azides with alkylzirconocenes

3.2.1 Synthesis of [Cp₂Zr(Bu)(N₃(Bu)(Mes))] **21**

The first route toward a zirconium nitrogen double bond was the synthesis of [Cp₂Zr=NMe]. The rationale behind the reaction was that upon generation of the Negishi reagent; 'Cp₂Zr' a Zr(II) species, oxidative addition with an azide would result in formation of the nitrogen double bond with the elimination of nitrogen gas being a driving force behind bond formation. This synthetic strategy has been used for a wide range of other metals for the formation of nitrogen double bonds including Fe, Co, Ge, Sn and Nb.^{41, 116-118}

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Scheme 28: Proposed synthetic route to imidozirconocenes from oxidative addition to the Negishi reagent.

However, when the reaction was carried out *via* the assumed generation of the Negishi reagent at -30 °C, upon addition of the azide the reaction gave the insertion product **21**. The formation of the triazenido ligand from azides is known in the literature for zirconium, however, the majority of triazenido complexes with zirconium are synthesised *via* deprotonation of the corresponding triazene followed by coordination opposed to insertion into the zirconium-alkyl bond.^{55, 120-121}

Scheme 29: Synthesis of triazenido complex **21.**

The ^1H NMR spectrum of **21** shows the chemical shift downfield (δ 3.26, 2H) of the triplet signal of one of the two *n*-Bu fragments. This resonance is attributed to the protons on the α -carbon of the butyl fragment of the triazenido ligand, which would be expected to have increased deshielding due to the adjacent nitrogen atom. The resonances associated with the mesityl group are shifted downfield (δ 6.81 (2H), 2.33 (6H), 2.15 (3H)) relative to the free mesityl azide (δ 6.54 (2H), 2.13 (6H), 2.01 (3H)), indicating a change to a more deshielded chemical environment. The presence of several signals in the high field of the spectrum indicates that there are two *n*-Bu fragments present in **21**, indicating that the β -hydrogen elimination of the dialkyl zirconocene to give the Negishi reagent never occurred, and instead the azide inserted into one of two zirconium alkyl fragments present.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated toluene solution of **21**. The X-ray crystal structure data of **21** shows 2 molecules in the asymmetric unit with approximately the same bond lengths and angles, hence only one molecule will be discussed here. The 5-coordinate zirconium metal centre is in a distorted trigonal bipyramidal geometry (Figure 47). The two alkyl fragments are oriented anti to each other, and the plane of the mesityl group is orientated almost orthogonal to the equatorial ZrN_3 plane, presumably to minimize steric repulsion. Comparing the structure to the most similar complex in the literature, **XXXIV**; the Zr-N distances in **21** are extremely similar (2.339 and 2.314 Å), indicating the delocalisation of electrons over the all three of the nitrogens. This differs from complexes **XXXIV**, which has one of the nitrogen-nitrogen bonds almost 0.2 Å shorter (2.388 compared to 2.197 Å), though this compound does not have delocalisation of electron density over all three nitrogen atoms, so a different bond length would be expected.⁵⁵ The bite angle of the triazenido ligand (53.63 Å) is comparable to the literature values for triazenido ligands on zirconium (IV).¹²² The two butyl groups are orientated anti each other (C(1)-(Zr(1)-N(3)-C(14) dihedral angle (DHA) = 178.13°).

Figure 47: ORTEP diagram of 21. 30% thermal probability, hydrogens omitted for clarity. Cyclopentadienyl ligands shown with centroids.

Table 24: Selected bond lengths and angles of 21.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(1)	2.339(2)	N(1)-N(2)-N(3)	107.0(2)
Zr(1)-N(3)	2.314(2)	N(1)-Zr(1)-N(3)	53.63(7)
Zr(1)-C(1)	2.325(2)	Zr(1)-N(1)-C(5)	147.41(16)
N(3)-C(14)	1.464(3)	Zr(1)-N(3)-C(14)	145.17(17)
N(1)-C(5)	1.437(3)	Cp(1)-Zr(1)-Cp(2)	127.90(5)
Zr(1)-Cp(1)	2.2251(11)	(N(1)-Zr(1)-C(1)	77.85(8)
Zr(1)-Cp(2)	2.2460(13)		

3.2.2 Synthesis of [Cp₂Zr(Me)(N₃(Me)(Mes))]

22

Having synthesised **21** it was decided that the other readily accessed bis-alkyl zirconocenes would be synthesised to gain some insight as to the effect of the alkyl fragment on the structure and bonding of the triazenido zirconocene complex. The reaction of [Cp₂ZrMe₂] with one equivalent of [MesN₃] in toluene generated the insertion product with high yield (85%).

Scheme 30: Synthesis of 22 via bismethylzirconocene.

The ¹H NMR spectrum of **22** shows the downfield chemical shift to δ 3.00 (3H) of one of the methyl singlets, which is attributed to the methyl going from the extremely shielded zirconium methyl present in [Cp₂ZrMe₂] (δ -0.12) to the more deshielded triazenido ligand due to the electronegative nitrogen atom. A second methyl environment is observed at δ -0.23 (3H). The chemical shift indicates increased shielding relative to the starting material. The methyl mesityl resonances are also downfield shifted relative to the azide starting material to δ 2.33 (6H) and 2.17 ppm (3H). The meta protons of the mesityl group resonate as a singlet at δ 6.82 ppm (2H), while the cyclopentadienyl resonance is a singlet at δ 5.62 ppm.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated diethyl ether solution of **22**. The solid-state crystal structure data reveals **22** has one molecule in the asymmetric unit. The

molecule has the same conformation as **21**, with the mesityl ring almost orthogonal to the plane on the three nitrogen atoms (the angle between planes $95.9(6)^\circ$). As per **21**, the crystal structure data for **22** reveals the two alkyl fragments are orientated anti to each other ($\text{C}(1)\text{-N}(3)\text{-Zr}(1)\text{-C}(2)$ DHA = 169.45°). This DHA is smaller than **21**, possibly due to the reduced steric bulk of the methyl ligand relative to the butyl ligand. The bite angle of the triazenido ligand in **20** is $53.7(2)^\circ$, effectively the same as **21** ($53.63(7)^\circ$). The $\text{Zr}(1)\text{-N}$ distances of $2.331(6)$ Å and $2.343(6)$ Å are similar to **21** ($2.339(2)$ Å and $2.314(2)$ Å), indicating the change of alkyl substituent has little effect on the coordination of the triazenido ligand. The $\text{Zr}(1)\text{-C}(2)$ distance of $2.297(9)$ Å is shorter than the $\text{Zr}(1)\text{-C}(1)$ distance of **21** ($2.325(2)$ Å). Other bond distances and angles are available in Table 25.

Figure 48: ORTEP diagram of 22. 30% thermal probability, hydrogens omitted for clarity. Cyclopentadienyl ligands shown with centroids.

Table 25: Selected bond lengths and angles of 22.

Bond Lengths (Å)		Bond Angles ($^\circ$)	
$\text{Zr}(1)\text{-N}(3)$	$2.331(6)$	$\text{N}(1)\text{-Zr}(1)\text{-N}(3)$	$53.7(2)$
$\text{Zr}(1)\text{-N}(1)$	$2.343(6)$	$\text{N}(3)\text{-Zr}(1)\text{-C}(2)$	$128.4(3)$
$\text{Zr}(1)\text{-C}(2)$	$2.297(9)$	$\text{Zr}(1)\text{-N}(1)\text{-C}(3)$	$144.1(6)$
$\text{N}(3)\text{-C}(1)$	$1.44(1)$	$\text{Zr}(1)\text{-N}(3)\text{-C}(1)$	$145.9(5)$
$\text{N}(2)\text{-N}(1)$	$1.333(8)$	$\text{N}(1)\text{-N}(2)\text{-N}(3)$	$107.4(6)$

Zr(1)-Cp(1)	2.230(5)	Cp(1)-Zr(1)-Cp(2)	130.4(2)
Zr(1)-Cp(2)	2.225(5)	Cp(1)-Zr(1)-C(2)	99.6(3)
N(1)-C(3)	1.416(10)	Cp(2)-Zr(1)-C(2)	98.2(3)

3.2.3 Synthesis of [Cp₂Zr(Me)(N₃(Me)(C₆H₅))] **23**

Compound **23** was synthesised from the addition mesitylazide to [Cp₂ZrMe₂] at -30 °C in diethyl ether. **23** was characterised by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, IR, elemental analysis and single crystal X-ray diffraction.

The ¹H NMR spectrum shows the characteristic downfield shift for the NMe environment at δ 3.14 ppm (3H), likely due to the increased deshielding from the α nitrogen atom. The zirconium bonded methyl environment is chemical shifted downfield to δ 0.04 ppm (3H) from δ -0.12 ppm and the cyclopentadienyl resonance is upfield shifted to δ 5.60 ppm (10H) from the starting material (δ 5.71 ppm). The aromatic signals are observed as two multiplet at δ 7.33-7.28 ppm (4H) for the *ortho* and *meta* protons and δ 7.01 ppm (1H) for the *para* substituted proton.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated diethyl ether solution of **23**. The solid-state crystal structure of **23** has 2 molecules of in the asymmetric unit. These molecules have extremely similar bond lengths and angles, as such only one molecule will be discussed in detail. There are 5 coordinated sites occupied resulting in a distorted trigonal pyramidal geometry around the central zirconium atoms with the Zr-methyl ligand and triazenido ligand occupying the equatorial plane. Unlike **22** the methyl groups are located syn to each other C(1),N(3)-Zr(2)-C(4) DHA = 2.99°. As **22** has the anti-DHA of the methyl ligands, it is indicated that the steric bulk of the azide the determines the syn or anti orientation of the alkyl groups. The zirconium nitrogen bond, Zr(1)-N(5), (2.356(3) Å) in which the nitrogen has an α phenyl substituent of is longer than the zirconium nitrogen bond length with an α methyl substituent; Zr(1)-N(4) of 2.296(3) Å, reflecting the non-symmetrical nature of the triazenido ligand. The

zirconium cyclopentadienyl bond distances are shorter than in **22**, though whether this is a steric or electronic effect is unknown. The angle between the cyclopentadienyl planes is similar to **22**.

Figure 49: ORTEP representation of **23**. 30% Thermal ellipsoids. Hydrogen atoms omitted for clarity.

Table 26: Selected bond lengths and angles of **23**.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-Cp(3)	2.2233(15)	Cp(1)-Cp(2) planes	129.17(15)
Zr(1)-Cp(4)	2.2244(16)	N(4)-Zr(1)-N(5)	53.84(10)
N(4)-N(6)	1.303(4)	Zr(1)-N(4)-C(14)	145.2(2)
N(6)-N(5)	1.319(4)	Zr(1)-N(6)-C(28)	146.9(2)
Zr(1)-C(9)	2.330(3)	Cp(3)-Cp(4) planes	129.52(7)
Zr(1)-N(5)	2.356(3)	N(4)-N(5)-N(6)	107.0(3)
Zr(1)-N(4)	2.296(3)		

3.2.4 Synthesis of [Cp₂Zr(Bn)(N₃(Bn)(Mes))]

24

24 was synthesised from the treatment of [Cp₂ZrBn₂] with mesitylazide at -30 °C. Following workup and purification by crystallisation the compound was characterised by ¹H NMR spectroscopy, ¹³C NMR spectroscopy and single crystal X-ray diffraction.

24

The ¹H NMR spectrum of **24** shows the significant chemical shift downfield from δ 1.83 ppm to δ 4.43 ppm (2H) for the methylene environment of the ZrBn group that the azide had inserted into. The other methylene CH₂ resonance has shifted upfield slightly to δ 1.70 ppm (2H). The phenyl aromatic resonances are visible as 5 signals at δ 7.25 (2H), 7.13 (4H), 7.09 (1H), 6.99 (2H), 6.85 ppm (1H) for 6 environments, while the *meta*-substituted phenyl protons that are part of the mesityl group resonate as a singlet at δ 6.80 ppm (2H), similar to **22** (δ 6.82 ppm (2H)). The equivalent cyclopentadienyl ligands resonate at δ 5.62 ppm (10H), upfield from **21** (δ 5.79 ppm) and **22** (δ 5.69 ppm), but downfield from **23** (δ 5.60 ppm). The mesityl methyl environments are visible in a 2:1 ratio at δ 2.33 ppm (6H) and δ 2.14 ppm (2H), downfield shifted from the free azide.

Crystals suitable for an X-ray diffraction study were obtained from a concentrated hexane solution of **24**. The solid-state crystal structure data indicates that **24** has one molecule present in the asymmetric unit. As per the other triazenido compounds the zirconium atom is 5 coordinate at the zirconium atom with a distorted trigonal bipyramidal geometry. The triazenido ligand and ZrBn ligand occupy the equatorial plane, while the of the cyclopentadienyl ligands (as measured from the centroid in the centre of each ring) are separated by an angle of 128.26(6)°. The bite angle (N(1)-Zr(1)-N(3)) of the triazenido ligand is 53.72°, similar to compounds **21** (53.63°), **22** (52.7°) and **23** (53.84°), indicating that the bite angle doesn't appear to the changing electronic and steric properties of the substituents. The Zr(1)-C(17) bond distance of 2.384(2) Å is slightly longer than the zirconium carbon bond of **21** (2.325(2) Å) and **22** (2.330(3) Å), though whether this is an electronic effect through increased σ-donation or a steric effect was unable to be determined. The benzyl groups are orientated anti to one another (C(10)-N(1)-Zr(1)-C(17) DHA = 172.84),

as would be expected if the observation that the orientation is dependent on the steric bulk of the azide is correct.

Figure 50: ORTEP diagram of 24 with 30% thermal probability, hydrogens omitted for clarity. Cyclopentadienyl ligands shown with centroids.

Table 27: Selected bond lengths and angles of 24.

Bond Lengths (Å)		Bond Angles (°)	
Zr(1)-N(3)	2.329(2)	N(1)-Zr(1)-N(3)	53.72(7)
Zr(1)-N(1)	2.342(2)	N(3)-Zr(1)-C(17)	74.24(8)
Zr(1)-C(17)	2.384(2)	Zr(1)-N(3)-C(6)	147.87(6)
N(2)-N(1)	1.294(3)	Zr(1)-N(1)-C(1)	146.26(16)
Zr(1)-Cp(1)	2.2193(12)	N(1)-N(2)-N(3)	107.76(18)
Zr(1)-Cp(2)	2.2305(13)	Cp(1)-Zr(1)-Cp(2)	128.26(6)
		Cp(1)-Zr(1)-C(17)	102.08(7)
		Cp(2)-Zr(1)-C(17)	102.35(7)

3.3 Summary of Results

The novel amidozirconocenes **14**, **15**, **16**, **17**, **18** and **19** were synthesised for their use in the synthesis of **1**. The amidozirconocenes have varying steric bulk on the amide ligand so that the effect of amide bulk on the synthesis of **1** can be investigated. The amides **14** ($[\text{Cp}_2\text{Zr}(\text{NHDipp})(\text{Me})]$), **15** ($[\text{Cp}_2\text{Zr}(\text{Me})(\text{NHA}r^*)]$) and **16** ($[\text{Cp}_2\text{Zr}(\text{Me})(\text{NH}(\text{DMP}))]$) indicated that as the steric bulk of the amide is increased, the Zr-N-C angle of the amide increases. The benzyl complexes **17** ($[\text{Cp}_2\text{Zr}(\text{NPh})(\text{Bn})]$) and **19** ($[\text{Cp}_2\text{Zr}(\text{NHDMP})(\text{Bn})]$) however indicate the opposite effect, with the Zr-N-C bond angle decreasing with increased steric bulk. Hence more information is needed in order to fully understand the relationship. The imidozirconocene **20** was synthesised from the thermolysis of **15** with THF, and crystal structure data showed similar bond lengths and angles to the literature complexes **XXX** and **XXXI(a)**. The insertion reactions of mesitylazide and phenyl azide into $[\text{Cp}_2\text{ZrMe}_2]$, $[\text{Cp}_2\text{ZrBn}_2]$ and $[\text{Cp}_2\text{ZrBu}_2]$ were investigated and it was determined that the steric bulk of the azide influences the structural configuration of the triazenido product. The synthesis of the butyl complex **21** indicated that the Negishi reagent was not generated and instead the azide moiety were inserting into the bis-alkylzirconocene.

4 Results and Discussion: Group 4 – Group 14 Heterobimetallics

4.1 Synthetic Strategy

The strategy employed towards synthesising an amido-bridged germanium zirconium complex was based on two main approaches. The first was the reaction of the imidozirconocene with a germylene, while the second was the reaction of reduced zirconium(II) with a germanimine. Since the reaction of imidozirconocene with a germylene was thought to be the more desirable synthetic route, the majority of reactions that were carried out used the attempted route of an imidozirconocene with a germylene, which was thought would either act as a donor to stabilise the zirconium nitrogen bond, or rearrange to provide the desired heterobimetallic.

Scheme 31: Proposed Synthetic Route to heterobimetallic 1.

