Bis(imino)phenyl group 13 - 14 complexes

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BIS(IMINO)PHENYL GROUP 13 – 14 COMPLEXES

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Abbreviations

Å	Angstrom
β	beta
δ	chemical shift
°	degree
°C	degree Celsius
η	‘eta’ (hapticity)
μ	Mu
Ar	2,6-diisopropylphenyl
Ar*	2,6-bis(diphenylmethyl)-4-methyl
br	broad
calcd	calculated
Cp	cyclopentadiene
Cp*	pentamethylcyclopentadiene
Cy	cyclohexyl
d	doublet
dec.	decomposed
EPR	Electron Paramagnetic Resonance
Et ₂ O	diethyl ether
equiv	equivalent
g	gram(s)
h	hour(s)
HOMO	Highest Occupied Molecular Orbital
<i>i</i> Pr	isopropyl
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital

m	multiplet
Me	methyl
MeCN	acetonitrile
mmol	millimole
M.p.	melting point
<i>n</i> BuLi	<i>n</i> -butyllithium
NMR	Nuclear Magnetic Resonance
OTf	triflate
Ph	phenyl
ppm	parts per million
s	singlet
t	triplet
<i>t</i> Bu	tert-butyl
THF	tetrahydrofuran

List of Synthesized Compounds

Formula	Numbering Scheme	Page	Structure
$C_{32}H_{46}BrInN_4$	1.1	31
$C_{39}H_{54}Cl_2In_2N_4$	1.2	33
$C_{52}H_{79}Cl_2In_3N_6O$	1.3	36
$C_{148}H_{118}Br_2In_2N_4$	1.4	38
$C_{148}H_{118}Br_2N_4Tl_2$	1.5	41
$C_{16}H_{23}ClGeN_2$	2.1	63
$C_{32}H_{46}Ge_2N_4$	2.2	66

$C_{38}H_{46}AuClGeIN_2OP$	3.8	106
$C_{55}H_{78}N_4OSi$	4.2	125

General Introduction

The chemistry of pincer ligands has been widely explored in the field of organometallic chemistry since its first utilization in the 1970s.¹⁻³ Pincer ligands can be used to modify the properties of the metal center to which it is bonded.⁴ Huge efforts have been dedicated in the exploration of pincer ligands coordinated to transition metals as these compounds have been found to be useful in catalysis and material sciences.^{5,6}

Chart A. Bis(imino)phenyl ligands

An example of a type of pincer ligand is the bis(imino)phenyl ligand (Chart A). Ir, Pt, and Pd pincer complexes with the bis(imino)phenyl ligands have been developed and investigated as catalysts for Heck coupling, transfer hydrogenation of ketones and C–C bond formation reactions.⁷⁻¹² Bis(imino)phenyl pincer lanthanide complexes were also synthesized and it was discovered that these complexes exhibit high catalytic activity and cis-1,4 selectivity for isoprene and butadiene polymerization.¹³ Recently, our group has successfully isolated group 14 (Ge, Sn, Pb) bis(imino)phenyl compounds, **A** – **C** (Chart B).¹⁴⁻¹⁶

Chart B. Examples of some group 14 bis(imino)phenyl compounds

Our group also isolated the corresponding bis(imino)phenyl germylidenide anion (**D**, Chart C),¹⁴ bis(imino)phenyl stannylidenide anion (**E**, Chart C)¹⁵ and an aromatic plumbylidenide anion (**F**, Chart C).¹⁶ The K atom is η^1 -coordinated to the low-valent germanium atom in compound **D**. There is also an electron delocalization in the germanium heterocycle in **D**, which stabilizes the negative charge at the germanium atom.¹⁴ In compound **E**, the potassium atom is η^5 -coordinated to the low-valent tin heterocycle and the negative charge at the tin atom is stabilized by the electron delocalization in the low valent tin heterocycle.¹⁵ The plumbylidenide anion **F**, is the first aromatic low-valent lead analogue of an indenyl anion. The negative charge of the compound is aromatically delocalized in the PbC_3N five-membered ring. The results obtained shows that the 2p orbitals of C/N atoms and a 6p orbital of a low valent lead atom, can sufficiently overlap to form an aromatic compound.¹⁶ Furthermore, a low valent germanium dianion radical (**G**, Chart C) was obtained by the reduction of the 2,6-bis(imino)-phenyl germanium(II) chloride (**A**, Chart B) with excess calcium.^{14,17}

Chart C. Examples of some Group 14 bis(imino)phenyl anions

Although our group has managed to synthesize group 14 (Ge, Sn, Pb) compounds and their respective anions, supported by bis(imino)phenyl ligands, there is limited exploration of the synthesis of low valent group 13 compounds supported by bis(imino)phenyl ligands. Recently, Vidovic's group synthesized several aluminium complexes supported by bis(imino)phenyl ligands (Scheme A and B).¹⁸⁻¹⁹

Scheme A. Synthesis of bis(imino)phenyl diethylaluminium (**H**) and bis(imino)phenyl aluminium dichloride (**I**)

The reaction of $\text{L}^{\text{Ar}}\text{Br}$ with $n\text{BuLi}$ afforded the lithigated product, $\text{L}^{\text{Ar}}\text{Li}$, which then further react with diethylaluminium chloride or aluminium trichloride to afford compounds **H** and **I**, respectively (Scheme A). Subsequent reaction of compound **I** and AgOTf led to the formation of compound **K**, where the Cl atoms were replaced with OTf. It is also noted that when compound **I** was subjected to reduced pressure over 12 hours, compound **J**, a THF-free analogue of compound **I** was afforded. When both compounds **I** and **J** reacted with $\text{Na}[\text{BPh}^{\text{Cl}}_4]$ ($\text{Ph}^{\text{Cl}} = 3,5\text{-Cl}_2\text{C}_6\text{H}_3$) separately in dichloromethane, compounds **L** and **M** were afforded respectively. Compound **L** comprises of a mononuclear cationic aluminium compound while compound **M** comprises of a dimer of compound **J** supported by a sodium cation (Scheme B).¹⁹

Scheme B. Synthesis of bis(imino)phenyl aluminium compounds **J** – **M**

In addition, bis(imino)phenyl aluminium compound **L** has been reported to possess catalytic activity for Diels–Alder cycloaddition reactions.¹⁹ Therefore, we are interested in utilizing the bis(imino)phenyl ligands to synthesize low valent group 13 compounds. In continuation to our previous studies, we are interested in the isolation of a bis(imino)phenyl germanium element(I) radical intermediate using *t*Bu substituent and also to explore the reactivity of the 2,6-bis(imino)phenylchlorogermylene with *t*Bu substituents. Lastly, to complete the study of group 14 compounds supported by bis(imino)phenyl ligands, we aim to isolate a 2-silaamidinate anion.

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Abstract

This thesis mainly describes the synthesis and reactivity of group 13 and group 14 complexes stabilized by bis(imino)phenyl ligands.

Chapter 1 describes the synthesis and characterization of indium and thallium compounds supported by bis(imino)aryl pincer ligands with Ar* (Ar* = 4-Me-2,6-CHPh₂-C₆H₂) and *t*Bu substituents. The reaction of bis(imino)aryl pincer ligand with Ar* bulky substituents and group 13 metal(I) bromide in toluene or THF led to the formation of a new metal(II) radical, [L^{Ar*}(Br)M•] (L^{Ar*} = C₆H₃-2,6-(HC=NAr*)₂; M = In (**1.4**) or Tl (**1.5**)). However, the reaction of bis(imino)phenyl pincer ligand with *t*Bu substituents and indium(I) bromide in toluene afforded a separated ion pair of bis(imino)phenylindium(III) bromide complex, [L^{*t*Bu}₂In]⁺Br⁻ (**1.1**, L^{*t*Bu} = C₆H₃-2,6-(HC=N*t*Bu)₂). When the reaction was done in Et₂O, an indium(I) trimer, [(L^{*t*Bu}InCl)₂L^{*t*Bu}In] (**1.3**) was afforded. In addition, the consecutive reaction of L^{*t*Bu}Br, *n*BuLi and indium(III) chloride afforded a bis(imino)phenylindium(II) dimer, [L^{*t*Bu}InCl]₂ (**1.2**).

Chapter 2 describes the synthesis and characterization of a 2,6-bis(imino)phenylchlorogermylene [$L^{tBu}GeCl$] (**2.1**, $L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$), and its reduction to afford a bis(germylene) [2-(HC–N*t*Bu)-6-(HC=N*t*Bu) C_6H_3Ge]₂ (**2.2**) and germylidenide anion [$L^{tBu}GeLi$]₂ (**2.3**). The reaction of the 2,6-bis(imino)phenyl bromide, **L^{tBu}Br** with *n*BuLi in THF at –78 °C, followed by addition to $GeCl_2 \cdot$ dioxane, afforded **2.1**. The reaction of **2.1** with lithium proceeded through a new reaction pathway, involving the reduction of the germanium(II) centers in **2.2**, concomitant with the homolytic cleavage of the C–C bond to afford **2.3**.

Chapter 3 describes the reactivity of $[L^{tBu}GeCl]$ (**3.1**, $L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$) towards group 11 metals. The reaction of **3.1** and AgOTf (OTf = $CF_3SO_3^-$) in toluene afforded a germylene-silver(I) complex, $[{L^{tBu}(TfO)Ge}]_2Ag(OTf)$ (**3.2**). Further reaction of **3.2** and 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (I_{Me}) in toluene afforded a bis(germyliumylidene cation)-silver(I) complex, $[{L^{tBu}(I_{Me})Ge}]_2Ag(OTf)]OTf_2$ (**3.3(OTf)**₂). The reaction of **3.1** and $(CuOTf)_2 \cdot C_7H_8$ afforded $[L^{tBu}(Cl)GeCu(\mu-Cl)]_2$ (**3.4**) instead. The reaction of **3.1** and CuI or AuI in acetonitrile afforded a dimeric germylene-copper(I) $[L^{tBu}(Cl)GeCu(\mu-I)]_2$ (**3.5**) and -gold(I) complex $[L^{tBu}(Cl)GeAuI]$ (**3.7**) respectively. Further reactivity of **3.5** and **3.7** with PPh_3 afforded a copper(I) $[L^{tBu}(Cl)GeCuI(PPh_3)]$ (**3.6**) and gold(I) complex $[L^{tBu}(Cl)GeAuI(PPh_3)]$ (**3.8**), respectively.

Chapter 4 describes the reaction of the N-heterocyclic carbene (NHC)-stabilized disilicon(0) complex $[\text{IPr} \rightarrow \text{Si}=\text{Si} \leftarrow \text{IPr}]$ (**4.1**; $\text{IPr} = :\text{C}\{\text{N}(\text{Ar})\text{CH}\}_2$) with ArN_3 in THF at room temperature to afford a mixture of the NHC-stabilized siladiimide $[\text{ArNSi}(\text{IPr})\text{NAr}]$ (**4.2**), triazene $[\{\text{CHN}(\text{Ar})\}_2\text{CN}_3\text{Ar}]$ (**4.3**) and the free carbene IPr .

Chapter 1.

A Bis(imino)phenyl-Stabilized Indium(II) and Thallium(II) Radical Complex

1.1 Introduction

Low valent indium and thallium complexes in the formal oxidation state of +1 and +2 have attracted much attention due to their unprecedented electronic structures.¹⁻¹² The indium and thallium centres in the formal oxidation state of +1 possess a lone pair of electrons and two vacant p orbitals, which enable them to show carbene-like properties. In addition, the indium and thallium centers in the formal oxidation state of +2 are paramagnetic due to the presence of a radical. In accordance to high tendency of main-group elements in generating closed-shell configurations, indium(II) and thallium(II) compounds are extremely rare and tend to dimerize to form a metal-metal bond in the form of $[R_2M-MR_2]$.¹³ However, the coordinative unsaturation of these low valent indium and thallium complexes, along with low metal-metal bond energies, especially indium(II) and thallium(II) dimers, facilitate disproportionation, which result in the formation of mixed valent indium and thallium compounds comprising more than one valence state.¹⁴ A broad variety of methods have been established for the synthesis of mixed valent salts, especially, disproportionation reaction of group 13 metal(I) halides with suitable organolithium and potassium compounds.¹⁵⁻²⁵ Recently, Power et al. synthesized a mixed valent organoindium subhalide stabilized by three m-terphenyl groups (**1.II**, Scheme 1.1), by the reaction of LiR (**1.I**, R = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂) and InCl, in the presence of LiI (Scheme 1.1).²²

Scheme 1.1 Synthesis of mixed-valent organoindium subhalide (**1.II**)

Chivers et al. also reported the reaction of $[\text{HC}(\text{PPh}_2\text{Se})_2]\text{Li} \cdot \text{TMEDA}$ and TlOEt and elemental selenium to afford a mixed-valent thallium(I)/thallium(III) salt $\{[\text{Tl}][\text{Tl}\{(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2\}_2]\}_\infty$ (**1.VI**, Scheme 1.2).²³

Scheme 1.2 Synthesis of a mixed-valent Tl(I)/Tl(III) salt $[\text{Tl}][\text{Tl}\{(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2\}_2]_\infty$ (**1.VI**)

However, there is no general rule to control the oxidation state and number of indium or thallium atoms in a mixed valent compound. Even a slight difference in reaction conditions and the nature of neutral or anionic ligands result in a variety of mixed valent indium or thallium complexes with unpredictable electronic structures. Under specific reaction conditions and ligands, disproportionation of indium(I) and thallium(I) halides can lead to the formation of indium(II) and thallium(II) dimers, respectively.²⁶⁻³⁵ It is evidenced in the reaction between $\{(\text{SiMe}_3)\text{NC}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{Li} \cdot \text{THF}$ and InBr in which the disproportionation of indium(I) bromide led to the formation of indium(II) dimer

$[\{(\text{SiMe}_3)\text{NC}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{InBr}]_2$ (**1.VIII**, Scheme 1.3) instead of an indium(I) compound.³⁵

Scheme 1.3 Synthesis of $[\{\text{SiMe}_3\text{NC}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{InBr}]_2$ (**1.VIII**)

Disproportionation of indium(I) and thallium(I) bromide were also observed in the reaction of MBr ($\text{M} = \text{In}, \text{Tl}$) and $\text{NaSi}(\text{tBu})_3$, leading to the formation of elemental metal (In or Tl) and $((\text{tBu})_3\text{Si})_2\text{M}-\text{M}(\text{Si}(\text{tBu})_3)_2$ ($\text{M} = \text{In}$ (**1.X**) or $\text{M} = \text{Tl}$ (**1.XI**), Scheme 1.4).³⁰

Scheme 1.4 Formation of a $((\text{tBu})_3\text{Si})_2\text{M}-\text{M}(\text{Si}(\text{tBu})_3)_2$ ($\text{M} = \text{In}$ (**1.X**) or Tl (**1.XI**))

MacDonald et al. also reported that the isolation of $[\text{In}_2\text{Cl}_4]$ with different donors ($\text{L} = \text{arene}, \text{THF}, 18\text{-crown-6}$), resulted in the formation of a variety of valence isomers, such as mixed-valent ionic form $[\text{L}_2\text{In}][\text{InCl}_4]$ (**1.XII**), isovalent covalent form $[\text{Cl}_2\text{In}(\text{L})-\text{In}(\text{L})\text{Cl}_2]$ (**1.XIII**) and mixed-valent donor-acceptor form $[\text{ClIn}(\text{L}) \rightarrow \text{InCl}_3]$ (**1.XIV**) (Scheme 1.5).³⁶

Scheme 1.5 The isolation of $[\text{In}_2\text{Cl}_4]$ with different donors

In addition, Jones et al. showed that steric hindered guanidinate ligands with different substituents underwent disproportionation reaction or salt-elimination reaction with InCl to form the corresponding In(II) dimer and monomeric In(I) complexes. Whereas, in case of thallium, only the monomeric guanidinato thallium(I) complex was afforded (Scheme 1.6 – 1.7).³⁷⁻³⁸

Scheme 1.6 Reaction of **1.XV** with InCl

Scheme 1.7 Reaction of **1.XV** and TlBr

Recently, our group demonstrated that bis(imino)phenyl ligands are able to isolate low valent group 14 elements in various oxidation states. A germylidenide anion, **1.XXVI**,

was synthesized from the reduction of the 2,6-bis(imino)phenyl germanium(II) chloride with excess KC_8 or the reduction of the germanium(I) dimer, **1.XXV** (Scheme 1.8).³⁹

Scheme 1.8 Synthesis of a digermylene (**1.XXV**) and an germylidenide anion (**1.XXVI**)

The reaction of **1.XXIV** with trimethyltin hydroxide afforded 2,6-diiminophenylgermanium(II) hydroxide, **1.XXVII**, which is stabilized by Me_3SnCl . A 2,6-diiminophenylgermanium(II) azide, **1.XXVIII**, was afforded by the reaction of **1.XXIV** with sodium azide. Further reaction of **1.XXVIII** with 1-adamantylphosphaalkyne led to the formation of a germanium(II) triazaphospole, **1.XXIX** (Scheme 1.9).⁴⁰

Scheme 1.9 Synthesis of a 2,6-diiminophenylgermanium(II) hydroxide (**1.XXVII**), azide (**1.XXVIII**), and triazaphospole (**1.XXIX**)

A low valent germanium dianion radical, **1.XXX**, was obtained by the reduction of the 2,6-bis(imino)-phenyl germanium(II) chloride, **1.XXIV** with excess calcium (Scheme 1.10).⁴¹ However, when **1.XXIV** reacted with excess magnesium, a germylidendiide anion, **1.XXXI**, was formed instead (Scheme 1.11).⁴¹

Scheme 1.10 Synthesis of germanium dianion radical (**1.XXX**)

Scheme 1.11 Synthesis of germylidenide anion (**1.XXXI**)

In addition, our group also isolated the 2,6-bis(imino)phenyl-stabilized stannylidenide and plumbylidenide anions, **1.XXXIV** and **1.XXXVI** respectively by the reduction of the respective tin(II) and lead(II) halides with alkali metal (Scheme 1.12 – 1.13).⁴²⁻⁴³

Scheme 1.12 Synthesis of a distannylene (**1.XXXIII**) and stannylidenide anion (**1.XXXIV**)

Scheme 1.13 Synthesis of lead(I) dimer (1.XXXVII) and plumbylidenide anion (1.XXXVI)

In continuation of utilizing the bis(imino)phenyl ligands and to research beyond group 14 complexes, we are interested in exploring the ability of bis(imino)phenyl ligands in controlling the disproportionation reactions of indium(I) and thallium(I) halides. Herein, the use of bis(imino)phenyl ligands in the synthesis of new indium(II) and thallium(II) radical complexes [M^{II•}], along with an indium(II) dimer, are reported.

1.2 Results and Discussion

1.2.1 Synthesis of $[L^{tBu}_2In]Br$

Scheme 1.14 Synthesis of **1.1**

The reaction of $L^{tBu}Br$ ⁴⁴ ($L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$) with $nBuLi$ in THF at -78 °C, followed by addition of the resulting solution to $InCl$ in toluene at -78 °C, proceeded through a lithiation reaction followed by a disproportionation mechanism to afford a mixture of indium metal, $L^{tBu}InCl_2$, $L^{tBu}H$ and the separated ion pair bis(imino)phenylindium(III) bromide complex $[L^{tBu}_2In]Br$ (**1.1**, Scheme 1.14) in 40% yield determined by NMR. Compound **1.1** was isolated as an extremely moisture- and air-sensitive colourless crystalline solid, soluble in hydrocarbon solvents. It was characterized by NMR spectroscopy and X-ray crystallography. Its 1H NMR spectrum exhibits a singlet at δ 1.12 ppm for the tBu substituents, a triplet at δ 7.23 ppm and a doublet at δ 7.69 ppm for the phenyl protons and another singlet at δ 8.76 ppm for the $CH=N$ protons. These suggest that the imino substituents are chemically equivalent in solution and in its solid state structure (Figure 1.1).

Figure 1.1 Molecular structure of **1.1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C17–In1 2.106(4), C1–In1 2.113(4), In1–N4 2.597(4), In1–N3 2.499(4), In1–N1 2.624(4), N2–In1 2.485(4), C12–N2 1.283(6), C7–N1 1.280(6), C23–N3 1.278(6), C28–N4 1.276(6), N3–In1–C17 74.21(15), C17–In1–N4 71.83(15), C17–In1–C1 173.41(17), N4–In1–N1 93.58(11), N1–In1–N3 95.31(12), N4–In1–N2 95.68(11), N3–In1–N2 95.35(12), C1–In1–N2 74.23(15), C1–In1–N1 71.20(15).

The molecular structure of **1.1** (Figure 1.1) illustrates that the central indium atom adopts a distorted octahedral geometry. The In...Br distance is 6.635(1) Å, which is longer than the sum of their van der Waal's radius (ca. 4.15 Å). This indicates that compound **1.1** is a separated ion pair. The C–In bond lengths (C1–In1: 2.113(4) Å, C17–In1: 2.106(4) Å) are comparable to that of the bis(amino)phenylindium(III) chloride [{2,6-[(C₂H₅)₂NCH₂]₂C₆H₃}In(CH₃)Cl] (**1.XXXVIII**, Chart 1.1, C–In: 2.156(4) Å).⁴⁵ The N1–In1 (2.624(4) Å) and N4–In1 (2.597(4) Å) bonds are longer than the N2–In1 (2.485(4) Å)

and N3–In1 (2.499(4) Å) bonds. The N1–In1 and N4–N1 bond lengths are also comparable to those of [$\{2,6-[(C_2H_5)_2NCH_2]_2C_6H_3\}In(CH_3)Cl\}$ (**1.XXXVIII**, Chart 1.1, In–N: 2.603(3), 2.607(3)].⁴⁵

Chart 1.1 Bis(amino)phenylindium(III) chloride [$\{2,6-[(C_2H_5)_2NCH_2]_2C_6H_3\}In(CH_3)Cl\}$]

1.2.2 Synthesis of $[L^{tBu}InCl]_2$

Scheme 1.15 Synthesis of **1.2**

The reaction of $L^{tBu}Br$ ⁴⁴ ($L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$) with $nBuLi$ in THF at -78 °C, followed by addition of the resulting solution to $InCl_3$ at -78 °C, to afford a yellow solution of $L^{tBu}InCl_2$, which was confirmed by crude NMR spectroscopy. The solution was added to KC_8 at -78 °C, where $L^{tBu}InCl_2$ was reduced to afford bis(imino)phenylindium(II) dimer, $[L^{tBu}InCl]_2$ (**1.2**, Scheme 1.15). $L^{tBu}H$ (observed from crude NMR) and indium metal were obtained as byproducts. Compound **1.2** was isolated as an extremely moisture- and air-sensitive colourless crystalline solid, in 42% yield. It is soluble in toluene and was characterized by NMR spectroscopy and X-ray crystallography. Its 1H NMR spectrum exhibits two singlets at δ 0.88 and 1.69 ppm, corresponding to two environmentally inequivalent groups of tBu protons and two singlets at δ 7.99 ppm and 8.29 ppm attributable

to two environmentally inequivalent groups of HC=N protons. These suggests that the imino substituents are chemically equivalent in solid state (Figure 1.2), whereas they are chemically inequivalent in solution, where only one set of imino substituent is coordinated to the central indium metal while the another set of imino substituent is not coordinated to the central indium metal.

