Chemistry of base-stabilized group 14 element (I) dimers

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2014

Yeong, C. H. (2014). Chemistry of base-stabilized group 14 element(I) dimers. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/55296>

<https://doi.org/10.32657/10356/55296>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CHEMISTRY OF BASE-STABILIZED
GROUP 14 ELEMENT(I) DIMERS**

**YEONG HUI-XIAN CRYSTAL
SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

2014

Chemistry of Base-Stabilized Group 14 Element(I) Dimers

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School of Physical and Mathematical Sciences

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

2014

Acknowledgements

First of all, I would like to acknowledge my supervisor, Dr. Cheuk-Wai So, for his invaluable advice and guidance throughout my PhD study. I am most grateful for his continuous patience and support over the past four years.

I would like to thank my colleagues, Yang Yifan, Guo Jiayi, Chia Siew Peng, Zhang Shu Hua and Ho Ying Fu Samuel for their encouragement and helpful discussions. A highly conducive research environment was made possible with their assistance and cooperation within the laboratory.

I am thankful towards the research groups of Professor Shigeru Nagase, Professor Kok Hwa Lim, Dr. Hong-Wei Xi, Professor Kai-Chung Lau and Dr. Hajime Hirao for their expertise in doing the theoretical calculations of the compounds in this thesis. I would like to express my heartfelt gratitude to Dr. Li Yongxin and Dr. Rakesh Ganguly for their expertise and assistance in the collection and analysis of X-ray crystallographic data. Thanks are also given to the technicians and administrative staffs of NTU for their kind assistance. Special thanks are given to Goh Ee Ling, Dr. Attapol Pinsa, Seow Ai Hua and Hum Wei Mei Celine.

I am grateful for the Nanyang President's Graduate Scholarship for supporting my graduate study and overseas conferences.

Lastly, I would like to thank my family for their unending support and encouragement.

Yeong Hui-Xian Crystal

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Symbols and Abbreviations

br	broad
<i>t</i> Bu	tert-butyl
calcd	calculated
d	doublet
DME	1,2-dimethoxyethane
decomp	decomposed
ϵ	molar absorptivity
<i>et al.</i>	and others (Latin <i>et alii</i>)
Et ₂ O	Diethyl ether
g	gram(s)
h	hour(s)
<i>i</i> Pr	iso-propyl
λ	lambda
m	multiplet
Me	methyl
Mes	2,4,6-Me ₃ C ₆ H ₂
M.p.	melting point
nm	nanometer
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
ppm	parts per million
q	quartet
s	singlet
sept	septet
THF	tetrahydrofuran
°	degree
°C	degree Celsius
Å	angstrom(s)
η	'eta' (hapticity)
μ	'mu'

Abstract

This thesis mainly describes the reactivity studies of an amidinate-stabilized silicon(I) dimer [LSi:-Si:L] (**4**; L = PhC(N*t*Bu)₂; Chart I). Density functional theory (DFT) calculations and topological analysis of the electron densities of **4** show that it comprises a Si¹-Si¹ single bond and a lone pair of electrons at each Si atom. Reaction of **4** with Br₂, PhC≡CH and PhC≡CPh, afforded [LSiBr] (**8**), *cis*-1,2-disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**14**) and [LSi(μ-C₂Ph₂)₂SiL] (**17**), respectively. Compounds **8**, **14** and **17** have been characterized by X-ray crystallography and NMR spectroscopy. X-ray crystallography and DFT calculations of **17** show that the singlet biradicals are stabilized by the amidinate ligand and the delocalization within the Si(μ-C₂Ph₂)₂Si six-membered ring.

Chart I. Compounds **4**, **8**, **14**, **17**, **29** and **32**.

In chapter 2, the syntheses of stable heavier group 14 cyclobutadiene analogues which comprise of heavier group 14 elements in the four-membered skeleton is described. The amidinate-stabilized germatrisilacyclobutadiene ylides [L_3Si_3GeL'] (**29**; $L' = :GeL$; **32**: $L' = :SiL$; Chart I) were prepared from the reaction of different equivalents of compound **4** with the amidinate-stabilized germanium(I) dimer [$LGe:-Ge:L$] (**7**). Furthermore, **32** can be prepared by the treatment of compound **29** with one equivalent of compound **4**. Compounds **29** and **32** were characterized by NMR spectroscopy and X-ray crystallography. Theoretical studies of compound **29** show that it is not anti-aromatic. The puckered Si_3Ge four-membered ring in **29** features a ylide structure, which is stabilized by amidinate ligands and the electron delocalization within the Si_3Ge four-membered ring.