4.2 Reactions between Group 4 and Group 14 Compounds

4.2.1 Addition of [Cp₂ZrMe₂] to [DippNH₂] in the presence of [Ge(NAPH^{TMS})]

The reaction of bismethylzirconocene with diisopropylaniline and [Ge(NAPH^{TMS})] was carried out in an NMR tube fitted with a young's tap and heated on an aluminium heating block to 75 °C. Reaction progress was monitored by ¹H NMR spectroscopy. After 2 days of heating the ¹H NMR resonances attributed to the zirconium amide could be seen growing in along with another set of diisopropyl peaks. Further heating resulted in a number of new resonances indicating a range of new products. The ¹H NMR spectrum did not give an indication of the desired reaction product, as although there was a new intense peak growing in, consistent with a isopropyl environment, there was no observed change to the TMS resonances of

[Ge(NAPH^{TMS})]. The low field zirconium alkyl resonance did also not disappear to give methane as desired. Although attempted, separation of the products was not successful.

4.2.2 Addition of [Cp₂Zr(Me)(NHDipp)] to [Ge(NAPH^{TMS})]

To investigate whether the THF stabilized imidozirconocene would react with [Ge(NAPH^{TMS})], giving an imido-bridged heterobimetallic, or germylene stabilized imidozirconocene, the addition of 2 equivalents of THF to [Cp₂Zr(Me)(NHDipp)] followed by heating formed the imidozirconocene *in situ*. Presence of the imidozirconocene was confirmed from comparison to literature ¹H NMR spectroscopy values.⁵⁴ To this solution was added [Ge(NAPH^{TMS})] and ¹H NMR spectra were taken after various temperature intervals.

Scheme 32: Proposed reaction to amide bridged heterobimetallic 1.

Analysis of the ¹H NMR spectra of the crude reaction mixture indicated that there was no change in chemical environment of the germylene or imidozirconocene (no change to a chemical shift or change in resonance multiplicity). The imidozirconocene species appeared to decompose after several days, with a range of new cyclopentadienyl peaks in the region δ 6.4 - 5.3 ppm while the characteristic isopropyl resonances at δ 3.70 (septet) and 1.38 (doublet) ppm slowly diminished. Although no single product could be isolated, the chemical shifts in the ¹H NMR spectra indicated the imidozirconocene [Cp₂Zr(NDipp)(THF)] had been synthesised before subsequently decomposing. Although not a success, this indicates that the THF stabilised imidozirconocene was more stable than the proposed germylene stabilised imidozirconocene. This is perhaps unsurprising, as THF is known to be a strong donor and coordinating

solvent. Although exchange of the THF molecule for the germylene was expected, the ^1H NMR spectra indicated that the lone pair on complex **3** is not a strong enough donor atom to displace THF.

4.2.3 Addition of $[\text{Cp}_2\text{Zr}(\text{NAr}^*)(\text{THF})]$ to $[\text{Ge}(\text{BIAN}^{\text{Mes}})]$

To investigate whether the THF stabilised imidozirconocenes were reactive towards a different germylene, a reaction similar to that above was carried out. To one equivalent of the bulky isolated imidozirconocene **20** was added one equivalent of the germylene $[\text{GeBIAN}^{\text{Mes}}]$. The reaction was carried out on an NMR scale so that the reaction could be monitored throughout by ^1H NMR spectroscopy.

The ^1H NMR spectrum indicated no change to the $[\text{GeBIAN}^{\text{Mes}}]$ resonances for the aromatic BIAN backbone at δ 7.20 (doublet), 6.90 (triplet), and 6.59 (doublet) ppm, or to the mesityl resonances at δ 6.94 (singlet), 2.29 (singlet) or 2.26 (singlet), indicating no change in environment in solution for any of the atoms present in $[\text{GeBIAN}^{\text{Mes}}]$. A new singlet at δ 1.23 ppm grew in over 5 days at 100 °C, this was assumed to be a new *tert*-butyl environment as the resonance of the *tert*-butyl peak of **18** (δ 1.17 ppm) decreased proportionally. Although this indicated the presence of one new product, a number of new resonances in the cyclopentadienyl region of chemical shifts (δ 5.59, 5.58 and 5.48 ppm) indicated a range of cyclopentadienyl environments, either indicating a number of products or possible loss of symmetry of the cyclopentadienyl ligands. Due to the high number of aromatic protons present in **18** the aromatic region a complex series of multiplets, and hence did not help identify the species present in solution. Attempts to isolate individual products proved unsuccessful, however it seems likely that the imidozirconocene was undergoing some sort of decomposition at 100 °C and did not proceed to the desired heterobimetallic complex.

4.2.4 Addition of [Cp₂Zr(NHAr*)(Me)] to [GeBIAN^{Mes}]

Since substitution of the relative donor molecules didn't occur from the treatment of the **18** with the germylenes **2** or **3**, thermal elimination by the alkyl-amidozirconocene in the presence of a germylene was attempted (eq. 31). Prior reactions had indicated that without the presence of THF present the thermal elimination of methane would not proceed to the imidozirconocene, hence the reaction of **15** with **2** was carried out to investigate whether the germylene would act as a donor molecule when a more suitable donor molecule such as THF was not present.

The reaction was carried out in an NMR tube fitted with a Young's tap in order to monitor the reaction by ¹H NMR spectroscopy. Over the period of 5 days up to 100 °C the methyl peak of **15** vanished, indicating the elimination of methane, which was confirmed from the increased intensity of a new signal attributed to methane at 0.16 ppm.⁷¹ The *tert*-butyl singlet resonance at δ 1.10 ppm became weaker over the 5 days while a new singlet at δ 1.24 ppm grew in proportion to the diminishing signal, indicating the presence of a single new *tert*-butyl environment (likely the same product as the reaction described by eq. 30). The cyclopentadienyl singlet of the amide (δ 5.59 ppm) diminishes over the 5 days, with two new singlets appearing in spectrum at δ 5.60 and 5.49 ppm respectively attributed to two new cyclopentadienyl environments. There was no observed change to the [Ge(BIAN^{Mes})] aromatic signals of δ 7.20 (doublet), 6.90 (triplet), and 6.59 (doublet) ppm, or to the mesityl resonances at 6.94 (singlet), 2.29 (singlet) or 2.26 (singlet), indicating no coordination or decomposition of the germylene over the 5 days. Interestingly, the signals at δ 5.49, and 1.24 ppm indicate that the reaction of the amide **15** with **2** and the reaction of the imidozirconocene **20** with **2** may go to the same product. This perhaps shouldn't be surprising as it is likely that the imidozirconocene is being generated *in situ*. However, there is no evidence of the imidozirconocene in the ¹H NMR spectrum, indicating that if the imidozirconocene is being generated, it is then reacting again instantly. This is in contrast to the THF stabilised imidozirconocene, which was observed to react over several days, even at 100 °C.

Scheme 33: Possible reaction of 15 to zirconium tetracycle.

Assuming generation of the imidozirconocene in situ, it seems most likely that the reaction product could be the [2+2] cycloaddition dimer (zirconium tetracycle) (Scheme 33). Complexes of this type are known (including **XXXI(d)** and **18**), although the zirconium atoms have previously only been reported supported by the dimethyl amide ligand with bridging amidosilyl or amidotertbutyl ligands, or with the relatively small 4-*tert*-butylphenyl amide supported with cyclopentadienyl ligands.^{49, 123-124} **15** was chosen for use in this reaction due to the large steric bulk of [NHAr*], which it was assumed would kinetically hinder the cycloaddition through steric stabilisation. A simple way to investigate Scheme 34 would be to heat **15** or **19** to see whether the same ¹H NMR resonance are seen in the ¹H NMR spectrum.

4.2.5 Addition of [DMPNH₂] to [Cp₂ZrBn₂] with [Ge(HMDS)₂]

To see whether using a smaller amine source [2,6-MeC₆H₃NH₂] and different germylene would promote formation of **1**, the reaction detailed in Scheme 34 was carried out. The reagents were heated together to 70 °C over 5 days in an NMR tube fitted with a Young's tap. ¹H NMR spectra were collected over the period to monitor the reaction in situ. Over this period, a change in the cyclopentadienyl resonance from δ 5.51 ppm to two new resonances in an approximate 1:10 ratio at δ 5.56 and 5.44 ppm was observed. The new major product cyclopentadienyl peak at δ 5.44 ppm was attributed to the benzyl amide species **19**, while the product at δ 5.56 was the suspected zirconium tetracycle, although this product could not be isolated for further analysis. The presence of a new singlet at δ 3.35 ppm which integrated in a 6:10 ratio for the 2,6 methyl positions relative to the new cyclopentadienyl resonance indicates either the synthesis of the imidozirconocene or the zirconium tetracycle shown in Scheme 34. In the high field the [Ge(HMDS)₂] resonance at δ 0.32 ppm fully disappears after the first 24 hours of heating at 70 °C, with a new singlet at δ 0.09 ppm appearing with an equivalent integral to the [Ge(HMDS)₂] starting material. This new resonance is likely the protonated free ligand [(HMDS)-H], which is known to appear at this chemical shift. This resonance could either occur through thermal degradation of [Ge(HMDS)₂], or ligand exchange with the 2,6-dimethylaniline. Thermal degradation requires the ligand to pick up a proton, while

ligand transfer would be expected to give the by-product $[\text{Ge}(\text{NHDMP})_2]$, which was not observed in the ^1H NMR spectrum. The low field shows a new triplet at δ 7.34 ppm, doublet at δ 7.22 ppm, attributed the new amide resonances, as well as toluene signals at δ 7.13 (multiplet), 7.02 (multiplet) and 2.11 ppm (singlet) indicating the hydride transfer from the free amine to the benzyl group to give toluene as a reaction by-product.

Scheme 34: Reaction of Bisbenzylzirconocene with 2,6-dimethylaniline and $[\text{Ge}(\text{HMDS})_2]$.

4.2.6 Addition of $[\text{Ge}(\text{HMDS})_2]$ to $[\text{Cp}_2\text{Zr}(\text{NHPH})(\text{Bn})]$

After the previous reaction had shown that $[\text{Cp}_2\text{Zr}(\text{NHPH})(\text{Bn})]$ thermally ejects toluene to give the amide bridged dimer **18**, the reaction was repeated in the presence of a germylene to investigate whether the germylene could act as a suitable donor or even react with the amide to the desired heterobimetallic. This approach would also avoid possible ligand exchange between $[\text{Ge}(\text{HMDS})_2]$ and the free amine, as was a possible side product as shown in the reaction in Scheme 35. Equal molar amounts of $[\text{Cp}_2\text{Zr}(\text{NHPH})(\text{Bn})]$ and $[\text{Ge}(\text{HMDS})_2]$ were dissolved in deuterated benzene heated to 40 °C in an NMR tube fitted with a Young's tap for 2 days, before being heated to 100 °C.

Analysis of the ^1H NMR spectra over the time period showed that the evolution of two small new cyclopentadienyl resonances at δ 5.67 and 5.85 ppm. For the high field resonances, the intensity of the methylene peak at δ 2.22 ppm decreased over time, while the methyl toluene resonance at 2.11 ppm grew in over time, indicating the elimination of the benzyl group from $[\text{Cp}_2\text{Zr}(\text{NHPH})(\text{Bn})]$. The HMDS resonance of **I** at δ 0.32 ppm decreased over time with the evolution of two new singlets in a 1:4 ratio at δ 0.53 and 0.09 ppm growing in over time. These peaks indicate that while most of the $[\text{Ge}(\text{HMDS})_2]$ is

likely decomposing to the free ligand HMDS-H, a small fraction of **1** may have reacted. The ^1H NMR spectra does not allow this signal to be assigned with any certainty, but one could speculate that it could either be the complexation of the germylene to the zirconium centre in a donor-accepter relationship, or could be ligand exchange between the free HMDS-H and the phenyl amide to give the zirconium coordinated HMDS ligand and free aniline (Scheme 35).

Scheme 35: Possible products of the reaction between phenylamide-benzylzirconocene and $[\text{Ge}(\text{HMDS})_2]$ at 100 °C.

The decomposition of $[\text{Ge}(\text{HMDS})_2]$ to give free protonated HMDS-H requires an acid or proton transfer. The only acidic proton available in the reaction (other than minute amounts of impurities) is the acidic α proton of the phenyl amide. This proton is required for the elimination of the benzyl fragment as toluene so the migration to HMDS seems unlikely. Upon further heating a green crystalline solid identified as **18** by single crystal X-ray diffraction was isolated in a 70% yield.

4.2.7 Reduction of $[\text{Cp}_2\text{ZrCl}_2]$ with magnesium in the presence of $[\text{Ge}(\text{BIAN}^{\text{Mes}})]$

Applying the synthetic strategy employed by Muller et al. in their synthesis of donor stabilised germanium-zirconium bonds, the reduction of zirconocene dichloride in the presence of a germylene was attempted to try and form a direct zirconium germanium bond without the use of a bridging amide ligand.⁶⁰ After 24 hours there was no magnesium metal left in the reaction leaving a purple black solution (eq. 33). The reaction was dried to remove volatiles, extracted into toluene and filtered to give a dark purple solution.

Analysis of the ^1H NMR spectrum of a dried aliquot of the purple solution showed the resonances of the free germylene in solution at δ 7.20 (doublet), 6.94 (singlet), 6.90 (triplet), 6.59 (doublet) 2.29 (singlet) and 2.26 ppm (singlet). Several resonances present in the chemical shift range δ 6.0 – 4.5 ppm indicated a range of cyclopentadienyl environments and hence a range of products. The major resonance at δ 5.72 ppm was shifted upfield from the starting material (δ 5.89 ppm). The singlet integrated for 10 protons relative to the known germylene environments, indicating this unknown peak was the major product of the zirconocene dichloride reduction. Attempts to isolate and crystallise the compound attributed to this peak were not successful.

4.2.8 Addition of $[(\text{HMDS})_2\text{Ge}(\text{NMes})]$ to $[\text{Cp}_2\text{Zr}(\text{Bu})_2]$

In an attempt to synthesise **1** by the reaction of a germanimine with a reduced source of zirconium (Scheme 1), zirconocene dichloride was treated with 2 equivalents of *n*-BuLi at $-30\text{ }^\circ\text{C}$ to generate the negishi reagent. After warming to room temperature over 30 minutes the orange solution was treated with a solution of *in situ* generated compound **9**. After 2 days the solvent was removed the dark brown residue was extracted into hexane and filtered to give a dark yellow solution. ^1H NMR spectroscopy indicated two new major products. The two products proved inseparable.

Scheme 36: Addition of germanimine **9** to the Negishi reagent.

4.2.9 Reduction of $[\text{Cp}_2\text{ZrCl}_2]$ with magnesium in the presence of $[(\text{HMDS})_2\text{Ge}(\text{NMes})]$

In an attempt to synthesise **1** by the reaction of a germanimine with a reduced source of zirconium (Scheme 1), zirconocene dichloride was treated with magnesium metal in THF. This suspension was then treated with an *in situ* generated solution of **9** in hexane. The suspension was left to stir for two days until no more solid magnesium was present, resulting in a dark orange solution. Following removal of the solvent the dark yellow residue was extracted into hexane and filtered to remove a black solid. ^1H NMR

spectroscopy of the hexane extraction indicated a range of products. Isolation of these products was not possible.

4.3 Summary of Results

The two synthetic routes to **1** were attempted; firstly, through the addition of a germylene to an imidozirconocene, secondly through the reactions of a germanimine with a Zr(II) species. However, neither route lead to the synthesis of the desired heterobimetallic complex **1**.

For the synthetic route to **1** from the imidozirconocene species it was proposed that the [2+2] cycloaddition amido-bridged tetracycle product could explain the products observed by ^1H NMR spectroscopy. This is known to occur when there is insufficient steric bulk on the arylamide, to give the compounds **XXIX** and **18**.

For the synthetic route to **1** from the germanimine, the reaction with the *in situ* generated Negishi reagent gave two observable products by ^1H NMR spectroscopy, though neither product indicated that compound **1** had been formed. Attempted isolation of these two compounds is ongoing.

In conclusion, the desired heterobimetallic complex **1** was not successfully synthesised from either of the theorised synthetic routes. However, as the chemistry of low valent group 14 compounds develops new and exciting synthetic methods, complex **1** is a viable synthetic target for the future.

5 Appendices

5.1 Experimental

5.1.1 General Procedures

Unless otherwise stated all manipulations were performed under a dry and oxygen free N₂ environment using Schlenk-line and cannula techniques, or in a nitrogen filled glovebox. Solvents were dried using a PureSolv. System (Innovative Technologies) and stored over 4 Å molecular sieves. ¹H and ¹³C spectra were recorded in deuterated benzene at 298 K using a Varian INOVA system at ¹H: 300 and 600 MHz or ¹³C: 125 MHz and internally referenced to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrometer using Nujol mineral oil. Absorption spectra were obtained on a Shimadzu UV-2600 Spectrophotometer. All chemicals were purchased from Sigma-Aldrich chemical company and used as received unless otherwise stated. Liquids were subjected to a minimum of three freeze-pump-thaw cycles before storage over 4 Å molecular sieves in the glovebox.