Figure 1.2 Molecular structure of **1.2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–In1 2.146(2), N1–In1 2.532(2), N2 – In1 2.662(2), In1–Cl1 2.4414(6), C7–N1 1.279(3), C12–N2 1.275(3), C17–In2 2.140(3), In2–Cl2 2.4489(6), N3–In2 2.504(2), N4–In2 2.636(2), C23–N3 1.277(3), C28–N4 1.276(4), In1–In2 2.7256(3), C17–In2–Cl2 110.27(7), C17–In2–N3 73.02(9), C17–In2–N4 70.78(9), C17–In2–In1 125.19(7), In1–In2–Cl2 123.303(18), N3–In2–In1 108.94(5), N4–In2–In1 95.38(5), C1–In1–Cl1 109.89(7), N1–In1–Cl1 90.58(5), C1–In1–In2 128.89(7), N1–In1–In2 111.50(5), C7–N1–In1 108.73(18), C23–N3–In2 109.25(17), C28–N4–In2 107.66(19).

The molecular structure of compound **1.2** (Figure 1.2) shows that it has a gauge-bent geometry (C1–In1–In2: 128.89(7)°, C17–In2–In1: 125.19(7)°), in which the indium atoms adopt a distorted trigonal bipyramidal geometry. The In1–Cl1 (2.4414(6) Å) and In2–Cl2 (2.4489(6) Å) bonds are comparable to those in the bis(amino)phenylindium(II) dimer [*i*Pr₂NC(NAr)₂InCl]₂ (**1.XVII**, Chart 1.2, In–Cl: 2.392(3), 2.375(3) Å) and [(2,6-Me₂C₅H₈)NC(NAr)₂InCl]₂ (**1.XVIII**, Chart 1.2, In–Cl: 2.3752(12) Å). The In–In bond length (2.7256(3) Å) is comparable to those of other indium(II) dimers such as [*i*Pr₂NC(NAr)₂InCl]₂ (**1.XVII**, Chart 1.2, In–In: 2.7196(13) Å), [(2,6-Me₂C₅H₈)NC(NAr)₂InCl]₂ (**1.XVIII**, Chart 1.2, In–In: 2.7085(7) Å), [PhC(CHNAr)₂InCl]₂ (**1.XXXIX**, Chart 1.2, In–In: 2.7575(4) Å), and [(CHNAr)₂InCl]₂ (**1.XXXX**, Chart 1.2, In–In: 2.7280(9) Å). The N1–In1 (2.532(2) Å) and N3–In2 (2.504(2) Å) bonds are shorter than the N4–In2 (2.636(2) Å) and N2–In1 bonds (2.662(2) Å). Similar difference in In–N bond lengths can be found in [{2,6-(Me₂NCH₂)₂C₆H₃}InCl]₂ (**1.XXXXI**, Chart 1.2, In–N: 2.554(3), 2.601(3) Å).

Chart 1.2 Examples of In(II) dimers

1.2.3 Synthesis of $[\text{L}^{\text{tBu}}\text{InCl}]_2\text{L}^{\text{tBu}}\text{In}$

Scheme 1.16 Synthesis of **1.3**

The reaction of $\text{L}^{\text{tBu}}\text{Br}$ with $n\text{BuLi}$ in THF at $-78\text{ }^{\circ}\text{C}$, followed by addition of the resulting solution to InCl in Et_2O at $-78\text{ }^{\circ}\text{C}$, afforded an indium trimer, $[\text{L}^{\text{tBu}}\text{InCl}]_2\text{InL}^{\text{tBu}}$ (**1.3**, Scheme 1.16), consisting of one In(I) and two In(II) atoms. Indium metal was also displaced out during the reaction. Compound **1.3** was isolated as an extremely moisture- and air-sensitive yellow crystalline solid. However, only one crystal was obtained for characterization by X-ray crystallography. Attempts to reproduce compound **1.3** were unsuccessful, which led to the formation of indium metal and $\text{L}^{\text{tBu}}\text{H}$.

Figure 1.3 Molecular structure of **1.3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths ($\text{\AA}$)

and angles (deg): In1–C1 2.166(8), In1–N1 2.621(8), In1–N2 2.654(7), In1–Cl1 2.435(2), C7–N1 1.280(11), C12–N2 1.267(11), In1–In2 2.7602(8), C17–In2 2.150(9), In2–N3 2.577(6), In2–N4 2.574(7), C28–N4 1.246(10), C23–N3 1.259(11), In2–In3 2.7767(8), C33–In3 2.199(8), N5–In3 2.325(7), In3–Cl2 2.449(3), C39–N5 1.307(11), C44–N6 1.264(11); In1–In2–In3 135.88(3), C1–In1–Cl1 111.2(2), N1–In1–Cl1 93.61(17), N2–In1–Cl1 91.1(2), C1–In1–N1 71.7(3), C1–In1–N2 70.2(3), C1–In1–In2 129.0(2), C7–N1–In1 107.5(6), C12–N2–In1 107.7(6), C17–In2–In1 112.5(2), C17–In2–N3 71.6(3), C17–In2–N4 71.3(3), C17–In2–In3 111.6(2), C23–N3–In2 107.7(6), C28–N4–In2 109.1(5), C33–In3–Cl2 105.8(2), C33–In3–N5 77.4(3), C34–C44–N6 118.1(9), C39–N5–In3 121.2(10), C33–In3–In2 126.8(2).

The molecular structure of **1.3** (Figure 1.3) illustrates that the central indium(I) atom adopts a distorted square pyramidal structure (sum of bond angles = 387.43°). The In1–In2 (2.7602(8) Å) and In2–In3 (2.7767(8) Å) bonds are comparable to those of the In–In bonded hexamer (**1.XXXXXII**, Chart 1.3, 2.8122 – 2.8535 Å)⁴⁶ and the In₄ cluster (**1.XXXXXIII**, Chart 1.3, 2.696(2) Å).²⁹ The In1–N1 (2.621(8) Å), In1–N2 (2.654(7) Å), In2–N3 (2.577(6) Å), In2–N4 (2.574(7) Å), and In3–N5 (2.325(7) Å) bond lengths are longer than those in **1.XXXXXII** (Chart 1.3, average In–N bond length: 2.212 Å).⁴⁶ The C1–In1 (2.166(8) Å), C17–In2 (2.150(9) Å) and C33–In3 (2.199(8) Å) bond lengths are longer than those of compounds **1.1** (C–In: 2.113(4), 2.106(4) Å) and **1.2** (C–In: 2.146(2), 2.140(3) Å). The In1–Cl1 (2.435(2) Å) and In3–Cl2 (2.449(3) Å) bond lengths are comparable to those in [{2,6-(Me₂NCH₂)₂C₆H₃}InCl]₂ (**1.XXXXXI**, Chart 1.2, In–Cl: 2.451 Å).³⁴ It is also observed that the In–Cl bond lengths in **1.3** are longer than those of the corresponding indium(III) compound, [L^tBuInCl₂] (In–Cl: 2.3852, 2.3787 Å, see appendix). This is expected as the oxidation state for the terminal indium atoms in compound **1.3** are +2.

Chart 1.3 Polymeric indium complexes

1.2.4 Synthesis of $[\text{L}^{\text{Ar}^*}(\text{Br})\text{In}^\bullet]$

Scheme 1.17 Synthesis of **1.4**

When the *t*Bu substituents were replaced with Ar^* ($\text{Ar}^* = 4\text{-Me-2,6-CHPh}_2\text{-C}_6\text{H}_2$), the reaction of $\text{L}^{\text{Ar}^*}\text{Br}$ ($\text{L}^{\text{Ar}^*} = 2,6\text{-(CH=NAr}^*)_2\text{C}_6\text{H}_3$) with *n*BuLi in THF at -78°C , followed by addition of the resulting solution to InBr in toluene at -78°C , afforded an indium(II) radical $[\text{L}^{\text{Ar}^*}(\text{Br})\text{In}^\bullet]$ (**1.4**, Scheme 1.17), in 90% yield, determined by NMR. $\text{L}^{\text{Ar}^*}\text{H}$ (from crude NMR) and indium metal were observed as byproducts. Compound **1.4** was isolated as an extremely moisture- and air-sensitive colourless crystalline solid, and is soluble in toluene. It was characterized by X-ray crystallography and NMR spectroscopy.

Figure 1.4 Molecular structure of **1.4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and CHPh_2 substituents are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles (deg): C5–N1 1.267(8), N1–In1 2.534(5), C1–In1 2.159(9), In1–Br1 2.5331(15), C5A–N1A 1.267(8), N1A–In1 2.534(5); C1–In1–N1 71.91(12), C1–In1–N1A 71.91(12), N1A–In1–N1 143.8(2), N1–In1–Br1 96.58(12), N1A–In1–Br1 96.58(12), C1–In1–Br1 108.4(2).

The molecular structure of **1.4** (Figure 1.4) illustrates that the indium atom adopts a “see-saw” geometry. The C1–In1 (2.159(9) $\text{\AA}$) bond length is almost identical and comparable to those of compounds **1.1** (C–In: 2.113(4), 2.106(4) $\text{\AA}$) and **1.2** (C–In: 2.146(2), 2.140(3) $\text{\AA}$). The N1–In1 (2.534(5) $\text{\AA}$) and N1A–In1 (2.534(5) $\text{\AA}$) bond lengths are comparable to those of **1.1** (In–N: 2.597(4), 2.624(4) $\text{\AA}$), indicating that the N–In bonds in **1.4** are coordinative covalent bonds. The ^1H NMR spectrum of compound **1.4** exhibits a set of signals for the ligand backbone, which differs from $\text{L}^{\text{Ar*}}\text{InBr}_2$. No fumes nor bubbles were observed upon addition of d-solvent for NMR analysis. There were also no observable signs of decomposition of compound **1.4** in d-solvent. No indium metal was displaced out from the solution and the solution colour remained unchanged. Compound **1.4** is EPR-silent in solution but EPR-active in solid state (Figure 1.5).

Figure 1.5 Solid EPR spectrum for compound **1.4**

Hence, based on the NMR, EPR results and observations, we suggest that compound **1.4** could exist as an indium(II) dimer in solution, analogous to the structure of compound **1.2**. We propose that the reaction proceeds through a possible disproportionation mechanism, via the formation of an indium(I) compound, $L^{Ar*}In$ and indium(III) compound, $L^{Ar*}InBr_2$, which further reacted to form a dimer, $[L^{Ar*}InBr]_2$ and byproducts $L^{Ar*}H$ and indium metal (Scheme 1.18). However, due to the bulkiness of the supporting substituent, Ar^* and the crystal packing effect, compound **1.4** exists as an indium(II) radical in the solid state.

Scheme 1.18 Proposed mechanism for the synthesis of **1.4**

1.2.5 Synthesis of $[\text{L}^{\text{Ar}^*}(\text{Br})\text{Tl}^{\bullet}]$

Scheme 1.19 Synthesis of **1.5**

The reaction of $\text{L}^{\text{Ar}^*}\text{Br}$ with $n\text{BuLi}$ in THF at $-78\text{ }^{\circ}\text{C}$, followed by addition of the resulting solution to TlBr at $-78\text{ }^{\circ}\text{C}$, afforded a thallium analogue of the metal(II) radical $[\text{L}^{\text{Ar}^*}(\text{Br})\text{Tl}^{\bullet}]$ (**1.5**, Scheme 1.19), in 98% yield, determined by NMR. Although thallium's preferred oxidation state is +1, compound **1.5** was afforded instead of a single thallium(I)

complex. $L^{Ar*}H$ (from crude NMR) and thallium metal were observed as byproducts. Compound **1.5** was isolated as an extremely moisture- and air-sensitive colourless crystalline solid. It is soluble in toluene and was characterized by NMR spectroscopy and X-ray crystallography.

Figure 1.6 Molecular structure of **1.5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and $CHPh_2$ substituents are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Tl1 2.129(12), C5A–N1A 1.287(10), N1A–Tl1 2.625(6), C5–N1 1.287(10), N1–Tl1 2.625(6), Tl1–Br1 2.6748(14); C1–Tl1–Br1 102.3(3), C1–Tl1–N1A 71.43(14), N1A–Tl1–Br1 93.44(13), C1–Tl1–N1 71.43(14), N1–Tl1–Br1 93.44(13), N1A–Tl1–N1 142.8(3).

The molecular structure of **1.5** (Figure 1.6) shows that the thallium atom adopts a “see-saw” (sum of bond angles = 329.74°). The C1–Tl1 (2.129(12) Å), and N–Tl (2.625(6) Å) bond lengths of **1.5** are comparable to those of $[\{ C_5H_5FeC_5H_3(2-CH_2NMe_2) \}_2TiCl]$ (**1.XXXXIV**, Chart 1.4, C–Ti: 2.121(8); N–Ti: 2.669 Å).⁴⁷ However, the Tl–N bond lengths in **1.5** (2.625(6) Å) are longer than the Tl–N bond lengths in other Tl(I) complexes such as $[CH\{(CH_3)_2CN(Ar)\}_2Tl]$ (**1.XXXXV**, Chart 1.4, average Tl–N bond length: 2.416 Å),⁴⁸ $[(2-C_5H_4N)C(CH_3)\{CH_2N(Tl)SiMe_3\}_2]$ (**1.XXXXVI**, Chart 1.4, average Tl–N bond

length: 2.445 Å),⁴⁹ CH₂[CH₂N(Tl)SiMe₃]₂ (**1.XXXXVII**, Chart 1.4, average Tl–N bond length: 2.452 Å) and CH₂[CH₂N(Tl)Si*t*BuMe₂]₂ (**1.XXXXVIII**, Chart 1.4, average Tl–N bond length: 2.443 Å).⁵⁰ These results indicate that the Tl–N bonds are coordinative covalent bonds. The Tl–Br bond length (2.6748(14) Å) in **1.5** is shorter than those in **1.XXXXIX** (Chart 1.5, Tl–Br: 3.214, 3.172 Å)⁵¹ but longer than the Tl–Br in **1.XXXXX** (Chart 1.5, Tl–Br: 2.542 Å).⁵²

Chart 1.4 Examples of N–Tl bonded complexes

Chart 1.5 Examples of thallium(III) complexes

The ^1H NMR spectrum of compound **1.5** exhibits a set of signals corresponding to the ligand backbone. No fumes nor bubbles were observed upon addition of d-solvent for NMR analysis and there were also no observable signs of decomposition of compound **1.5** in d-solvent. No colour change was observed and thallium metal was not displaced out in the solution. Similar to compound **1.4**, compound **1.5** is also EPR-silent in solution but EPR-active in the solid state (Figure 1.7).

Figure 1.7 Solid EPR spectrum of compound **1.5**

With reference to the NMR and EPR results and observations, we propose that compound **1.5** is the thallium analogue of compound **1.4**, formed via a similar reaction mechanism (Scheme 1.20). Similarly, due to the bulkiness of the supporting substituent, Ar^* and the crystal packing effect, compound **1.5** exists as a thallium(II) radical in the solid state but as a dimer in solution (Scheme 1.20).

Scheme 1.20 Proposed mechanism for the synthesis of compound **1.5**

1.3 Conclusion

In conclusion, various reactions of bis(imino)phenyl pincer anionic ligands with group 13 metal halides led to the formation of compounds **1.1** – **1.5**. The reaction of bis(imino)phenyl pincer anionic ligand with 4-Me-2,6-CHPh₂-C₆H₂ (Ar*) bulky substituents and group 13 metal(I) halide led to the formation of a new metal(II) radical, [L^{Ar*}(Br)M•] (L^{Ar*} = C₆H₃-2,6-(HC=NAr*)₂, M = In (**1.4**) or Tl (**1.5**)). By replacing the Ar* substituents on the ligand with a less bulky substituent, *t*Bu, a separated ion pair bis(imino)phenylindium(III) bromide complex, [L^{*t*Bu}₂In]Br (**1.1**, L^{*t*Bu} = C₆H₃-2,6-(HC=N*t*Bu)₂) was afforded. It was also noted that a change in reaction solvent resulted in the formation of an indium(I) trimer, [(L^{*t*Bu}InCl)₂L^{*t*Bu}In] (**1.3**). In addition, the consecutive reaction of L^{*t*Bu}Br, *n*BuLi and indium(III) chloride led to the formation of a bis(imino)phenylindium(II) dimer, [L^{*t*Bu}InCl]₂ (**1.2**).

1.4 Experimental Section

General Procedures. All operations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Et₂O, THF and toluene were dried and distilled over Na/K alloy prior to use. Compound **L^{tBu}Br** was prepared as described in the literature.⁴⁴ The ¹H and ¹³C were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H and ¹³C. Elemental analyses were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

Synthesis of compound L^{Ar*}Br. A 250 mL round bottom flask equipped with a magnetic stirrer was charged with 2-bromoisophthalaldehyde (2.71 g, 12.7 mmol) in THF (130 mL). 2,6-bis(diphenylmethyl)-4-methylaniline⁵³ (12.3 g, 28.0 mmol), *p*-toluenesulfonic acid (0.241 g, 1.27 mmol) and 4 Å molecular sieves were added to the solution. The reaction mixture was refluxed for 16 hours. ¹H NMR spectroscopic analysis showed complete conversion. The reaction mixture was filtered and volatiles were removed under reduced pressure. Compound **L^{Ar*}Br** was crystallized from ethyl acetate and dried in vacuo. Yellow crystals of compound **L^{Ar*}Br** (9.51 g, 71%) were obtained. M.p.: 273 °C. Elemental analysis (%) calcd for C₇₄H₅₉N₂Br: C, 84.15; H, 5.63; N, 2.65. Found: C, 84.83; H, 5.79; N, 2.79. ¹H NMR (399.5 MHz, C₆D₆, 25 °C): δ 1.93 (s, 6H, CH₃), 5.75 (s, 4H, CH(Ph)₂), 7.0–7.15 (m, 45H, Ph), 7.84 (s, 2H, CH=N), 8.32 (d, ³J_{HH} = 7.68 Hz, 2H, Ph). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ 21.22 (CH₃), 52.63 (s, 4H, CH(Ph)₂), 126.55, 127.30, 128.63, 129.53, 130.13, 131.65, 133.34, 133.92, 135.25, 144.41, 148.92 (Ph), 163.33 (CH=N).

Synthesis of [L^{tBu}₂In]Br (1.1). *n*BuLi (1.64 M in *n*-hexanes, 0.73 mL, 1.2 mmol) was added dropwise to a solution of **L^{tBu}Br** (0.323 g, 1.00 mmol) in THF (20 mL) at –78 °C

and stirred for 3 h. Volatiles were removed under vacuum and toluene (10 mL) was added. The reaction mixture was added dropwise to a solution of InCl (0.180 g, 1.20 mmol) in toluene (10 mL) at $-78\text{ }^{\circ}\text{C}$. The resulting yellow solution was gradually warmed to room temperature and stirred for 16 hours. LiCl and indium metal was filtered off, and the yellow filtrate was concentrated to afford colourless crystals of **1.1**, $\text{L}^{\text{tBu}}\text{H}$ and $\text{L}^{\text{tBu}}\text{InCl}_2$. Pure NMR spectrum of **1.1** could not be obtained. On the basis of the ^1H resonances of $\text{L}^{\text{tBu}}\text{H}$, $\text{L}^{\text{tBu}}\text{InCl}_2$, the ^1H NMR resonances of **1.1** can be identified in the spectra (see appendix for ^1H NMR of $\text{L}^{\text{tBu}}\text{H}$, $\text{L}^{\text{tBu}}\text{InCl}_2$). ^1H NMR (395.9 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): 1.12 (s, 36H, CH_3), 7.23 (t, $^3J_{\text{H-H}} = 7.70\text{ Hz}$, 2H, *p*-Ph), 7.69 (d, $^3J_{\text{H-H}} = 7.72\text{ Hz}$, 4H, *m*-Ph), 8.76 (s, 4H, $\text{CH}=\text{N}$).

Synthesis of $[\text{L}^{\text{tBu}}\text{InCl}]_2$ (1.2**).** $n\text{BuLi}$ (1.64 M in *n*-hexanes, 2.2 mL, 3.6 mmol) was added dropwise to a solution of $\text{L}^{\text{tBu}}\text{Br}$ (0.969 g, 3.00 mmol) in THF (30 mL) at $-78\text{ }^{\circ}\text{C}$ and stirred for 3 h. A solution of InCl_3 (0.796 g, 3.60 mmol) in THF (30 mL) was then added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. The resulting yellow solution was gradually warmed to room temperature and stirred for 16 h. The resulting solution of $\text{L}^{\text{tBu}}\text{InCl}_2$ (based on crude NMR) was then added dropwise to KC_8 (0.818 g, 6.05 mmol) at $-78\text{ }^{\circ}\text{C}$ and gradually warmed to room temperature and stirred for another 16 h. Crude ^1H NMR showed the formation of $\text{L}^{\text{tBu}}\text{H}$. KC_8 and indium metal was filtered off, and the yellow filtrate was extracted from toluene to afford colourless crystals of **1.2** (0.549 g, 42%). M.p.: $254\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis (%) calcd for $\text{C}_{39}\text{H}_{54}\text{N}_4\text{In}_2\text{Cl}_2$: C, 53.26; H, 6.19; N, 7.12. Found: C, 53.62; H, 6.57; N, 7.05. ^1H NMR (399.5 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 0.88 (s, 18H, CH_3), 1.69 (s, 18H, CH_3), 7.10-7.13 (m, 3H, Ph-*H*), 7.17-7.20 (m, 3H, Ph-*H*), 7.99 (s, 2H, $\text{CH}=\text{N}$), 8.29 (s, 2H, $\text{CH}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 30.45 (CH_3), 31.33 (CH_3), 57.85 ($\text{C}(\text{CH}_3)_3$), 58.94 ($\text{C}(\text{CH}_3)_3$), 132.32, 132.43, 141.65, 158.06 (Ph), 159.49 ($\text{CH}=\text{N}$), 160.99 ($\text{CH}=\text{N}$).

Synthesis of $[\text{L}^{\text{Bu}}\text{InCl}]_2\text{InL}^{\text{Bu}}$ (1.3**).** $n\text{BuLi}$ (1.64 M in *n*-hexanes, 0.73 mL, 1.2 mmol) was added dropwise to a solution of $\text{L}^{\text{Bu}}\text{Br}$ (0.323 g, 1.00 mmol) in THF (20 mL) at -78°C and stirred for 3 h. Volatiles were removed under vacuum and Et_2O (10 mL) was added. The reaction mixture was added dropwise to a solution of InCl (0.180 g, 1.20 mmol) in Et_2O (10 mL) at -78°C . The resulting yellow solution was gradually warmed to room temperature and stirred for 16 h. LiCl and indium metal was filtered off, and the yellow filtrate was concentrated to afford a yellow crystal of **1.3**. Due to irreproducibility of crystals, M.p., elemental analysis and NMR spectra could not be obtained.

Synthesis of $[\text{L}^{\text{Ar*}}(\text{Br})\text{In}^\bullet]$ (1.4**).** $n\text{BuLi}$ (1.64 M in *n*-hexanes, 1.2 mmol, 0.73 mL) was added dropwise to a solution of $\text{L}^{\text{Ar*}}\text{Br}$ (1.06 g, 4.00 mmol) in THF (10 mL) at -78°C and stirred for 16 h. Volatiles were removed under vacuum and toluene was added. The reaction mixture was added dropwise to a solution of InBr (0.180 g, 1.20 mmol) in toluene (10 mL) at -78°C . The resulting red solution was gradually warmed to room temperature and stirred overnight. LiBr and indium metal was filtered off, and the red filtrate was concentrated to afford colourless crystals of **1.4** (1.05 g, 90% (as determined by NMR)). M.p.: 283°C (dec.). Elemental analysis (%) calcd for $\text{C}_{74}\text{H}_{59}\text{BrInN}_2$: C, 75.90; H, 5.08; N, 2.39. Found: C, 78.93; H, 6.70; N, 2.49. Attempts to obtain acceptable elemental analysis data for compound **1.4** failed as the sample decomposed at high temperatures. ^1H NMR (395.9 MHz, C_6D_6 , 25°C): δ 1.87 (s, 12H, tol-CH_3), 5.61 (s, 8H, CHPh_2), 6.78–6.84 (m, 18H, Ph), 6.88–6.90 (m, 10H, Ph), 6.92 (s, 4H, CH=N), 6.98–7.06 (m, 26H, Ph) 7.11–7.13 (m, 16H, *o/m*-Ph) 7.20 (d, $^3J_{\text{HH}} = 6.87$ Hz, 8H, *o*-Ph), 7.30 (d, $^3J_{\text{HH}} = 7.31$ Hz, 8H, *o*-Ph), 7.67 (d, $^3J_{\text{HH}} = 7.79$ Hz, 8H, *o*-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, C_6D_6 , 25°C): δ 21.21 (CH_3), 21.43 (CH_3), 51.92 (CHPh_2), 53.39 (CHPh_2), 126.18, 126.58, 127.03, 129.14, 130.28, 130.51, 130.82, 134.22, 134.61, 135.75, 137.17, 139.66, 143.22, 144.00, 144.15, 144.54, 145.40, 147.05 (Ph), 170.99 (CH=N).