Furthermore, stable heavier group 14 cyclobutadiene analogues that consist of germanium and tin atoms in the four-membered framework were also isolated and characterized. The reaction of the amidinate-stabilized Ge^I dimer **7** with two equivalents of the amidinate tin(II) chloride [$LSnCl$] and KC_8 afforded the zwitterionic base-stabilized digermadistannacyclobutadiene [$L_2Ge_2Sn_2L'_2$] (**36**; $L' = :GeL$; Chart II). Compound **36** can also be prepared by the reaction of **7** with [$L^{Ar}SnCl$] ($L^{Ar} = tBuC(NAr)_2$; $Ar = 2,6-iPr_2C_6H_3$). Additionally, the reaction of **7** with the “onio-substituent transfer” reagent [4-NMe₂-C₅H₄NSiMe₃]OTf and 4-dimethylaminopyridine (DMAP) afforded the zwitterionic base-stabilized tetragermacyclobutadiene [L_4Ge_4] (**45**; Chart II). X-ray structural data and theoretical studies show conclusively that compounds **36** and **45** have a planar and rhombic charge-separated structure. They are also non-aromatic.

Chart II. Compounds **36** and **45**.

In chapter 3, the synthesis and reactivity of a silyliumylidene cation stabilized by amidinate ligand $[\text{PhC}(\text{N}t\text{Bu})_2]$ and DMAP are described. The reaction of compound **4** with one equivalent of $[\text{4-NMe}_2\text{-C}_5\text{H}_4\text{NSiMe}_3]\text{OTf}$ and two equivalents of DMAP afforded $[\text{LSi}(\text{DMAP})]\text{OTf}$ (**54**; Chart III). DFT calculations of compound **54**⁺ indicate the presence of a lone pair of electrons on the positively charged silicon(II) atom. The Lewis ambiphilic character of **54** is demonstrated from its reactivity. Treatment of **54** with **4**, $[\text{K}\{\text{HB}(i\text{Bu})_3\}]$ and elemental sulphur, afforded the disilylenylsilylium triflate $[\text{L}'_2(\text{L})\text{Si}]\text{OTf}$ (**55**; $\text{L}' = \text{LSi:}$), silylsilylene $[\text{LSiSi}(\text{H})\{\text{(N}t\text{Bu})_2\text{C}(\text{H})\text{Ph}\}]$ (**56**) and the base-stabilized silanethionium triflate $[\text{LSi}(\text{S})\text{DMAP}]\text{OTf}$ (**57**), respectively. Thereafter, the reactivity of compound **54** with transition metal complexes was explored. The results further highlighted the lewis acidity of **54**, as well as its functionality to serve as a two electron σ donating ligand with good π accepting ability. Treatment of compound **54** with $[\text{Rh}(\text{cod})\text{Cl}]_2$ and $\text{W}(\text{CO})_5\text{THF}$ afforded $[\{\text{L}(\text{DMAP})\text{Si}\}_2\{\mu\text{-Rh}(\mu\text{-Cl}_2)\text{Rh}(\text{cod})\}]\text{OTf}_2$ (**71**) and $[\text{L}(\text{DMAP})\text{Si}\rightarrow\text{W}(\text{CO})_5]\text{OTf}$ (**72**), respectively. Compounds **54**, **55**, **57**, **71** and **72** have been characterized by X-ray crystallography and NMR spectroscopy.

Chart III. Compounds **54**, **55**, **56**, **57**, **71** and **72**.

Lastly in chapter 4, the synthesis and characterization of a germanium(I) dimer $[L^1Ge:-Ge:L^1]$ (**97**; Chart IV) supported by the 2-imino-5,6-methylenedioxyphenyl ligand (L^1) is described. Compound **97** was synthesized by the reaction of $[L^1GeCl]$ (**94**) with KC_8 . Additionally, treatment of the Ge^I dimer **97** with excess KC_8 in THF resulted in the cleavage of the Ge^I-Ge^I bond to afford the germylidenide anion $[L^1GeK]$ (**98**). Compound **98** can also be synthesized by the reaction of $[L^1GeCl]$ (**94**) with excess KC_8 . Compounds **94**, **97** and **98** have been characterized by X-ray crystallography and NMR spectroscopy. The molecular structure of the germylidenide anion **98** shows that the potassium atom is η^1 -coordinated with the low-valent

germanium atom. Moreover, the negative charge at the germanium center in compound **98** is stabilized by the electron-delocalization in the germanium heterocycle.