Samples suitable for X-ray diffraction were grown in a concentrated solution of the sample using at -30 °C unless stated otherwise. Crystals were covered in inert oil and suitable crystals were selected under a microscope and mounted on an Agilent SuperNova X-ray Diffraction system fitted with an Atlas detector. Data were collected at the temperature indicated using focused Mo K α radiation at 0.71073 Å or Cu K α radiation at 1.54128 Å as specified. Intensities were collected for Lorentz and polarisation effects and for absorption using multi-scan methods. Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXT or SHELXL, refined on F² using all data by full matrix least-squares procedures with SHELXL-97, within OLEX-2.3.¹²⁵ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate unless otherwise stated. The functions minimized were $\sum w(F_2o - F_2c)^2$, with $w = [\sigma^2(F_2o) + aP^2 + bP]^{-1}$, where $P = [\max(F_2o)^2 + 2F_2c^2]/3$. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

The lithium salts of the following: hexamethyldisilazane, 2,6 diisopropylphenylamine, 2,6 dimethylphenylamine, N1,N8-bis(trimethylsilyl)naphthalene-1,8-diamine, 2,6-dibenzhydryl-4-(*tert*-

butyl)aniline and aniline were synthesised from the slow addition of 2.0 M *n*-BuLi (4 mmol) or 2.0 M *n*-BuLi (8.0 mmol) (for *N*¹,*N*⁸-bis(trimethylsilyl)naphthalene) in cyclohexane to a solution of the amine (4 mmol) in hexane at -30 °C. The solvent was removed under reduced pressure to yield the products as white, yellow or red solids.

5.1.2 [(C₅H₅)₂ZrN(2,6-*i*Pr₂C₆H₃)(C₄H₈O)] [Cp₂Zr(NDipp)(THF)]

This compound was made with modification to the literature procedure.⁵⁴ To an NMR tube fitted with a Young's tap was added [Cp₂Zr(Me)(NHDipp)] (22 mg, 0.05 mmol) in C₆D₆ (300 μL) along with 2 drops of deuterated THF. The reaction was heated on an aluminium heating block for 5 days and monitored by ¹H NMR spectroscopy until no starting material remained. No yield was taken for this complex due to it being used immediately in subsequent reactions.

¹H NMR (C₆D₆, 600MHz) δ 7.22 (d, *J*_{HH} = 7.2 Hz, 2H, *meta*-ArH); 6.90 (t, *J*_{HH} = 7.4 Hz, 1H, *para*-ArH); 6.07 (s, 10H, C₅H₅); 3.70 (sept, *J*_{HH} = 6.8 Hz, 2H, CH(CH₃)₃); 1.38 (d, *J*_{HH} = 6.8 Hz, 12H). A small amount of starting material was still observable in the ¹H NMR spectrum as an impurity.

5.1.3 [2,4,6-(Me)₃C₆H₂N₃] [MesN₃] C₉H₁₁N₃

In a modification of the literature procedure, 2,4,6 trimethyl aniline (6.80 mL, 0.05 mol) was added to a 250 mL RB (round-bottomed) flask with 9.7 mL of concentrated HCl (12M, 0.12 mol) and 50 mL of H₂O. The suspension was stirred for 30 minutes until a solution obtained. The solution was cooled to 0 °C with an ice bath and to the solution was added a prepared solution of sodium nitrite (6.89 g, 0.10 mol) in H₂O (5 mL) dropwise over 2 minutes. The resulting solution was left to stir for 1 hour. The solution had the pH adjusted to 7 with saturated sodium bicarbonate solution. The solution was again cooled to 0 °C with an ice bath and treated with a solution of sodium azide (6.50 g, 0.10 mol) in 5 mL water dropwise over 10 minutes. The resulting solution was left to stir for 2 hours. The compound was extracted into diethyl ether (2 x 50 mL), washed with H₂O (2 x 50 mL) and saturated sodium chloride solution (2 x 50 mL) before having the solvent removed under reduced pressure. Due to the potential risk of explosion a blast shield was used to isolate the azide any time the compound was put under reduced pressure. The resulting dark orange liquid was purified by vacuum distillation to give [MesN₃] as a dense yellow liquid. The solution discoloured over the next week so was stored under N₂ in the glovebox at -30 °C to minimise further degradation. ¹H NMR data for the compound agreed with literature values.¹²⁶

Yield: 6.74 g (87%).

^1H NMR (CDCl_3 , 300MHz) δ 6.83 (s, 2H, $\text{NC}_6\text{-2,6-(Me)-4-(Me)H}_2$); 2.32 (s, 6H, , $\text{NC}_6\text{-2,6-(Me)-4-(Me)H}_2$); 2.25 (s, 3H, , $\text{NC}_6\text{-2,6-(Me)-4-(Me)H}_2$).

5.1.4 [$\text{C}_6\text{H}_5\text{N}_3$] [PhN_3] $\text{C}_6\text{H}_5\text{N}_3$

In a modification of the literature procedure, aniline (4.66 g, 0.05 mol) was added to a 250 mL RB flask with 10.0 mL of concentrated HCl (12M, 0.12 mol) in H_2O (50 mL). The solution was stirred for 30 minutes before being cooled to 0 °C with an ice bath. A solution of sodium nitrite (4.82 g, 0.07mol) in H_2O (4 mL) was added dropwise over 2 minutes. The resulting solution was left to stir for 1 hour. The pH was adjusted to 7 sodium with sodium bicarbonate solution. The solution was cooled to 0 °C with an ice bath and treated with sodium azide (5.20 g, 0.08 mol) in H_2O (2 mL) dropwise over 10 minutes. The compound was extracted into diethyl ether (2 x 50 mL), washed with H_2O (2 x 50 mL) and saturated sodium chloride solution (2 x 50 mL) before solvent removal under reduced pressure. Due to the potential risk of explosion a blast shield was used to isolate the azide any time it was put under reduced pressure. The resulting orange liquid was purified by vacuum distillation to give [PhN_3] as a yellow liquid. Due to the short lifetime of the azide the product was stored under N_2 in the glovebox at -30 °C to minimise degradation.¹²⁷ ^1H NMR data for the compound agreed with the literature values.¹²⁸

Yield: 5.65 g (91 %).

^1H NMR (CDCl_3 , 300 MHz) δ 7.36 (t, J_{HH} = 8.2 Hz, 2H, *meta*- C_6H_5); 7.15 (t, J_{HH} = 8.1 Hz, 1H, *para*- C_6H_5); 7.04 (d, J_{HH} = 8.4 Hz, 2H, *ortho*- C_6H_5).

5.1.5 [$2,6\text{-((C}_6\text{H}_5)_2\text{CH)}_2\text{-4-((CH}_3)_3\text{C)C}_6\text{H}_2\text{NH}_2$] [Ar^*NH_2] $\text{C}_{36}\text{H}_{35}\text{N}$

This compound was made In a modification to the literature procedure.¹²⁹ To a 250 mL RB flask with 4-*tert*-butyl-aniline (2.50 g, 0.02 mol) was added 2 equivalents of diphenyl-methanol (6.17 g, 0.03 mol). The suspension was heated to 125 °C for 40 minutes. The resulting solution was treated with $[\text{ZnBr}_2]$ (2.09 g, 9.28 mmol) in HCl (12.1M, 1.4 mL) and the reaction was left to stir overnight. The resulting crude solid was filtered and washed with methanol using a Buchner funnel and dried in a heating pistol for 1 week (60 °C) to give the compound as a white solid. The compound agreed with literature ^1H NMR spectral data.

^1H NMR (CDCl_3 , 300 MHz) δ 7.29 (t, J_{HH} = 7.5 Hz, 8H, *meta*- C_6H_5); 7.22 (t, J_{HH} = 7.3 Hz, 4H, *para*- C_6H_5); 7.10 (d, J_{HH} = 7.3 Hz, 8H, *ortho*- C_6H_5); 6.58 (s, 2H, *meta*- C_6H_2); 5.47 (s, 2H, $(\text{CHPh}_2)_2$); 3.28 (s, 2H, NH_2); 0.98 (s, 9H, $\text{C}(\text{CH}_3)_3$).

^1H NMR (C_6D_6 , 300 MHz) δ 7.15-6.99 (m, 20H, ArH); 6.93 (s, 2H, ArH); 5.47 (s, 2H, $(\text{CHPh}_2)_2$); 1.11 (s, 9H, $\text{C}(\text{CH}_3)_3$).

5.1.6 [2,6- $((\text{C}_6\text{H}_5)_2\text{CH})_2$ -4- $((\text{CH}_3)_3\text{C})\text{C}_6\text{H}_2\text{N}_3$] [Ar*N₃] 25 C₃₆H₃₃N₃

In a 250 mL RB flask with stirring, [Ar*NH₂] (2.68g, 5.57 mmol) was dissolved in 1:2 H₂O (50 mL) to THF (100 mL) mixture. Concentrated HCl was added (10 mL, 12 M) and the temperature of the reaction was brought down to 0 °C using an ice bath. The solution was treated with 4 equivalents of sodium nitrite (1.50 g, 22.3 mmol) in H₂O (10mL) added dropwise over 5 minutes before being left to stir for four hours, after which time the solution had turned yellow. A solution of [NaN₃] (1.44 g, 0.02 mol) in H₂O (10 mL) was added dropwise over 5 minutes while maintaining an internal reaction temperature of under 5 °C. The reaction was left to stir for four hours. The compound was extracted into toluene (3 x 50 mL) and washed with sodium bicarbonate (2 x 100 mL), H₂O (2 x 50 mL) and brine (2 x 50 mL) before the toluene fraction was dried over MgSO₄ and filtered. The volatiles removed under reduced pressure to give the azide as an off white powder. A small amount (300 mg) of compound was recrystallised from the minimum value of toluene (2 mL) for single crystal X-ray diffraction. The compound was analysed by ^1H and ^{13}C NMR, liquid chromatography mass spectrometry (LC-MS) and single crystal X-ray diffraction.

Yield: 4.39 g (51%)

^1H NMR (CDCl_3 , 600MHz) δ 7.28 (t, $J_{\text{HH}} = 7.3$ Hz, 8H, *meta*-C₆H₅); 7.21 (t, $J_{\text{HH}} = 7.4$ Hz, 4H, *para*-C₆H₅); 7.07 (d, $J_{\text{HH}} = 7.0$ Hz, 8H, *ortho*-C₆H₅); 6.80 (s, 2H, *meta*-C₆H₂); 5.85 (s, 2H, $(\text{CHPh}_2)_2$); 1.02 (s, 9H, $\text{C}(\text{CH}_3)_3$).

^1H NMR (C_6D_6 , 600MHz) δ 7.14-7.08 (m, 18H, ArH); 7.01 (t, $J_{\text{HH}} = 7.3$ Hz, 4H, ArH); 6.06 (s, 2H, $(\text{CHPh}_2)_2$); 1.02 (s, 9H, $\text{C}(\text{CH}_3)_3$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 149.1 (ArC); 143.6 (ArC); 139.7 (ArC); 135.4 (ArC); 129.8 (ArC); 128.8 (ArC); 126.9 (ArC); 126.7 (ArC); 53.3 (CHPh_2); 34.7 ($\text{C}(\text{CH}_3)_3$); 31.1 ($\text{C}(\text{CH}_3)_3$).

LC-MS (Q-TOF): m/z [M⁺] calculated for C₃₆H₃₃N₃: 507.2674; found: 507.2670.

5.1.7 [Ge(HMDS)₂] [((SiMe₃)₂N)₂Ge] C₁₂H₃₆GeN₂Si₄

This compound was made with a modification to the literature procedure.¹³⁰ To a solution of stirred [(HMDS)-H] (600 mg, 3.71 mmol) in hexane (13 mL) at -30 °C was added one equivalent of *n*-Buli in cyclohexane solution (1.49 mL, 3.71 mmol). The solution was allowed to come to room temperature and

left to stir overnight. The solvent was removed under reduced pressure and the solid was redissolved in THF (6 mL). The new solution was added dropwise to a stirred solution of $\text{GeCl}_2 \cdot \text{dioxane}$ (0.430 g, 1.85 mmol) at $-30\text{ }^\circ\text{C}$ in THF (6 mL). The solution was left to stir for 12 hours, over which time a strong orange colour developed. The solvent was removed under reduced pressure and the residue was extracted into hexane (2 x 5 mL) and filtered through celite. The solvent was removed under reduced pressure to give an oily orange solid which was characterised by ^1H NMR spectroscopy. The compound was used without further purification.

^1H NMR (C_6D_6 , 300 MHz) δ 0.32 (s, 36H, $[\text{Ge}(\text{N}(\text{TMS})_2)_2]$).

5.1.8 $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{Me})_2]$ $[\text{Cp}_2\text{ZrMe}_2]$ $\text{C}_{12}\text{H}_{16}\text{Zr}$

This compound was synthesised in a modification to the literature procedure.¹³¹ To a solution of $[\text{Cp}_2\text{ZrCl}_2]$ (500 mg, 1.71 mmol) in THF (15 mL) at $-30\text{ }^\circ\text{C}$ was added 2.1 equivalents of MeLi (3M, 1.19 mL, 3.59 mmol) in dimethoxyethane. The solution was left to stir for a minimum of 6 hours before the volatiles were removed under reduced pressure. The residue was extracted into toluene (3 x 3 mL) and filtered through celite to give a pale yellow/green solution. The solution had the solvent removed under reduced pressure to give the product as a white powder. ^1H NMR data agreed with literature values.

Yield: 349 mg (81%)

^1H NMR (C_6D_6 , 300 MHz) δ 5.71 (s, 10H, C_5H_5); - 0.12 (s, 6H, ZrMe_2).

5.1.9 $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{Cl})]$ $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ $\text{C}_{12}\text{H}_{16}\text{ZrCl}$

This compound was made with a modification to the literature procedure.¹³¹ To a stirred solution of $[\text{Cp}_2\text{ZrMe}_2]$ (400 mg, 1.59 mmol) in toluene (5 mL) was added 1 equivalent of trityl chloride (440 mg, 1.59 mmol) and the reaction was left to stir overnight. Over this time the solution went from pale yellow/green to bright yellow. The solvent was removed under reduced pressure and the residue was washed with hexane (3 x 10 mL). The product was dried under reduced pressure to give the $[\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})]$ as an off white solid. ^1H NMR data agreed with the literature values.

Yield: 0.329 mg (76%).

^1H NMR (C_6D_6 , 300 MHz) δ 5.74 (s, 10H, C_5H_5); 0.45 (s, 3H, ZrMe).

5.1.10 $[(C_5H_5)_2Zr(CH_2C_6H_5)_2]$ $[Cp_2ZrBn_2]$ $C_{24}H_{24}Zr$

This compound was made using a modification to the literature procedure.¹³² To a stirred solution of $[Cp_2ZrCl_2]$ (550mg, 1.71 mmol) in diethyl ether (10 mL) at -30 °C was added a solution of benzylmagnesiumchloride in diethyl ether (1M, 3.71 mL, 3.71 mmol). The resulting orange suspension was left to stir overnight before the solvent was removed under reduced pressure. The compound was extracted into hexane (4 x 5 mL) and filtered through celite to give a vibrant orange solution. Removal of the solvent under reduced pressure gave $[Cp_2ZrBn_2]$ as an orange solid. 1H NMR data agreed with literature values.

1H NMR (C_6D_6 , 300 MHz) δ 7.25 (t, J_{HH} = 7.8 Hz, 4H, *meta*-ArH); 6.93 (t, J_{HH} = 7.5 Hz, 2H, *para*-ArH); 6.88 (d, J_{HH} = 8.9 Hz, 4H, *ortho*-ArH); 5.51 (s, 10H, C_5H_5); 1.83 (s, 4H, CH_2Ph).

5.1.11 $[Zr(CH_2C_6H_5)_4]$ $[Zr(Bn)_4]$ $C_{28}H_{28}Zr$

This compound was made using a modification to the literature procedure.¹³³ To a stirred suspension of $[ZrCl_4]$ (1.00 g, 4.29 mmol) in diethyl ether at -78 °C was added an excess of benzylmagnesiumchloride solution (1M, 20 mL, 5 mmol). The solution was allowed to come to temperature overnight. The suspension was filtered through a glass frit packed with celite and the solvent was removed under reduced pressure. The residue was extracted into toluene (4 X 5 mL), filtered through celite and left to crystallise at -30 °C to give the compound as intense orange crystals. Due to light sensitivity it is recommended this compound is stored in a light free environment. The compound was confirmed as $[Zr(Bn)_4]$ by 1H NMR spectroscopy.

1H NMR (C_6D_6 , 300 MHz) δ 7.06 (m, 12 H, ArH); 6.39 (d, J_{HH} = 7.3 Hz, 8H, *ortho*-ArH); 1.54 (s, 8H, CH_2Ph).

5.1.12 Bis(trimethylsilyl)-4,10-bis((trimethylsilyl)imino)-4,10-dihydroperylene-3,9-diamine

A previously prepared sample of $[Li_2NAPH]$ (260 mg, 0.85 mmol) in THF (7 mL) was added dropwise to a stirred solution of $[PbCl_2]$ (230 mg, 0.85 mmol) in THF (5 mL) at -30 °C and the solution was left to stir overnight. The solvent was removed under reduced pressure and the compound was extracted into toluene (3 x 5 mL). The extraction was filtered through celite to give a yellow solution which was concentrated and stored at -30 °C to crystallise. Over several days the solution went dark green. The

solvent was removed under reduced pressure to give the named compound. ^1H NMR spectroscopy resonances agree with the literature values.⁶⁹

^1H NMR (C_6D_6 , 600 MHz) δ 14.13 (s, 2H, NH); 8.13 (d, 4H, $J_{\text{HH}} = 10.0$ Hz, C_{20}H_8); 7.19 (d, $J_{\text{HH}} = 9.7$ Hz, 4H, C_{20}H_8); 0.48 (s, 36H, $(\text{SiMe}_3)_4$).