Synthesis of [L^{Ar*}(Br)Tl•] (1.5). *n*BuLi (1.64 M in *n*-hexanes, 0.73 mL, 1.20 mmol) was added dropwise to a solution of L^{Ar*}Br (1.06 g, 1.00 mmol) in THF (10 mL) at −78 °C and stirred for 16 h. A solution of TlBr (0.341 g, 1.20 mmol) in THF (10 mL) was then added to the reaction mixture at −78 °C. The resulting red solution was gradually warmed to room temperature and stirred overnight. LiBr and thallium metal was filtered off and the red filtrate was concentrated to afford colourless crystals of **1.5** (1.24 g, 98% (as determined by NMR)). M.p.: 278 °C (dec.). Elemental analysis (%) calcd for C₇₄H₅₉BrTlN₂: C, 70.51; H, 4.72; N, 2.22. Found: C, 76.12; H, 5.77; N, 1.91. Attempts to obtain acceptable elemental analysis data for compound **1.5** failed as the sample decomposed at high temperatures. ¹H NMR (399.5 MHz, C₆D₆, 25 °C): δ 1.89 (s, 12H, *tol*-CH₃), 5.49 (s, 8H, CHPh₂), 6.81 (t, ³J_{HH} = 7.77 Hz, 12H, *p*-Ph), 6.87–6.89 (m, 12H, Ph), 6.93 (s, 4H, CH=N), 6.94–6.97 (m, 10H, Ph), 7.00 (t, ³J_{HH} = 6.85 Hz, 16H, *m*-Ph), 7.05 (d, ³J_{HH} = 6.87 Hz, 2H, *o*-Ph), 7.11–7.13 (m, 18H, Ph-*H*), 7.19–7.21 (d, ³J_{HH} = 7.31 Hz, 8H, *o*-Ph), 7.39 (d, ³J_{HH} = 7.31 Hz, 8H, *o*-Ph), 7.71 (d, ³J_{HH} = 7.79 Hz, 8H, *o*-Ph). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ 21.22 (CH₃), 21.44 (CH₃), 51.78 (CHPh₂), 53.15 (CHPh₂), 126.10, 126.55, 126.62, 127.19, 128.82, 128.94, 130.02, 130.17, 130.55, 130.93, 134.21, 134.74, 136.26, 140.45 (br), 142.93, 144.00, 145.95, 147.39 (Ph), 168.54 (br) (CH=N).

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Chapter 2.

Synthesis of a Germylidenide Anion from the C–C Bond Activation of a Bis(germylene)[†]

2.1 Introduction

Low-valent group 14 element anionic complexes, namely germylidenide, stannylidenide, and plumbylidenide anions, of composition $[\text{R}\ddot{\text{E}}:]^-$ (E = Ge, Sn, Pb; R = supporting ligands), which possess two lone pair of electrons on the metal centers, have drawn much interest in recent years due to their uncommon structures and potential application in metathesis reactions for the formation of metal–metal bonds.^{1–4} The first example of such a complex was reported by Driess and Jones, where the N-heterocyclic germylidenide (**2.VI**) was synthesized by the reaction of β -diketiminato chlorogermylene $[\text{HC}\{\text{C}(\text{Me})\text{N}(\text{Ar})_2\}_2\ddot{\text{Ge}}\text{Cl}]$ (**2.I**) with 2 equiv of potassium (Scheme 2.1).¹ It is suggested that a series of steps, including reductive ring contraction reactions, occur in the reaction mechanism.

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Scheme 2.1 Reaction mechanism for the synthesis of N-heterocyclic germylidenide **2.VI**

The reaction of $[\text{HC}\{\text{C}(t\text{Bu})\text{N}(\text{Ar})\}_2\text{GeCl}]$ (**2.VIII**) or $[\text{HC}\{\text{C}(t\text{Bu})\text{N}(\text{Ar})\}_2\text{SnCl}]$ (**2.IX**) with 2 equiv of lithium undergo a similar reaction mechanism to afford analogous N-heterocyclic germylidenide complex **2.XIV** and stannylidenide complex **2.XV** respectively (Scheme 2.2).²

Scheme 2.2 Reaction mechanism for the synthesis of N-heterocyclic germylidenide **2.XIV** and stannylidenide **2.XV**

The application of low-valent group 14 element anionic complexes toward M–M bond formation was studied, but only one example has been reported as yet. The reaction of complex **2.VI** and 1 equiv of β -diketiminato chlorogermylene or chlorostannylene $[\text{HC}\{\text{C}(\text{Me})\text{N}(\text{Ar})\}_2\text{ECl}]$ ($\text{E} = \text{Ge}, \text{Sn}$) afforded new M(I)–M(I) compounds, an unsymmetric digermylene **2.XVII** and a germylene-stannylene **2.XIX** respectively (Scheme 2.3).³

Scheme 2.3 Reactivity of complex **2.VI**

Saito and co-workers have also isolated low valent tin dianions, the dilithiostannole, **2.XXI** by the treatment of **2.XX** with excess lithium in Et_2O (Scheme 2.4).⁵ The lithium metals in **2.XXI** are coordinated to the SnCCCC ring in an η^5 -fashion, similar to complex **2.XV** where the lithium metal is η^5 -coordinated to the SnCCCN ring.

Scheme 2.4 Synthesis of dilithiostannole **2.XXI**

The application of **2.XXI** towards transition metals was studied. When **2.XXI** was treated with 2 equiv of Cp_2HfCl_2 in toluene, the stannole dianion ligand coordinated to each

hafnium atom in an η^1 -fashion, affording **2.XXII**, the first example of a complex containing two Sn–Hf bonds (Scheme 2.5).⁶ However, when **2.XXI** was treated with 0.5 equiv of $[\text{Cp}^*\text{RuCl}]_4$ in Et_2O , the stannole dianion ligand coordinates to the ruthenium metals in an η^5 -fashion to afford a triple-decker type ruthenocene **2.XXIV**.⁷ In complex **2.XXII**, significant C–C bond alternation (1.362(4) to 1.500(5) Å) was observed in the SnC_4 ring, indicating non-aromatic, 1,3-diene character. In contrast, there is no C–C bond alternation observed in the SnC_4 of complex **2.XXIV**, indicating an aromatic character. The dilithiostannole **2.XXI** has different coordination modes (η^1 or η^5) towards transition metals, leading to different electronic structures of the stannole dianion ligand.

Scheme 2.5 Reaction of **2.XXI** with Cp_2HfCl_2 and $[\text{Cp}^*\text{RuCl}]_4$

Besides the above-mentioned examples, our group have also isolated the 2,6-bis(imino)phenyl-stabilized stannylidenide and plumbylidenide anions $[\{2,6-(\text{HCNR})_2\text{C}_6\text{H}_3\}\ddot{\text{E}}:]^-$ ($\text{R} = t\text{Bu}$, Ar; $\text{E} = \text{Sn}$, Pb) (Scheme 2.6 – 2.7) by the reduction of the respective tin(II) and lead(II) halides with alkali metal.^{4, 8} These stannylidenide and

plumbylidenide anions can also be afforded by the reduction of the tin(II) or lead(II) dimer $[\{2,6-(\text{HCNR})_2\text{C}_6\text{H}_3\}\ddot{\text{E}}]_2$ ($\text{R} = t\text{Bu}, \text{Ar}$; $\text{E} = \text{Sn}, \text{Pb}$) with alkali metal.

Scheme 2.6 Synthesis of stannylidenide anion $[\{2,6-(\text{HCN}t\text{Bu})_2\text{C}_6\text{H}_3\}\ddot{\text{Sn}}:]^-$ (**2.XXVII**)

Scheme 2.7 Synthesis of plumbylidenide anion $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\ddot{\text{Pb}}:]^-$ (**2.XXIX**)

Furthermore, the low valent germanium dianion radical $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\text{Ge:}]^{\bullet-}$ (**2.XXXII**) was obtained by the reduction of the 2,6-bis(imino)-phenyl germanium(II) chloride $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\text{GeCl}]$ (**2.XXXI**) with excess calcium (Scheme 2.8).⁹⁻¹⁰

Scheme 2.8 Synthesis of germanium dianion radical $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\text{Ge:}]^{\bullet-}$ (**2.XXXII**)

The mechanism for the formation of the stannylidenide and plumbylidenide anions $[\{2,6-(\text{HCNR})_2\text{C}_6\text{H}_3\}\ddot{\text{E}}:]^-$ ($\text{R} = \text{Ar}$ or $t\text{Bu}$; $\text{E} = \text{Sn}, \text{Pb}$) is proposed. It is suggested that the reduction of $[\{2,6-(\text{HCNR})_2\text{C}_6\text{H}_3\}\ddot{\text{E}}\text{X}]$ ($\text{R} = \text{Ar}$ or $t\text{Bu}$; $\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$; $\text{X} = \text{Cl}$ or Br) with alkali metal goes through the formation of a group 14 element(I) radical intermediate, $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\ddot{\text{E}}^\bullet]$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$), which consequently either dimerizes in a head-to-head manner to form the group 14 element(I) dimer $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\ddot{\text{E}}]_2$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) or undergoes a further one-electron reduction to form the anion in the presence of excess alkali metal. It is proposed that the formation of the germanium dianion radical **2.XXXII** undergoes a similar reaction, where a germanium(I) radical $[\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\text{Ge}^\bullet]$ intermediate is formed, followed by a two-electron reduction with calcium to afford **2.XXXII**.

The proposition of a group 14 element(I) radical intermediate compelled us to explore whether its isolation is possible. Therefore, we replaced the Ar substituents on the 2,6-bis(imino)phenyl ligand with 4-Me-2,6-CHPh₂-C₆H₂ (Ar*) and *t*Bu substituents and studied the resulting effects. However, Ar* substituents resulted in the formation of the germanium(I) dimer [{2,6-(HCNAr*)₂C₆H₃} $\ddot{\text{Ge}}$]₂ and attempts to isolate a germanium(I) radical intermediate failed. Thus, we focused on the effects of *t*Bu substituent.

Herein, we report the synthesis of a 2,6-bis(imino)phenylchlorogermylene bearing two *t*Bu substituents at the imine backbone. Its reaction with lithium afforded a germylidenide anion through a new reaction pathway, the C–C bond activation of a bis(germylene).

2.2 Results and Discussion

2.2.1 Synthesis of the Chlorogermylene

The reaction of the 2,6-bis(imino)phenyl bromide **L^{*t*Bu}Br**¹¹ ($L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$) with *n*BuLi in THF at $-78\text{ }^{\circ}\text{C}$, followed by addition to $GeCl_2 \cdot$ dioxane, led to the formation of the 2,6-bis(imino)phenylchlorogermylene [$L^{tBu}GeCl$] (**2.1**, Scheme 2.9), in 47% yield. It was isolated as an extremely air- and moisture-sensitive orange crystalline solid. It is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. Its 1H NMR spectrum exhibits a singlet at δ 1.36 ppm, a multiplet at δ 7.10 – 7.14 ppm, and another singlet at δ 8.01 ppm corresponding to the *t*Bu, Ph, and $HC=N$ protons, respectively. These suggests that the imino substituents are chemically equivalent in solution, whereas they are chemically inequivalent in its solid state structure (Figure 2.1).

Scheme 2.9 Synthesis of **2.1**

Figure 2.1 Molecular structure of **2.1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–C1 2.0004(19), Ge1–N1 2.2981(17), C7–N1 1.281(3), C6–C7 1.466(3), C1–C6 1.394(3), Ge1–Cl1 2.3477(5); C1–Ge1–N1 76.68(7), C7–N1–Ge1 111.41(13), N1–C7–C6 117.81(18), C7–C6–C1 115.92(18), C1–Ge1–Cl1 93.95(5), N1–Ge1–Cl1 88.94(4).

The molecular structure of **2.1** (Figure 2.1) is isostructural to the 2,6-bis(imino)phenyl stabilized germanium(II) chloride [$\{2,6-(\text{HCNAr})_2\text{C}_6\text{H}_3\}\text{GeCl}$] (**2.XXXI**, Chart 2.1),⁹ where Ar substituents are attached to the N_{imine} atoms. The Ge1 atom has a distorted trigonal pyramidal geometry. The sum of the bond angles at the Ge1 atom (259.57°) is similar to that in **2.XXXI** (267.40°). This implies that there is a stereoactive lone pair at the Ge1 atom. The Ge1–C1 (2.0004(19) Å) and Ge1–N1 (2.2981(17) Å) bonds are similar to those in **2.XXXI** (Chart 2.1, Ge–C: 2.028(3) Å; Ge–N: 2.247(3) Å). The Ge1 $\cdots$ N2 distance (2.57(1) Å) is considerably longer than the Ge1–N1 bond length (2.2981(17) Å), but shorter than the sum of the van der Waals radii (ca. 3.55 Å). These results imply that there is a weak interaction between the Ge1 and N1 atoms.

Chart 2.1 2,6-bis(imino)phenyl stabilized germanium(II) chloride [$\{2,6\text{-(HCNAr)}_2\text{C}_6\text{H}_3\}\text{GeCl}$]

To gain further insight on the bonding nature, compound **2.1** was explored by means of quantum chemical calculations (Section 2.5). The HOMO of compound **2.1** illustrates the lone pair orbital on the germanium atom (Figure 2.2). The LUMO shows π^* orbitals on the ligand backbone. Accordingly, the natural bond-orbital (NBO) analysis supports that the lone pair electrons at the Ge atom is high in s-character and possesses some directionality ($\text{sp}^{0.23}$, occupancy: 1.94).

(a) HOMO of **2.1**

(a) LUMO of **2.1**

Figure 2.2 Selected molecular orbitals of **2.1** (isovalue = 0.02)

2.2.2 Synthesis of the Bis(germylene)

The reduction of **2.1** was studied. Compound **2.1** reacted with 1 equiv of lithium in THF at room temperature to form the bis(germylene) [2-(HC–N*t*Bu)-6-(HC=N*t*Bu)C₆H₃Ge:]₂ (**2.2**, Scheme 2.10), in 49% yield. On the basis of the LUMO of **2.1**, it is proposed that the reaction advances through the reduction of the imine moiety of the ligand backbone to form an imine radical anion intermediate, followed by a C–C coupling reaction and salt elimination of LiCl, resulting in the formation of compound **2.2**.

Scheme 2.10 Synthesis of **2.2**

Compound **2.2** was isolated as an extremely air- and moisture-sensitive colorless crystalline solid. It is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. Its ¹H NMR spectrum displays four singlets at δ 1.10, 1.35, 3.80 and 8.48 ppm, corresponding to two chemically nonequivalent *t*Bu substituents, HC–N and HC=N protons respectively.

Figure 2.3 Molecular structure of **2.2** with thermal ellipsoids at the 50% probability level.

Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg):

Ge1–C1 1.991(3), Ge1–N2 2.127(2), Ge2–N2 2.081(2), Ge2–N1 2.119(2), Ge1–N1 2.082(2), C12–N1 1.489(4), C17–N2 1.490(4), C12–C17 1.562(4), C12–C11 1.519(4), Ge2–C23 1.995(3), C17–C18 1.512(4); C1–Ge1–N2 93.37(11), C1–Ge1–N1 85.00(10), C12–N1–Ge1 99.36(15), N1–C12–C11 111.0(2), N2–C17–C12 103.8(2), C17–N2–Ge1, 111.28(16), N1–Ge1–N2 69.17(9), N2–Ge2–N1 69.33(8), Ge1–N1–Ge2 86.20(8), C17–N2–Ge2 98.82(17), C23–Ge2–N2 85.96(11), N2–C17–C18 111.5(2), C23–C18–C17 113.7(3).

2.XXXIII

Chart 2.2 N-donor stabilized chlorogermylene [$\{ \text{ArN}=\text{C}(\text{Me})\text{C}(\text{Me})_2\text{-N}(\text{Ar}) \} \text{GeCl}$]

The molecular structure of **2.2** (Figure 2.3) shows that the germanium atoms adopt a distorted trigonal pyramidal geometry (sum of the bond angles = 247.7°, 248.4°), indicating that there is a lone pair of electrons on each of the germanium atoms. The C–Ge bond lengths (C1–Ge1: 1.991(3) Å; C23–Ge2: 1.995(3) Å) are comparable to that of **2.1** (C–Ge: 2.0004(19) Å). The C12–N1 (1.489(4) Å) and C17–N2 bond lengths (1.490(4) Å), are longer than the C3–N3 (1.265(4) Å) and C24–N4 bond lengths (1.256(4) Å), indicating that they are single bonds. Also, the C12–C17 bond (1.562(4) Å) is a C–C single bond. The N–Ge bonds (2.081(2), 2.119(2), 2.127(2), and 2.082(2) Å) are comparable to the N–Ge coordinative covalent bond (2.0634(18) Å) in the N-donor stabilized chlorogermylene [$\{\text{ArN}=\text{C}(\text{Me})\text{C}(\text{Me})_2\text{N}(\text{Ar})\}\text{GeCl}$] (**2.XXXIII**, Chart 2.2).¹² The N–Ge (2.081(2), 2.119(2), 2.127(2), and 2.082(2) Å) bond lengths are considerably longer than those of the germanium(II) amido compound [$\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Ge}$] (N–Ge: 1.873(5), 1.878(5) Å).¹³ These imply that compound **2.2** has resonance structures **2.2A** and **2.2B**, resulting in weak N_{amino}–Ge bonds (Scheme 2.11).

Scheme 2.11 Resonance Structures of **2.2**

Compound **2.2** was investigated by means of quantum chemical calculations (Section 2.5). The HOMO illustrates the lone pair orbitals on the germanium atoms. The LUMO illustrates the π^* orbitals on the ligand backbone and the C–Ge bonds (Figure 2.4).

Figure 2.4 Selected molecular orbitals of **2.2** (isovalue = 0.02)

2.2.3 Synthesis of the Germylidenide Anion by the C–C Bond Activation of **2.2**

The reaction of **2.2** with 2 equiv of lithium in THF led to the formation of the lithium germylidenide $[L^{tBu}GeLi]_2$ (**2.3**, Scheme 2.12), in 27% yield. With reference to the LUMO of **2.2**, it suggests that the reaction advances through the reduction of the germanium(II) centers in **2.2**, followed by the homolytic cleavage of the C–C bond to form **2.3** (Scheme 2.13). Compound **2.3** can also be afforded by the reaction of 2 equiv of **2.1** with 4 equiv of lithium in THF, whereby the reaction progresses through the reduction of **2.2**.

Scheme 2.12 Synthesis of **2.3**

N1 1.939(3), C7–N1 1.380(5), C6–C7 1.401(6), Ge1–C1 1.946(4), C1–C6 1.463(5), Ge1–Li1A 2.897(8), Ge1–Li1 2.680(7), Li1–N2 2.101(9); C7–N1–Ge1 115.1(3), N1–Ge1–C1 83.31(16), C6–C1–Ge1 112.1(3), C7–C6–C1 114.0(4), N1–C7–C6 115.0(4), N1–Ge1–Li1 126.1(2), N1–Ge1–Li1A 59.35(18), N2–Li1–Ge1 157.2(4).

Compound **2.3** was characterized by X-ray crystallography (Figure 2.5). The Li1 atom is η^1 -coordinated to both Ge1 and N2 atom, and η^5 -coordinated to the GeCCCN ring of another molecule. The Li1–Ge1 bond (2.680(7) Å) is comparable to those in the dianionic germole complex $[(\mu, \eta^5\text{-GeC}_4\text{Ph}_4)\{\text{Li}(\text{dioxane})_2\}_2]$ (**2.XXXIV**, Chart 2.3, average Ge–Li bond length: 2.706 Å).¹⁴ However, the Ge1–Li1A (2.897(8) Å) bond length of **2.3** is longer than those of the dianionic germole complex **2.XXXIV**. Comparing the Ge1–C1 (1.946(4) Å), C1–C6 (1.463(5) Å), C6–C7 (1.401(6) Å), C7–N1 (1.380(5) Å), and Ge1–N1 (1.939(3) Å) bond lengths of compound **2.3** with those of compound **2.1** (Ge1–C1: 2.0004(19); C1–C6: 1.394(3); C6–C7: 1.466(3); C7–N1: 1.281(3); Ge1–N1: 2.2981(17) Å), it proposes that the negative charge on the germanium center is stabilized by an electron delocalization in the GeCCCN five-membered ring.

Chart 2.3 $[(\mu, \eta^5\text{-GeC}_4\text{Ph}_4)\{\text{Li}(\text{dioxane})_2\}_2]$

The bonding nature of compound **2.3** was explored by means of quantum chemical calculations (Section 2.5). The LUMO shows the π^* orbital of the ligand backbone (Figure

2.6c). The HOMO-2 and HOMO specifically show that each germanium atom comprises two lone pair orbitals being perpendicular to and lying on the same plane as the germanium-containing five membered ring (Figure 2.6a and 2.6b). The HOMO also depicts the π -delocalization. Additionally, the negative nucleus-independent chemical shift¹⁵⁻¹⁶ (NICS(1): -12.8 ppm) of the germanium-containing five-membered ring and the natural charge of the germanium atoms (0.75) support that the negative charge at the germanium atom is stabilized by an aromatic delocalization in the germanium-containing five-membered ring.

Figure 2.6 Selected molecular orbitals of **2.3** (isovalue = 0.02)

In addition, the ^7Li NMR of compound **2.3** has a signal at $\delta -2.27$ ppm. This low frequency resonance of compound **2.3** is contributed by the strong shielding effect of the diatropic ring current from the aromatic germanium-containing five-membered ring.¹⁷⁻¹⁹ Hence, based on compound **2.3**'s solid structure, NMR spectra and its bonding nature, we proposed a solution structure for **2.3** (Chart 2.4).

Chart 2.4 Proposed solution structure for **2.3**

2.3 Conclusion

In conclusion, by replacing the Ar substituents on the 2,6-bis(imino)phenyl ligand with *t*Bu substituents resulted in the discovery of a new reaction pathway, where the germylidenide anion **2.3** was obtained by the reduction of the germanium(II) centers in **2.2**, concomitant with the homolytic cleavage of the C–C bond.