Chart IV. Compounds **94**, **97** and **98**.

Chapter 1

Reactivity of an Amidinate-Stabilized Silicon(I) Dimer towards Bromine and Unsaturated Molecules

Introduction

The synthesis of heavier group 14 alkyne analogues $\text{RE}\equiv\text{ER}$ (R = bulky terphenyl or silyl ligand; E = Si, Ge, Sn, Pb) has attracted much attention over the past decades due to their uncommon structures and bonding.^[1] The latter has been studied extensively via time dependent-density functional theory (TD-DFT) calculations, UV/Vis spectroscopy studies and reactivity studies.^[2] The silicon analogue of an alkyne is known as a disilyne. The central $\text{Si}\equiv\text{Si}$ moieties in **1** and **2** (Chart 1) are stabilized by a bulky silyl and terphenyl substituent, respectively.^[1k, 1o] The $\text{Si}\equiv\text{Si}$ bond lengths in **1** and **2** are 2.0622(9) and 2.108(5) Å, respectively. They are shorter than the typical $\text{Si}=\text{Si}$ double bond lengths (2.14 Å) in a disilene and the average Si-Si single bond lengths (2.34 Å).^[3] Hence, the short $\text{Si}\equiv\text{Si}$ bonds of **1** and **2** are indicative of the triple bond character of the $\text{Si}\equiv\text{Si}$ bonds. In addition, **1** and **2** feature a slightly *trans*-bent geometry around the $\text{Si}\equiv\text{Si}$ moieties (**1**: $\text{Si}'\text{-Si-Si}$ angle is $137.44(4)^\circ$; **2**: C-Si-Si angle is $133.0(3)^\circ$). This is in contrast to their lighter analogues, which consist of a linear geometry about the $\text{C}\equiv\text{C}$ triple bond.

Chart 1. Disilynes **1** and **2**.

This deviation from linearity of a disilyne is a consequence of mixing of σ^* and in-plane π orbitals that are of the same symmetry.^[1b] Moreover, the energy gap of

the bonding π orbital and the anti-bonding σ^* orbital is approximately half or less than half of that in the carbon analogues. This $\sigma^*-\pi$ mixing results in accumulation of non-bonding electron density at the silicon centers and hence the *trans*-bent geometry of a disilyne (Chart 2).

Chart 2. $\sigma^*-\pi$ mixing in the C_{2h} -symmetric *trans*-bent $RSi\equiv SiR$ molecule.

Alternatively, the $Si\equiv Si$ triple bond can be described as one π bond and two donor-acceptor bonds between the silicon atoms (Chart 3).^[1b] Consider each silicon atom in multiple-bonded derivative **M** as sp hybridized (Chart 4). One sp hybrid is used to form the $R-Si$ σ bond. The unpaired electron in the remaining sp hybrid of each silicon atom will then couple to form a $Si-Si$ π bond. The lone pair of electrons in the p orbital of each silicon atom will then be donated into the vacant p orbital of the other Si atom to form a donor-acceptor bond.

Chart 3. Bonding model of multiple-bonded disilyne derivative **M**.

Chart 4. Multiple-bonded **M** and single-bonded **S** derivatives of a disilyne.

As the *trans*-bending angle (R-Si-Si) approaches 90°, the two donor-acceptor bonds become two lone pair of electrons at each silicon atom and the Si-Si π bond is converted to a Si-Si σ bond. Thus, each silicon atom in the resulting single-bonded derivative **S** (Chart 4) will have a vacant p orbital (Chart 5). If donor ligands are incorporated at the silicon centers of derivative **S**, a lone pair of electrons from each donor ligand will be donated into the vacant p orbitals of the silicon atoms. Hence, the octet rule at each silicon atom in **S** is fulfilled and it is base-stabilized. Such compounds are known as base-stabilized silicon(I) dimers.

Chart 5. Bonding model of single-bonded disilyne derivative **S**.