5.1.13 $[\text{Zr}(2,6-((\text{CH}_3)_2\text{CH})_2\text{NHC}_6\text{H}_4)_4]$ $[\text{Zr}(\text{NHDipp})_4]$ $\text{C}_{48}\text{H}_{72}\text{Zr}$

This compound was made using a modification to the literature procedure.¹³⁴ To a solution of $[\text{Zr}(\text{Bn})_4]$ (50 mg, 0.11 mmol) in C_6D_6 (0.20 mL) was added 4 equivalents of 2,6-diisopropylaniline (77 mg, 0.44 mmol, 0.08 mL). The solution went from orange to a vibrant yellow. The solution was transferred into an NMR tube fitted with a Young's tap and heated to 100 °C for 3 days until only one product was identifiable by ^1H NMR spectroscopy. No yield was taken as the product was used immediately for another reaction.

^1H NMR (C_6D_6 , 300 MHz) δ 7.14-6.85 (m, 12H, ArH); 6.98 (s, 4H, ZrNH); 3.26 (sep, $J_{\text{HH}} = 7.3$ Hz, 8H, $(\text{CH}(\text{CH}_3)_2)_2$); 1.18 (d, $J_{\text{HH}} = 6.8$ Hz, 48H, $(\text{CH}(\text{CH}_3)_2)_2$).

5.1.14 $[\text{Ge}((2,6-((\text{CH}_3)_2\text{CH})_2\text{NC}_6\text{H}_4)_3]$ $[(\text{GeNDipp})_3]$ $\text{C}_{36}\text{H}_{51}\text{Ge}_3\text{N}_3$

This compound was made using a modification from the literature procedure.¹³⁵ To a solution of $[\text{Zr}(\text{NHDipp})_4]$ (88 mg, 0.11 mmol) in C_6D_6 (0.30 mL) was added 2 equivalents of $[\text{Ge}(\text{NAPH}^{\text{TMS}})]$ (86 mg, 0.22 mmol). The solution was transferred into an NMR tube fitted with a Young's tap and heated 50 °C for 5 days. The NMR tube was taken into a glove box and the solvent was removed under reduced pressure. The residue was extracted into minimal toluene (3 mL) and heated to give a clear solution. This solution was transferred to the -30 °C freezer to crystallise. The named compound was identified by single crystal X-ray crystallography and ^1H NMR spectroscopy. ^1H NMR spectroscopy resonances agreed with literature values.¹³⁵

^1H NMR (C_6D_6 , 300 MHz) δ 7.16 (m, 6H, *meta*-ArH); 7.10 (m, 3H, *para*-ArH); 3.40 (s, 6H, $(\text{CHMe}_2)_2$); 1.12 (d, $J_{\text{HH}} = 6.6$ Hz, 36H, $(\text{CHMe}_2)_2$).

5.1.15 $[(\text{TMS})\text{NH}]_2\text{C}_{10}\text{H}_6]$ $[\text{NAPH}^{\text{TMS}}-\text{H}]$

This compound was made in a modification to the literature procedure.¹³⁶ To a stirred solution of 1,8-diaminonaphthalene (3.98 g, 25 mmol) in THF (25 mL) at -30 °C was added MeLi (16.1 mL, 50 mmol)

dropwise by cannula transfer resulting in a green solution after 1 hour. The solution was heated to reflux then cooled to -30 °C. TMSCl (6.35 mL, 67 mmol) was added dropwise by cannula transfer. The solution turned purple and was left to stir overnight. The solution was concentrated to half volume and cooled to -30 °C to give $[(\text{TMS})\text{NH}]_2\text{C}_{10}\text{H}_6$ ($\text{NAPH}^{\text{TMS}}\text{-H}$) as colourless crystals.

Yield 3.86g (51%)

^1H NMR (CDCl_3 , 300 MHz) δ 7.15 (m, 4H, ArH); 6.71 (dd, $J_{\text{HH}} = 6.8, 1.8$ Hz, 2H, ArH); 5.55 (br s, 2H, NH); 0.29 (s, 18H, TMS).

^1H NMR (C_6D_6 , 300 MHz) δ 7.36 (d, $J_{\text{HH}} = 7.9$ Hz, 2H, ArH); 7.20 (t, $J_{\text{HH}} = 7.2$ Hz, 2H, ArH); 6.72 (d, $J_{\text{HH}} = 7.6$ Hz, 2H, ArH); 5.39 (s, 2H, NH); 0.18 (s, 18H, TMS).

5.1.16 $[\text{Ge}((\text{N}(\text{SiMe}_3))_2\text{C}_{10}\text{H}_6)] [\text{Ge}(\text{NAPH}^{\text{TMS}})] \quad 3 \text{ C}_{16}\text{H}_{24}\text{GeN}_2\text{Si}_2$

A stirred solution of $[\text{NAPH}^{\text{TMS}}\text{-H}]$ (500 mg, 1.65 mmol) in Et_2O (5 mL) at -30 °C was treated with *n*-BuLi (1.32 mL, 2.5 M in cyclohexane) dropwise over 3 minutes. The resulting solution was left to stir for 1 hour at room temperature before the solution was added dropwise to a solution of $[\text{GeCl}_2\text{.dioxane}]$ (380 mg, 1.65 mmol) in THF (8 mL). The pale yellow solution was left to stir for 15 hours before having the solvent removed under reduced pressure. The compound was extracted into toluene (10 mL), filtered through celite and concentrated to 2 mL. After 24 hours at -30 °C orange crystals were deposited, identified as **3** by single crystal X-ray diffraction. Yield 0.45g (73%).

^1H NMR (C_6D_6 , 600 MHz) δ 7.21 (dd, $J_{\text{HH}} = 8.3, 0.8$ Hz, 2H, *p*-CH), 7.13 (t, $J_{\text{HH}} = 8.6$ Hz, 2H, *m*-CH), 6.71 (dd, $J_{\text{HH}} = 7.1, 0.9$ Hz, 2H, *o*-CH), 0.34 (s, 18H, $\text{Si}(\text{CH}_3)_3$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 142.3, 137.6, 128.0, 125.5, 120.5, 112.3 (C_{10}H_6), 2.5 (SiCH_3).

UV-vis (Hexane, 25 °C) [λ_{max} , nm (ϵ , $\text{mol}^{-1}\text{L cm}^{-1}$): 235 (33,800), 349 (13,500).

Elemental analysis was not able to be obtained due to the extreme oxophilicity of this compound.

5.1.17 $[\text{Ge}(\text{N}(2,4,6\text{-CH}_3(\text{C}_6\text{H}_2)_2(\text{C}_{12}\text{H}_6))] [\text{Ge}(\text{BIAN}^{\text{Mes}})] \quad 2 \text{ C}_{30}\text{H}_{28}\text{GeN}_2$

A stirred solution of $[\text{GeCl}_2\text{.dioxane}]$ (167 mg, 0.67 mmol) in THF (5 mL) was treated with $[\text{Mg}(\text{BIAN}^{\text{Mes}})(\text{THF})_3]$ (490 mg, 0.67 mmol) in THF (5 mL) at -30 °C. The solution changed from dark green to a dark brown over 4 hours. The reaction was left to stir overnight before being concentrated to dryness under reduced pressure. The residue was extracted into toluene and filtered through celite to give a dark

brown solution. This solution was concentrated and cooled to -30 °C to give dark brown crystals. Yield: 0.247g (74%).

^1H NMR (C_6D_6 , 600 MHz) δ 7.20 (d, $J_{\text{HH}} = 7.6\text{ Hz}$, 2H, *p*-CH); 6.94 (s, 4H (C_6H_2)₂); 6.90 (t, $J_{\text{HH}} = 7.4\text{ Hz}$, 2H, *m*-CH); 6.59 (d, $J_{\text{HH}} = 6.6\text{ Hz}$, 2H, *o*-CH); 2.29 (s, 12H, (*o*-CH₃)₂(C_6H_2 (*p*-CH₃))); 2.26 (s, 6H, (*o*-CH₃)₂(C_6H_2 (*p*-CH₃))).

^{13}C NMR (C_6D_6 , 125 MHz) δ 140.1 (N-C), 138.9, 136.01, 134.2, 132.0, 132.1, 129.6, 129.4, 127.7, 125.6, 118.2, 21.2, 18.7.

Anal. Calcd. for $\text{C}_{30}\text{H}_{28}\text{GeN}_2$: C, 73.66; H, 5.77; N, 5.73. Found: C, 70.02; H, 5.43; N, 5.09.

UV-vis (Hexane, 25 °C) [λ_{max} , nm (ϵ , $\text{mol}^{-1}\text{L cm}^{-1}$): 324 (15,900), 422 (16,800).

5.1.18 $[\text{Ge}(\text{NAPH}^{\text{TMS}})\text{Ge}(\text{NAPH}^{\text{TMS}})(\text{Bu})(\text{NAPH})][\text{Li}(\text{THF})_4]$ 4 $\text{C}_{52}\text{H}_{86}\text{Ge}_2\text{N}_4\text{Si}_4\text{LiO}_4$

5.1.18.1 Method A:

n-BuLi (2.0 mL, 4.0 mmol) was added dropwise to a purple stirred solution of $[\text{NAPH}^{\text{TMS}}\text{-H}]$ (610 mg, 2.0 mmol) at -30 °C in Et_2O (7 mL) and left for 1 hour. The resulting solution was added dropwise to a stirred solution of $[\text{GeCl}_2\text{.dioxane}]$ (460 mg, 2.0 mmol) in THF (5mL) at -30 °C. The solution was left to stir overnight before the solvent was removed under reduced pressure. The residue was extracted with toluene (2 x 5mL), filtered and reduced to dryness.

Yield: 620 mg (56%)

5.1.18.2 Method B

To a solution of $[\text{Ge}(\text{NAPH}^{\text{TMS}})]$ (40 mg, 0.11 mmol) in THF (5 mL) was added 0.5 equivalents of *n*-BuLi solution in cyclohexane (0.03 mL, 0.05mmol). The solution went from a dark orange to yellow. The solution was concentrated and stored in the freezer resulting in yellow crystals. Yield 38 mg (63%).

^1H NMR (C_6D_6 , 600 MHz) δ 7.27 (d, $J_{\text{HH}} = 7.4\text{ Hz}$, 2H); 7.22 (d, $J_{\text{HH}} = 8.0\text{ Hz}$, 2H); 7.15-7.12 (m, 4H); 6.93 (d, $J_{\text{HH}} = 8.1\text{ Hz}$, 2H); 6.84 (d, $J_{\text{HH}} = 6.98\text{ Hz}$, 2H), 3.29 (m, 8H); 1.23 (m, 8H); 1.19-1.14 (m, 2H); 0.75 (t, $J_{\text{HH}} = 6.54\text{ Hz}$, 3H); 0.54 (s, 18H); 0.50 (m, 4H); 0.44 (s, 18H).

^{13}C NMR (C_6D_6 , 125 MHz) δ 149.3 (ArC); 138.3 (ArC); 137.7 (ArC); 128.4 (ArC); 126.0 (ArC); 125.7 (ArC); 125.3 (ArC); 120.5 (ArC); 120.2 (ArC); 116.7 (ArC); 113.8 (ArC); 27.8; 27.0; 25.5; 15.6; 14.2; 3.3. Other aromatic carbon signal assumed to be obscured by solvent resonance.

5.1.19 [Ge(NAPH^{TMS})Ge(NAPH)(Me)(NAPH^{TMS})] [Li(THF)₄] 5
C₅₂H₈₆Ge₂N₄Si₄LiO₄

5.1.19.1 Method A:

MeLi (1.00 mL, 3.1 mmol, 3.1M in dimethoxyethane) was added dropwise to a stirred solution of [NAPH^{TMS}-H] (400 mg, 1.32 mmol) at -30 °C in Et₂O (7 mL) and left for 1 hour. The resulting solution was added dropwise to a stirred solution of GeCl₂.dioxane (306 mg, 1.32 mmol) in THF (5 mL) at -30 °C. The reaction was left to stir overnight before the solvents were removed in *vacuo*. The residue was extracted with toluene (2 x 5 mL), filtered through celite and concentrated to dryness to give the compound as a yellow powder.

Yield: 132 mg (19%)

5.1.19.2 Method B

To a solution of **2** (46 mg, 0.04 mmol) in THF (5 mL) was added 0.5 equivalents of *n*-BuLi solution (0.02 mmol, 0.01 mL). The solution went from a dark orange to yellow over several hours. The solution was concentrated to dryness to give a yellow solid. Yield: 26 mg (62%).

¹H NMR (C₆D₆, 600 MHz) δ 7.34 (d, , *J*_{HH} = 8.4Hz, 2H); 7.25 (d, , *J*_{HH} = 8.9 Hz, 2H); 7.21 (t, , *J*_{HH} = 7.7 Hz, 2H); 7.15 – 7.13 (m, 2H); 7.03 – 6.99 (m, 2H); 6.85 (d, , *J*_{HH} = 7.7 Hz, 2H), 3.11 (m, 8H); 1.09 (m, 8H); 0.38 (s, 18H); 0.37 (s, 18H); -0.03 (br s, 3H).

¹³C NMR (C₆D₆, 125 MHz) δ 150.7 (ArC); 138.3 (ArC); 137.5 (ArC); 134.3 (ArC); 134.3 (ArC); 128.0 (ArC); 125.3 (ArC); 124.8 (ArC); 120.4 (ArC); 120.2 (ArC); 113.8 (ArC); 67.8; 65.5; 63.8; 24.8; 15.1; 3.1; 3.0. Other aromatic carbon signal assumed to be present under the solvent signal.

5.1.20 [(Ge(2,6-CH(C₆H₅)₂)-4-(C(CH₃)₃)C₆H₂N)₂] [(Ge(NAr*))₂] 6
C₇₂H₆₆Ge₂N₂

To a solution of [GeCl₂.dioxane] (48 mg, 0.21 mmol) in THF (5 mL) was added two equivalents of [LiNHAr*] (0.20 g, 0.42 mmol) in THF (5 mL). The solution turned yellow overnight. The solvent was removed under reduced pressure and the residue was extracted with toluene (3 x 5 mL). The solution was filtered through celite, then concentrated under reduced pressure before being transferred to a -30 °C freezer from which X-ray quality crystals were grown.

Yield 0.72g, 31%.

^1H NMR (C_6D_6 , 600 MHz) δ 7.27-7.25 (m, 12H); 7.15-7.11 (m, 16H); 7.06-7.00 (m, 16H), 6.43 (s, 4H); 1.13 (s, 18H).

^{13}C NMR (C_6D_6 , 125 MHz) δ 145.7, 138.5, 130.4, 129.9, 129.2, 127.0, 125.7, 125.5, 54.2 (CHPh_2), 31.6 (CH_3), 30.1 (CCH_3).

5.1.21 $[(\text{Cl})\text{Ge}(\text{N}(\text{Cy})\text{C}(\text{NHCy})\text{NAr}^*)] \quad 7 \quad \text{C}_{43}\text{H}_{45}\text{ClGeN}_3$

To a stirred solution of $[\text{GeCl}_2\cdot\text{dioxane}]$ (0.23 g, 1.0 mmol) and dicyclohexylcarbodiimide (0.21 g, 1.0 mmol) in THF (6 mL) was added a solution of LiNHAr^* (0.500 g, 1.1 mmol) in THF (2 mL) and the resulting solution was left to stir overnight. The solution was diluted with toluene (2 mL) and the solvent was removed under reduced pressure. The residue was extracted into hexane (5 mL) and filtered through celite to give a yellow solution. The solution was cooled to $-30\text{ }^\circ\text{C}$ until X-ray quality crystals were grown.

Yield: 402 mg (56%)

^1H NMR (C_6D_6 , 600 MHz) δ 7.64 (d, $J_{\text{HH}} = 7.6\text{ Hz}$, 2H); 7.47 (d, $J_{\text{HH}} = 8.1\text{ Hz}$, 2H); 7.45 (d, $J_{\text{HH}} = 2.7\text{ Hz}$, 1H); 7.38 (s, 1H); 7.25 (d, $J_{\text{HH}} = 7.3\text{ Hz}$, 2H); 7.05 (t, $J_{\text{HH}} = 6.9\text{ Hz}$, 8H); 6.95 (m, 2H); 5.95 (s, 1H); 2.01 (m, 2H, Cy-H); 1.87 (m, 2H, Cy-H); 1.66 (m, 2H, Cy-H); 1.45 (m, 2H, Cy-H); 1.32 (m, 8H, Cy-H); 1.08 (s, 9H, $\text{C}(\text{CH}_3)_3$); 0.81 (m, 2H, Cy-H); 0.72 (m, 2H, Cy-H); 0.46 (m, 1H, *ipso*-Cy-H); 0.10 (m, 1H, *ipso*-Cy-H).

Other ^1H signals assumed to be hidden under toluene impurity.

^{13}C NMR (C_6D_6 , 125 MHz) δ 203.7 (NCN); 148.4 (ArC); 132.7 (ArC); 130.5 (ArC); 130.3 (ArC); 130.2 (ArC); 129.8 (ArC); 129.5 (ArC); 129.4 (ArC); 128.7 (ArC); 128.6 (ArC); 128.5 (ArC); 128.4 (ArC); 126.7 (ArC); 35.8 (CyC); 35.7 (CyC); 33.2 (CyC); 31.3 (CCH_3); 30.1 (CPh_2); 24.8 (CyC); 25.1 (CyC); 25.3 (CyC); 25.6 (CyC); 25.9 (CyC); 26.5 (CyC). Toluene impurity present. Other ^{13}C signals assumed to be hidden by the solvent signal.