2.4 Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF, toluene, and Et₂O were dried over and distilled over Na/K alloy prior to use. CH₂Cl₂ was dried over and distilled over CaH₂ prior to use. **L^{tBu}Br** was prepared as described in the literature.¹¹ The ¹H, ¹³C, and ⁷Li NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H and ¹³C and LiCl for ⁷Li. Elemental analyses were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

Synthesis of 2.1. *n*BuLi (2.0 M in cyclohexane, 2.75 mL, 5.5 mmol) was added dropwise to a solution of **L^{tBu}Br** (1.62 g, 5.00 mmol) in THF (50 mL) at −78 °C. The reaction mixture was stirred for 3 h. A solution of GeCl₂·dioxane (1.27 g, 5.50 mmol) in THF (5 mL) was then added to the reaction mixture at −78 °C. The resulting reddish-brown solution was gradually warmed to room temperature and stirred overnight. Solvent was removed under vacuum, and the residue was extracted with dichloromethane. LiCl was filtered off, and the reddish-brown filtrate was concentrated to afford orange crystals of **2.1** (0.824 g, 47%). M.p.: 163 °C (dec.). Elemental analysis (%) calcd for C₁₆H₂₃N₂GeCl: C, 54.68; H, 6.60; N, 7.97. Found: C, 54.30; H, 6.58; N, 7.80. ¹H NMR (395.9 MHz, C₆D₆, 25 °C): δ 1.36 (s, 18H, C(CH₃)₃), 7.10–7.14 (m, 3H, Ph), 8.01 (s, 2H, CH=N). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 25 °C): δ 30.53 (CH₃), 59.30 (C(CH₃)₃), 130.20, 141.38, 157.69, 158.14 (Ph), 166.82 ppm (C=N–C).

Synthesis of 2.2. THF (20 mL) was added to a mixture of compound **2.1** (0.351 g, 1.00 mmol) and lithium metal (0.00694 g, 1.00 mmol) at 0 °C. The resulting red reaction mixture

was gradually warmed to room temperature and stirred for 15 h. Solvent was removed under vacuum, and the dark green residue was extracted with Et₂O. LiCl was filtered off and tmeda (0.15 mL, 1.00 mmol) was added at 0 °C. The resulting green solution was stirred at room temperature for 2 h. The solution was then filtered and concentrated, affording dark green crystals of compound **2.2** (0.156 g, 49%). M.p.: 218 °C (dec.). Elemental analysis (%) calcd for C₃₂H₄₆Ge₂N₄: C, 60.81; H, 7.33; N, 8.87. Found: C, 60.72; H, 7.14; N, 8.67. ¹H NMR (395.9 MHz, C₆D₆, 25 °C): δ 1.10, (s, 18H, C(CH₃)₃), 1.35 (s, 18H, C(CH₃)₃), 3.80 (s, 2H, CH–N), 7.16–7.24 (m, 4H, Ph), 7.39 (d, ³J_{HH} = 6.79 Hz, 2H, Ph), 8.48 (s, 2H, CH=N). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 25 °C): δ 30.21 (CH₃), 31.33 (CH₃), 55.86 (C(CH₃)₃), 57.87 (C(CH₃)₃), 73.46 (HC–N), 122.43, 127.11, 142.60, 155.82, 159.01 (Ph), 159.33 ppm (C=N–C).

Synthesis of 2.3. Method A: THF (20 mL) was added to a mixture of compound **2.2** (0.253 g, 0.40 mmol) and lithium granules (0.0056 g, 0.80 mmol) at 0 °C. The resulting red reaction mixture was gradually warmed to room temperature and stirred for 15 h to afford a dark green solution. Solvent was removed under vacuum, and compound **2.3** was obtained quantitatively.

Method B: THF (40 mL) was added to a mixture of compound **2.1** (1.41 g, 4.00 mmol) and lithium granules (0.0555 g, 8.00 mmol) at room temperature. The red reaction mixture turned blue initially and became dark green after 15 h of stirring. Solvent was removed under vacuum, and the residue was extracted with toluene. LiCl was filtered off, and the filtrate was concentrated to form dark green crystals of compound **2.3** (0.349 g, 27%). M.p.: 249 °C (dec.). Elemental analysis (%) calcd for C₃₂H₄₆Ge₂Li₂N₄: C, 59.51; H, 7.18; N, 8.67. Found: C, 59.32; H, 6.97; N, 8.44. ¹H NMR (399.5 MHz, C₆D₆, 25 °C): δ 1.49, (s, 36H, C(CH₃)₃), 6.67 (t, ³J_{HH} = 7.55 Hz, 2H, Ph), 6.78 (d, ³J_{HH} = 7.35 Hz, 4H, Ph), 8.03 (s, 4H, CH=N). ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25 °C): δ 32.55 (CH₃), 57.46 (C(CH₃)₃), 120.42,

125.41, 136.53 (Ph), 160.15 ppm (C=N–C). $^7\text{Li}\{^1\text{H}\}$ NMR (155.3 MHz, C_6D_6 , 25 °C): δ
–2.27 ppm.

2.5 Theoretical studies

In order to have a better understanding of the bonding nature of compounds **2.1** – **2.3**, compounds were investigated using DFT²⁰⁻²¹ B3PW91²²⁻²³ method with the 6-31+G(d) level. All calculations were carried out using the Gaussian 09 packages.²⁴ The NBO analyses were performed using the NBO 5.0 program at the same level. The optimized geometry is in good agreement with the X-ray crystallographic data of **2.1** – **2.3**.

Figure 2.7 Calculated structure of **2.1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–C1 1.971, Ge1–N1 2.368, C7–N1 1.279, C6–C7 1.464, C1–C6 1.396, Ge1–Cl1 2.310; C1–Ge1–N1 75.59, C7–N1–Ge1 110.02, N1–C7–C6 118.13, C7–C6–C1 115.75, C1–Ge1–Cl1 94.40, N1–Ge1–Cl1 90.10.

Figure 2.8 Calculated structure of **2.2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–C1 1.981, Ge1–N2 2.097, Ge2–N2 2.068, Ge2–N1 2.097, Ge1–N1 2.068, C12–N1 1.483, C17–N2 1.483, C12–C17 1.573, C12–C11 1.508, Ge2–C23 1.981, C17–C18 1.508; C1–Ge1–N2 94.43, C1–Ge1–N1 85.77, C12–N1–Ge1 98.64, N1–C12–C11 111.04, N2–C17–C12 104.00, C17–N2–Ge1 110.39, N1–Ge1–N2 70.08, N2–Ge2–N1 70.08, Ge1–N1–Ge2 86.61, C17–N2–Ge2 98.64, C23–Ge2–N2 85.77, N2–C17–C18 111.04, C23–C18–C17 113.04.

Figure 2.9 Calculated structure of **2.3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–N1 1.926, C7–N1 1.368, C6–C7 1.400, Ge1–C1 1.906, C1–C6 1.500, Ge1–Li1A 2.768, Ge1–Li1 2.631, Li1–N2 2.093; C7–N1–Ge1 114.64, N1–Ge1–C1 83.95, C6–C1–Ge1 112.43, C7–C6–C1 113.87, N1–C7–C6 114.81, N1–Ge1–Li1 134.32, N1–Ge1–Li1A 60.85, N2–Li1–Ge1 82.38.

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Chapter 3.

The coordination chemistry of a germylene and germyliumylidene cation toward coinage metals

3.1 Introduction

Germyliumylidene cations of composition $[\text{RGe:}]^+$ have attracted much attention due to their distinctive properties.¹ They consist of two vacant orbitals and a lone pair of electrons on the germanium(II) cations, possess the properties of highly Lewis acidic germyl ions and the ambiphilic character of germylenes. These characteristics allow germyliumylidene ions to show extraordinary synthetic potential. However, its high reactivity hampers their isolation. For the past decades, several research groups have tackled the difficulties and utilized the concepts of thermodynamic and/or kinetic stabilization to afford stable germyliumylidene cation. The most spectacular example is the amido germyliumylidene cation $[\text{Ar}^*(\text{Me}_3\text{Si})\text{NGe}]^+$ (**3.I**, Chart 3.1, $\text{Ar}^* = 4\text{-Me-2,6-CHPh}_2\text{-C}_6\text{H}_2$),² in which the low valent germanium centre is stabilized by a steric hindered monodentate ligand, along with a weak arene interaction. Due to pronounced electron deficiency at the germanium centres, a series of germyliumylidene cations were synthesized with the aid of anionic ligands with strong electron pair donors.³⁻¹¹ In addition, neutral multidentate ligands and a carbodiphosphorane ligand were introduced to synthesize germyliumylidene cations via auto-ionisation of germanium dichloride (Chart 3.1).

Chart 3.1 Gerymiumylidene cations

Since a gerymlene and gerymiumylidene cation consist of a lone pair of electrons and vacant p orbital on the low valent germanium atoms, they can serve as ancillary ligands in transition metal complexes such as the group 11 metals.¹²⁻¹⁵ However, until now, only gerymlene-group 11 metal complexes were reported (Chart 3.2 – 3.3).¹⁶⁻²⁷

R = Me, X = C₆F₅, **3.XV**

R = OtBu, X = I, **3.XVI**

Chart 3.2 Examples of germylene-copper complexes

M = Ag, R = C(SiMe₃)N₂, **3.XXII**

M = Au, R = CCPh, **3.XXIII**

3.XXIV

3.XXV

X = Cl (**3.XXVI**)
or I (**3.XXVII**)

3.XXVIII

Chart 3.3 Examples of germylene-silver and germylene-gold complexes

More recently, Cabeza, García-Álvarez and co-workers successfully synthesized the first amidinatogermylene complexes of copper, silver and gold (Scheme 3.1).²⁸

Scheme 3.1 Synthesis of amidinatogermylene complexes of copper, silver and gold

Recent results show that transition metal-germylene complexes (Chart 3.4) were capable of catalyzing organic transformations, such as hydrogenation reactions,²⁹⁻³⁰ Suzuki-Miyaura cross-coupling of aryl bromides,³¹ Heck arylation of olefins,³¹ Sonogashira cross-coupling reaction³² and N-alkylation of aniline.³⁰

R = ethyl (**3.XXXV**)
R = Ph (**3.XXXVI**)

R = ethyl (**3.XXXVII**)
R = Ph (**3.XXXVIII**)

3.XXXIX

3.XXXX

3.XXXXI

3.XXXXII

3.XXXXIII

Chart 3.4 Examples of germylene-transition metal complexes with catalytic activities

It is anticipated that transition metal-germyliumylidene cation complexes should have synthetic potential, but they are still unknown as yet. In the previous chapter, we have

reported the reduction of the 2,6-bis(imino)phenylchlorogermylene [$L^{tBu}GeCl$] (**3.1**, $L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$, Scheme 3.2) with alkali metal to afford the corresponding germylidenide anion.³³ In this chapter, the reactivity of **3.1** for the formation of a 2,6-bis(imino)phenylgermyliumylidene cation was investigated. We report the synthesis of a 2,6-bis(imino)phenylgermyliumylidene cation in the coordination sphere of an N-heterocyclic carbene (NHC) and AgOTf (OTf = $CF_3SO_3^-$). The coordination chemistry of the 2,6-bis(imino)phenylchlorogermylene [$L^{tBu}GeCl$] towards other group 11 metals is also described.

3.2 Results and Discussion

3.2.1 Attempt to synthesize $[L^{tBu}Ge]^+$

The reaction of the 2,6-bis(imino)phenylchlorogermylene $[L^{tBu}GeCl]$ (**3.1**, $L^{tBu} = C_6H_3-2,6-(HC=NtBu)_2$) with sodium trifluoromethanesulfonate (NaOTf, OTf = $CF_3SO_3^-$), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) or MeOTf did not afford a germyliumylidene cation, instead an insoluble white precipitate was formed. It is suggested that a germyliumylidene cation cannot be accessed by a simple metathesis reaction as the LUMO of **3.1** is the π^* orbitals on the ligand backbone. In this context, another strategy was then introduced.

3.2.2 Synthesis of $[{L^{tBu}(TfO)Ge}]_2Ag(OTf)$

Scheme 3.2 Synthesis of **3.2**

The reaction of compound **3.1** and silver(I) trifluoromethanesulfonate (AgOTf) in a molar ratio of 2:3 in toluene, afforded a mixture of the germylene-silver(I) complex $[{L^{tBu}(TfO)Ge}]_2Ag(OTf)$ (**3.2**, Scheme 3.2) in 31% yield, and AgCl. Other germylene-silver(I) complexes were not observed in the reaction mixture, which was confirmed by 1H NMR spectroscopy. When **3.1** reacted with one equiv of AgOTf, $[L^{tBu}(Cl)Ge-AgOTf]$ was not afforded and instead, compound **3.2** was formed. The reaction appears that AgOTf undergoes a salt elimination reaction with **3.1** to form a $L^{tBu}GeOTf$ intermediate, which then coordinates with another molecule of AgOTf to form **3.2**.

Compound **3.2** was isolated as an extremely moisture- and air-sensitive colourless crystalline solid. It is soluble in THF and CH₂Cl₂. It was characterized by NMR spectroscopy and X-ray crystallography. Its ¹H NMR spectrum exhibits a singlet at δ 1.62 for the *t*Bu substituents, a singlet at δ 7.90 ppm and triplet at δ 7.70 ppm for the phenyl protons, and another singlet at δ 8.86 ppm corresponding to HC=N protons. The ¹³C NMR spectrum shows one set of resonances due to the ligand backbone and another quartet arising from the OTf substituents. The ¹⁹F{¹H} NMR spectrum exhibits a signal at δ = −78.61 ppm, which is inconsistent with the solid state structure, indicating that in solution, there is fast exchange between free and bound triflate groups on the NMR time scale. A similar observation was made for the 2-6-bis(imino)pyridine-bound stannylumylidene cation [C₅H₅N-2,6-(MeCN(Ar)SnOTf)OTf]OTf (**3.XXXXIV**, Chart 3.5).³⁴

3.XXXXIV

Chart 3.5 2-6-bis(imino)pyridine-bound stannylumylidene complex

Figure 3.1 Molecular structure of **3.2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and *t*Bu substituents are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1–Ge1 2.5009(5), Ag1–Ge2 2.4782(5), Ge1–O1 1.951(3), Ag1–O4 2.492(5), Ge2–O7 1.930(13), C1–Ge1 1.933(3), C18–Ge2 1.933(4), Ge1–N1 2.332(3), Ge1–N2 2.329(3), Ge2–N3 2.358(3), Ge2–N4 2.309(3), C12–N2 1.276(4), C7–N1 1.273(5), C29–N4 1.285(5), C24–N3 1.268(5); Ge1–Ag1–Ge2 139.459(18), Ge1–Ag1–O4 97.26(12), O4–Ag1–Ge2 123.27(12), C1–Ge1–Ag1 145.58(10), C1–Ge1–O1 102.9(2), O1–Ge1–Ag1 111.5(2), C18–Ge2–Ag1 137.59(10), Ag1–Ge2–O7 116.8(7), C18–Ge2–O7 105.6(7).

The molecular structure of **3.2** (Figure 3.1) illustrates that the 2,6-bis(imino)phenyl ligands are in a staggered conformation. The germanium atom adopts a pseudo trigonal bipyramidal geometry with the imino nitrogen atoms at the axial position, while the silver atoms adopt a distorted trigonal planar geometry (sum of bond angles = 360.00°). The C–

Ge (C1–Ge1: 1.933(3) Å; C18–Ge2: 1.933(4) Å) and Ge–N_{imino} (2.309(3), 2.358(3), 2.329(3), 2.332(3) Å) bond lengths are comparable to those of **3.1** (Ge–C: 2.0004(19) Å; Ge–N: 2.2981(17) Å). The Ge–O bond lengths (1.930, 1.950 Å) are slightly shorter than that of the aminotroponimate-stabilized triflatogermylene-silver complex (**3.XIX**, Chart 3.3, Ge–O: 2.020(6) Å).²² The Ag1–O4 bond length (2.492(5) Å) is comparable to that of AgOTf (Ag–O: 2.485(5), 2.504(5) Å).³⁵ The Ag–Ge bond lengths (2.5009(5), 2.4782(5) Å) are unequal, which are comparable to those of base-stabilized germylene-silver(I) cation complexes such as [{PhC(NtBu)₂Ge(*t*Bu)}₂Ag]⁺ (**3.XXXIV**, Scheme 3.1, Ag–Ge: 2.4539(3) Å)²⁸ and [{HC(MeCNAr)₂Ge(PhC≡C)}₂Ag][Ag(C₆F₅)₂] (**3.XX**, Chart 3.3, Ag–Ge: 2.4732(10), 2.4731(10) Å).²³

3.2.3 Synthesis of [{L^{*t*Bu}Ge(I_{Me})}₂Ag(OTf)]OTf₂

Scheme 3.3 Synthesis of **3.3(OTf)₂**

The reaction of **3.2** with 2 equiv of 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (I_{Me}) in toluene afforded the dicationic bis(germyliumylidene)silver(I) complex [{L^{*t*Bu}(I_{Me})Ge}₂Ag(OTf)]OTf₂ (**3.3(OTf)₂**, Scheme 3.3), in 32% yield. Compound **3.3** is the first example of a germlyiumylidene cation-transition metal complex, following a previous example of the germanium(II) dication-silver(I) complex [{(H₂CN=C(Me)C₅H₄N)₂Ge}₂Ag(OTf)]⁴⁺ (**3.XXI**, Chart 3.3).²⁴ Compound **3.3(OTf)₂** was isolated as an extremely moisture- and air-sensitive yellow crystalline solid. It is soluble in

CH₂Cl₂ and 1,2-difluorobenzene. Compound **3.3**(OTf)₂ was characterized by NMR spectroscopy and X-ray crystallography. Its ¹H NMR spectrum exhibits a singlet at δ 1.11 ppm for the *t*Bu substituents, four other singlets at δ 2.08, 2.27, 2.57 and 4.28 ppm for the methyl protons on the I_{Me}, a triplet at δ 7.95 ppm and a doublet at δ 8.09 ppm for the phenyl protons, and another singlet at δ 8.56 ppm for the HC=N protons. These results suggest that the imino substituents are chemically equivalent in solution but otherwise in the solid state structure (Figure 3.2). In addition, the four singlets corresponding to the methyl protons on I_{Me}, suggest that the I_{Me} ligands do not freely rotate, resulting in chemically inequivalent in solution. The ¹³C NMR spectrum exhibits one set of resonances corresponding to the ligand backbone, one set of resonances due to the I_{Me} and another quartet arising from the OTf substituents. The ¹⁹F{¹H} NMR spectrum exhibits a signal at δ –78.55 ppm, indicating the exchange between free and bound triflate groups to be fast on the NMR time scale.

Figure 3.2 Molecular structure of **3.3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and *t*Bu substituents are omitted for clarity. Selected bond lengths (Å) and

angles (deg): Ag1–Ge1 2.5003(8), Ag1–Ge2 2.4881(8), C8–Ge1 1.941(7), C31–Ge2 1.937(7), N3–Ge1 2.081(6), N7–Ge2 2.099(5), C1–Ge1 2.001(6), C24–Ge2 1.987(6), Ag1–O1 2.417(12); Ge1–Ag1–Ge2 134.33(3), Ge1–Ag1–O1 102.8(10), Ge2–Ag1–O1 122.9(10), C31–Ge2–Ag1 116.14(18), C31–Ge2–N7 81.8(2), C31–Ge2–C24 109.9(3), Ag1–Ge2–C24 126.47(18), C24–Ge2–N7 97.5(2), Ag1–Ge2–N7 114.35(14), C8–Ge1–Ag1 115.69(19), C8–Ge1–N3 82.4(3), C8–Ge1–C1 109.9(3), N3–Ge1–Ag1 111.84(16), N3–Ge1–C1 98.6(2), C1–Ge1–Ag1 127.41(19).

The molecular structure of **3.3** (Figure 3.2) comprises two molecules in the asymmetric unit and only one of them is discussed herein. The silver atom adopts a trigonal planar geometry (sum of bond angles = 360.05°), while the germanium atoms adopt a pseudo trigonal pyramidal geometry with the N_{imino} atoms at the axial position. The Ge1–N3 (2.081(6) Å) and Ge2–N7 (2.099(5) Å) bond lengths are significantly shorter than the Ge1...N4 (2.740(7) Å) and Ge2...N8 (2.704(6) Å) distances. The Ge1–N3 (2.081(6) Å) and Ge2–N7 (2.099(5) Å) bond lengths are intermediate values between those of the Ge–N_{imino} coordinative covalent bonds in the pyridinylimino-stabilized chlorogermylumylidene cations [$\{C_5H_3N-2-OMe-6-(MeCNAr)\}GeCl\}^+$ (**3.X**, Chart 3.1, Ge–N: 2.045(4), 2.070(4) Å),¹⁰ and [$\{C_5H_3N-2,6-MeCNAr\}GeCl\}^+$ (**3.XI**, Chart 3.1, Ge–N: 2.255(2), 2.267(2) Å).¹¹ They are shorter than those of **3.2** due to the presence of Ge(II) cations. The Ge1...N4 (2.740(7) Å) and Ge2...N8 (2.704(6) Å) distances are shorter than the sum of their van der Waals radii (ca. 3.55 Å), indicating a weak interaction between these germanium and nitrogen atoms. The C_{aryl}–Ge (C8–Ge1: 1.941(7), C31–Ge2: 1.937(7) Å) and Ag–Ge (Ag1–Ge1: 2.5003(8), Ag1–Ge2: 2.4881(8) Å) bond lengths are comparable to those of **3.2** (C–Ge: 1.933(3), 1.933(4); Ge–Ag: 2.5009(5), 2.4782(5) Å). The C_{Ime}–Ge bond lengths (C1–Ge1: 2.0016 Å; C24–Ge2: 1.987(6) Å) are longer than the C_{aryl}–Ge bond lengths. The C_{Ime}–Ge bond lengths are comparable to that of the NHC-stabilized

germyliumylidene cation such as $[I_{Ar}-GeCH(SiMe_3)_2]^+$ (**3.VI**, Chart 3.1, $C_{I_{Ar}}-Ge$: 2.082(1) Å)⁷ and $[N(Mes)\{C(H)\}_2N\{(CH_2)_2NMe\}C-Ge]^+$ (**3.VIII**, Chart 3.1, $C-Ge$: 2.062(2) Å).⁹ These results show that the C1–Ge1 and C24–Ge2 bonds are coordinative covalent bonds.

3.2.4 Synthesis of $[L^{tBu}(Cl)GeCu(\mu-Cl)]_2$

Scheme 3.4 Synthesis of **3.4**

The reaction of **3.1** with CuOTf in fluorobenzene afforded a reddish-brown suspension. The insoluble residue was filtered. The filtrate was then mixed with 1,2-difluorobenzene and the resulting solution was concentrated to afford an extremely moisture- and air-sensitive orange crystalline solid of $[L^{tBu}(Cl)GeCu(\mu-Cl)]_2$ (**3.4**, Scheme 3.4), in 5% yield. Other germylene-copper(I) complexes were not observed in the mother liquor, which was confirmed by 1H NMR spectroscopy. However, the residue is insoluble in solvents such as MeCN, fluorobenzene, 1,2-difluorobenzene and CH_2Cl_2 and could not be characterized by NMR spectroscopy.

Compound **3.4** comprises a three coordinate Cu centre complexed by a germylene donor. Such feature is rare and only one example with this structural character, $[HC\{C(Me)N(Ar)\}_2(tBuO)GeCu(\mu-I)]_2$ (**3.XVI**, Chart 3.2)¹⁹ has been reported. Compound **3.4** is soluble in CH_2Cl_2 and MeCN. It was characterized by NMR spectroscopy and X-ray crystallography. Its 1H NMR spectrum exhibits a singlet at δ 1.64 ppm for the *t*Bu substituents, a triplet at δ 7.67 ppm and a doublet at δ 7.79 ppm for the phenyl protons, and

another singlet at δ 8.56 ppm for the HC=N protons. These results suggest that the imino substituents are chemically equivalent in solution but otherwise in the solid state structure (Figure 3.3).