Several research groups have successfully synthesized and structurally characterized base-stabilized silicon(I) dimers. For example, the carbene-stabilized silicon(I) dimer (**3**; Chart 6) was formed from the KC_8 reduction of the neutral tetrachloro-silicon-carbene precursor.^[4a] Following that, the amidinate-stabilized silicon(I) dimers $[\text{LSi}:-\text{Si}: \text{L}]$ (**4**: $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$; **5**: $\text{L} = \text{Ar}'\text{C}(\text{NAr})_2$; $\text{Ar}' = 4$ - $t\text{BuC}_6\text{H}_4$; $\text{Ar} = 2,6$ - $i\text{Pr}_2\text{C}_6\text{H}_3$) (Chart 6), were obtained from the reduction of their corresponding trichlorosilane precursors with KC_8 and $[(^{\text{Mes}}\text{Nacnac})\text{Mg}]_2$ ($^{\text{Mes}}\text{Nacnac} = [(\text{MesNCMe})_2\text{CH}]^-$; Mes = mesityl), respectively.^[4b, 4c] Lastly, the

phosphine-stabilized silicon(I) dimer (**6**; Chart 6) was formed from the Li reduction of its trichlorosilane precursor.^[4d] Compounds **3-6** comprise of a Si:–Si: single bond and a lone pair of electrons at each Si atom. Each silicon atom has a formal oxidation state of +1. These prompted our interest in studying the bonding nature of a base-stabilized silicon(I) dimer via theoretical studies and thereafter, its reactivity. In Section 1.1, the theoretical studies of the amidinate-stabilized silicon(I) dimer [LSi:–Si:L] (**4**; L = PhC(N*t*Bu)₂) is described. Moreover, the reactivity of **4** was investigated with the aim to explore its potential as a functionalized silylene in metathesis reactions. The reactivity of **4** towards bromine is described in Section 1.2.1. Following that, the reactivity of **4** with unsaturated substrates like phenylacetylene and diphenylacetylene is described in Section 1.2.2.

Chart 6. Base-stabilized silicon(I) dimers.

Results and Discussion

1.1. Theoretical Studies of Amidinate-Stabilized Silicon(I) Dimer [LSi:-Si:L] (**4**; L = PhC(NtBu)₂).

In order to understand the bonding nature of **4**, it was investigated by means of quantum chemical calculations. The calculations were performed by the density functional theory (DFT)^[5] B3LYP^[6] with the 6-311+G(d,p) basis set^[7] as implemented in the Gaussian 03^[8] program. The calculated structural parameters (Si-Si': 2.472 Å, Si-N: 1.903 Å, Si-N' = 1.905 Å and N-Si-N' = 68.5°) are in good agreement with the crystallographic data.^[4b] The natural-bond-orbital (NBO)^[9] analysis (Table 1) shows that the Si-Si bond is derived from the overlapping of p-rich hybrids (sp^{7.48}, 87.8% p character) on the Si atoms. The Wiberg bond index (WBI)^[10] shows that the Si-Si bond (0.923) in **4** has single-bond character. The lone pair of electrons at the silicon centers are high in s character (sp^{0.43}, 69.9% s character) with some directionality.

Table 1. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of **4**.

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Wiberg bond index
Si-Si' (σ)	Si	50.0	sp ^{7.48}	Si'	50.0	sp ^{7.48}	0.923
Si-N (σ)	Si	13.7	sp ^{9.54}	N	86.3	sp ^{2.42}	0.489
Si-N' (σ)	Si	13.8	sp ^{9.52}	N'	86.2	sp ^{2.51}	0.496
C-N (π)	C	39.4	sp ^{2.17}	N	60.6	sp ^{1.92}	1.359
C-N' (π)	C	39.0	sp ^{2.19}	N'	61.0	sp ^{1.91}	1.328

The presence of a π bond in a molecule can be measured by the chemical shift anisotropy (CSA).^[11] Large CSA values indicate the presence of π bonds. When the calculated ²⁹Si CSA of **4** (δ = 80.5 ppm) is compared to that of [H₂Si=SiH₂] (δ = 362.6

ppm), it is suggested that the Si-Si bond in **4** does not have multiple-bond character (Table 2).

Table 2. The calculated chemical shift tensors (in ppm) and chemical shift anisotropy (CSA) (in ppm) at the GIAO (Gauge independent atomic orbital)/B3LYP/6-311+G(d,p) relative to calculated TMS (for Si, $\sigma_{\text{iso}} = 340.82$ ppm).