5.1.22 $[\text{Ge}(\text{HMDS})_2(\text{NMe}_3)] \quad \text{C}_{21}\text{H}_{47}\text{GeN}_3\text{Si}_4$

To a stirred solution of $[\text{Ge}(\text{HMDS})_2]$ (140 mg, 0.36 mmol) in hexane 5 mL at $-30\text{ }^\circ\text{C}$ was added $[\text{NMe}_3]$ (57 mg, 0.35 mmol) in hexane (3 mL). The resulting orange solution was immediately transferred into the freezer at $-30\text{ }^\circ\text{C}$ and X-ray quality crystals were grown overnight.

Yield: 102 mg, 55%

^1H NMR (C_6D_6 , 600 MHz) δ 6.99 (s, 2H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.47 (s, 6H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.28k (s, 3H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$), 0.29 (s, 36H, $(\text{SiMe}_3)_4$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 149.8 (N-C), 129.3 (ArC), 129.2 (ArC), 20.7 ($\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 4.5 ($(\text{SiMe}_3)_4$), 4.2 ($\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$). The final aromatic signal was assumed to be obscured by the solvent resonance.

5.1.23 **[Ge(HMDS) $_2$ (N $_4$ Ph $_2$)] 10 $\text{C}_{24}\text{H}_{46}\text{GeN}_6\text{Si}_4$**

To a solution of $[\text{Ge}(\text{HMDS})_2]$ (100 mg, 0.25 mmol) in C_6D_6 (0.15 mL) was added one equivalent of phenylazide $[\text{PhN}_3]$ (30 mg, 0.25 mmol) in C_6D_6 (0.15 mL). The solution was mixed by extracting into and out of a pipette for one minute before the now orange solution was put into an NMR tube and sealed with a Young's tap. The reaction was monitored by ^1H NMR spectroscopy until there was no more phenylazide left in solution (10 minutes). The NMR tube was taken back into the glovebox where toluene (1 mL) was added and the solvent was removed under reduced pressure. The residue was extracted into hexane (4 mL) and filtered through celite. The solvent was removed under reduced pressure to give the product as a yellow/orange solid.

Yield: 58 mg (76%)

^1H NMR (C_6D_6 , 600 MHz) δ 7.62 (d, $J_{\text{HH}} = 8.1$ Hz, 2H, para ArH); 7.00-6.93 (m, 4H, ArH); 6.89-6.80 (m, 4H, ArH); 0.24 (s, 36H, $(\text{N}(\text{SiMe}_3)_2)_2$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 145.7; 138.5; 130.4; 129.3; 127.0; 125.7; 31.6 ; 30.1.

5.1.24 **[Ge(NAPH)(N $_4$ Mes $_2$)] 8 $\text{C}_{34}\text{H}_{46}\text{GeN}_6\text{Si}_2$**

To a solution of $[\text{Ge}(\text{NAPH}^{\text{TM}})]$ (30 mg, 0.08 mmol) in C_6D_6 (0.20 mL) was added a solution of $[\text{MesN}_3]$ in C_6D_6 (0.10 mL). The solution immediately went from orange to burnt orange. The solution was transferred into an NMR tube fitted with a Young's tap and monitored by ^1H NMR spectroscopy. When no free azide was observed by ^1H NMR spectroscopy (1 minute) the NMR tube was taken into the glove box, diluted with toluene (1 mL) and the volatiles were removed under reduced pressure to give the compound as an orange solid.

Yield: 22 mg (87%).

^1H NMR (C_6D_6 , 600 MHz) δ 7.19 (d, $J_{\text{HH}} = 7.9$ Hz, 2H, ArH); 7.03 (t, $J_{\text{HH}} = 7.9$ Hz, 2H, ArH); 6.87 (d, $J_{\text{HH}} = 7.9$ Hz, 2H, ArH); 6.74 (s, 4H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.58 (s, 12H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.09 (s, 6H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 0.09 (s, 18H, $(\text{SiMe}_3)_2$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 144.0 (ArC); 139.0 (ArC); 136.8 (ArC); 133.6 (ArC); 131.9 (ArC); 130.6 (ArC); 125.7 (ArC); 121.5 (ArC); 116.3 (ArC); 112.7 (ArC); 22.7 ($\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 20.5 ($\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.2 ($(\text{SiCH}_3)_3$).

5.1.25 [(TMSN)Ge(HMDS)(N(TMS)Ar*)] 11 $\text{C}_{48}\text{H}_{69}\text{GeN}_3\text{Si}_4$

To a solution of $[\text{Ge}(\text{HMDS})_2]$ (58 mg, 0.15 mmol) in hexane (2 mL) was added $[\text{N}_3\text{Ar}^*]$ (90 mg, 0.18 mmol) at -30°C . The solution was heated up to room temperature and an orange/yellow solid precipitated over an hour. The suspension was heated to supersaturate the solution. The solution was cooled to -30°C to give crystals suitable for X-ray diffraction overnight.

^1H NMR (C_6D_6 , 600 MHz) δ 7.66 (d, $J_{\text{HH}} = 7.2$ Hz, 4H, ArH); 7.51 (d, $J_{\text{HH}} = 7.0$ Hz, 4H, ArH); 7.26 (t, $J_{\text{HH}} = 7.5$ Hz, 4H, ArH); 6.35 (s, 2H, $(\text{CHPh}_2)_2$); 1.04 (s, 9H, $\text{C}(\text{CH}_3)_3$); 0.49 (s, 9H, SiMe_3); 0.42 (s, 18H, $\text{N}(\text{SiMe}_3)_2$); -0.15 (s, 9H, SiMe_3).

Other aromatic proton resonances are obscured by $[\text{Ar}^*\text{Cl}]$ (26) and assumed $[(\text{HMDS})_2\text{Ge}(\text{NAr}^*)]$ impurities in the NMR. ^{13}C NMR data was not obtained for this compound.

5.1.26 $[(\text{HMDS})_2\text{Ge}(\text{N}_2\text{OPhNC(O)NMe}_3)]$ 13 $\text{C}_{28}\text{H}_{51}\text{GeN}_5\text{O}_3\text{Si}_4$

In an NMR tube fitted with a Young's tap, $[\text{Ge}(\text{HMDS})_2]$ (70 mg, 0.18 mmol), $[\text{MesN}_3]$ (29 mg, 0.18 mmol) and 4-nitrophenylisocyanate (29 mg, 0.18 mmol) were added together in C_6D_6 (0.30 mL). The solution was monitored by ^1H NMR spectroscopy until no free azide was observed (20 hours). The NMR tube was taken back into a nitrogen glovebox where toluene (1 mL) was added before the solvent was evaporated under reduced pressure. The residue was extracted into hexane (2 mL), filtered through celite and reduced to dryness to give an off-white solid.

Yield: 72 mg (59%).

^1H NMR (C_6D_6 , 600 MHz) δ 8.07 (d, $J_{\text{HH}} = 6.4$ Hz, 2H, *meta*- $\text{C}_6\text{H}_4\text{NO}_2$); 7.64 (d, $J_{\text{HH}} = 8.1$ Hz, 2H, *ortho*- $\text{C}_6\text{H}_4\text{NO}_2$); 6.80 (s, 2H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.43 (s, 6H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.13 (s, 3H $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 0.20 (s, 36H, $(\text{N}(\text{TMS})_3)_2$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 142.8 (C=O); 135.8 (ArC); 129.9 (ArC); 128.6 (ArC); 124.7 (ArC); 121.6 (ArC); 32.0 (MeC), 21.7 (MeC), 5.8 (TMS). Other ^{13}C signals assumed to be hidden under the solvent signal.

Anal. Calcd. for $\text{C}_{28}\text{H}_{51}\text{GeN}_5\text{O}_3\text{Si}_4$ (691.23): C, 48.69; H, 7.44; N, 10.14; Found: C, 48.78; N, 7.39; H, 9.96.

5.1.27 [(HMDS) $_2$ Ge(CCPH)(NHPH)] 12 $\text{C}_{29}\text{H}_{53}\text{GeN}_3\text{Si}_4$

To a stirred solution of $[\text{Ge}(\text{HMDS})_2]$ (60 mg, 0.16 mmol) in hexane (6 mL) was added dropwise a solution of $[\text{MesN}_3]$ (25 mg, 0.16 mmol) in hexane (2 mL). A colourless gas was released and the solution turned from orange to yellow. After 10 minutes a suspension of phenylacetylene (16 mg, 0.16 mmol) in hexane (2 mL) was added dropwise. The reaction was left to stir overnight before being concentrated under reduced pressure and cooled to $-30\text{ }^\circ\text{C}$ to grow crystals suitable for single crystal X-ray diffraction.

Yield: 68 mg, (67%).

^1H NMR (C_6D_6 , 600 MHz) δ 7.61 (m, 1H, *para*-ArH); 7.43 (m, 2H, ArH); 6.93 (m, 2H, ArH); 6.82 (s, 2H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 3.11 (br s, 1H, NH); 2.53 (s, 6H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 2.17 (s, 3H, $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$); 0.47 (s, 36H, $(\text{N}(\text{SiMe}_3)_2)_2$).

^{13}C NMR (C_6D_6 , 125 MHz) δ 163.6 (ArC); 141.5 (ArC); 131.6 (ArC); 130.1 (ArC); 130.0 (ArC); 129.6 (ArC); 129.2 (ArC); 128.8 (ArC); 128.8 (ArC); 123.1 (ArC); 106.0 (C $\equiv$ C); 98.0 (C $\equiv$ C); 20.7 $\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$; 6.4 ($\text{N}(\text{SiMe}_3)_2$); 3.7 ($\text{NC}_6\text{-}2,6\text{-(Me)-}4\text{-(Me)H}_2$).

5.1.28 [$\text{Cp}_2\text{Zr}(\text{Bn})(\text{NHPH})$] 17 $\text{C}_{23}\text{H}_{23}\text{NZr}$

To a solution of $[\text{Bn}_2\text{ZrCp}_2]$ (75 mg, 0.19 mmol) in C_6D_6 (0.20 mL) was added a solution of aniline (17 mg, 0.18 mmol) in C_6D_6 (0.20 mL). The resulting orange solution was transferred into an NMR tube fitted with a Young's tap and heated to $100\text{ }^\circ\text{C}$ for two days using an aluminium heating block to give a yellow solution and a green solid (**18**). The NMR tube was taken back into the glovebox and the yellow solution was the green solid was decanted from the solution. Toluene was added (2 mL) to the solution before the solvent was removed under reduced pressure. The residue was extracted into hexane (3 mL), filtered through celite and placed in the freezer at $-30\text{ }^\circ\text{C}$ from which yellow plates suitable for X-ray diffraction were grown. Yield: 52 mg, 69%.

^1H NMR (C_6D_6 , 600 MHz) δ 7.26-7.19 (m, 4H, ArH); 7.06 (d, $J_{\text{HH}} = 7.8$ Hz, 2H, ArH); 6.90-6.86 (m, 2H, ArH); 6.76 (d, $J_{\text{HH}} = 7.6$ Hz, 2H, ArH); 5.51 (s, 10H, C_5H_5); 3.58 (br s, 1H, NH); 2.24 (s, 2H, CH_2Ph).

^{13}C NMR (C_6D_6 , 125 MHz) δ 156.1 (ArC), 153.9 (ArC), 129.0 (ArC), 128.3 (ArC), 126.1 (ArC), 121.0 (ArC), 120.4 (ArC), 120.2 (ArC), 110.7 (C_5H_5), 50.0 ($\text{CH}_2\text{C}_6\text{H}_5$).

5.1.29 $[(\text{Cp}_2\text{Zr}(\mu\text{-NPh}))_2]$ 18 $\text{C}_{32}\text{H}_{30}\text{N}_2\text{Zr}_2$

To a solution of $[\text{Bn}_2\text{ZrCp}_2]$ (75 mg, 0.19 mmol) in C_6D_6 (0.20 mL) was added a solution of aniline (17 mg, 0.18 mmol) in C_6D_6 (0.20 mL). The resulting orange solution was transferred into an NMR tube fitted with a Young's tap and heated to 100 °C for two days to give a yellow solution and a green solid (**18**). The green solid was decanted from the solution and washed with THF (2 x 2 mL). The crystals were insoluble in all available NMR solvents (D6-benzene, D8-THF, D3-acetonitrile, heavy water, D6-DMSO and D8-toluene). However, the product was identified by single crystal X-ray diffraction.

5.1.30 $[\text{Cp}_2\text{Zr}(\text{Bu})(\text{N}_3(\text{Bu})(\text{Mes}))]$ 21 $\text{C}_{27}\text{H}_{39}\text{N}_3\text{Zr}$

To a stirred solution on $[\text{Cp}_2\text{ZrCl}_2]$ (0.29 g, 1.0 mmol) in THF (5 mL) at -30 °C was added dropwise a 2M solution *n*-BuLi in cyclohexane (1.0 mL, 2.0 mmol), resulting in a yellow solution. After letting this solution come up to room temperature over 15 minutes a solution of $[\text{MesN}_3]$ (0.17 g, 1.0 mmol) in hexane was added to the solution dropwise. After 1.5 hours the dark orange solution had the solvent removed under reduced pressure to give a dark oily residue. This oil was redissolved in a minimum volume of diethyl ether (2 mL) and cooled to -30 °C to grow X-ray quality crystals.

Yield: 352 mg (71%)

^1H NMR (C_6D_6 , 600 MHz) δ 6.81 (s, 2H, $\text{NC}_6\text{-}2,6\text{-(Me)}_2\text{-}4\text{-(Me)H}_2$); 5.79 (s, 10H, C_5H_5); 3.26 (t, $J_{\text{HH}} = 6.1$ Hz, 2H, Bu), 2.33 (s, 6H, $\text{NC}_6\text{-}2,6\text{-(Me)}_2\text{-}4\text{-(Me)H}_2$); 2.15 (s, 3H, $\text{NC}_6\text{-}2,6\text{-(Me)}_2\text{-}4\text{-(Me)H}_2$); 1.67-1.62 (m, 2H, Bu); 1.31 (sex, $J_{\text{HH}} = 7.6$ Hz, 2H, Bu); 1.18-1.11 (m, 5H, Bu); 0.86 (t, $J_{\text{HH}} = 7.1$ Hz, 3H, Bu); 0.33-0.30 (m, 2H, Bu).

^{13}C NMR (C_6D_6 , 125 MHz) δ 144.8 (ArC), 134.0 (ArC), 133.9 (ArC), 128.3 (ArC), 109.3 (C_5H_5), 67.0 (BuC), 55.8 (BuC), 48.0 (BuC), 36.8 (BuC), 32.6 (BuC), 30.3 (BuC), 20.9 (BuC), 19.7 (*ortho*-Me), 15.6 (*para*-Me), 14.1 (BuC).

5.1.31 [Cp₂Zr(Me)(N₃(Me)(Mes))] 22 C₂₁H₂₇N₃Zr

To a stirred solution on [Cp₂ZrMe₂] (93 mg, 0.32 mmol) in toluene (5 mL) at -30 °C was added a solution of [MesN₃] (0.17 g, 1.0 mmol) in toluene (2 mL) dropwise. The solution was left to stir at room temperature overnight. The solvent was reduced to approximately 1.5 mL before being placed in the freezer at -30 °C overnight to give the product as crystals.

Yield 0.11 g (85%).

¹H NMR (C₆D₆, 600 MHz) δ 6.82 (s, 2H, (N-2,4,6-MeC₆H₂)); 5.69 (s, 10H, C₅H₅), 3.00 (s, 3H, (NMe)); 2.33 (s, 6H, (N-2,4,6-MeC₆H₂)); 2.17 (s, 3H, (N-2,4,6-MeC₆H₂)); -0.23 (s, 3H, (ZrMe)).

¹³C NMR (C₆D₆, 125 MHz) δ 144.8 (ArC), 134.2 (ArC), 133.6 (ArC), 129.4 (ArC), 109.1 (C₅H₅), 43.0 (NMe), 28.3 (ZrMe), 21.0 (N-2,4,6-MeC₆H₂), 19.6 (N-2,4,6-MeC₆H₂).

5.1.32 [Cp₂Zr(Me)(N₃(Me)(C₆H₅))] 23 C₁₈H₂₁N₃Zr

To a stirred solution on [Cp₂ZrMe₂] (0.67 g, 2.66 mmol) in diethyl ether (5 mL) at -30 °C was added a solution of [PhN₃] (0.32 g, 2.66 mmol) in diethyl ether (2 mL) dropwise. The solution was left to for 5 days at room temperature. The solvent was removed under reduced pressure. The residue was extracted into hexane (2mL). The resulting suspension was filtered through celite, concentrated to 1 mL and cooled to -30 °C overnight to give the product as colourless crystals.

¹H NMR (C₆D₆, 600 MHz) δ 7.33-7.28 (m, 4H, *ortho*, *meta* ArH); 7.01 (m, 1H, *para*-ArH); 5.60 (s, 10H, C₅H₅); 3.14 (s, 3H, NMe); -0.04 (s, 3H, ZrMe).