Figure 3.3 Molecular structure of **3.4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Ge1 1.943(5), Ge1–N1 2.202(4), C7–N1 1.269(7), C12–N2 1.259(6), Ge1–Cl1 2.2388(12), Ge1–Cu1 2.2679(8), Cu1–Cl2 2.3120(12), Cu1–Cl2A 2.2931(13), C1–Ge1–Cl1 102.43(13), C1–Ge1–N1 79.30(17), C1–Ge1–Cu1 133.79(13), Cu1–Ge1–N1 108.68(11), Cu1–Ge1–Cl1 122.21(4), Ge1–Cu1–Cl2 125.66(4), Ge1–Cu1–Cl2A 133.40(4), Cu1–Cl2A–Cu1A 79.06(4), Cu1–Cl2–Cu1A 79.06(4), Cl2A–Cu1–Cl2 100.94(4).

The molecular structure of **3.4** (Figure 3.3) illustrates that the Cu₂Cl₂ four-membered ring is bridged between two 2,6-bis(imino)phenyl chlorogermylene donors. The 2,6-bis(imino)phenyl ligands are tilted with respect to the Cu₂Cl₂ ring, while the Ge atoms adopt a pseudo trigonal bipyramidal geometry. The Ge1–N1 bond length (2.202(4) Å) is

comparable to that of **3.1** (Ge1–N1: 2.2981(17) Å) and is shorter than the Ge1⋯N2 distance (2.502(4) Å). The Ge1⋯N2 distance (2.502(4) Å) is shorter than the sum of their van der Waals radii (ca. 3.55 Å), indicating a weak interaction between the Ge1 and N2 atoms. Similar observation can be found in **3.1**. The Ge–Cu bond length (2.2679(8) Å) is comparable to that of the dimeric germylene-copper(I) complex [HC{C(Me)N(Ar)}₂(*t*BuO)GeCu(μ-I)]₂ (**3.XVI**, Chart 3.2, Ge–Cu: 2.3341(10) Å).¹⁹ The Cu₂Cl₂ ring has a rhomboidal shape. The Cu–Cl bond lengths (2.293, 2.312 Å) are shorter than those of the amidinato germylene-copper(I) tetramer with a cubic (CuCl)₄ cluster [{PhC(N*t*Bu)₂}(*t*Bu)GeCuCl]₄ (**3.XXX**, Scheme 3.1, Cu–Cl: 2.364(2)–2.549(2) Å).²⁸ The obtuse Cu–Cl–Cu bond angle (79.06°) and long Cu⋯Cu distance (2.931 Å),³⁶ indicating that there is no Cu–Cu bonding in **3.4**.

The mechanism for the formation of **3.4** is proposed. The reaction of **3.1** with CuOTf proceeded through a substitution to form L^{*t*Bu}GeOTf and CuCl. The latter was coordinated with **3.1**, along with dimerization to form **3.4**. The mechanism is evidenced by the reaction of CuCl with **3.1** in MeCN to afford **3.4**.

3.2.5 Synthesis of [L^{*t*Bu}(Cl)GeCu(μ-I)]₂

Scheme 3.5 Synthesis of **3.5**

Similar reaction of **3.1** with CuI in MeCN afforded [L^{*t*Bu}(Cl)GeCu(μ-I)]₂ (**3.5**, Scheme 3.5), in 16% yield. It was isolated as an extremely moisture- and air-sensitive

orange crystalline solid. It is soluble in THF and MeCN. Compound **3.5** was characterized by NMR spectroscopy and X-ray crystallography. Its ^1H NMR spectrum exhibits a singlet at δ 1.60 ppm for the *t*Bu substituents, a triplet at δ 7.54 ppm and a doublet at δ 7.75 ppm for the phenyl protons and another singlet at δ 8.64 ppm for the CH=N protons. These results suggest that the imino substituents are chemically equivalent in solution but otherwise in the solid state structure (Figure 3.4).

Figure 3.4 Molecular structure of **3.5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Ge1 1.965(9), Ge1–N1 2.290(13), C7–N1 1.311(17), C12–N2 1.252(14), Ge1–Cl1 2.276(2), Ge1–Cu1 2.3029(17), Cu1–Cu1A 2.645(3), Cu1–I1A 2.521(2), Cu1–I1 2.572(2); C1–Ge1–Cl1 103.0(3), C1–Ge1–N1 79.0(5), C1–Ge1–Cu1 132.0(3), Cu1–Ge1–N1 106.2(9), Ge1–Cu1–I1A 129.52(8), Ge1–Cu1–I1 113.01(7), Ge1–Cu1–Cu1A 170.67(12), Cu1A–I1A–Cu1 62.55(6), Cu1–I1–Cu1A 62.55(6), I1A–Cu1–Cu1A 59.66(6), I1A–Cu1–I1 117.45(6), Cu1–Cu1A–I1 59.66(6), I1A–Cu1A–Cu1 57.78(6), Cu1A–Cu1–I1 57.78(6).

The molecular structure of **3.5** (Figure 3.4) resembles that of **3.4**, except the Cu₂I₂ four-membered ring. Since the bridging I substituents are better electron donors in comparison with the Cl donors in **3.4**,³⁷ the Cu–Cu bond length (2.645 Å) is shorter and the Cu–I–Cu bond angle (62.55(6)°) is more acute than those of **3.4** (Cu–Cl–Cu: 79.06°).³⁶

The Cu–Cu bond length (2.645(3) Å) of **3.5** is shorter than that of the dimeric base-stabilized germylene-copper(I) complex [HC{C(Me)N(Ar)}₂(*t*BuO)GeCu(μ-I)]₂ **3.XVI** (Chart 3.2, Cu–Cu: 3.297(2) Å)¹⁹ but comparable to those of **3.XXXV** (Chart 3.6, Cu–Cu: 2.6739(9) Å),³⁸ **3.XXXVI** (Chart 3.6, Cu–Cu: 2.6869(8) Å),³⁹ **3.XXXVII** (Chart 3.6, Cu–Cu: 2.587(1) Å).⁴⁰ The Cu–I bond lengths (2.572(2), 2.521(2) Å) are shorter than that of **3.XVI**, Chart 3.2, Cu–I: 2.5791(9), 2.6382(9) Å,¹⁹ but comparable to those of **3.XXXV** (Chart 3.6, Cu–I: 2.6065(10) Å, 2.6248(7) Å),³⁸ **3.XXXVI** (Chart 3.6, Cu–I: 2.581(2), 2.631(2), 2.604(2), 2.571(2) Å)³⁹ and **3.XXXVII** (Chart 3.6, Cu–I: 2.599(1), 2.555(1) Å).⁴⁰

In addition, the Cu–I–Cu (62.55(6)°) and I–Cu–I (117.45(6)°) bond angles of **3.5** are comparable to those of **3.XXXV** (Chart 3.6, Cu–I–Cu: 61.48(2)°, I–Cu–I: 118.52(2)°),³⁸ **3.XXXVI** (Chart 3.6, Cu–I–Cu: 59.75(5)°, 59.98(5)°; I–Cu–I: 120.83(6)°, 119.44(6)°),³⁹ **3.XXXVII** (Chart 3.6, Cu–I–Cu: 60.25(2)°; I–Cu–I: 119.75(3)°).⁴⁰ It is also noted that the Cu–Cu bond length (2.645 Å) is shorter than the sum of their van der Waals radii (ca. 4.06 Å). Hence, these suggest the presence of Cu^I...Cu^I, d¹⁰–d¹⁰ interaction.

3.XXXXV

3.XXXXVI

3.XXXXVII

Chart 3.6 Examples of complexes containing Cu₂I₂ bridging unit

3.2.6 Synthesis of [L^tBu(Cl)GeCuI(PPh₃)]₂

Scheme 3.6 Synthesis of **3.6**

A monomeric 2,6-bis(imino)phenyl chlorogermylene-copper(I) complex [L^tBu(Cl)GeCuI(PPh₃)] (**3.6**, Scheme 3.6), in 76% yield, can be afforded by reacting **3.5** with triphenylphosphine (PPh₃) in THF at room temperature. It was isolated as an extremely moisture- and air-sensitive yellow crystalline solid. It is soluble in polar solvent such as THF, MeCN and CH₂Cl₂. Compound **3.6** was characterized by NMR spectroscopy and X-

ray crystallography. Its ^1H NMR spectrum exhibits a singlet at δ 1.45 ppm for the *t*Bu substituents, a set of signals [δ 7.27–7.38 (multiplet); 7.49 (triplet); 7.57 (triplet); 7.70 (doublet) ppm] for the phenyl protons and another singlet at δ 8.58 ppm for the CH=N protons. These results are consistent with the solid state structure (Figure 3.5). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a signal at δ –4.85 ppm corresponding to PPh_3 , which is comparable to $(\text{Ph}_3\text{P})_2\text{CuI}$ ($^{31}\text{P}\{^1\text{H}\}$ NMR = δ –5 ppm).⁴¹

Figure 3.5 Molecular structure of **3.6** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Ge1 1.945(6), Ge1–Cl1 2.2847(16), Ge1–Cu1 2.3385(9), Cu1–I1 2.5142(8), Cu1–P1 2.2356(15), C17–P1 1.818(6), C23–P1 1.805(6), C29–P1 1.828(6); C1–Ge1–Cl1 99.56(17), C1–Ge1–Cu1 139.50(17), Cu1–Ge1–Cl1 120.87(5), I1–Cu1–Ge1 109.79(3), P1–Cu1–I1 117.81(5), P1–Cu1–Ge1 132.23(5), C17–P1–Cu1 111.21(18), C23–P1–Cu1 116.0(2), C29–P1–Cu1 116.92(19), C17–P1–C23 104.1(3), C23–P1–C29 105.0(3).

The molecular structure of **3.6** (Figure 3.5) illustrates that the copper and germanium atoms adopt a trigonal planar (sum of bond angles = 359.8°) and pseudo trigonal pyramidal geometry, respectively. The bond lengths around the germanium atom (C1–Ge1: 1.945(6) Å; Ge1–Cl1: 2.2847(16) Å; Ge1–Cu1: 2.3385(9) Å; Cu1–I1: 2.5142(8) Å) are comparable to those of compounds **3.4** (C–Ge: 1.943(5) Å; Ge–Cl: 2.2388(12) Å; Ge–Cu: 2.2679(8) Å) and **3.5** (C–Ge: 1.965(9) Å; Ge–Cl: 2.276(2) Å; Ge–Cu: 2.3029(17) Å; Cu–I: 2.521(2), 2.572(2) Å). The Cu1–P1 bond length (2.2356(15) Å) is comparable to that of the phosphine-copper(I) complexes **3.XXXXXVIII** (Chart 3.7, Cu–P: 2.2138(15) Å),⁴² **3.XXXXXIX** (Chart 3.7, Cu–P: 2.2001(11) Å),⁴³ **3.XXXXXX** (Chart 3.7, Cu–P: 2.2277(8), 2.2254(7) Å),⁴⁴ and **3.XXXXXXI** (Chart 3.7, Cu–P: 2.259(2), 2.267(1), 2.220(1) Å).⁴⁵ These show that the P1–Cu1 bond is a coordinative covalent bond.

Chart 3.7 Examples of triphenylphosphine coordinated copper complexes

3.2.7 Synthesis of $[L^{tBu}(Cl)GeAuI]$

Scheme 3.7 Synthesis of **3.7**

In contrast, the reaction of **3.1** with AuI in $MeCN$ at room temperature, afforded the monomeric 2,6-bis(imino)phenyl chlorogermylene-gold(I) complex $[L^{tBu}(Cl)GeAuI]$ (**3.7**, Scheme 3.7), in 53% yield. It was isolated as an extremely moisture- and air-sensitive colourless crystalline solid. It is soluble in toluene, THF and $MeCN$. Compound **3.7** was characterized by NMR spectroscopy and X-ray crystallography. Its 1H NMR spectrum exhibits a singlet at δ 1.68 ppm for the tBu substituents, a triplet at δ 7.46 ppm and a doublet at δ 7.72 ppm for the phenyl protons and another singlet at δ 8.86 ppm for the $CH=N$ protons. These results suggest that the imino substituents are chemically equivalent in solution but otherwise in the solid state structure (Figure 3.6).

Figure 3.6 Molecular structure of **3.7** with thermal ellipsoids at the 50% probability level.

Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Ge1 1.826(11), N2–Ge1 2.229(11), Ge1–Cl1 2.216(7), Ge1–Au1 2.356(5), Au1–I1 2.561(2), C1–Ge1–N2 79.2(5), C–Ge1–Cl1 104.8(6), C1–Ge1–Au1 131.1(6), N2–Ge1–Cl1 90.0(4), N2–Ge1–Au1 98.6(4), Ge1–Au1–I1 171.46(17), Au1–Ge1–Cl1 124.1(3).

The molecular structure of **3.7** (Figure 3.6) illustrates that the germanium atom adopts a distorted tetrahedral geometry (sum of bond angles = 274.15°), while the gold atom adopts an almost linear geometry (Ge1–Au1–I1: 171.46(17)°). The C1–Ge1 (1.826(11) Å), N2–Ge1 (2.229(11) Å) and Ge1–Cl1 (2.216(7) Å) bond lengths are shorter than those of **3.1** (C–Ge: 2.004(19) Å; N–Ge: 2.2981(17) Å, Ge–Cl: 2.3477(5) Å). The Ge1–Au1 (2.356(5) Å) and Au1–I1 (2.561(2) Å) bond lengths are comparable to those of the oxobis(germylene)-gold(I) complex (**3.XXVIII**, Chart 3.3, Ge–Au: 2.347(2), 2.345(2) Å; Au–I: 2.577(1), 2.582(1) Å)²⁷ and the base-stabilized chlorogermylene-gold(I) complex [Ge(AuI){N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Cl] (**3.XXIV**, Chart 3.3, Ge–Au: 2.346(2) Å; Au–I: 2.561(1) Å)²¹.

3.2.8 Synthesis of $[L^{tBu}(Cl)GeAuI(PPh_3)]_2$

Scheme 3.8 Synthesis of **3.8**

The reaction of **3.7** with PPh_3 in THF at room temperature afforded the rare example of a gold(I) complex $[L^{tBu}(Cl)GeAuI(PPh_3)]$ comprising both germylene and phosphine ligands (**3.8**, Scheme 3.8), in 62% yield. In contrast, research groups of Schmidbaur and Sharp show that $(\text{Ph}_3\text{P})\text{AuCl}$ underwent an oxidative addition with GeCl_2 -dioxane and $\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2$ to form $(\text{Ph}_3\text{P})\text{AuGeCl}_3$ and $(\text{Ph}_3\text{P})\text{AuGe}(\text{Cl})\{\text{N}(\text{SiMe}_3)_2\}_2$, respectively.⁴⁶⁻⁴⁷

Compound **3.8** was isolated as an extremely moisture- and air-sensitive yellow crystalline solid. It is soluble in THF and MeCN. Compound **3.8** was characterized by NMR spectroscopy and X-ray crystallography. Its ^1H NMR spectrum exhibits a singlet at δ 1.55 ppm for the *t*Bu substituents, a multiplet at δ 7.38–7.58 ppm and a doublet at δ 7.79 ppm for the phenyl protons and another singlet at δ 8.70 ppm for the $\text{CH}=\text{N}$ protons. These results suggest that the imino substituents are chemically equivalent in solution but otherwise in the solid state structure (Figure 3.7). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a signal at δ 28.30 ppm corresponding to PPh_3 , which is comparable to that of the phosphine-stabilized Au(I)-Ge(IV) complex $(\text{Ph}_3\text{P})_3\text{AuGeCl}_3$ ($^{31}\text{P}\{^1\text{H}\}$ NMR = δ 27.2 ppm).⁴⁶

Figure 3.7 Molecular structure of **3.8** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Ge1 1.942(4), N1–Ge1 2.292(3), Ge1–Cl1 2.2649(10), Ge1–Au1 2.4144(4), Au1–I1 2.7720(3), Au1–P1 2.3037(9), C29–P1 1.827(4), C23–P1 1.819(4), C17–P1 1.817(4); C1–Ge1–N1 77.96(13), C1–Ge1–Cl1 101.68(10), C1–Ge1–Au1 142.19(10), N1–Ge1–Cl1 91.55(8), N1–Ge1–Au1 103.69(8), Cl1–Ge1–Au1 115.92(3), Ge1–Au1–P1 138.59(3), Ge1–Au1–I1 105.114(12), I1–Au1–P1 116.18(2), Au1–P1–C29 113.12(12), Au1–P1–C23 117.36(12), Au1–P1–C17 111.07(12), C29–P1–C23 106.02(16), C23–P1–C17 105.16(17).

The molecular structure of **3.8** (Figure 3.7) illustrates that the germanium atom adopts a pseudo trigonal bipyramidal geometry, while the gold atom adopts a distorted trigonal planar geometry (sum of bond angles = 359.89°). The C1–Ge1 (1.942(4) Å), Ge1–Au1 (2.4144(4) Å), Ge1–Cl1 (2.2649(10) Å) and Ge1–N1 (2.292(3) Å) bond lengths are comparable to those of **3.7** (C–Ge: 1.826(11) Å; Ge–Au: 2.356(5) Å; Ge–Cl: 2.216(7) Å; Ge–N (2.229(11) Å). The Ge1···N2 distance (2.423(3) Å) shows that there is a weak

interaction between the Ge1 and N2 atoms. The Au1–P1 bond length (2.3037(9) Å) is comparable to that of the phosphine-Au(I)-Ge(IV) complexes (Ph₃P)AuGe(Cl){N(SiMe₃)₂}₂ (Au–P: 2.3177(13) Å),⁴⁷ and (Ph₃P)AuGeCl₃ (Au–P: 2.312(1) Å).⁴⁶ These show that the Au1–P1 bond is a coordinative covalent bond. The Au1–I1 bond length (2.7720(3) Å) is longer than that of **3.7** (Au–I: 2.577(1) Å) but it is comparable to that of the three-coordinate bis(triphenylphosphine)gold(I) complex, (PPh₃)₂AuI (Au–I: 2.754(1) Å).^{41, 48}

3.3 Conclusion

In conclusion, the reactivity of $[L^{tBu}GeCl]$ (**3.1**, $L^{tBu} = 2,6-(HCNtBu)_2C_6H_3$) towards group 11 metals have been explored. The reaction of **3.1** and AgOTf (OTf = $CF_3SO_3^-$) afforded the germylene-silver(I) complex $[{L^{tBu}(TfO)Ge}]_2Ag(OTf)$ (**3.2**). Further reaction of **3.2** with 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (I_{Me}) afforded the bis(germyliumylidene cation)-silver(I) complex $[{L^{tBu}(I_{Me})Ge}]_2Ag(OTf)OTf_2$ (**3.3(OTf)₂**). However, the reaction of **3.1** with $(CuOTf)_2 \cdot C_7H_8$ afforded $[L^{tBu}(Cl)GeCu(\mu-Cl)]_2$ (**3.4**) instead. Dimeric germylene-copper(I) $[L^{tBu}(Cl)GeCu(\mu-I)]_2$ (**3.5**) and monomeric gold(I) complexes $[L^{tBu}(Cl)GeAuI]$ (**3.7**) react with PPh_3 to afford copper(I) $[L^{tBu}(Cl)GeCuI(PPh_3)]$ (**3.6**) and gold(I) complexes $[L^{tBu}(Cl)GeAuI(PPh_3)]$ (**3.8**), respectively.

3.4 Experimental Section

General Procedures. All operations were conducted under an inert atmosphere of argon gas using standard Schlenk techniques. THF, toluene, and Et₂O were dried and distilled over Na/K alloy prior to use. CH₂Cl₂, 1,2-difluorobenzene and fluorobenzene were dried and distilled over CaH₂ prior to use. [L^{Bu}GeCl] (**3.1**) was prepared as described in the literature.³³ The ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H and ¹³C, CCl₄ for ¹⁹F and 85% H₃PO₄ for ³¹P. Elemental analyses were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

Synthesis of [(L^{Bu}(TfO)Ge)₂Ag(OTf)] (3.2**).** Toluene (20 mL) was added to a mixture of **3.1** (0.351 g, 1.00 mmol) and AgOTf (0.385 g, 1.50 mmol) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 15 h in the absence of sunlight. Solvent was removed under vacuum, and the residue was extracted with CH₂Cl₂. AgCl was filtered off, and the pale-yellow filtrate was concentrated to afford colourless crystals of **3.2**. (0.200 g, 31%). M.p.: 170 °C (dec.). Elemental analysis (%) calcd for C₃₆H₄₈AgCl₂F₉Ge₂N₄O₉S₃: C, 34.01; H, 3.81; N, 4.41; S, 7.57. Found: C, 34.05; H, 3.92; N, 4.34; S, 7.90. ¹H NMR (399.5 MHz, THF-*d*₈, 27.2 °C): δ 1.62 (s, 36H, C(CH₃)₃), 7.90 (s, 4H, Ph), 7.70 (t, ³J_{HH} = 7.55 Hz, 2H, Ph), 8.86 (s, 4H, CH=N). ¹³C{¹H} NMR (100.5 MHz, THF-*d*₈, 27.4 °C): δ 30.92 (CH₃), 60.97 (C(CH₃)₃), 120.6 (q, ³J_{CF} = 319.81 Hz, CF₃), 132.76, 140.28 (Ph), 161.99 ppm (C=N-C). ¹⁹F{¹H} NMR (375.9 MHz, THF-*d*₈, 27.0 °C): δ -78.61 ppm.

Synthesis of $[\text{L}^{\text{tBu}}(\text{Ime})\text{Ge}]_2\text{Ag}(\text{OTf})\text{OTf}_2$ (3.3**(OTf)₂).** Ime (0.127 g, 1.03 mmol) in toluene (10 mL) was added dropwise to **3.1** (0.636 g, 0.50 mmol) in toluene (20 mL) at room temperature. The resulting yellow solution was stirred for 15 h in the absence of sunlight. Solvent was removed under vacuum, and the residue was extracted with 1,2-difluorobenzene. Insoluble precipitate was filtered off and the yellow filtrate was concentrated to afford yellow crystals of **3.3**(OTf)₂ (0.300 g, 32%). M.p.: 207 °C (dec.). Elemental analysis (%) calcd for C₆₁H₇₈AgF₁₃Ge₂N₈O₉S₃: C, 44.04; H, 4.73; N, 6.74; S, 5.78. Found: C, 44.31; H, 4.49; N, 6.67; S, 5.47. ¹H NMR (399.5 MHz, CD₂Cl₂, 22.9 °C): δ 1.11 (s, 36H, C(CH₃)₃), 2.08 (s, 6H, N-CH₃), 2.27 (s, 6H, N-CH₃), 2.57 (s, 6H, N-CH₃), 4.28 (s, 6H, N-CH₃), 7.95 (t, ³J_{HH} = 7.55 Hz, 2H, Ph), 8.09 (d, ³J_{HH} = 319.81 Hz, 4H, Ph), 8.56 (s, 4H, CH=N). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, 23.2 °C): δ 9.23 (C-CH₃), 9.43 (C-CH₃), 31.15 (C(CH₃)₃), 33.70 (N-CH₃), 36.40 (N-CH₃), 60.56 (C(CH₃)₃), 116.47 (CF₃), 119.66, 122.86 (C=C), 126.05, 129.46, 130.29, 132.16 (Ph), 134.69, 138.16 (NCN), 160.80 ppm (C=N-C). ¹⁹F{¹H} NMR (375.9 MHz, CD₂Cl₂, 23.3 °C): δ -78.55 ppm.