	δ_{11}	δ_{22}	δ_{33}	δ_{iso}^a	$\Delta\delta$	CSA ^b
4	73.83	151.80	193.33	201.163	139.65	80.51
H ₂ Si=SiH ₂	-76.17	-13.92	317.57	75.83	393.75	362.62
H ₃ Si-SiH ₃	-103.42	-103.41	-113.73	-106.85	10.31	10.32

^a $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. ^b CSA = $\delta_{33} - (\delta_{11} + \delta_{22})/2$.

The topological analysis of the electron densities of **4** and [H₃Si-SiH₃] according to Bader's quantum theory of atoms in molecules was performed using the optimized structure at the B3LYP/6-31+G(d) level (Table 3).^[12] The Laplacian of the electron density $\nabla^2\rho$ and the total energy density H at the (3, -1) bond critical point (BCP) show that the Si-Si bonds in **4** and [H₃Si-SiH₃] are nonpolar and covalent (Figure 1). The electron density is locally concentrated between two Si atoms in **4** and [H₃Si-SiH₃]. The bond strength of the Si-Si bond in **4** is weaker than that in [H₃Si-SiH₃]. There are four valence-shell charge concentrations at the Si atoms. One of them in the non-bonding region is regarded as the lone pair (LP) density. The result shows that the LP of electrons is stereochemically active, consistent with the NBO analysis.

Table 3. Theoretical topological features at the BCP of **4** and [H₃Si-SiH₃].^c

Bond	ρ	$\nabla^2\rho$	G	H	$ V $
4					
Si-Si'	0.52	-2.29	0.06	-0.22	0.27
Si-N	0.59	6.87	0.72	-0.24	0.96
Si-N'	0.59	7.06	0.73	-0.23	0.96
N-C	2.25	-24.56	1.72	-3.49	5.21
N'-C	2.27	-24.92	1.86	-3.60	5.46
[H ₃ Si-SiH ₃]					
Si-Si	0.63	-3.91	0.04	-0.31	0.36

^c Units: ρ , e $\text{\AA}^{-3}$; $\nabla^2\rho$, e $\text{\AA}^{-5}$; H , G , $|V|$, hartree $\text{\AA}^{-3}$. **Figure 1.** $\nabla^2\rho$ in the (a) SiSiN plane and (b) SiSiC plane in compound **4**. The N atom on the left of part (a) is slightly off the plane. LP stands for the lone pair of electrons on silicon. Green lines indicate negative values in $\nabla^2\rho$, and black lines stand for positive values.

It is noteworthy that the germanium analogue of **4**, [LGe:-Ge:L] (**7**) was also reported by Roesky *et al.*^[13] The Ge-Ge single bond length in **7** is 2.569(5) Å and it has no multiple-bond character. Moreover, compounds **4** and **7** adopt a *gauche*-bent structure (**4**: C-Si-Si-C torsion angle: 96.6°; **7**: C-Ge-Ge-C torsion angle: 113.0°). DFT calculations of compound **7** at the B3LYP/6-31G level show that the HOMO comprise of σ bonding interaction between the Ge p orbitals. In the LUMO, empty p orbitals at the Ge centers overlap to form a strong Ge-Ge π_y bonding, with additional Ge-N π^* interactions. Considering that compounds **4** and **7** are isostructural, and that the Ge-Ge bond is also derived from the overlapping of p-rich hybrids (14.4% s character; 85.3% p character) on the Ge atoms, there is reason to believe that the frontier orbitals of **4** will be similar to that of **7**.