¹³C NMR (C₆D₆, 125 MHz) δ 150.1 (ArC), 129.4 (ArC), 122.5 (ArC), 115.9 (ArC), 109.1 (C₅H₅), 42.4 (NMe), 28.5 (ZrMe).

Anal. Calcd. for C₁₈H₂₁N₃Zr (369.08): C, 58.34; H, 5.71; N, 11.34. Found: C, 58.26; H, 5.90; N, 11.37.

IR (Nujol, cm⁻¹): 3093 (w), 2950 (s Nujol), 2920 (s, Nujol), 2850 (s, Nujol), 2729 (w), 1590 (w), 1464 (s, Nujol), 1380 (s, Nujol), 1290 (m), 1166 (w), 1020 (w), 802 (m), 756 (w), 725 (w), 694 (w), 520 (w).

5.1.33 [Cp₂Zr(Bn)(N₃(Bn)(Mes))] 24 C₃₃H₃₅N₃Zr

To a stirred solution of [Cp₂ZrBn₂] (180 mg, 0.45 mmol) in hexane (3 mL) at -30 °C was added a solution of [MesN₃] (53 mg, 0.45 mmol) in hexane (2 mL) dropwise. The reaction was left to stir for 24 hours. The

solution was filtered through celite and reduced to 1 mL volume before being placed in the freezer at -30 °C from which X-ray quality crystals were grown.

Yield: 147 mg (58%)

¹H NMR (C₆D₆, 600 MHz) δ 7.25 (d, *J*_{HH} = 6.9 Hz, 2H, ArH); 7.14-7.12 (m, 4H, ArH); 7.09 (t, *J*_{HH} = 7.9 Hz, 1H, ArH); 6.99 (d, *J*_{HH} = 7.7 Hz, 2H, ArH); 6.85 (t, *J*_{HH} = 7.1, 1H, ArH); 6.80 (s, 2H, ArH); 5.62 (s, 10H); 4.43 (s, 2H NCH₂Ph); 2.33 (s, 6H, 2,4,6-MeC₆H₂); 2.14 (s, 3H, 2,4,6-MeC₆H₂); 1.70 (s, 2H, ZrCH₂Ph).

¹³C NMR (C₆D₆, 125 MHz) δ 153.5 (ArC), 144.1 (ArC), 139.7 (ArC), 135.0 (ArC), 134.0 (ArC), 129.6 (ArC), 129.0 (ArC), 129.0 (ArC), 128.0 (ArC), 126.3 (ArC), 120.7 (ArC), 110.6 (C₅H₅), 61.7 (CH₂Ph), 54.0 (CH₂Ph), 21.0 (N-2,4,6-MeC₆H₂), 19.5 (N-2,4,6-MeC₆H₂).

5.1.34 [Cp₂Zr(NHDipp)(Me)] 14 C₂₃H₃₁NZr

To a stirred solution of [Cp₂Zr(Cl)(Me)] (110 mg, 0.42 mmol) in diethyl ether (5 mL) at -30 °C was added [LiNHDipp] (77 mg, 0.42 mmol) in diethyl ether (5 mL). Upon addition of the lithiated 2,6 diisopropylaniline the solution went yellow and a white solid precipitated. The suspension mixture was left to stir at room temperature overnight. The suspension was then left to settle and the yellow solution was decanted from the white solid and filtered through celite to give a clear yellow solution. The solvent was removed under reduced pressure and the resulting residue was extracted into toluene (3 x 5 mL). The extracted solution was filtered through celite and concentrated under reduced pressure to 2 mL. The vial was cooled to -30 °C to give the product as yellow crystals after 2 days.

Yield: 112 mg (64%)

¹H NMR (C₆D₆, 600 MHz) δ 7.16 (d, 2H, *m*-C₆H₃); 7.11 (t, 1H, *p*-C₆H₃); 6.22 (br s, 1H, NH); 5.62 (s, 10H, C₅H₅); 3.41 (m, 2H, CH(CH₃)₂); 1.24 (d, *J*_{HH} = 6.5 Hz, 12H, CH(CH₃)₂); 0.23 (s, 3H, ZrCH₃).

¹³C NMR (C₆D₆, 125 MHz) δ 152.3 (ArC); 126.0 (ArC); 123.7 (ArC); 123.0 (ArC); 110.0 (C₅H₅); 28.2 ((CH₃)₂CH); 23.5 ((CH₃)₂CH); 18.9 (ZrMe).

5.1.35 [Cp₂Zr(Me)(NHar*)] 15 C₄₇H₄₇NZr

To a stirred solution of [Cp₂Zr(Me)(Cl)] (270 mg, 0.99 mmol) in diethyl ether (5 mL) at -30 °C was added [LiNHar*] (480 mg, 1.0 mmol) in diethyl ether (5 mL) dropwise over 1 minute. The addition of the red [LiNHar*] to the colourless solution of [Cp₂Zr(Me)(Cl)] resulted in a green solution developing over 20 minutes. The reaction was left to stir overnight before being filtered through celite. The resulting green

solution was concentrated to dryness under reduced pressure then extracted into toluene (2 x 2 mL). The toluene solution was filtered through celite, layered with hexane and cooled to -30 °C to give the product as green crystals.

^1H NMR (C_6D_6 , 600 MHz) δ 7.24 (br s, 8H, ArH); 7.19 (m, 8H, ArH); 7.06-6.99 (m, 6H, ArH); 6.01 (br s, 2H, $(\text{CHPh}_2)_2$); 5.58 (s, 10H, C_5H_5); 2.79 (br s, 1H, NH); 1.09 (s, 9H, $\text{C}_6\text{H}_2^t\text{Bu}$); 0.30 (s, 3H, ZrMe).

^{13}C NMR (C_6D_6 , 125 MHz) δ 152.63 (ArC); 145.0 (ArC); 130.0 (ArC); 128.6 (ArC); 126.5 (ArC); 125.7 (ArC); 112.8 (ArC); 110.0 (C_5H_5); 34.5 (CHPh_2); 31.5 ($\text{C}_6\text{H}_2\text{C}(\text{CH}_3)_3$); 31.5 ($\text{C}_6\text{H}_2\text{C}(\text{CH}_3)_3$); 21.0 (ZrCH₃).

5.1.36 [Cp₂Zr(Me)(NHDMP)] 16 C₁₉H₂₃NZr

5.1.36.1 Method A:

To a solution of [Cp₂ZrMe₂] (100 mg, 0.40 mmol) in toluene (10 mL) was added 2,6-Dimethylaniline (48mg, 0.40 mmol). The solution was transferred to an ampule fitted with a Young's tap and heated using an oil bath at 110°C for 4 days. The solvent was removed under reduced pressure and the residue was extracted into hexane and filtered through celite. The solution was layered with toluene (1 mL) and cooled to -30 °C to give crystals the product as orange crystals.

5.1.36.2 Method B:

To a stirred solution of [Cp₂Zr(Me)(Cl)] ((490 mg, 1.82 mmol) in ether (10 mL) was added [LiNHDMP] (230 mg, 1.82 mmol), the reaction was left to stir overnight. The suspension was filtered through celite to before having the solvent removed under reduced pressure. The residue was extracted into toluene (2 x 5 mL) filtered through celite and reduced to dryness under reduced pressure to give the compound as an orange solid.

^1H NMR (C_6D_6 , 600 MHz) δ 7.11-7.07 (m, 3H); 5.34 (s, 10H, C_5H_5); 2.04 (s, 6H, NPhMe₂); 0.54 (s, 3H, ZrMe). Toluene is also present in the ^1H and ^{13}C NMR spectral data.

^{13}C NMR (C_6D_6 , 125 MHz) δ 149.1 (ArC), 128.8 (ArC), 128.8 (ArC), 128.2 (ArC), 110.4 (C_5H_5), 52.5 (*ortho*-CH₃), 13.9 (ZrMe).

Anal. Calcd. for C₁₉H₂₃NZr (355.09): C, 63.99; H, 6.50; N, 3.93; Found: C, 61.26; N, 3.86; H, 6.49.

5.1.37 [Cp₂Zr(NAr*)(THF)] 20 C₅₀H₅₀NOZr

In a NMR tube fitted with a young's tap was added [Cp₂Zr(Me)(NAr*)] (60 mg, 0.08 mmol) in C₆D₆ (0.30 mL) and 5 drops of THF. The NMR tube was sealed and heated on an aluminium heating block for 5 days at 100 °C (the author notes this is above the boiling point of deuterated benzene, hence caution is advised). The NMR tube was taken back into the glovebox where hexane (1 mL) was added and the solvent was removed under reduced pressure. The residue was extracted into toluene (2 mL) and filtered through celite. The solution was concentrated to 1 mL under reduced pressure before being cooled to -30 °C to give the compound as orange crystals.

¹H NMR (C₆D₆, 600 MHz) δ 7.39 (d, *J*_{HH} = 7.9 Hz, 8H, ArH); 7.20 (t, *J*_{HH} = 7.9 Hz, 8H, ArH); 7.08 (t, *J*_{HH} = 7.2 Hz, 4H, ArH); 7.05 (s, 2H, ArH); 6.43 (s, 2H, (CHPh₂)₂); 5.74 (s, 10H, C₅H₅); 3.44 (m, 4H, THF); 1.17 (s, 9H, C(CH₃)₃); 1.10-1.07 (m, 4H, THF).

¹³C NMR (C₆D₆, 125 MHz) δ 165.7 (ArC); 152.8 (ArC); 144.7 (ArC); 137.9 (ArC); 130.2 (ArC); 129.3 (ArC); 128.6 (ArC); 125.7 (ArC); 111.8 (C₅H₅); 86.4 (THF); 34.6 (C(CH₃)₃); 31.5 (C(CH₃)₃); 30.1 (THF); 24.0 ((CH(Ph₂))₂).

5.1.38 [Cp₂Zr(Bn)(NHDMP)] 19 C₂₅H₂₇NZr

To a stirred solution of [Bn₂ZrCp₂] (100 mg, 0.03 mmol) in C₆D₆ (0.30 mL) was added [DMPNH₂] (30 mg, 0.03 mmol) and the reaction was transferred to a NMR tube fitted with a Young's tap. The reaction was heated at 80 °C for 2 days until there was no remaining evidence of the free amine by ¹H NMR spectroscopy. The NMR tube was taken into a nitrogen filled glovebox where it was diluted with toluene (1 mL) and the solvent was removed under reduced pressure. The residue was extracted into minimal hexane (4 mL) and cooled to -30 °C to give the product as pale yellow crystals.

¹H NMR (C₆D₆, 600MHz) δ 7.34 (t, *J*_{HH} = 6.9 Hz, 2H, ArH); 7.22 (d, *J*_{HH} = 7.7 Hz, 2H, ArH); 7.11 (m, 2H, ArH); 7.05 (t, *J*_{HH} = 7.2 Hz, 1H, ArH); 6.95 (t, *J*_{HH} = 8.1 Hz, 1H, ArH); 5.44 (s, 10H, C₅H₅); 3.50 (br s, 1H, NH); 2.25 (s, 2H, CH₂Ph); 2.14 (s, 6H, 2,6-MeC₆H₃).

¹³C NMR (C₆D₆, 125 MHz) δ 155.7 (ArC); 154.8 (ArC); 137.9 (ArC); 131.3 (ArC); 129.3 (ArC); 125.7 (ArC); 122.8 (ArC); 120.9 (ArC); 110.8 (C₅H₅); 47.0 (CH₂Ph); 20.9 (2,6-MeC₆H₃).

5.1.39 [Ar*Cl] 26 C₃₆H₃₃Cl

In a 250 mL RB flask with stirring, [Ar*NH₂] (2.68g, 5.57 mmol) was dissolved in 1:2 H₂O (50 mL) to THF (100 mL) mixture. Concentrated HCl was added (10 mL, 12.1M) and the temperature of the reaction was brought down to 0 °C using an ice bath. The solution was treated with 4 equivalents of sodium nitrite (1.50 g, 22.3 mmol) in H₂O (10mL) added dropwise over 5 minutes before being left to stir for four hours, after which time the solution had turned yellow. A solution of [NaN₃] (1.44 g, 0.02 mol) in H₂O (10 mL) was added dropwise over 5 minutes while maintaining an internal reaction temperature of under 5 °C. The reaction was left to stir for four hours. The target compound was extracted into toluene (3 x 50 mL) and washed with sodium bicarbonate (2 x 100 mL), H₂O (2 x 50 mL) and brine (2 x 50 mL) before the toluene fraction was dried over [MgSO₄] and filtered through celite. The volatiles were removed to give an off-white powder. The compound was purified by fractional recrystallisation from minimal toluene. Yield 1.19 g (14%).

¹H NMR (C₆D₆, 300 MHz) δ 7.14 - 6.98 (m, 22H, ArH); 6.19 (s, 2H (CHPh₂)₂); 1.02 (s, 9H, C(CH₃)₃).

¹³C NMR (C₆D₆, 125 MHz) δ 153.9 (ArC); 144.9 (ArC); 143.9 (ArC); 139.5 (ArC); 138.5 (ArC); 129.0 (ArC); 128.8 (ArC); 126.8 (ArC); 52.4 (CHPh₂) ; 35.2 (C(CH₃)₃); 21.3 ((CH₃)₃).

5.2 ¹H And ¹³C NMR Spectra for Novel Compounds

The following compounds were all run in deuterated benzene at 25°C. Impurities in the spectra are noted on each individual sample. All spectra were internally referenced to the residual solvent signal.

5.2.1 ^1H NMR and ^{13}C Spectra of 2 (THF impurity)

5.2.2 ^1H NMR and ^{13}C Spectra of 3

5.2.3 ^1H NMR and ^{13}C Spectra of 4

5.2.4 ^1H NMR and ^{13}C Spectra of 6

5.2.5 ^1H NMR and ^{13}C Spectra of 7

5.2.6 ^1H NMR and ^{13}C Spectra of 8

5.2.7 ^1H NMR and ^{13}C Spectra of 9

5.2.8 ^1H NMR and ^{13}C Spectra of 10

5.2.9 ^1H NMR and ^{13}C Spectra of 11(Toluene impurity)

5.2.10 ^1H NMR and ^{13}C Spectra of 12 (Toluene impurity)

5.2.11 ^1H NMR and ^{13}C Spectra of 13

5.2.12 ^1H NMR and ^{13}C Spectra of 14

5.2.13 ^1H NMR and ^{13}C Spectra of 15

5.2.14 ^1H NMR and ^{13}C Spectra of 16

5.2.15 ^1H NMR and ^{13}C Spectra of 17

5.2.16 ^1H NMR and ^{13}C Spectra of 19 (Toluene impurity)

5.2.17 ^1H NMR and ^{13}C Spectra of 20 (Toluene impurity)

5.2.18 ^1H NMR and ^{13}C Spectra of 21

5.2.19 ^1H NMR and ^{13}C Spectra of 22 (Toluene impurity)

5.2.20 ^1H NMR and ^{13}C Spectra of 23

5.2.21 ^1H NMR and ^{13}C Spectra of 24

5.2.22 ^1H NMR and ^{13}C Spectra of 25

5.2.23 ^1H NMR and ^{13}C Spectra of 26

5.3 Crystal Structure and Refinement Data

Crystal structure refinement data is located on the following pages. Data collection SuperNova, Dual, Cu at zero, EOS , Program package WinGX , Abs. correction 'MULTISCAN' Refinement using SHELXL-2013 , Drawing using ORTEP-3 for Windows

Crystal data and structure refinement for [Ge(BIAN ^{Me}) ₂] (2)		Crystal data and structure refinement for [Ge(NAPH ^{Me})] (3)		Crystal data and structure refinement for [Ge(NAPH ^{Me})]Ge(Bu)(NAPH)] [U(HF ₂) ₂] (4)	
Identification code	PC_01_045a	PC_01_055b	[U(HF ₂) ₂] (4)	PC_01_047a	
Empirical formula	C ₂₀ H ₁₆ GeN ₂	C ₂₀ H ₁₆ GeN ₂ Si ₂		C ₂₃ H ₂₀ Ge ₂ LiN ₂ O ₂ Si ₄	
Formula weight	489.13	373.14		1098.75	
Temperature/K	120.00(10)	120.01(10)		120.01(10)	
Crystal system	Triclinic	Triclinic		Monoclinic	
Space group	<i>P</i> -1	<i>P</i> -1		<i>P</i> 2 ₁ / <i>n</i>	
<i>a</i> /Å	11.7208(4)	9.4520(4)		25.8458(5)	
<i>b</i> /Å	14.6630(4)	9.6819(7)		19.1420(2)	
<i>c</i> /Å	16.3750(5)	10.7207(6)		14.1769(3)	
α /°	70.084(3)	69.454(6)		90	
β /°	70.932(3)	78.082(4)		123.749(3)	
γ /°	73.992(3)	88.297(5)		90	
Volume/Å ³	2453.34(15)	897.90(10)		5831.9(2)	
<i>Z</i>	4	2		4	
$\rho_{\text{calc}}/\text{cm}^3$	1.324	1.380		1.251	
μ/mm^{-1}	1.834	3.548		2.394	
<i>F</i> (000)	1016.0	388.0		2336.0	
Crystal size/mm ³	0.126 × 0.083 × 0.041	0.0937 × 0.0853 × 0.0512		0.2772 × 0.2133 × 0.205	
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)		Cu K α (λ = 1.54184)	
2 θ range for data collection/°	8.748 to 143.706	9.008 to 143.656		8.76 to 143.676	
Index ranges	-14 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 18, -19 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -13 ≤ <i>l</i> ≤ 12		-31 ≤ <i>h</i> ≤ 31, -23 ≤ <i>k</i> ≤ 21, -17 ≤ <i>l</i> ≤ 16	
Reflections collected	29804	7838		45608	
Independent reflections	9564 [<i>R</i> _{int} = 0.0366, <i>R</i> _{sigma} = 0.0384]	3508 [<i>R</i> _{int} = 0.0289, <i>R</i> _{sigma} = 0.0367]		11411 [<i>R</i> _{int} = 0.0235, <i>R</i> _{sigma} = 0.0191]	
Data/restraints/parameters	9564/0/607	3508/0/196		11411/0/617	
Goodness-of-fit on <i>P</i> ²	1.157	1.058		1.025	
Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0373, <i>wR</i> ₂ = 0.1096	<i>R</i> ₁ = 0.0294, <i>wR</i> ₂ = 0.0766		<i>R</i> ₁ = 0.0262, <i>wR</i> ₂ = 0.0661	
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0486, <i>wR</i> ₂ = 0.1136	<i>R</i> ₁ = 0.0316, <i>wR</i> ₂ = 0.0783		<i>R</i> ₁ = 0.0281, <i>wR</i> ₂ = 0.0674	
Largest diff. peak/hole / e Å ⁻³	0.50/-0.55	0.67/-0.68		0.62/-0.51	
Data collected and solved by Dr J.R Fulton		Data collected and solved by Dr J.R Fulton		Data collected and solved by Dr J.R Fulton	