Synthesis of $[\text{L}^{\text{tBu}}(\text{Cl})\text{GeCu}(\mu\text{-Cl})_2]$ (3.4**).** Fluorobenzene (30 mL) was added to a mixture of [LGeCl] (0.351 g, 1.00 mmol) and copper(I) trifluoromethane toluene complex (0.285 g, 0.55 mmol) at 0 °C. The reaction mixture was then warmed to room temperature and stirred overnight in the absence of sunlight. Insoluble precipitate was filtered and the orange solution was concentrated to approximately 5 mL. 1,2-difluorobenzene (10 mL) was added to the orange solution and concentrated to afford orange crystals of **3.4** (0.023 g, 5%). Mp: 260 °C (dec.). Elemental analysis (%) calcd for C₃₂H₄₆Cl₄Cu₂Ge₂N₄: C, 42.66; H, 5.15; N, 6.22. Found: C, 40.07; H, 5.05; N, 4.69. Attempts to obtain acceptable elemental analysis data for compound **3.4** failed as the sample decomposed at high temperatures. ¹H NMR (395.9 MHz, CD₂Cl₂, 24.6 °C): δ 1.64 (s, 36H, C(CH₃)₃), 7.67 (t, ³J_{HH} = 7.46 Hz, 2H, *p*-

Ph), 7.79 (d, $^3J_{\text{HH}} = 7.68$ Hz, 4H, *m*-Ph), 8.56 (s, 4H, $\text{CH}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: Due to poor solubility of crystals, $^{13}\text{C}\{^1\text{H}\}$ NMR could not be obtained.

Synthesis of $[\text{L}^{\text{tBu}}(\text{Cl})\text{GeCu}(\mu\text{-I})_2]$ (3.5**).** Acetonitrile (50 mL) was added to a mixture of $[\text{L}^{\text{tBu}}\text{GeCl}]$ (0.702 g, 2.00 mmol) and CuI (0.419 g, 2.20 mmol) at room temperature and stirred overnight in the absence of sunlight. Insoluble precipitate was filtered off and the orange filtrate was concentrated to afford orange crystals of **3.5** (0.17 g, 16%). M.p.: 270 °C (dec.). Elemental analysis (%) calcd for $\text{C}_{33}\text{H}_{48}\text{Cl}_4\text{Cu}_2\text{Ge}_2\text{N}_4\text{I}_2$: C, 33.91; H, 4.14; N, 4.80. Found: C, 34.01; H, 3.95; N, 4.44. ^1H NMR (395.9 MHz, $\text{THF-}d_8$, 25.3 °C): δ 1.60 (s, 36H, $\text{C}(\text{CH}_3)_3$), 7.54 (t, $^3J_{\text{HH}} = 7.48$ Hz, 2H, *p*-Ph), 7.75 (d, $^3J_{\text{HH}} = 7.68$ Hz, 4H, *m*-Ph), 8.64 (s, 4H, $\text{CH}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, $\text{THF-}d_8$, 24.5 °C): δ 31.40 (CH_3), 60.25 ($\text{C}(\text{CH}_3)_3$), 130.33, 131.58, 140.34 (Ph), 159.33 ppm ($\text{C}=\text{N}-\text{C}$).

Synthesis of $[\text{L}^{\text{tBu}}(\text{Cl})\text{GeCuI}(\text{PPh}_3)]_2$ (3.6**).** THF (30 mL) was added to a mixture of **3.5** (0.217 g, 0.20 mmol) and PPh_3 (0.105 g, 0.4 mmol) and stirred overnight at room temperature. Insoluble precipitate was filtered off and the orange filtrate was concentrated to afford yellow crystals of **3.6** (0.267 g, 76%). M.p.: 238 °C. Elemental analysis (%) calcd for $\text{C}_{34}\text{H}_{38}\text{ClCuGeIN}_2\text{P}$: C, 50.78; H, 4.76; N, 3.48. Found: C, 50.52; H, 4.21; N, 3.83. ^1H NMR (399.5 MHz, $\text{THF-}d_8$, 23.9 °C): δ 1.45 (s, 18H, $\text{C}(\text{CH}_3)_3$), 7.27–7.38 (m, 9H, Ph), 7.49 (t, $^3J_{\text{HH}} = 7.31$ Hz, 1H, Ph), 7.57 (t, $^3J_{\text{HH}} = 8.91$ Hz, 6H, Ph), 7.70 (d, $^3J_{\text{HH}} = 7.31$ Hz, 2H, Ph), 8.58 (s, 2H, $\text{CH}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, $\text{THF-}d_8$, 24.3 °C): δ 31.00 (CH_3), 59.78 ($\text{C}(\text{CH}_3)_3$), 129.08 (d, $^3J_{\text{HH}} = 9.58$ MHz, Ph), 129.44, 130.37, 131.19, 133.61, 133.92 (Ph), 134.94 (d, $^3J_{\text{PC}} = 12.37$ Hz, Ph), 141.19 (Ph), 159.30 ppm ($\text{C}=\text{N}-\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, $\text{THF-}d_8$, 24.5 °C): δ -4.85 ppm.

Synthesis of $[L^{tBu}(Cl)GeAuI]$ (3.7**).** Acetonitrile (20 mL) was added to a mixture of $[L^{tBu}GeCl]$ (0.351 g, 1.00 mmol) and AuI (0.323 g, 1.00 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 h in the absence of sunlight. Insoluble precipitate was filtered off and the yellow filtrate was concentrated to afford colourless crystals of **3.7** (0.355 g, 53%). M.p.: 188 °C. Elemental analysis (%) calcd for $C_{16}H_{23}N_2AuClGeI$: C, 28.45; H, 3.43; N, 4.15. Found: C, 28.51; H, 3.56; N, 3.83. 1H NMR (395.9 MHz, THF- d_8 , 25.1 °C): δ 1.68 (s, 18H, $C(CH_3)_3$), 7.72 (t, $^3J_{HH} = 7.46$ Hz, 1H, *p*-Ph), 7.93 (d, $^3J_{HH} = 7.72$ Hz, 2H, *m*-Ph), 8.86 (s, 2H, $CH=N$). $^{13}C\{^1H\}$ NMR (99.5 MHz, THF- d_8 , 25.7 °C): δ 31.49 (CH_3), 61.29 ($C(CH_3)_3$), 132.65, 133.10, 138.98, 146.50 (Ph), 160.23 ppm ($C=N-C$).

Synthesis of $[L^{tBu}(Cl)GeAuI(PPh_3)]_2$ (3.8**).** THF (40 mL) was added to a mixture of **3.7** (0.270 g, 0.40 mmol) and PPh_3 (0.105 g, 0.40 mmol) at room temperature and stirred overnight. Insoluble precipitate was filtered off and the orange filtrate was concentrated to afford orange crystals of **3.8** (0.250 g, 62%). M.p.: 214 °C. Elemental analysis (%) calcd for $C_{38}H_{46}N_2AuClGeIOP$: C, 45.20; H, 4.59; N, 2.78. Found: C, 44.88; H, 4.50; N, 2.37. 1H NMR (399.5 MHz, THF- d_8 , 24.3 °C): δ 1.55 (s, 18H, $C(CH_3)_3$), 7.38–7.58 (m, 16H, Ph), 7.79 (d, $^3J_{HH} = 7.31$ Hz, 2H, Ph), 8.70 (s, 2H, $CH=N$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF- d_8 , 22.7 °C): δ 31.09 (CH_3), 60.46 ($C(CH_3)_3$), 129.50 (d, $^3J_{PC} = 10.55$ Hz, Ph), 130.86, 131.19, 132.03, 133.29, 133.65 (Ph), 134.72 (d, $^3J_{PC} = 15.33$ Hz, Ph), 139.99 (Ph), 159.67 ppm ($C=N-C$). $^{31}P\{^1H\}$ NMR (161.7 MHz, THF- d_8 , 22.9 °C): δ 28.30 ppm.

3.5 References

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Chapter 4.

Synthesis of an N-Heterocyclic-Carbene-Stabilized Siladiimide[†]

4.1 Introduction

Heavier group 14 compounds containing two double bonds of composition $E=M=E$ ($M = \text{Si, Ge, Sn, Pb}$; $E = \text{O, S, NR, PR, or } MR_2$; $R = \text{supporting substituent}$) are rare.¹⁻⁶ Theoretical studies show that such compounds are highly unstable due to the presence of two reactive $M=E$ double bonds, which lead to oligomerization or rearrangement easily because of the lesser kinetic stabilization at the central M atoms. As a result, it is a formidable challenge to isolate a stable $E=M=E$ moiety. Until now, only three groups of compounds containing an $E=M=E$ skeleton have been isolated using different strategies. One of them is the heavier allene analogues $[\{H_2CC(SiMe_3)_2\}_2M=M=M\{C(SiMe_3)_2CH_2\}_2]$ (**4.I**, Chart 4.1),⁷⁻¹⁰ in which the central two-coordinate M atom of the allene skeletons is strongly bent. Another one is the heavier base-stabilized 2-allene analogues $[(PPh_2S)_2C=M=C(PPh_2S)_2]$ (**4.II**, Chart 4.1),¹¹⁻¹³ in which the four-coordinate M atom is stabilized by two thiophosphinoyl substituents. Therefore, it is indispensable to look for novel synthetic strategies for the isolation of other stable $E=M=E$ moieties.

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Chart 4.1 Compounds containing E=M=E skeleton

Recently, the third strategy using base-stabilized group 14 element(0) complexes to construct a E=M=E skeleton has been developing. Base-stabilized group 14 element(0) complexes are divided into two groups.¹⁴⁻¹⁵ The first group is the diatomic group 14 element(0) moieties :M=M:, which comprise a M=M double bond and a lone pair of electrons on each M atom, stabilized by coordinating with two N-heterocyclic carbenes (NHCs) or N-heterocyclic silylenes [LSiN(SiMe₃)₂] [L = PhC(N*t*Bu)₂] or cyclic alkylaminocarbenes (cAACs) (Chart 4.2).¹⁶⁻²⁰

Chart 4.2 Examples of diatomic group 14 element(0) moieties

Another group is monoatomic group 14 element(0) moieties, which retain their valence electrons as two lone pairs. They were synthesized by coordinating with the

bis(NHC) ligand [$\text{bis(NHC)} = \text{H}_2\text{C}[\{\text{NC(H)C(H)N(Ar)}\}\text{C:}]_2$] or cyclic alkylaminocarbenes (cAACs) to form silylones and germylones of composition $[\{\text{bis(NHC)}\} \rightarrow \text{M}]$ or $[\text{cAAC} \rightleftharpoons \text{M} \rightleftharpoons \text{cAAC}]$ ($\text{M} = \text{Si}, \text{Ge}$), respectively (Chart 4.3).²¹⁻²⁵

Chart 4.3 Examples of monoatomic group 14 element (0) moieties

These group 14 element(0) complexes serve as a synthon to provide a “ M^0 ” moiety, which comprises two lone pairs of electrons and can undergo oxidation reactions to afford a stable $\text{E}=\text{M}=\text{E}$ skeleton. The feasibility of this strategy was illustrated by Driess et al. for the silicon and germanium derivatives, in which treatment of the bis(NHC)-stabilized silylone or germylone with GaCl_3 , followed by oxidation with elemental chalcogens (S, Se, Te), afforded the bis(NHC)/ GaCl_3 -stabilized monomeric silicon or germanium chalcogenide complexes $[\text{bis(NHC)} \rightarrow \text{ME}_2 \rightarrow \text{GaCl}_3]$ ($\text{M} = \text{Si}, \text{Ge}$; $\text{E} = \text{S}, \text{Se}$) or $[\text{bis(NHC)} \rightarrow \text{SiTe}_2]$ (Scheme 4.1).²⁶⁻²⁸

Scheme 4.1 Synthesis of a bis(NHC)/GaCl₃-stabilized monomeric group 14 chalcogenide complexes

In contrast, research groups of Robinson and Roesky showed that oxidation of NHC or cAAC-stabilized disilicon(0) compounds with O₂ or elemental chalcogens cannot afford the monomeric silicon dichalcogenide [NHC→SiE₂] or [cAAC→SiE₂] (E = O, S, Se), respectively, but instead dimeric derivatives were formed (Scheme 4.2 – Scheme 4.3).²⁹⁻³¹

Scheme 4.2 Reaction of NHC stabilized disilicon(0) with O₂

Scheme 4.3 Reaction of cAAC-stabilized disilicon(0) compounds with elemental sulfur or selenium

Previously, our research group successfully isolated the first siladithiocarboxylate $[\{\text{PhC}(\text{N}t\text{Bu})_2\text{Si}(\text{S})_2\}\text{K}(\text{THF})_2]_2$ (**4.XXII**) by the reaction of the amidinate-stabilized silylene $[\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}]$ (**4.XXI**) with two equivalents of elemental sulfur and four equivalents of KC_8 in THF (Scheme 4.4).³² More recently, Roesky et al. also isolated a 1,3-diphospha-2-silaallyl anion (**4.XXIII**) by the reaction of the amidinate-stabilized silylene (**4.XXI**) with two equivalents of 2,4,6-*i*Pr₃C₆H₂PCl₂ and six equivalents of KC_8 in the presence of one equivalent of 18-crown-6 (Scheme 4.5).³³

Scheme 4.4 Synthesis of siladithiocarboxylate

Scheme 4.5 Synthesis of a 1,3-diphospha-2-silaallyl anion

In Chapters 1, 2 and 3, we have utilized the bis(imino)phenyl ligands to synthesize group 13 and group 14 metal complexes. In continuation of our research using bis(imino)phenyl ligands, we were interested in isolating a 2-silaamidinate anion (**4.XXIV**, Scheme 4.6) using the bis(imino)phenyl ligand system. However, attempts to synthesize any bis(imino)phenyl coordinated silicon complexes failed. Hence, we decided to use the NHC-stabilized disilicon(0) compound as a synthon to isolate a siladiimide $\text{RN}=\text{Si}=\text{NR}$, which then reacts with $\text{L}^{\text{R}}\text{Li}$ ($\text{L}^{\text{R}} = \text{C}_6\text{H}_3\text{-2,6-(HC=NR)}_2$; $\text{R} = t\text{Bu}$, Ar or Ar^* ; $\text{Ar}^* = 4\text{-Me-2,6-CHPh}_2\text{-C}_6\text{H}_2$) to form **4.XXIV** (Scheme 4.6). However, stable siladiimides, which comprise two $\text{Si}=\text{N}$ double bonds, are rare. Only $[\text{Me}_3\text{SiN}=\text{Si}=\text{NSiMe}_3]$ was observed in the low-temperature matrix by West et al.³⁴ Its existence was evidenced by UV-vis spectroscopy and trapping experiments. In this context, we are interested in investigating whether a room-temperature-stable siladiimide can be isolated.

Scheme 4.6 Failed attempts to synthesize bisimino(phenyl) silicon complexes

Herein, we report the synthesis of an NHC-stabilized monomeric siladiimide, which possesses strong Si=N double-bond character, from the oxidation of a disilicon(0) complex.

4.2 Results and Discussion

4.2.1 Synthesis of the NHC-stabilized siladiimide

Scheme 4.7 Synthesis of **4.2**

The reaction of the NHC-stabilized disilicon(0) complex $[\text{IPr} \rightarrow \text{Si}=\text{Si} \leftarrow \text{IPr}]$ (**4.1**; $\text{IPr} = :\text{C}\{\text{N}(\text{Ar})\text{CH}\}_2$)¹⁶ with ArN_3 in THF at room temperature afforded a mixture of the NHC-stabilized siladiimide $[\text{ArNSi}(\text{IPr})\text{NAr}]$ (**4.2**, Scheme 4.7) and the free carbene IPr, which was confirmed by NMR spectroscopy. Although compound **4.1** was isolated along with around 5% of IPr (see appendix for the spectrum of compound **4.1**), the formation of IPr in the synthesis of compound **4.2** should be due to the displacement of IPr during the oxidation of compound **4.1** with ArN_3 . Furthermore, a small amount of triazene $[\{\text{CHN}(\text{Ar})\}_2\text{CN}_3\text{Ar}]$ (**4.3**, yield 8.7%, Scheme 4.7) was observed in the reaction mixture. It is suggested that the free carbene IPr formed in the reaction subsequently reacted with ArN_3 to form **4.3** (see Scheme 4.8 for mechanism). The reaction mixture was filtered, and the filtrate was concentrated to afford a mixture of compound **4.2** and the free carbene IPr, which was isolated as air- and moisture-sensitive orange cocrystals of compound **4.2**·IPr (yield 34.6%). An attempt to separate compound **4.2** and the free carbene IPr by recrystallization failed. It is postulated that if all free carbene IPr formed in the reaction can be consumed by ArN_3 to form **4.3**, pure compound **4.2** may be isolated. As such, compound **4.1** was treated with excess ArN_3 in THF at room temperature, and a mixture of compounds **4.2** and **4.3** was afforded. However, only a few pieces (ca. 3–7 pieces) of yellow crystals

of **4.2** can be isolated by recrystallization from the reaction mixture in THF, enabling us to characterize compound **4.2** by IR spectroscopy and X-ray crystallography only.

Our group has recently isolated a dimeric NHC-silicon monotelluride from the reaction of **4.1** and tellurium.³⁵ With reference to the reaction mechanism of the formation of the NHC-silicon monotelluride, we suggest that the formation of **4.2** undergoes a similar reaction mechanism. Two equivalents of 2,6-diisopropylphenyl azide reacted with **4.1** to form **4.1A**, which then isomerized to form **4.1B**, as the Si=Si bond is believed to be weak, similar to those of the dimeric NHC-silicon monotelluride (Si=Si: 2.343(14)Å), which is longer than the Si=Si bond lengths (2.144 – 2.2890(14) Å)³⁶ reported. The Si–Si bond would be broken to form a stable form of **4.2** (Scheme 4.8).

Scheme 4.8 Proposed mechanism for the formation of **4.2** and **4.3**

Orange crystals of **4.2·IPr** decomposed at 215 °C. They were analyzed by NMR spectroscopy. On the basis of the ^1H and ^{13}C NMR resonances of **IPr**, the NMR resonances

of **4.2** can be identified in the spectra. The ^1H NMR spectrum of **4.2·IPr** shows a set of resonances due to the ligand backbone of **4.2**. The ^{13}C NMR spectrum of **4.2·IPr** shows a signal for the Si-bonded C_{NHC} atom of **4.2** (δ 145.7 ppm), which is upfield-shifted compared to that of compound **4.1** (δ 196.3 ppm).¹⁶ The signal is intermediate between that of IPr (δ 220.6 ppm) and the imidazolium salt [IPr-H]Cl (δ 139.3 ppm).³⁷ The ^{29}Si NMR spectrum of **4.2·IPr** shows a resonance (δ -65.0 ppm) for **4.2** that is upfield-shifted compared with the dimeric silaisonitrile $[\text{Ar}'\text{NSi:}]_2$ [**4.XXV**, $\text{Ar}' = 2,6\text{-bis}(2,4,6\text{-triisopropylphenyl})\text{phenyl}$, Chart 4.4, δ 183.3 ppm] and the $\text{Ar}'\text{NSi}=\text{N}$ moiety of the bis(silaimine) $[\text{Ar}'\text{NSi}=\text{NSiMe}_3]_2$ (**4.XXVI**, Chart 4.4, δ -56.8 ppm).³⁸ The upfield Si NMR signal implies that the allylic $\text{N}=\text{Si}^+-\text{N}^-$ skeleton (see Scheme 4.9) leads to a much stronger electron donating effect of IPr to the Si center.

Chart 4.4 Example of a dimeric silaisonitrile (**4.XXV**) and a bis(silaimine) (**4.XXVI**)

Compound **4.2·IPr** was characterized by X-ray crystallography. Due to its small crystal size ($0.14 \times 0.18 \times 0.22$ mm), the $R1$ (all data) value obtained for compound **4.2·IPr** is large (15.2%). The molecular structure of **4.2·IPr** (Figure 4.1) shows that the Si1 atom adopts a distorted trigonal-planar geometry with a $\text{N}-\text{Si}-\text{N}$ bond angle of $146.84(19)^\circ$. The $\text{Si}-\text{N}$ bonds ($1.591(3)$ and $1.594(3)$ Å) are significantly shorter than the $\text{Si}-\text{N}$ single bonds

in $[\text{Ar}'\text{NSi:}]_2$ (**4.XXV**, Chart 4.4, Si–N: 1.755(1) Å), but they are comparable to the Si=N double bonds in $[\text{Ar}'\text{NSi}=\text{NSiMe}_3]_2$ (**4.XXVI**, Chart 4.4, Si=N: 1.564(2) Å).³⁸ This indicates that the Si–N bonds in **4.2** have considerable double-bond character. The C25–Si1 (1.887(4) Å) bond length is shorter than those of compound **4.1** (C–Si: 1.9271(15) Å)¹⁶ and is comparable to normal Si–C single bonds (1.87–1.91 Å).³⁹

Figure 4.1 Molecular structure of **4.2·IPr** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–N1 1.591(3), Si1–N2 1.594(3), Si1–C25 1.887(4), N3–C25 1.362(4), N4–C25 1.352(5), N5–C52 1.376(4), N6–C52 1.375(5); N2–Si1–N1 146.71(17), C25–Si1–N1 107.16(15), C25–Si1–N2 106.11(16), N5–C52–N6 100.0(3).

The molecular structure of compound **4.2** (Figure 4.2) is comparable to that of **4.2·IPr**. Similarly, due to its small crystal size (0.01 × 0.30 × 0.40 mm), the R1 (all data) value obtained for compound **4.2** is large (14.7%). The Si1 atom in compound **4.2** adopts a trigonal-planar geometry. The C25–Si1 (1.889(5) Å), N1–Si1 (1.591(5) Å), and N2–Si1 (1.593(5) Å) bonds are comparable to those of **4.2·IPr** (Si–C: 1.887(4); Si–N: 1.591(3),

1.594(3) Å). The N1–Si1–N2 bond angle is 147.7(2)°, which is similar to that of **4.2·IPr** (146.71(17)°).

Figure 4.2 Molecular structure of **4.2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C25–Si1 1.889(5), N1–Si1 1.591(5), N2–Si1 1.593(5); N1–Si1–C25 102.7(3), N2–Si1–C25 109.5(2), N1–Si1–N2 147.7(2).

Compound **4.2** was analysed by IR spectroscopy. The IR signal for the SiN stretch ($\nu(\text{SiN}) = 1461 \text{ cm}^{-1}$, see appendix), which is consistent with the theoretical value of 1447 cm^{-1} (Si–N unsymmetric stretch and C–H bending; see appendix), shows a hypsochromic shift compared with that of $[\textit{t}\text{Bu}_2\text{Si}=\text{N}-\text{Si}\textit{t}\text{Bu}_3]$ (1326 cm^{-1}).⁴⁰ This indicates that the Si–N bonds in **4.2** possess strong multiple-bond character.

4.3 Theoretical calculations for compound 4.2

Compound **4.2** was investigated using DFT⁴¹⁻⁴² B3PW91⁴³⁻⁴⁴ method with the 6-31G* level. All calculations were carried out using the Gaussian 09 packages.⁴⁵ There is no imaginary frequency in the structure. The absolute energy is -2493.25253 Hartree. The NBO analyses were performed using the NBO 3.1 program at the same level. The optimized geometry is in good agreement with the X-ray crystallographic data of **4.2**.

Figure 4.3 Calculated molecular structure of **4.2**. Hydrogen atoms are omitted for clarity.

Selected bond lengths (Å) and angles (deg): C25–Si1 1.920, N1–Si1 1.610, N2–Si1 1.602, N1–Si1–C25 105.86, N2–Si1–C25 105.63, N1–Si1–N2 148.36.