1.2. Reactivity Studies of Amidinate-Stabilized Silicon(I) Dimer [LSi:-Si:L] (**4**; L = PhC(N*t*Bu)₂).

1.2.1. Reactivity of Amidinate-Stabilized Silicon(I) Dimer **4** with Bromine.

The treatment of **4** with one equivalent of bromine in toluene for 2 h afforded the monomeric bromosilylene [LSiBr] (**8**; Scheme 1) in 11.9 % yield. The Si^I-Si^I bond in **4** was cleaved by bromine in the reaction. It is noteworthy that the lone pair of electrons at the Si^I center in **4** did not undergo an oxidative addition reaction with bromine. In contrast, the reaction of [:Si{(NCH₂*t*Bu)₂C₆H₄-1,2}] or **1** (Chart 1) with bromine gave [SiBr₂{(NCH₂*t*Bu)₂C₆H₄-1,2}] (**9**; Chart 7) and [R¹SiBr₂-SiBr₂R¹] (**10**; R¹ = Si^{*i*}Pr{CH(SiMe₃)₂})₂), respectively.^[14, 1k] Power and co-workers have reported that the reaction of [Ar'MMAr'] [M = Ge, Sn; Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*Pr₂)₂] with PhN=NPh resulted in the complete cleavage of the M-M bond, and a lone pair of electrons was found at the metal centers in the product [Ar'M{(Ph)N-N(Ph)}MAr'].^[2c] Similar results can be found in the reaction of [Ar'SnSnAr'] with N₃SiMe₃ to form

$[\text{Ar}'\text{Sn}\{\mu_2\text{-N}(\text{SiMe}_3)\}\text{SnAr}']$.^[12c] The chloro-analogue of **8**, the amidinate-stabilized chlorosilylene $[\text{LSiCl}]$ (**11**; Chart 7) can be synthesized by the reaction of $[\text{LSiCl}_3]$ with potassium or by the reaction of $[\text{LSiHCl}_2]$ with $\text{LiN}(\text{SiMe}_3)_2$.^[15] Carbene-stabilized dihalosilylenes $[\text{L}'\rightarrow\text{SiX}_2]$ (**12**: $\text{X} = \text{Cl}$; **13**: $\text{X} = \text{Br}$; $\text{L}' = :\text{C}\{\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) have also been synthesized by the reaction of $[\text{L}'\rightarrow\text{SiCl}_4]$ or $[\{\text{L}'\rightarrow\text{SiBr}_3\}\text{Br}]$ with potassium graphite.^[16]

Scheme 1. Synthesis of **8**.

Chart 7. Examples of mono- and dihalo-silylenes.

Compound **8** was isolated as an air- and moisture-sensitive pale-yellow crystalline solid. It is soluble in toluene and THF. **8** is stable in solution and the solid state at room temperature in an inert atmosphere. It has been characterized by elemental analysis, spectroscopic methods and X-ray crystallography. The ^1H and ^{13}C

NMR spectra of **8** display resonances due to the amidinate ligand. The ^{29}Si NMR signal of **8** ($\delta = 18.6$ ppm) shows an upfield shift compared to that of **4** ($\delta = 76.3$ ppm).^[4b] It is comparable with that of **11** ($\delta = 14.6$ ppm)^[15a] and **13** ($\delta = 10.9$ ppm).^[16b]

The molecular structure of **8** (Figure 2) shows that the amidinate ligand is bonded in a *N,N'*-chelate fashion to the silicon(II) center, which displays a trigonal pyramidal geometry. The sum of bond angles at the silicon center is 255.0° , which is comparable with that of the three-coordinated chlorosilylene **11** (260.7°).^[15a] This geometry is consistent with a stereoactive lone pair of electrons at the silicon center. The phenyl group is orthogonally arranged to the four-membered Si1-N1-C1-N1A ring. The Si1-Br1 bond ($2.326(3)$ Å) is comparable to those of **13** ($2.3379(8)$ and $2.3607(8)$ Å),^[16b] but is longer than that of gaseous silicon dibromide (2.243 Å).^[17]

Figure 2. ORTEP drawing of compound **8** (50% thermal ellipsoids). Selected bond distances [Å] and angles [$^\circ$]: Si1-Br1 $2.326(3)$, Si1-N1 $1.971(5)$, Si1-N1A $1.882(5)$, C1-N1 $1.331(5)$; N1-Si1-N1A $66.9(2)$, N1A-Si1-Br1 $93.3(2)$, N1-Si1-Br1 $94.8(2)$, Si1-N1-C1 $88.5(3)$, N1-C1-N1A $105.9(6)$.