Crystal data and structure refinement for [Ge(NAPH ^{mm})[Ge(Me)(NAPH ^{mm})] [Lu(THF ₂) ⁺](5)				Crystal data and structure refinement for [HMDS ₂ Ge(N ₂ O)PnNC(=O)NMe ₂](7)				Crystal data and structure refinement for [Ge(NAPH)(NLMes ₂)] (8)			
Identification code	PC_01_040a			Identification code	PC-02-052a			Identification code	PC_01_61a		
Empirical formula	C ₆ H ₈ GeLiN ₂ O ₂ Si ₄			Empirical formula	C ₂₈ H ₃₂ N ₈ O ₄ GeSi ₄			Empirical formula	C ₂₇ H ₂₅ GeLiN ₂ Si		
Formula weight	1056.77			Formula weight	552.56			Formula weight	445.05		
Temperature/K	120.01(10)			Temperature/K	120.00(10)			Temperature/K	120.00(10)		
Crystal system	Monoclinic			Crystal system	Triclinic			Crystal system	Monoclinic		
Space group	P2 ₁ /c			Space group	P-1			Space group	C2/c		
a/Å	16.1154(6)			a/Å	11.3532(2)			a/Å	21.2543(3)		
b/Å	17.2489(3)			b/Å	17.4676(3)			b/Å	11.7910 (1)		
c/Å	27.6328(10)			c/Å	18.7517(3)			c/Å	13.6459(1)		
α/°	90			α/°	83.951(2)			α/°	90		
β/°	133.792(7)			β/°	87.967(2)			β/°	97.808(1)		
γ/°	90			γ/°	76.058(2)			γ/°	90		
Volume/Å ³	5544.7(7)			Volume/Å ³	3588.86(11)			Volume/Å ³	3388.09(6)		
Z	4			Z	5			Z	8		
ρ _{calc} /cm ³	1.2658			ρ _{calc} /cm ³	1.2782			ρ _{calc} /cm ³	1.3086		
μ/mm ⁻¹	2.499			μ/mm ⁻¹	2.719			μ/mm ⁻¹	2.155		
F(000)	2240.0			F(000)	1466.8			F(000)	1408.7		
Crystal size/mm ³	0.1452 × 0.0953 × 0.0757			Crystal size/mm ³	0.283 × 0.183 × 0.059			Crystal size/mm ³	0.159 × 0.126 × 0.069		
Radiation	Cu Kα (λ = 1.54184)			Radiation	Cu Kα (λ = 1.54184)			Radiation	Cu Kα (λ = 1.54184)		
2θ range for data collection/°	8.32 to 143.58			2θ range for data collection/°	6.7 to 147.2			2θ range for data collection/°	8.4 to 143.62		
Index ranges	-18 ≤ h ≤ 19, -21 ≤ k ≤ 19, -34 ≤ l ≤ 28			Index ranges	-14 ≤ h ≤ 9, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23			Index ranges	-26 ≤ h ≤ 24, -14 ≤ k ≤ 14, -10 ≤ l ≤ 16		
Reflections collected	41816			Reflections collected	48835			Reflections collected	8890		
Independent reflections	10835 [R _{int} = 0.0260, R _{sigma} = 0.0234]			Independent reflections	14407 [R _{int} = 0.0501, R _{sigma} = 0.0393]			Independent reflections	3307 [R _{int} = 0.0210, R _{sigma} = 0.0232]		
Data/restraints/parameters	10835/0/590			Data/restraints/parameters	14407/0/769			Data/restraints/parameters	3307/0/202		
Goodness-of-fit on F ²	1.040			Goodness-of-fit on F ²	1.022			Goodness-of-fit on F ²	1.030		
Final R indexes [I>2σ(I)]	R ₁ = 0.0532, wR ₂ = 0.1449			Final R indexes [I>2σ(I)]	R ₁ = 0.0640, wR ₂ = 0.1670			Final R indexes [I>2σ(I)]	R ₁ = 0.0251, wR ₂ = 0.0655		
Final R indexes [all data]	R ₁ = 0.0500, wR ₂ = 0.1483			Final R indexes [all data]	R ₁ = 0.0664, wR ₂ = 0.1730			Final R indexes [all data]	R ₁ = 0.0271, wR ₂ = 0.0669		
Largest diff. peak/hole / e Å ⁻³	1.94/-0.94			Largest diff. peak/hole / e Å ⁻³	1.08/-1.31			Largest diff. peak/hole / e Å ⁻³	0.29/-0.28		
Data collected and solved by Dr J.R Fulton				Data collected and solved by Dr J.R Fulton				Data collected and solved by Dr J.R Fulton			

Crystal data and structure refinement for [(HMDS) ₂ Ge(NMes)] (9)			
Identification code	PC-02-023a	Identification code	PC-02-038a
Empirical formula	C ₂₁ H ₁₇ GeN ₂ Si ₄	Empirical formula	C ₄₈ H ₃₉ Ge ₂ N ₁₂ Si ₈
Formula weight	526.58	Formula weight	1207.23
Temperature/K	120.00(10)	Temperature/K	120.00(10)
Crystal system	Monoclinic	Crystal system	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	Space group	<i>P</i> -1
<i>a</i> /Å	16.1293(6)	<i>a</i> /Å	11.9310(7)
<i>b</i> /Å	24.4676(7)	<i>b</i> /Å	17.1724(9)
<i>c</i> /Å	8.1398(3)	<i>c</i> /Å	17.2934(12)
α /°	90	α /°	64.755(6)
β /°	93.045(3)	β /°	76.856(5)
γ /°	90	γ /°	78.861(5)
Volume/Å ³	3207.80(19)	Volume/Å ³	3102.1(4)
<i>Z</i>	4	<i>Z</i>	2
$\rho_{\text{calc}}/\text{cm}^3$	1.0903	$\rho_{\text{calc}}/\text{cm}^3$	1.292
μ/mm^{-1}	2.807	μ/mm^{-1}	1.166
<i>F</i> (000)	1129.5	<i>F</i> (000)	1280.0
Crystal size/mm ³	0.637 × 0.189 × 0.073	Crystal size/mm ³	0.383 × 0.153 × 0.13
Radiation	Cu K α (λ = 1.54184)	Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	7.22 to 147.46	2 θ range for data collection/°	6.574 to 58.928
Index ranges	-19 ≤ <i>h</i> ≤ 20, -30 ≤ <i>k</i> ≤ 29, -10 ≤ <i>l</i> ≤ 8	Index ranges	-15 ≤ <i>h</i> ≤ 16, -21 ≤ <i>k</i> ≤ 22, -16 ≤ <i>l</i> ≤ 23
Reflections collected	21629	Reflections collected	29037
Independent reflections	6410 [<i>R</i> _{int} = 0.0500, <i>R</i> _{sigma} = 0.0473]	Independent reflections	14470 [<i>R</i> _{int} = 0.0446, <i>R</i> _{sigma} = 0.0657]
Data/restraints/parameters	6410/0/277	Data/restraints/parameters	14470/0/655
Goodness-of-fit on <i>F</i> ²	1.027	Goodness-of-fit on <i>F</i> ²	1.143
Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0618, <i>wR</i> ₂ = 0.2025	Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.1298, <i>wR</i> ₂ = 0.3703
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0671, <i>wR</i> ₂ = 0.2117	Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1443, <i>wR</i> ₂ = 0.3776
Largest diff. peak/hole / <i>e</i> Å ⁻³	2.36/-0.65	Largest diff. peak/hole / <i>e</i> Å ⁻³	6.15/-1.64
Data collected and solved by Dr J.R Fulton			
Largest diff. peak/hole/ <i>e</i> Å ⁻³ possible solvent accessible void.			
Residual electron density located around germanium atoms.			

Crystal data and structure refinement for [(HMDS)GeI=NTMS](NTMS)Ar ⁻] (11)			
Identification code	PC-02-038a	Identification code	PC-02-038a
Empirical formula	C ₅₅ H ₇₁ N ₃ GeSi ₄	Empirical formula	C ₅₅ H ₇₁ N ₃ GeSi ₄
Formula weight	965.20	Formula weight	965.20
Temperature/K	120.00(10)	Temperature/K	120.00(10)
Crystal system	Triclinic	Crystal system	Triclinic
Space group	<i>P</i> 1	Space group	<i>P</i> 1
<i>a</i> /Å	22.5739(3)	<i>a</i> /Å	22.5739(3)
<i>b</i> /Å	21.1247(3)	<i>b</i> /Å	21.1247(3)
<i>c</i> /Å	11.44235(18)	<i>c</i> /Å	11.44235(18)
α /°	90	α /°	90
β /°	90	β /°	90
γ /°	90	γ /°	90
Volume/Å ³	5456.48(18)	Volume/Å ³	5456.48(18)
<i>Z</i>	4	<i>Z</i>	4
$\rho_{\text{calc}}/\text{cm}^3$	1.175	$\rho_{\text{calc}}/\text{cm}^3$	1.175
μ/mm^{-1}	1.884	μ/mm^{-1}	1.884
<i>F</i> (000)	2064.0	<i>F</i> (000)	2064.0
Crystal size/mm ³	0.422 × 0.228 × 0.161	Crystal size/mm ³	0.422 × 0.228 × 0.161
Radiation	Cu K α (λ = 1.54184)	Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	7.726 to 133.1994	2 θ range for data collection/°	7.726 to 133.1994
Index ranges	-26 ≤ <i>h</i> ≤ 26, -25 ≤ <i>k</i> ≤ 18, -11 ≤ <i>l</i> ≤ 13	Index ranges	-26 ≤ <i>h</i> ≤ 26, -25 ≤ <i>k</i> ≤ 18, -11 ≤ <i>l</i> ≤ 13
Reflections collected	12767	Reflections collected	12767
Independent reflections	4961 [<i>R</i> _{int} = 0.0273, <i>R</i> _{sigma} = 0.0384]	Independent reflections	4961 [<i>R</i> _{int} = 0.0273, <i>R</i> _{sigma} = 0.0384]
Data/restraints/parameters	4961/20/308	Data/restraints/parameters	4961/20/308
Goodness-of-fit on <i>F</i> ²	1.056	Goodness-of-fit on <i>F</i> ²	1.056
Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0340, <i>wR</i> ₂ = 0.0877	Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0340, <i>wR</i> ₂ = 0.0877
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0364, <i>wR</i> ₂ = 0.0896	Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0364, <i>wR</i> ₂ = 0.0896
Largest diff. peak/hole / <i>e</i> Å ⁻³	0.46/-0.45	Largest diff. peak/hole / <i>e</i> Å ⁻³	0.46/-0.45
Data collected by Dr J.R Fulton, Solved by Acc. Prof. M. Coles			

The molecule lies on a mirror plane. One of the methyl groups of the silyl-imido group is disordered and was modelled over two positions. The toluene solvate is located on an inversion centre and was modelled as a rigid body at 50% occupancy

Crystal data and structure refinement for [(HMDs)Ge(CCPH)(NHMe)] (12)	
Identification code	PC-02-048a
Empirical formula	C ₂₈ H ₃₃ GeN ₃ Si ₂
Formula weight	628.69
Temperature/K	120.00(10)
Crystal system	Triclinic
Space group	P-1
a/Å	10.4463(5)
b/Å	12.1246(4)
c/Å	15.6432(6)
α/°	100.157(3)
β/°	95.351(3)
γ/°	113.005(4)
Volume/Å ³	1766.19(14)
Z	2
ρ _{calc} /cm ³	1.1821
μ/mm ⁻¹	2.622
F(000)	672.0
Crystal size/mm ³	0.751 × 0.394 × 0.257
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.1448 to 133.1936
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 11, -18 ≤ l ≤ 19
Reflections collected	10911
Independent reflections	6243 [R _{int} = 0.0229, R _{sigma} = 0.0291]
Data/restraints/parameters	6243/1/353
Goodness-of-fit on F ²	1.069
Final R indexes [I>2σ(I)]	R ₁ = 0.0437, wR ₂ = 0.1195
Final R indexes [all data]	R ₁ = 0.0448, wR ₂ = 0.1209
Largest diff. peak/hole / e Å ⁻³	1.15/-1.15

Data collected by Dr J.R Fulton, Solved by Acc. Prof. M. Coles

Crystal data and structure refinement for [(HMDs)Ge(N ₂ OPhNC(O)NMe)] (13)	
Identification code	PC-02-052a
Empirical formula	C ₂₈ H ₂₃ N ₃ O ₂ GeSi ₂
Formula weight	552.56
Temperature/K	120.00(10)
Crystal system	Triclinic
Space group	P-1
a/Å	11.3532(2)
b/Å	17.4676(3)
c/Å	18.7517(3)
α/°	83.951(2)
β/°	87.967(2)
γ/°	76.058(2)
Volume/Å ³	3588.86(11)
Z	5
ρ _{calc} /cm ³	1.2782
μ/mm ⁻¹	2.719
F(000)	1466.8
Crystal size/mm ³	0.283 × 0.183 × 0.059
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.7 to 147.2
Index ranges	-14 ≤ h ≤ 9, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23
Reflections collected	48835
Independent reflections	14407 [R _{int} = 0.0501, R _{sigma} = 0.0393]
Data/restraints/parameters	14407/0/769
Goodness-of-fit on F ²	1.022
Final R indexes [I>2σ(I)]	R ₁ = 0.0640, wR ₂ = 0.1670
Final R indexes [all data]	R ₁ = 0.0684, wR ₂ = 0.1730
Largest diff. peak/hole / e Å ⁻³	1.08/-1.31

Data collected and solved by Dr J.R Fulton

Crystal data and structure refinement for [(Cp ₂ Zr(NHDipp)(Me)] (14)	
Identification code	PC_01_106
Empirical formula	C ₂₃ H ₂₃ NZr
Formula weight	412.11
Temperature/K	120.01(10)
Crystal system	Monoclinic
Space group	P112 ₁ /a
a/Å	11.6490(3)
b/Å	15.3295(4)
c/Å	11.6356(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2077.81(10)
Z	4
ρ _{calc} /cm ³	1.3173
μ/mm ⁻¹	4.343
F(000)	862.6
Crystal size/mm ³	0.539 × 0.264 × 0.212
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	10.74 to 145.84
Index ranges	14 ≤ h ≤ 6, -18 ≤ k ≤ 17, -13 ≤ l ≤ 13
Reflections collected	4156
Independent reflections	2840 [R _{int} = 0.0164, R _{sigma} = 0.0186]
Data/restraints/parameters	2840/0/269
Goodness-of-fit on F ²	0.981
Final R indexes [I>2σ(I)]	R ₁ = 0.0715, wR ₂ = 0.1873
Final R indexes [all data]	R ₁ = 0.723, wR ₂ = 0.1876
Largest diff. peak/hole / e Å ⁻³	1.21/-1.46

Data collected and solved by Dr J.R Fulton

Cyclopentadienyl ligands modelled as isotropic. Residual electron density located around zirconium atom.