Table 4.1 Comparison of experimental and calculated bond lengths and angles

	Experimental bond lengths (Å) and angles (°)	Calculated bond lengths (Å) and angles (°)
C25–Si1	1.889(5)	1.920
N1–Si1	1.591(5)	1.610
N2–Si1	1.593(5)	1.602
N1–Si1–C25	102.7(3)	105.86
N2–Si1–C25	109.5(2)	105.63
N1–Si1–N2	147.7(2)	148.36

The HOMO–4, HOMO, and LUMO (Figure 4.4) primarily show the allylic π -type molecular orbitals of the NSiN skeleton. In addition, the HOMO shows that one of the lone-pair orbitals on the N atoms interacts with the C–Si σ^* orbital (natural bond orbital second-order perturbation energy: 12.7 kcal mol^{–1}). The LUMO also shows the C–Si π orbital. Moreover, the Wiberg bond indices (WBI) of the Si–N bonds in **4.2** (WBI: 1.14 and 1.17) are larger than those in N(SiMe₃)-2,6-*i*Pr₂C₆H₃Si(SH)₃ (WBI at M06-2X/def2-TZVPP levels: 0.56 (Si_{SiMe}–N); 0.61 (Si_{SiS}–N)),⁴⁶ which implies that the Si–N bonds in **4.2** possess some multiple-bond character, which is consistent with their bond lengths. The WBI value of the C–Si bond is 0.64. The bond dissociation energy of the C–Si bond is 159 kJ mol^{–1}, which is smaller than those of alkylsilanes (ca. 370 kJ mol^{–1}).⁴⁷ These suggest that the C–Si bond is labile. Moreover, the natural population analysis charges of the N atoms in the N1–Si1–N2 skeleton are –1.14 and –1.15, while those of the C25 and Si1 atoms are 0.06 and 1.86, respectively.

Figure 4.4 Selected molecular orbitals of **4.2** (isovalue = 0.02)

Thus, from the results of NMR spectroscopy, IR spectroscopy, X-ray crystallography, and theoretical studies, the NSiN skeleton is dominated by the allylic-like skeleton and the negative hyperconjugation between the lone pairs at the N_{imine} atom and the C-Si σ^* orbital (Scheme 4.9).

Scheme 4.9 Resonance structures of **4.2**

4.4 Conclusion

In conclusion, the NHC-stabilized siladiimide [ArNSi(IPr)NAr] (**4.2**) was prepared by simple procedures. The N–Si–N skeleton in **4.2** possesses considerable double-bond character, and the Si atom is three-coordinate. The reaction of **4.2** with $\mathbf{L^R Li}$ is currently under investigation and the results will be reported in due course.

4.5 Experimental Section

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF and toluene were dried and distilled over K prior to use. **4.1** was prepared as described in the literature.¹⁶ It contained around 5% of IPr, which was illustrated by the following ¹H NMR spectrum of **4.1** (see appendix). The ¹H, ¹³C and ²⁹Si spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si. Elemental analyses were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

Synthesis of 4.2·IPr. A solution of 2,6-diisopropylphenyl azide (0.061 g, 0.30 mmol) in THF (10 mL) was added dropwise to a solution of compound **4.1** (0.125 g, 0.15 mmol) in THF (8 mL). The red solution changed to blue-green upon addition and the resulting solution was stirred at room temperature for 3 hours to afford an orange solution. The solution was filtered and the filtrate was concentrated to afford pale yellow crystals of **4.2·IPr** (0.06 g). Yield: 34.6 %. M.p.: 215 °C (dec.). Elemental analysis calcd (%) for C₇₈H₁₀₆N₆Si: C, 81.06; H, 9.25; N, 7.27. Found: C, 80.92; H, 9.08; N, 7.16. With reference to the ¹H and ¹³C NMR spectra of IPr, the NMR resonances of **4.2** can be identified. ¹H NMR: (395.9 MHz, C₆D₆, 25 °C): δ 0.89 (d, ³J_{H-H} = 6.80 Hz, 12H, CH(CH₃)₂), 1.11 (d, ³J_{H-H} = 6.77 Hz, 12H, CH(CH₃)₂), 1.18 (d, ³J_{H-H} = 6.77 Hz, 12H, CH(CH₃)₂), 1.27 (d, ³J_{H-H} = 6.80 Hz, 12H, CH(CH₃)₂), 2.97 (sept, ³J_{H-H} = 6.80 Hz, 4H, CH(CH₃)₂), 3.15 (sept, ³J_{H-H} = 6.80 Hz, 4H, CH(CH₃)₂), 6.19 (s, 2H, NCH), 6.88 (t, ³J_{H-H} = 7.46 Hz, 2H, Ph), 7.05 (t, ³J_{H-H} = 6.79 Hz, 2H, Ph), 7.17 (d, ³J_{H-H} = 7.68 Hz, 4H, Ph), 7.29 ppm (d, ³J_{H-H} = 7.24 Hz, 4H, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 25 °C): δ 22.69 (CH(CH₃)₂), 23.10 (CH(CH₃)₂), 24.54 (CH(CH₃)₂), 25.66 (CH(CH₃)₂), 28.04 (CH(CH₃)₂), 29.38 (CH(CH₃)₂), 117.25,

121.44, 122.28, 124.79, 125.40, 128.87, 131.77, 134.45 (Ph), 138.42 (CHN), 145.73 ppm (NCN). ^{29}Si NMR (78.65 MHz, C_6D_6): δ -65.0 ppm.

Synthesis of 4.2 and 4.3. A solution of 2,6-diisopropylphenyl azide (0.122 g, 0.60 mmol) in THF (10 mL) was added dropwise to a solution of **4.1** (0.125 g, 0.15 mmol) in THF (8 mL). The resulting solution was stirred at room temperature for 1 hour. Volatiles were removed under vacuo and the residue was extracted with toluene. The solution was filtered and the filtrate was concentrated to afford pale yellow crystals of compound **4.3** (0.107 g, 30 % yield). The residue was extracted with THF and the filtrate was concentrated to afford a few pieces (ca. 3 – 7 pieces) of yellow crystals of **4.2**.

4.2: IR (Nujol) ν = 721 (w), 747 (w), 756 (w), 800 (w), 937 (w), 1061 (w), 1103 (w), 1261 (w), 1377 (m, C-H bending at *i*Pr substituents), 1461 (m, unsymmetric N-Si-N stretch and C-H bending at NAr substituents), 2854 (s, unsymmetric C-H stretch of *i*Pr of NAr substituents), 2924 cm^{-1} (s, unsymmetric C-H stretch of *i*Pr at IPr).

4.3: M.p.: 241 °C. Elemental analysis (%) calcd for $\text{C}_{78}\text{H}_{106}\text{N}_{10}$: C, 79.10; H, 9.03; N, 11.80. Found: C, 78.86; H, 9.01; N, 11.72. ^1H NMR (395.9 MHz, C_6D_6 , 25 °C): δ 1.08 (d, $^3J_{\text{H-H}} = 6.77$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, $^3J_{\text{H-H}} = 6.80$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $^3J_{\text{H-H}} = 6.77$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.68 (sept, $^3J_{\text{H-H}} = 6.80$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.00 (sept, $^3J_{\text{H-H}} = 6.79$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 5.90 (s, 2H, NCH), 6.99–7.06 ppm (m, 9H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, C_6D_6 , 25 °C): δ 23.00 ($\text{CH}(\text{CH}_3)_2$), 23.38 ($\text{CH}(\text{CH}_3)_2$), 24.22 ($\text{CH}(\text{CH}_3)_2$), 27.02 ($\text{CH}(\text{CH}_3)_2$), 29.28 ($\text{CH}(\text{CH}_3)_2$), 117.58, 122.32, 124.02, 124.97, 129.97, 134.44, 139.75, 146.68 (Ph), 150.12 (CHN), 155.61 ppm (NCN).

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Appendix

X-ray Data Collection and Structural Refinement. Intensity data for compounds **1.1–1.5** were collected using a Bruker APEX II diffractometer. The crystals of **1.1–1.5** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .¹ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

1. Table S1.1 Crystallographic data for compounds 1.1 – 1.3

	1.1	1.2	1.3
Formula	C ₃₂ H ₄₆ InN ₄ Br	C ₃₉ H ₅₄ Cl ₂ In ₂ N ₄	C ₅₂ H ₇₉ Cl ₂ In ₃ N ₆ O
Mr	681.46	879.40	1219.57
Color	Colourless	Colourless	Yellow
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21/ <i>c</i> 1
<i>a</i> /Å	14.4630(19)	11.8468(7)	10.3040(7)
<i>b</i> /Å	14.2367(19)	17.2307(9)	30.128(2)
<i>c</i> /Å	16.4327(19)	20.1342(12)	19.0458(12)
α /deg	90	90	90
β /deg	103.070(4)	91.464(2)	100.4725(18)
γ /deg	90	90	90
<i>V</i> /Å ³	3295.9(7)	4108.6(4)	5814.1(7)
<i>Z</i>	4	4	4
<i>d</i> _{calcd} /g cm ^{−3}	1.373	1.422	1.393
μ / mm ^{−1}	1.955	1.283	1.310
<i>F</i> (000)	1400	1792	2488
Crystal size/ mm ³	0.180 x 0.200 x 0.210	0.320 x 0.400 x 0.420	0.120 x 0.140 x 0.260
Index range	−20 ≤ <i>h</i> ≤ 20	−18 ≤ <i>h</i> ≤ 18	−12 ≤ <i>h</i> ≤ 12,
	−20 ≤ <i>k</i> ≤ 20	−26 ≤ <i>k</i> ≤ 26	0 ≤ <i>k</i> ≤ 36
	−23 ≤ <i>l</i> ≤ 23	−27 ≤ <i>l</i> ≤ 31	0 ≤ <i>l</i> ≤ 22
No. of reflections collected	10446	95019	10508
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0696, 0.1210	0.0424, 0.0875	0.0764, 0.1707
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1492, 0.1532	0.0689, 0.0987	0.1286, 0.1893
GOF, <i>F</i> ²	0.974	1.027	1.028
no. of data/ restraints/ param	10446 / 175/ 386	16487 / 0/ 437	10508/ 89/ 627
largest diff peak, hole/ eÅ ^{−3}	1.881, −1.613	1.681, −1.279	1.591, −0.965

2. Table S1.2 Crystallographic data for compounds 1.4 – 1.5

	1.4	1.5
Formula	C ₁₄₈ H ₁₁₈ Br ₂ In ₂ N ₄	C ₁₄₈ H ₁₁₈ Br ₂ N ₄ Tl ₂
Mr	2341.92	2521.02
Color	Colourless	Colourless
Crystal System	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> /Å	15.4400(10)	15.2049(14)
<i>b</i> /Å	26.9225(18)	26.674(3)
<i>c</i> /Å	18.5891(12)	18.5110(18)
α /deg	90	90
β /deg	103.0891(18)	102.4090(19)
γ /deg	90	90
<i>V</i> /Å ³	7526.4(9)	7332.4(12)
<i>Z</i>	4	4
<i>d</i> _{calcd} /g cm ^{−3}	1.033	1.142
μ /mm ^{−1}	0.880	2.784
<i>F</i> (000)	2404	2532
Crystal size/ mm ³	0.360 x 0.240 x 0.140	0.320 x 0.120 x 0.060
Index range	−21 ≤ <i>h</i> ≤ 20	−22 ≤ <i>h</i> ≤ 21,
	0 ≤ <i>k</i> ≤ 37	0 ≤ <i>k</i> ≤ 38
	0 ≤ <i>l</i> ≤ 25	0 ≤ <i>l</i> ≤ 26
No. of reflections collected	21352	23429
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0839, 0.2127	0.0772, 0.1434
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1889, 0.2742	0.1932, 0.1768
GOE, <i>F</i> ²	1.041	1.038
no. of data/ restraints/ param	21352/ 1138/ 840	23429/ 317/ 761
largest diff peak, hole/ eÅ ^{−3}	2.021, −2.088	5.388, −4.031

3. Molecular structure of $L^{tBu}InCl_2$

Figure S1.1 Molecular structure of $L^{tBu}InCl_2$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–In1 2.1297, N1–In1 2.5002, N2–In2 2.5066, C7–N1 1.2635, C12–N2 1.2944, In1–Cl1 2.3852, In1–Cl2 2.3787; C1–In1–N1 72.99, C1–In1–Cl1 123.28, C1–In1–Cl2 128.95, C1–In1–N2 74.20, N1–In1–Cl1 95.95, N1–In1–Cl2 102.25, N2–In1–Cl2 101.25, N2–In1–Cl1 98.64, Cl1–In1–Cl2 107.75.

4. NMR spectra of compounds $L^{tBu}InCl_2$, $L^{tBu}H$, 1.1 – 1.2, $L^{Ar^*}Br$ and 1.4 – 1.5

(a) ^1H NMR spectrum of $\text{L}^t\text{BuInCl}_2$

(b) ^1H NMR spectrum of L^tBuH

$[L^{tBu}_2In]^+Br^-$

$L^{tBu}InCl_2$

$L^{tBu}H$

$[L^{tBu}_2In]^+Br^-$

$[L^{tBu}_2In]^+Br^-$

$L^{tBu}H$

$L^{tBu}InCl_2$

$L^{tBu}H$

$[L^{tBu}_2In]^+Br^-$

$L^{tBu}InCl_2$

(c) 1H NMR spectrum of **1.1**

(d) ^1H NMR spectrum of **1.2**

(e) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1.2**

(f) ^1H NMR spectrum of $\text{L}^{\text{Ar}^*}\text{Br}$

(g) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{L}^{\text{Ar}^*}\text{Br}$

(h) ^1H NMR spectrum of **1.4**

(i) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1.4**

(j) ¹H NMR spectrum of **1.5**

(k) ¹³C{¹H} NMR spectrum of **1.5**

5. IR spectrum of compound 1.4

SHIMADZU

6. IR spectrum of compound 1.5

SHIMADZU

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2.1–2.3** were collected using a Bruker APEX II diffractometer. The crystals of **2.1–2.3** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .¹ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

7. Table S2.1 Crystallographic data for compounds 2.1 – 2.3

	2.1	2.2	2.3
Formula	C ₁₆ H ₂₃ ClGeN ₂	C ₃₂ H ₄₆ Ge ₂ N ₄	C ₃₂ H ₄₆ Ge ₂ Li ₂ N ₄
Mr	351.40	631.91	645.79
Color	Orange	Colourless	Dark Green
Crystal System	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> 21 21 21	<i>P</i> c c a
<i>a</i> /Å	8.7947(6)	8.5992(6)	15.099(4)
<i>b</i> /Å	16.4126(11)	18.2258(12)	10.770(3)
<i>c</i> /Å	11.7594(8)	20.4920(14)	20.223(5)
α /deg	90	90	90
β /deg	95.918(2)	90	90
γ /deg	90	90	90
<i>V</i> /Å ³	1688.4(2)	3211.7(4)	3288.6(14)
<i>Z</i>	4	4	4
<i>d</i> _{calcd} /g cm ⁻³	1.382	1.307	1.304
μ /mm ⁻¹	1.965	1.897	1.854
<i>F</i> (000)	728	1320	1344
Crystal size/ mm	0.180 x 0.220 x 0.420	0.200 x 0.220 x 0.420	0.200 x 0.220 x 0.420
Index range	-12 ≤ <i>h</i> ≤ 13 -24 ≤ <i>k</i> ≤ 24 -17 ≤ <i>l</i> ≤ 13	-6 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26 -29 ≤ <i>l</i> ≤ 29	-20 ≤ <i>h</i> ≤ 21 -15 ≤ <i>k</i> ≤ 13 -16 ≤ <i>l</i> ≤ 28
No. of reflections collected	29237	26890	23643
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0377, 0.0868	0.0353, 0.0646	0.0728, 0.1523
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0592, 0.0946	0.0494, 0.0684	0.1222, 0.1724
GOF, <i>F</i> ²	1.044	0.991	1.090
no. of data/ restraints/ param	5968/ 0/ 187	10261/ 0/ 356	5041/ 0/ 187
largest diff peak, hole/ eÅ ⁻³	1.104, -0.774	0.589, -0.339	1.868, -0.874

8. NMR spectra of compounds 2.1 – 2.3

(a) ^1H NMR spectrum of **2.1**

(b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2.1**

(c) ^1H NMR spectrum of **2.2**

(d) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2.2**

(e) ^1H NMR spectrum of **2.3**

(f) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2.3**

(g) ${}^7\text{Li}\{ {}^1\text{H} \}$ NMR spectrum of **2.3**

9. Table S2.2 Optimized geometries of compound 2.1

Standard orientation:

Atom	Coordinates (Angstroms)		
	X	Y	Z
Ge	-0.658933	-0.243546	0.000000
C	1.302235	-0.046117	0.000000
C	2.007358	-0.011467	-1.204831
C	3.406696	0.065021	-1.210749
H	3.955507	0.092286	-2.150957
C	4.100476	0.105170	0.000000
H	5.185516	0.169677	0.000000
C	3.406696	0.065021	1.210749
H	3.955507	0.092286	2.150957
C	2.007358	-0.011467	1.204831
C	1.194778	-0.096915	2.420132
H	1.698375	-0.143246	3.392115
C	-1.017149	-0.311788	3.406247
C	-0.375304	-0.165880	4.789453
H	0.370238	-0.945871	4.987039
H	-1.148776	-0.254588	5.559871
H	0.102101	0.814310	4.909877
C	-1.621051	-1.718015	3.246837
H	-2.076934	-1.826939	2.257885
H	-2.390734	-1.885886	4.009356
H	-0.850268	-2.490085	3.356031
C	-2.118112	0.740687	3.218342
H	-1.708501	1.753577	3.285783
H	-2.890508	0.618423	3.986420
H	-2.583699	0.639865	2.233706
C	1.194778	-0.096915	-2.420132
H	1.698375	-0.143246	-3.392115
C	-1.017149	-0.311788	-3.406247
C	-0.375304	-0.165880	-4.789453
H	0.102101	0.814310	-4.909877
H	-1.148776	-0.254588	-5.559871
H	0.370238	-0.945871	-4.987039
C	-2.118112	0.740687	-3.218342
H	-2.583699	0.639865	-2.233706
H	-2.890508	0.618423	-3.986420
H	-1.708501	1.753577	-3.285783
C	-1.621051	-1.718015	-3.246837
H	-0.850268	-2.490085	-3.356031
H	-2.390734	-1.885886	-4.009356
H	-2.076934	-1.826939	-2.257885
N	-0.076585	-0.143452	2.293104
N	-0.076585	-0.143452	-2.293104
Cl	-1.066113	2.030260	0.000000

10. Table S2.3 Optimized geometries of compound 2.2

Standard orientation:

Atom	Coordinates (Angstroms)		
	X	Y	Z
Ge	1.404564	-0.662153	0.259620
Ge	-1.405012	-0.661753	-0.261103
C	2.421223	0.982278	0.692729
C	3.802083	1.189075	0.822585
C	4.783931	0.148224	0.479301
H	5.811991	0.342000	0.820811
C	5.411822	-1.973586	-0.450593
C	5.326097	-2.228256	-1.963533
H	5.672087	-1.351985	-2.524527
H	4.291199	-2.433342	-2.255674
H	5.946955	-3.086129	-2.247915
C	6.868033	-1.695623	-0.056676
H	6.981879	-1.544328	1.023784
H	7.268349	-0.814546	-0.573718
H	7.492507	-2.552627	-0.332926
C	4.890712	-3.208164	0.305234
H	3.841913	-3.392629	0.052439
H	4.956549	-3.056216	1.389031
H	5.482055	-4.094582	0.044843
C	4.272233	2.421665	1.303759
H	5.343405	2.580524	1.422265
C	3.383596	3.448657	1.622566
H	3.762587	4.401240	1.985718
C	2.007780	3.249921	1.484320
H	1.312780	4.049497	1.738476
C	1.544790	2.009578	1.040923
C	0.099470	1.666172	0.780341
H	-0.588065	2.387662	1.237364
C	-0.578671	0.031807	2.602394
C	-2.019172	0.518169	2.817588
H	-2.721179	-0.036156	2.183309
H	-2.128322	1.583536	2.584168
H	-2.320604	0.375078	3.862533
C	0.359068	0.742329	3.589209
H	0.315343	1.832054	3.493045
H	1.400565	0.432507	3.453098
H	0.061145	0.491239	4.614167
C	-0.520550	-1.476317	2.876992
H	0.495700	-1.864631	2.746058
H	-1.179727	-2.032517	2.202011
H	-0.835043	-1.675139	3.908049
C	-0.099812	1.667523	-0.777912
H	0.587749	2.389804	-1.233656
C	-1.545133	2.011305	-1.038023

C	-2.008328	3.252244	-1.479517
H	-1.313470	4.052349	-1.732390
C	-3.384181	3.450961	-1.617504
H	-3.763295	4.404062	-1.979160
C	-4.272705	2.423352	-1.300370
H	-5.343891	2.582236	-1.418710
C	-3.802361	1.190110	-0.821100
C	-2.421478	0.983362	-0.691495
C	-4.783834	0.148399	-0.479377
H	-5.811860	0.341915	-0.821137
C	-5.410986	-1.974556	0.448471
C	-5.325715	-2.230391	1.961230
H	-5.671887	-1.354542	2.522777
H	-4.290902	-2.435665	2.253560
H	-5.946632	-3.088490	2.244777
C	-4.888996	-3.208227	-0.308207
H	-3.840082	-3.392188	-0.055538
H	-4.954878	-3.055584	-1.391899
H	-5.479750	-4.095232	-0.048449
C	-6.867189	-1.697003	0.054203
H	-6.980619	-1.544588	-1.026132
H	-7.268297	-0.816771	0.572070
H	-7.491225	-2.554737	0.329188
C	0.578600	0.036167	-2.602629
C	2.019264	0.522549	-2.816622
H	2.721019	-0.033299	-2.183399
H	2.128651	1.587379	-2.580881
H	2.320838	0.381577	-3.861812
C	-0.358737	0.748714	-3.588343
H	-0.314573	1.838256	-3.490313
H	-1.400365	0.439073	-3.452867
H	-0.060798	0.499258	-4.613696
C	0.520126	-1.471444	-2.879857
H	-0.496280	-1.859688	-2.749964
H	1.178887	-2.028993	-2.205591
H	0.834939	-1.668585	-3.911148
N	-0.196045	0.268959	1.179610
N	0.195784	0.270959	-1.179491
N	4.456576	-0.901070	-0.162920
N	-4.456154	-0.901279	0.162075

Rotational constants (GHZ): 0.1505909 0.0609292 0.0584602

11. Table S2.4 Optimized geometries of compound 2.3

Standard orientation:

Atom	Coordinates (Angstroms)		
	X	Y	Z
Ge	-1.882754	0.110415	0.970475
C	-1.991787	-0.630652	-0.782154
C	-2.110735	0.024606	-2.047324
C	-2.405995	-0.693329	-3.197956
H	-2.524525	-0.168489	-4.144756
C	-2.563807	-2.101906	-3.161649
H	-2.793826	-2.641120	-4.077504
C	-2.446875	-2.778781	-1.970730
H	-2.594088	-3.857994	-1.936930
C	-2.176754	-2.068223	-0.764308
C	-2.110735	-2.632209	0.515524
H	-2.274889	-3.686067	0.719844
C	-1.967637	-2.210464	2.933745
C	-3.274385	-2.973733	3.206350
H	-4.138752	-2.338273	2.983185
H	-3.325188	-3.270860	4.260471
H	-3.354886	-3.882596	2.601088
C	-0.752291	-3.115675	3.187508
H	-0.771338	-4.000178	2.540443
H	-0.740167	-3.463272	4.227546
H	0.178475	-2.568779	2.996440
C	-1.900962	-1.007142	3.876943
H	-0.989844	-0.426293	3.705797
H	-1.902480	-1.351057	4.917532
H	-2.757875	-0.340735	3.728635
C	-2.015621	1.471626	-2.179384
H	-2.440365	1.870982	-3.110503
C	-1.761273	3.727565	-1.481593
C	-3.270769	4.019239	-1.474854
H	-3.777989	3.545880	-2.323282
H	-3.452246	5.098914	-1.534839
H	-3.728525	3.640780	-0.554020
C	-1.121660	4.225365	-2.785494
H	-0.055819	3.975890	-2.814571
H	-1.225598	5.314212	-2.864107
H	-1.596999	3.786063	-3.669862
C	-1.117625	4.439020	-0.287850
H	-1.536544	4.062329	0.652905
H	-1.296552	5.519566	-0.332283
H	-0.032594	4.279716	-0.271875
Li	-0.000179	1.666935	-0.007302
N	-1.949616	-1.730951	1.532374
N	-1.546830	2.267312	-1.282844
Ge	1.882754	-0.110415	0.970475

C	1.991787	0.630652	-0.782154
C	2.110735	-0.024606	-2.047324
C	2.405995	0.693329	-3.197956
H	2.524525	0.168489	-4.144756
C	2.563807	2.101906	-3.161649
H	2.793826	2.641120	-4.077504
C	2.446875	2.778781	-1.970730
H	2.594088	3.857994	-1.936930
C	2.176754	2.068223	-0.764308
C	2.110735	2.632209	0.515524
H	2.274889	3.686067	0.719844
C	1.967637	2.210464	2.933745
C	3.274385	2.973733	3.206350
H	4.138752	2.338273	2.983185
H	3.325188	3.270860	4.260471
H	3.354886	3.882596	2.601088
C	0.752291	3.115675	3.187508
H	0.771338	4.000178	2.540443
H	0.740167	3.463272	4.227546
H	-0.178475	2.568779	2.996440
C	1.900962	1.007142	3.876943
H	0.989844	0.426293	3.705797
H	1.902480	1.351057	4.917532
H	2.757875	0.340735	3.728635
C	2.015621	-1.471626	-2.179384
H	2.440365	-1.870982	-3.110503
C	1.761273	-3.727565	-1.481593
C	3.270769	-4.019239	-1.474854
H	3.777989	-3.545880	-2.323282
H	3.452246	-5.098914	-1.534839
H	3.728525	-3.640780	-0.554020
C	1.121660	-4.225365	-2.785494
H	0.055819	-3.975890	-2.814571
H	1.225598	-5.314212	-2.864107
H	1.596999	-3.786063	-3.669862
C	1.117625	-4.439020	-0.287850
H	1.536544	-4.062329	0.652905
H	1.296552	-5.519566	-0.332283
H	0.032594	-4.279716	-0.271875
Li	0.000179	-1.666935	-0.007302
N	1.949616	1.730951	1.532374
N	1.546830	-2.267312	-1.282844

X-ray Data Collection and Structural Refinement. Intensity data for compounds **3.2–3.8** were collected using a Bruker APEX II diffractometer. The crystals of **3.2–3.8** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .¹ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

12. Table S3.1 Crystallographic data for compounds 3.2 – 3.3(OTf)₂

	3.2	3.3(OTf)₂
Formula	C ₃₆ H ₄₈ AgCl ₂ F ₉ Ge ₂ N ₄ O ₉ S ₃	C ₇₃ H ₈₆ AgF ₁₇ Ge ₂ N ₈ O ₉ S ₃
Mr	1271.91	1891.72
Color	Colourless	Yellow
Crystal System	Monoclinic	Monoclinic
Space group	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21 1
<i>a</i> /Å	9.6584(14)	14.9794(3)
<i>b</i> /Å	20.346(3)	37.8961(8)
<i>c</i> /Å	25.508(4)	15.1055(3)
α /deg	90	90
β /deg	98.811(3)	105.3550(10)
γ /deg	90	90
<i>V</i> /Å ³	4953.4(13)	8268.7(3)
<i>Z</i>	4	4
<i>d</i> _{calcd} /g cm ⁻³	1.706	1.520
μ /mm ⁻¹	1.918	1.129
<i>F</i> (000)	2552	3856
Crystal size/ mm	0.200 x 0.240 x 0.360	0.100 x 0.200 x 0.420
Index range	-13 ≤ <i>h</i> ≤ 14 -29 ≤ <i>k</i> ≤ 29 -37 ≤ <i>l</i> ≤ 37	-21 ≤ <i>h</i> ≤ 21, -53 ≤ <i>k</i> ≤ 53 -20 ≤ <i>l</i> ≤ 21
No. of reflections collected	75268	149743
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0560, 0.1039	0.0584, 0.1245
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0994, 0.1180	0.0993, 0.1435
GOF, <i>F</i> ²	1.021	1.014
no. of data/ restraints/ param	15826/ 1169/ 854	49467 /2400/ 2515
largest diff peak, hole/ eÅ ⁻³	1.448, -0.889	1.252, -0.773

13. Table S3.2 Crystallographic data for compounds 3.4 – 3.6

	3.4	3.5	3.6
Formula	C ₃₂ H ₄₆ Cl ₄ Cu ₂ Ge ₂ N ₄	C ₃₂ H ₄₆ Cl ₂ Cu ₂ Ge ₂ I ₂ N ₄	C ₃₈ H ₄₆ ClCuGeIN ₂ OP
Mr	900.79	1083.69	876.22
Color	Orange	Orange	Yellow
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21/ <i>n</i> 1
<i>a</i> /Å	12.2768(3)	12.2246(3)	12.1257(4)
<i>b</i> /Å	9.6238(2)	10.4357(3)	17.5281(5)
<i>c</i> /Å	16.7905(4)	16.7820(4)	17.6204(7)
α /deg	90	90	90
β /deg	104.1459(18)	106.535(2)	91.1060(18)
γ /deg	90	90	90
<i>V</i> /Å ³	1923.63(8)	2052.38(9)	3744.4(2)
<i>Z</i>	2	2	4
<i>d</i> _{calcd} /g cm ⁻³	1.555	1.754	1.554
μ /mm ⁻¹	5.810	16.059	2.341
<i>F</i> (000)	912	1056	1768
Crystal size/mm	0.100 x 0.120 x 0.320	0.020 x 0.120 x 0.200	0.100 x 0.180 x 0.200
Index range	-14 ≤ <i>h</i> ≤ 12 -11 ≤ <i>k</i> ≤ 11 -18 ≤ <i>l</i> ≤ 20	-14 ≤ <i>h</i> ≤ 13 -12 ≤ <i>k</i> ≤ 12 -19 ≤ <i>l</i> ≤ 18	-17 ≤ <i>h</i> ≤ 17 -25 ≤ <i>k</i> ≤ 25 -23 ≤ <i>l</i> ≤ 25
No. of reflections collected	16041	14316	75502
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0492, 0.1256	0.0863, 0.2246	0.0628, 0.1618
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0670, 0.1415	0.1078, 0.2532	0.1402, 0.1945
GOF, <i>F</i> ²	1.079	1.009	1.047
no. of data/restraints/param	3425/ 0/ 205	3607/ 204/ 254	12050/ 421/ 519
largest diff peak, hole/ eÅ ⁻³	1.024, -0.898	2.674, -1.302	1.624, -1.234

14. Table S3.3 Crystallographic data for compounds 3.7 – 3.8

	3.7	3.8
Formula	C ₁₆ H ₂₃ AuClGeIN ₂	C ₃₈ H ₄₆ AuClGeIN ₂ OP
Mr	675.27	1009.64
Color	Colourless	Orange
Crystal System	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 1 21/ <i>n</i> 1
<i>a</i> /Å	8.9116(6)	12.2926(4)
<i>b</i> /Å	13.0031(13)	17.6363(6)
<i>c</i> /Å	17.8205(13)	17.8250(6)
α /deg	101.551(7)	90
β /deg	101.227(7)	90.0526(12)
γ /deg	97.616(7)	90
<i>V</i> /Å ³	1952.6(3)	3864.4(2)
<i>Z</i>	4	4
<i>d</i> _{calcd} /g cm ⁻³	2.297	1.735
μ /mm ⁻¹	29.464	5.510
<i>F</i> (000)	1256	1968
Crystal size/ mm	0.040 x 0.060 x 0.120	0.140 x 0.240 x 0.340
Index range	-10 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15 0 ≤ <i>l</i> ≤ 21	-18 ≤ <i>h</i> ≤ 17 -25 ≤ <i>k</i> ≤ 22 -26 ≤ <i>l</i> ≤ 22
No. of reflections collected	6954	82108
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0612, 0.1621	0.0361, 0.0627
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0759, 0.1710	0.0689, 0.0710
GOF, <i>F</i> ²	0.984	1.046
no. of data/ restraints/ param	6954/ 2168/ 819	12753/ 236/ 467
largest diff peak, hole/ eÅ ⁻³	1.123, -1.339	1.977, -1.129

15. NMR spectrum of 3.1 – 3.2, 3.3(OTf)₂, 3.4 – 3.8

(a) ¹H NMR spectrum of 3.1

(b) ¹³C{¹H} NMR spectrum of 3.1

(c) ^1H NMR spectrum of **3.2**

(d) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.2**

(e) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3.2**

(f) ^1H NMR spectrum of **3.3(OTf)₂**

(g) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.3(OTf)₂**

(h) $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3.3(OTf)₂**

(i) ^1H NMR spectrum of **3.4**

(j) ^1H NMR spectrum of 3.5

(k) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3.5

(l) ^1H NMR spectrum of **3.6**

(m) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.6**

(n) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3.6**

(o) ^1H NMR spectrum for **3.7**

(p) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **3.7**

(q) ^1H NMR spectrum of **3.8**

(r) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.8**

(s) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3.8**

X-ray Data Collection and Structural Refinement. Intensity data for compounds **4.2** and **4.2.IPr** were collected using a Bruker APEX II diffractometer. Their crystals were measured at 103(2) K. The structures were solved by a direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .¹ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

16. Table S4.1 Crystallographic data for compounds 4.2 and 4.2·IPr

	4.2	4.2·IPr
Formula	C ₅₅ H ₇₈ N ₄ OSi	C ₇₈ H ₁₀₆ N ₆ Si
M	839.30	1155.77
Color	Yellow	Orange
Crystal System	Orthorhombic	Monoclinic
Space group	<i>P n a</i> 21	<i>P</i> 1 21/ <i>c</i> 1
a/Å	19.024(4)	15.153(2)
b/Å	18.708(4)	23.334(3)
c/Å	14.086(3)	20.830(3)
α/deg	90	90
β/deg	90	110.043(4)
γ/deg	90	90
V/Å ³	5013.2(18)	6919.0(18)
Z	4	4
d _{calcd} /g cm ⁻³	1.112	1.109
μ/ mm ⁻¹	0.088	0.080
F(000)	1832	2520
Crystal size/ mm ³	0.010 x 0.300 x 0.400	0.140 x 0.180 x 0.220
2θ range (deg)	2.40 – 25.37	2.22 – 24.99
Index range	-22 ≤ <i>h</i> ≤ 22	-17 ≤ <i>h</i> ≤ 17,
	-18 ≤ <i>k</i> ≤ 22	-27 ≤ <i>k</i> ≤ 27
	-16 ≤ <i>l</i> ≤ 16	-24 ≤ <i>l</i> ≤ 24
No. of reflections collected	43439	86762
no. of indep rflns	9071	12115
R1, wR2 [<i>I</i> > 2σ(<i>I</i>)]	0.0516, 0.0803	0.0699, 0.1665
R1, wR2 (all data)	0.1470, 0.0993	0.1515, 0.2093
GOF, F ²	0.809	1.014
no. of data/ restraints/ param	9071/ 1/ 566	12115/ 569/ 903
largest diff peak, hole/ eÅ ⁻³	0.392, -0.304	0.302, -0.392

17. Figure S4.1 IR spectrum of compound 4.2

18. Figure S4.2 The Si-N unsymmetric stretch and C-H bending at the theoretical value of 1447 cm⁻¹

Green arrow represents vibrational direction

		252
		Å
Frequencies	--	1447.0320
Red. masses	--	2.4735
Frc consts	--	3.0515
IR Inten	--	103.1622

Atom	AN	X	Y	Z
1	6	-0.01	0.00	-0.02
2	6	-0.08	-0.04	-0.11
3	6	0.00	0.05	0.05
4	6	-0.01	-0.04	0.00
5	6	0.01	-0.01	-0.02
6	6	-0.01	0.06	0.04
7	6	0.04	-0.03	0.01

8	6	0.00	-0.05	-0.04
9	6	-0.10	0.12	0.01
10	6	0.01	-0.06	-0.04
11	6	0.00	0.01	0.02
12	6	0.01	0.02	0.00
13	6	-0.01	-0.01	0.01
14	6	-0.03	0.03	0.05
15	6	0.00	-0.03	-0.01
16	6	-0.01	0.02	0.00
17	6	0.00	0.01	0.00
18	6	0.00	-0.03	0.00
19	6	0.01	0.00	-0.02
20	6	0.00	0.03	0.01
21	6	-0.02	-0.05	0.03
22	6	0.00	0.03	0.00
23	6	-0.01	-0.01	-0.01
24	6	0.00	-0.01	0.00
25	6	0.01	0.01	0.00
26	6	0.01	0.00	0.02
27	6	0.01	0.01	-0.01
28	6	0.00	0.00	0.00
29	6	0.00	0.00	0.00
30	6	0.00	0.00	0.00
31	6	0.00	0.00	0.00
32	6	0.00	0.00	0.00
33	6	0.00	0.00	0.00
34	6	0.00	0.00	0.00
35	6	0.00	0.00	0.00
36	6	0.00	0.00	0.00
37	6	0.00	0.00	0.00
38	6	0.00	0.00	0.01
39	6	-0.01	0.01	-0.01
40	6	0.00	0.00	0.00
41	6	0.00	0.00	0.00
42	6	0.00	0.00	0.00
43	6	0.01	-0.01	-0.01
44	6	0.00	-0.01	0.01
45	6	0.00	0.00	0.00
46	6	0.00	0.00	0.00
47	6	0.00	0.00	0.00
48	6	0.01	0.00	0.00
49	6	0.00	0.00	0.00
50	6	0.00	0.00	0.00
51	6	0.00	0.00	0.00
52	1	0.07	-0.30	-0.19
53	1	0.01	0.14	0.06
54	1	0.10	0.06	-0.04
55	1	0.03	0.14	0.01
56	1	0.02	-0.03	0.06
57	1	-0.05	0.03	0.05
58	1	-0.04	0.07	0.08
59	1	0.31	-0.21	0.08

60	1	0.05	0.00	0.05
61	1	0.31	0.00	0.26
62	1	0.04	0.25	0.30
63	1	0.00	-0.07	-0.06
64	1	0.03	0.02	-0.02
65	1	-0.04	-0.03	-0.07
66	1	-0.03	-0.07	-0.02
67	1	0.02	-0.04	0.04
68	1	-0.04	-0.08	-0.03
69	1	0.02	0.14	0.00
70	1	0.06	-0.01	-0.01
71	1	0.03	-0.08	-0.02
72	1	0.05	-0.05	0.02
73	1	-0.03	-0.03	0.01
74	1	-0.01	0.00	-0.03
75	1	-0.01	-0.05	0.00
76	1	0.08	0.09	-0.12
77	1	0.01	0.01	-0.02
78	1	0.08	-0.02	-0.14
79	1	0.02	-0.11	-0.05
80	1	0.01	0.04	0.02
81	1	0.03	0.01	0.00
82	1	0.02	0.03	0.02
83	1	0.00	0.01	-0.02
84	1	-0.01	0.01	0.02
85	1	0.00	0.04	0.01
86	1	-0.04	-0.02	-0.04
87	1	-0.03	-0.04	0.02
88	1	0.01	-0.02	0.00
89	1	0.00	0.00	0.01
90	1	-0.01	0.00	0.00
91	1	-0.01	0.00	0.00
92	1	0.00	0.01	0.00
93	1	0.00	0.00	-0.01
94	1	0.00	0.01	0.00
95	1	-0.01	-0.01	0.00
96	1	0.00	0.00	0.00
97	1	-0.02	0.00	0.00
98	1	-0.01	0.00	0.00
99	1	-0.01	-0.01	-0.02
100	1	-0.01	-0.01	-0.02
101	1	0.01	0.01	-0.02
102	1	0.01	0.00	0.00
103	1	0.00	-0.03	0.07
104	1	0.07	-0.04	0.00
105	1	0.00	0.00	0.00
106	1	0.00	0.03	0.04
107	1	-0.02	0.05	0.04
108	1	-0.04	0.00	0.06
109	1	-0.01	0.03	-0.02
110	1	0.01	0.02	-0.03
111	1	-0.02	0.01	-0.03

112	1		-0.01	0.00	0.00	
113	1		0.00	0.00	0.00	
114	1		-0.01	-0.02	-0.01	
115	1		0.01	-0.01	-0.02	
116	1		-0.01	0.01	0.01	
117	1		0.00	0.00	0.01	
118	1		0.00	0.01	0.01	
119	1		-0.01	0.01	0.00	
120	1		0.00	-0.01	0.00	
121	1		-0.01	-0.01	0.01	
122	7		0.13	-0.06	0.05	
123	7		0.07	0.00	-0.06	
124	7		-0.01	-0.01	0.00	
125	7		-0.01	-0.01	-0.01	
126		14		-0.06	0.02	0.01

19. NMR spectra of compounds 4.1 and 4.2·IPr.

(a) ^1H NMR spectrum of **4.1**

(b) ^1H NMR of **4.2·IPr**

(c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4.2·IPr**

(d) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **4.2-IPr**

20. Table S4.2 The bond dissociation energy of the C-Si bond in 4.2

	4.2	IPr	ArNSiNAr
B3PW91/6-31G*	-2493.252532	-1159.608814	-1333.575395
Zero point correction (ZPVE)	1.109313	0.572946	0.531521
B3PW91/6-311+G(2d,p)//B3PW91/6-31G*	-2493.853079	1159.910154	-1333.877715
B3PW91/6-311+G(2d,p)//B3PW91/6-31G* + scaled ZPVE[a], 6	-2492.768836	-1159.350157	-1333.358206

Remark: [a] scaling factor = 0.9774

Bond dissociation energy with zero point correction

$$= (-1333.358206) + (-1159.350157) - (-2492.768836)$$

$$= 0.06047326 \text{ Hartree/mol} = 38.0 \text{ kcal/mol}$$

21. Table S4.3 The optimized geometry of compound 4.2

Standard orientation:

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.553869	-1.256135	1.230237
C	3.088201	-0.552745	2.354136
C	2.400248	0.662738	2.949529
C	3.335410	1.866228	3.122533
C	1.733020	0.295241	4.284121
C	4.251368	-1.020546	2.969180
C	4.910820	-2.164049	2.535073
C	4.366530	-2.877604	1.474568
C	3.204681	-2.460570	0.824719
C	2.643023	-3.325775	-0.291212
C	3.550085	-3.337572	-1.529583
C	2.383038	-4.761919	0.186488
C	-2.139225	-0.212026	2.210694
C	-2.644847	0.844859	3.024607
C	-2.359282	2.290986	2.662668
C	-3.534998	3.237237	2.932363
C	-1.097965	2.793895	3.379092
C	-3.370864	0.545901	4.177643
C	-3.642446	-0.765675	4.550062
C	-3.193647	-1.796475	3.734037
C	-2.463099	-1.553854	2.568963
C	-2.021569	-2.735020	1.722953
C	-3.169215	-3.708658	1.423338
C	-0.841799	-3.473716	2.369864
C	-0.122910	0.520744	-1.401326
C	0.287908	1.594415	-3.334503
C	-0.727511	0.728102	-3.558332
C	-2.063293	-0.874167	-2.254822
C	-3.331467	-0.391538	-1.876699
C	-3.587163	1.062307	-1.516763
C	-4.575447	1.226433	-0.358158
C	-4.073761	1.842849	-2.749652
C	-4.391079	-1.301275	-1.904109
C	-4.202096	-2.619606	-2.300488
C	-2.940886	-3.060803	-2.676675
C	-1.838287	-2.200274	-2.665675
C	-0.481821	-2.706984	-3.130637
C	-0.390751	-2.709550	-4.665866
C	-0.167233	-4.105326	-2.586268
C	1.574626	2.405976	-1.402699
C	1.059691	3.673578	-1.064027
C	-0.390892	4.078301	-1.284765
C	-1.010066	4.744915	-0.051087
C	-0.511827	5.006053	-2.505447

C	1.958579	4.618946	-0.560559
C	3.305743	4.320918	-0.417377
C	3.786936	3.071132	-0.789415
C	2.941880	2.081964	-1.301590
C	3.511201	0.753839	-1.775703
C	3.756691	0.778874	-3.294743
C	4.806314	0.365986	-1.054060
H	1.612031	0.971541	2.253122
H	3.808818	2.141521	2.174127
H	2.774460	2.735877	3.486527
H	4.131334	1.664944	3.849773
H	1.215899	1.157929	4.720364
H	0.999410	-0.507211	4.153808
H	2.481185	-0.049782	5.008376
H	4.646745	-0.473166	3.822721
H	5.819079	-2.502800	3.027093
H	4.855377	-3.791560	1.141551
H	1.683109	-2.882745	-0.577587
H	4.552486	-3.708191	-1.281907
H	3.144153	-3.990830	-2.313086
H	3.661486	-2.333806	-1.952462
H	1.747521	-4.773344	1.077475
H	1.889758	-5.352216	-0.595958
H	3.317458	-5.276622	0.440760
H	-2.155594	2.299674	1.584651
H	-3.328432	4.229228	2.511012
H	-4.464643	2.863485	2.489475
H	-3.711795	3.379239	4.005370
H	-0.228876	2.187714	3.107548
H	-0.880696	3.840405	3.126468
H	-1.223014	2.733981	4.467247
H	-3.732895	1.359658	4.802030
H	-4.203963	-0.980008	5.456050
H	-3.415265	-2.825446	4.010675
H	-1.683853	-2.334480	0.760032
H	-4.024655	-3.188363	0.979767
H	-2.838514	-4.483249	0.720312
H	-3.519006	-4.220171	2.328061
H	-0.529606	-4.327486	1.755060
H	0.023392	-2.814833	2.497160
H	-1.119963	-3.858162	3.359014
H	0.776762	2.303290	-3.983026
H	-1.303200	0.515315	-4.444506
H	-2.639355	1.492341	-1.177705
H	-5.593053	0.928353	-0.637397
H	-4.263816	0.645500	0.513688
H	-4.621088	2.280931	-0.065186
H	-5.024730	1.437750	-3.116188
H	-4.235512	2.896729	-2.494144
H	-3.355715	1.804552	-3.576267
H	-5.382126	-0.969376	-1.611796
H	-5.043768	-3.307133	-2.315659

H	-2.807356	-4.092574	-2.986135
H	0.288516	-2.027862	-2.746332
H	-0.540455	-1.711927	-5.091790
H	0.594116	-3.066485	-4.988177
H	-1.148868	-3.373208	-5.098377
H	-0.812195	-4.871466	-3.031307
H	0.865717	-4.374049	-2.828385
H	-0.284479	-4.150046	-1.499764
H	-0.978217	3.177016	-1.491578
H	-2.078266	4.922133	-0.218745
H	-0.903695	4.116481	0.836122
H	-0.549472	5.716200	0.162029
H	-0.123562	4.540637	-3.417783
H	-1.560925	5.270430	-2.681685
H	0.047092	5.935347	-2.345208
H	1.594280	5.604143	-0.284644
H	3.988704	5.067889	-0.021073
H	4.844526	2.857585	-0.681109
H	2.768283	-0.018521	-1.544076
H	4.474489	1.564899	-3.559656
H	4.173740	-0.179994	-3.623868
H	2.839606	0.953056	-3.867099
H	5.645039	1.011973	-1.343002
H	4.691159	0.397293	0.032908
H	5.084492	-0.657248	-1.321686
N	1.490510	-0.779888	0.500339
N	-1.418825	0.092883	1.069877
N	-0.974833	0.078086	-2.365297
N	0.651856	1.462270	-2.008881
Si	0.020210	-0.153392	0.390996

22. References

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