Crystal data and structure refinement for [Cp ₂ Zr(Me) ₂ (NHAr ⁺)] (15)		Crystal data and structure refinement for [Cp ₂ Zr(Me) ₂ (NHDMP)] (16)		Crystal data and structure refinement for [Cp ₂ Zr(Bn) ₂ (NHPn)] (17)	
Identification code	PC-01_114a	Identification code	PC-01_127a	Identification code	PC-02-017b
Empirical formula	C ₂₁ H ₁₈ NZr	Empirical formula	C ₂₁ H ₂₃ NZr	Empirical formula	C ₂₁ H ₂₃ NZr
Formula weight	717.13	Formula weight	356.62	Formula weight	404.64
Temperature/K	120.00(10)	Temperature/K	120.01(10)	Temperature/K	120.01(10)
Crystal system	Monoclinic	Crystal system	Monoclinic	Crystal system	Monoclinic
Space group	C2	Space group	P2 ₁	Space group	P2 ₁ /c
a/Å	18.9269(4)	a/Å	9.6469(2)	a/Å	7.6402(4)
b/Å	15.6045(3)	b/Å	7.8808(2)	b/Å	19.7091(7)
c/Å	13.2499(3)	c/Å	10.6232(3)	c/Å	16.6625(9)
α/°	90	α/°	90	α/°	90
β/°	108.564(2)	β/°	90.047(2)	β/°	121.587(8)
γ/°	90	γ/°	90	γ/°	90
Volume/Å ³	3709.69	Volume/Å ³	807.63(4)	Volume/Å ³	2137.2
Z	4	Z	2	Z	5
ρ _{calc} /cm ³	1.2839	ρ _{calc} /cm ³	1.4664	ρ _{calc} /cm ³	1.572
μ/mm ⁻¹	2.666	μ/mm ⁻¹	5.496	μ/mm ⁻¹	5.277
F(000)	1506.7	F(000)	368.4	F(000)	1040.0
Crystal size/mm ³	0.172 × 0.14 × 0.078	Crystal size/mm ³	0.186 × 0.082 × 0.063	Crystal size/mm ³	0.184 × 0.109 × 0.072
Radiation	Cu Kα (λ = 1.54184)	Radiation	Cu Kα (λ = 1.54184)	Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.04 to 146.92	2θ range for data collection/°	8.32 to 147.06	2θ range for data collection/°	7.676 to 146.928
Index ranges	-22 ≤ h ≤ 23, -18 ≤ k ≤ 19, -16 ≤ l ≤ 15	Index ranges	-12 ≤ h ≤ 11, -9 ≤ k ≤ 6, -13 ≤ l ≤ 10	Index ranges	-7 ≤ h ≤ 9, -24 ≤ k ≤ 23, -20 ≤ l ≤ 15
Reflections collected	12042	Reflections collected	6342	Reflections collected	12875
Independent reflections	6132 [R _{int} = 0.0170, R _{sigma} = 0.0231]	Independent reflections	2315 [R _{int} = 0.0389, R _{sigma} = 0.0412]	Independent reflections	4284 [R _{int} = 0.0499, R _{sigma} = 0.0511]
Data/restraints/parameters	6132/1/436	Data/restraints/parameters	2315/1/193	Data/restraints/parameters	4284/0/226
Goodness-of-fit on F ²	1.013	Goodness-of-fit on F ²	1.027	Goodness-of-fit on F ²	1.056
Final R indexes [I>2σ(I)]	R ₁ = 0.0461, wR ₂ = 0.1151	Final R indexes [I>2σ(I)]	R ₁ = 0.0310, wR ₂ = 0.0823	Final R indexes [I>2σ(I)]	R ₁ = 0.0753, wR ₂ = 0.2403
Final R indexes [all data]	R ₁ = 0.0488, wR ₂ = 0.1181	Final R indexes [all data]	R ₁ = 0.0313, wR ₂ = 0.0827	Final R indexes [all data]	R ₁ = 0.0842, wR ₂ = 0.2490
Largest diff. peak/hole / e Å ⁻³	0.83/-0.48	Largest diff. peak/hole / e Å ⁻³	0.86/-0.61	Largest diff. peak/hole / e Å ⁻³	0.95/-1.04
Data collected and solved by Dr J.R. Fulton		Data collected and solved by Dr J.R. Fulton		Data collected and solved by Dr J.R. Fulton	

Crystal data and structure refinement for [Cp2Zr(bn)(NHDMP)] (19)		Crystal data and structure refinement for [Cp ₂ Zr(NAr ⁺)(THF)] (20)		Crystal data and structure refinement for [Cp ₂ Zr(Bu)(N ₄ (Bu)(Me-s))] (21)	
Identification code	PC-02-040a	PC_01_152	PC_01_047a	PC_01_047a	
Empirical formula	C ₂₄ H ₂₈ N ₂ Zr	C ₂₇ H ₂₆ NOZr	C ₂₄ H ₂₆ N ₄ Zr ₂	C ₂₄ H ₂₆ N ₄ Zr ₂	
Formula weight	564.89	865.31	993.66	993.66	
Temperature/K	120.00(10)	120.01(10)	120.00(10)	120.00(10)	
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	Pc	Pc	
a/Å	8.2119(16)	12.4346(2)	7.7737(7)	7.7737(7)	
b/Å	15.9032(3)	25.2264(4)	22.09318(18)	22.09318(18)	
c/Å	21.1374(4)	15.4288(3)	14.91475(14)	14.91475(14)	
α/°	90	90	90	90	
β/°	90	108.804(2)	101.6432(8)	101.6432(8)	
γ/°	90	90	90	90	
Volume/Å ³	2784.01(9)	4581.40(15)	2510.02(4)	2510.02(4)	
Z	4	4	2	2	
ρ _{calc} /cm ³	1.3476	1.2545	1.315	1.315	
μ/mm ⁻¹	3.421	2.265	3.709	3.709	
F(000)	1177.9	1827.7	1048.0	1048.0	
Crystal size/mm ³	0.172 × 0.144 × 0.097	0.205 × 0.081 × 0.079	0.3056 × 0.2528 × 0.1112	0.3056 × 0.2528 × 0.1112	
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	
2θ range for data collection/°	6.94 to 147.18	7 to 147.34	10.04 to 143.526	10.04 to 143.526	
Index ranges	-9 ≤ h ≤ 10, -14 ≤ k ≤ 19, -26 ≤ l ≤ 22	14 ≤ h ≤ 15, -31 ≤ k ≤ 31, -19 ≤ l ≤ 18	-5 ≤ h ≤ 9, -24 ≤ k ≤ 27, -18 ≤ l ≤ 18	-5 ≤ h ≤ 9, -24 ≤ k ≤ 27, -18 ≤ l ≤ 18	
Reflections collected	10982	37366	15016	15016	
Independent reflections	5432 [R _{int} = 0.0274, R _{sigma} = 0.0370]	9209 [R _{int} = 0.0380, R _{sigma} = 0.0327]	6191 [R _{int} = 0.0188, R _{sigma} = 0.0219]	6191 [R _{int} = 0.0188, R _{sigma} = 0.0219]	
Data/restraints/parameters	5342/0/337	9209/0/545	6191/2/569	6191/2/569	
Goodness-of-fit on F ²	1.014	1.038	0.961	0.961	
Final R indexes [I>2σ(I)]	R ₁ = 0.0270, wR ₂ = 0.0686	R ₁ = 0.0518, wR ₂ = 0.1302	R ₁ = 0.0183, wR ₂ = 0.0472	R ₁ = 0.0183, wR ₂ = 0.0472	
Final R indexes [all data]	R ₁ = 0.0275, wR ₂ = 0.0691	R ₁ = 0.0571, wR ₂ = 0.1333	R ₁ = 0.0184, wR ₂ = 0.0473	R ₁ = 0.0184, wR ₂ = 0.0473	
Largest diff. peak/hole / e Å ⁻³	0.34/-0.59	1.26/-1.09	0.41/-0.54	0.41/-0.54	
Flack Parameter	-0.003(8)		-0.005(6)	-0.005(6)	
Data collected and solved by Dr J.R Fulton		Data collected and solved by Dr J.R Fulton		Data collected and solved by Dr J.R Fulton	
Residual electron density located around zirconium atom.					

Crystal data and structure refinement for [Cp ₂ Zr(Me) ₂ (Me)(Mes)] (22)		Crystal data and structure refinement for [Cp ₂ Zr(Me)(N ₃ Ph)(Me)] (23)		Crystal data and structure refinement for [Cp ₂ Zr(Bn) ₂ (N ₃ Mes)(Bn)] (24)	
Identification code	PC-01_051a	Identification code	PC-01-142a	Identification code	PC-02-018
Empirical formula	C ₂₁ H ₁₇ N ₃ Zr	Empirical formula	C ₂₆ H ₂₂ N ₃ Zr ₂	Empirical formula	C ₃₁ H ₂₃ N ₃ Zr
Formula weight	412.67	Formula weight	329.43	Formula weight	564.89
Temperature/K	120.01(10)	Temperature/K	120.01(10)	Temperature/K	120.00(10)
Crystal system	Orthorhombic	Crystal system	Orthorhombic	Crystal system	Orthorhombic
Space group	<i>P</i> no ₂	Space group	<i>P</i> 2 ₁ 2 ₁	Space group	<i>P</i> 2 ₁ 2 ₁
<i>a</i> /Å	8.06960(14)	<i>a</i> /Å	8.15625(10)	<i>a</i> /Å	8.21197(16)
<i>b</i> /Å	30.9521(5)	<i>b</i> /Å	15.64749(17)	<i>b</i> /Å	15.9032(3)
<i>c</i> /Å	7.76058(13)	<i>c</i> /Å	25.5913(3)	<i>c</i> /Å	21.1374(4)
<i>α</i> /°	90	<i>α</i> /°	90	<i>α</i> /°	90
<i>β</i> /°	90	<i>β</i> /°	90	<i>β</i> /°	90
<i>γ</i> /°	90	<i>γ</i> /°	90	<i>γ</i> /°	90
Volume/Å ³	1938.37(6)	Volume/Å ³	3266.09(7)	Volume/Å ³	2784.01(9)
<i>Z</i>	4	<i>Z</i>	4	<i>Z</i>	4
$\rho_{\text{calc}}/\text{cm}^3$	1.414	$\rho_{\text{calc}}/\text{cm}^3$	1.5073	$\rho_{\text{calc}}/\text{cm}^3$	1.3476
μ/mm^{-1}	4.689	μ/mm^{-1}	5.499	μ/mm^{-1}	3.421
<i>F</i> (000)	856.0	<i>F</i> (000)	1521.7	<i>F</i> (000)	1177.9
Crystal size/mm ³	0.268 × 0.17 × 0.134	Crystal size/mm ³	0.52 × 0.107 × 0.092	Crystal size/mm ³	0.172 × 0.144 × 0.097
Radiation	Cu K α (λ = 1.54184)	Radiation	Cu K α (λ = 1.54184)	Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	11.332 to 143.404	2 θ range for data collection/°	6.9 to 145.74	2 θ range for data collection/°	6.94 to 147.18
Index ranges	9 ≤ <i>h</i> ≤ 9, -37 ≤ <i>k</i> ≤ 37, -5 ≤ <i>l</i> ≤ 9	Index ranges	-8 ≤ <i>h</i> ≤ 10, -19 ≤ <i>k</i> ≤ 19, -31 ≤ <i>l</i> ≤ 30	Index ranges	-9 ≤ <i>h</i> ≤ 10, -14 ≤ <i>k</i> ≤ 19, -26 ≤ <i>l</i> ≤ 22
Reflections collected	10599	Reflections collected	10745	Reflections collected	10982
Independent reflections	2820 [<i>R</i> _{int} = 0.0219, <i>R</i> _{sigma} = 0.0183]	Independent reflections	5742 [<i>R</i> _{int} = 0.0253, <i>R</i> _{sigma} = 0.0342]	Independent reflections	5432 [<i>R</i> _{int} = 0.0274, <i>R</i> _{sigma} = 0.0370]
Data/restraints/parameters	2820/1/181	Data/restraints/parameters	5742/0/401	Data/restraints/parameters	5342/0/357
Goodness-of-fit on <i>F</i> ²	1.098	Goodness-of-fit on <i>F</i> ²	1.038	Goodness-of-fit on <i>F</i> ²	1.014
Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0584, <i>wR</i> ₂ = 0.1378	Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0268, <i>wR</i> ₂ = 0.0745	Final <i>R</i> indexes [<i>i</i> > 2 σ (<i>i</i>)]	<i>R</i> ₁ = 0.0270, <i>wR</i> ₂ = 0.0686
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0587, <i>wR</i> ₂ = 0.1381	Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0273, <i>wR</i> ₂ = 0.0747	Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0275, <i>wR</i> ₂ = 0.0691
Largest diff. peak/hole / e Å ⁻³	1.59/-0.86	Largest diff. peak/hole / e Å ⁻³	0.50/-0.67	Largest diff. peak/hole / e Å ⁻³	0.34/-0.59
Flack Parameter		Flack Parameter	-0.002(9)	Flack Parameter	-0.003(8)
Data collected and solved by Dr J.R Fulton		Data collected and solved by Dr J.R Fulton		Data collected and solved by Dr J.R Fulton	
Cyclopentadienyl ligands modelled as isotropic. Residual electron density located on cyclopentadienyl ligand		Residual electron density located around zirconium atom.			

Crystal data and structure refinement for [Ar ⁺ N ₃] (25)		Crystal data and structure refinement for [Ar ⁺ Cl] (26)	
Identification code	PC-01-075a	Identification code	PC-01-157
Empirical formula	C ₁₆ H ₁₃ N ₃	Empirical formula	C ₁₆ H ₁₃ S ⁺ Cl
Formula weight	507.65	Formula weight	250.54
Temperature/K	120.00(10)	Temperature/K	120.00(10)
Crystal system	Monoclinic	Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	Space group	<i>P</i> mmn
<i>a</i> /Å	5.7482(3)	<i>a</i> /Å	18.8345(2)
<i>b</i> /Å	19.9651(10)	<i>b</i> /Å	24.6993(5)
<i>c</i> /Å	25.4995(15)	<i>c</i> /Å	5.8667(2)
α /°	90	α /°	90
β /°	103.730(6)	β /°	90
γ /°	90	γ /°	90
Volume/Å ³	2842.8(3)	Volume/Å ³	2729.18(13)
<i>Z</i>	4	<i>Z</i>	8
$\rho_{\text{calc}}/\text{cm}^3$	1.186	$\rho_{\text{calc}}/\text{cm}^3$	1.219
μ/mm^{-1}	0.531	μ/mm^{-1}	1.392
<i>F</i> (000)	1080.0	<i>F</i> (000)	1064.0
Crystal size/mm ³	0.189 × 0.072 × 0.037	Crystal size/mm ³	0.424 × 0.191 × 0.06
Radiation	Cu K α (λ = 1.54184)	Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	8.402 to 146.97	2 θ range for data collection/°	7.158 to 147.038
Index ranges	-7 ≤ <i>h</i> ≤ 5, -24 ≤ <i>k</i> ≤ 24, -29 ≤ <i>l</i> ≤ 31	Index ranges	-23 ≤ <i>h</i> ≤ 20, -30 ≤ <i>k</i> ≤ 23, -6 ≤ <i>l</i> ≤ 7
Reflections collected	10835	Reflections collected	9781
Independent reflections	5154 [<i>R</i> _{int} = 0.0528, <i>R</i> _{sigma} = 0.0693]	Independent reflections	2814 [<i>R</i> _{int} = 0.0313, <i>R</i> _{sigma} = 0.0295]
Data/restraints/parameters	5154/0/355	Data/restraints/parameters	2814/0/177
Goodness-of-fit on <i>F</i> ²	1.064	Goodness-of-fit on <i>F</i> ²	1.057
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1152, <i>wR</i> ₂ = 0.3220	Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0410, <i>wR</i> ₂ = 0.1015
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1388, <i>wR</i> ₂ = 0.3423	Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0455, <i>wR</i> ₂ = 0.1044
Largest diff. peak/hole / e Å ⁻³	0.47/-0.71	Largest diff. peak/hole / e Å ⁻³	0.24/-0.35

Data collected and solved by Dr J.R Fulton

Data collected and solved by Dr J.R Fulton

5.4 Partial Charges for 4 and 5

Figure 51: Partial charges calculated for 4 showing negative (red) and positive (blue) partial atom charges.

Table 28: Molecular orbital energies of I.

	[Ge(HMDS) ₂]
HOMO-1 (kJ mol ⁻¹)	-682.61
HOMO(kJ mol ⁻¹)	-585.47
LUMO(kJ mol ⁻¹)	-144.40
LUMO+1 (kJ mol ⁻¹)	68.26
HOMO-LUMO (kJ mol ⁻¹)	441.07
HOMO-LUMO (eV)	4.57

HOMO

HOMO-1

LUMO

LUMO+1

Figure 53: Frontier molecular orbitals of [Ge(HMDS)₂].

5.6 Crystal Structure Data for [Ar*N₃]

Figure 54: ORTEP representation of 25. 30% Thermal ellipsoids. Hydrogens omitted for clarity.

Table 29: Selected bond lengths and angles for 25.

Bond Lengths (Å)		Bond Angles (°)	
N(1)-N(2)	1.133(7)	N(1)-N(2)-N(3)	169.9(6)
N(2)-N(3)	1.198(8)	N(2)-N(1)-C(1)	117.7(4)
N(1)-C(1)	1.485(6)		

5.7 Crystal Structure Data for [Ar*Cl]

Figure 55: ORTEP representation of 26, 30% thermal ellipsoids. Hydrogens omitted for clarity.

Table 30: Selected bond lengths and angles for 26.

Bond Lengths (Å)	
C(1)-Cl(1)	1.748

5.8 Crystal Structure Diagram for $[(\text{Cp}_2\text{Zr}(\text{NPh}))_2]$

Figure S6: ORTEP diagram for $[(\text{Cp}_2\text{Zr}(\text{NPh}))_2]$. Shown for connectivity purposes only. Isotropic model.

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