The C1-N1 and C1-N1A bond lengths in **8** ($1.331(5)$ Å) are approximately intermediate between the C-N double and C-N(sp^2) single bond lengths. This geometry shows considerable delocalization throughout the NCN backbone of the ligand. The Si-N bonds in **8** ($1.882(5)$ and $1.971(5)$ Å) are slightly longer than those of **4** ($1.866(4)$ and $1.874(4)$ Å).^[4b]

1.2.2. Reactivity of Amidinate-Stabilized Silicon(I) Dimer **4 with Phenylacetylene and Diphenylacetylene: Synthesis of an Amidinate-Stabilized *cis*-1,2-Disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**14**) and a Singlet Delocalized Biradicaloid [LSi(μ -C₂Ph₂)₂SiL] (**17**).**

The reaction of **4** with one equivalent of PhC≡CH in toluene for 2 h afforded the novel *cis*-1,2-disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**14**; Scheme 2). Its stereoisomer, *trans*-1,2-disilylenylethene, was not observed. It is suggested that the reaction involved an initial [1+2] cycloaddition between the HOMO [Si-Si' (σ)] of **4** and the LUMO of PhC≡CH, instead of a concerted [2+2] cycloaddition. In other words, the reaction initiates via a [1+2] cycloaddition of a Si^I center in **4** with PhC≡CH to form a silacyclopropene intermediate, which then undergoes an insertion with another Si^I center to form **14** (Scheme 3). In contrast, the reaction of **4** with two equivalents of PhC≡CH in toluene afforded a mixture of products that cannot be identified. Similar to the bromosilylene [LSiBr] (**8**; Section 1.2.1), the formation of compound **14** also involved a cleavage of the Si^I-Si^I bond of **4**. Furthermore, Tokitoh and co-workers showed that the reaction of [BbtSi≡SiBbt] (**2**; Chart 1) with ethylene may proceed through a disilylene intermediate [BbtSi(CH₂CH₂)SiBbt] to form a bis(silacyclopropane) (Chart 8).^[18] It is noteworthy that there is no reaction between **4** and Me₃SiC≡CH or Me₃SiC≡CSiMe₃ in toluene. The larger steric repulsion between the SiMe₃ substituent of the latter alkynes and the *t*Bu group of **4** might have deterred the reactions.

Scheme 2. Synthesis of **14**.

Scheme 3. Proposed mechanism for the formation of **14**.

Chart 8. Reaction of disilyne **2** with ethylene.

Compound **14** was isolated as a highly air- and moisture-sensitive yellow crystalline solid in 13.6% yield. It is soluble in toluene. **14** is stable in solution and the solid state at room temperature in an inert atmosphere. It has been characterized by elemental analysis, spectroscopic methods and X-ray crystallography. The ^1H NMR spectrum of **14** displays resonances due to the amidinate ligand and $-\text{C}(\text{H})=\text{C}(\text{Ph})-$ substituent. The ^{29}Si NMR spectrum of **14** displays two singlets at $\delta = 15.1$ and 29.5 ppm for the non-equivalent silicon centers. Both values are downfield shifted as compared to that of $[\text{LSiR}^2]$ ($\text{R}^2 = \text{NMe}_2$: $\delta = -2.62$ ppm; $\text{R}^2 = \text{O}^i\text{Pr}$: $\delta = -13.4$ ppm).^[19] The ^{29}Si NMR signals of **14** are comparable to the theoretical ^{29}Si NMR chemical shift ($\delta = 22.7, 49.6$ ppm) at the B3LYP/6-31+G(d) level.

The molecular structure of **14** is shown in Figure 3. The amidinate ligands are bonded in a N,N' -chelate fashion to the silicon centers, which display a trigonal pyramidal geometry. The sum of bond angles at the Si1 and Si2 centers are 263.1° and

269.5°, respectively. They are comparable with that of the three-coordinated chlorosilylene **11** (260.7°; Chart 7).^[15a] This geometry is consistent with a stereoactive lone pair of electrons at the silicon centers. The Si1 atom is displaced from the N1-C1-N2 least squares plane by 0.282 Å, whereas the Si2 atom is displaced from the N3-C24-N4 least squares plane by 0.337 Å. The Si1-C16 (1.905(2) Å) and Si2-C17 (1.927(2) Å) bonds are slightly shorter than the Si^{II}-C_{aryl} bond (1.973(2) Å) in [*Si*{C₆H₃-2,6-(Trip)₂}(η³-Cp*)] (**15**; Trip = 2,4,6-*i*Pr₃C₆H₂; Cp* = C₅Me₅; Chart 9).^[20] The Si1-C16 and Si2-C17 bonds are comparable with the Si^{IV}-C(sp²) bonds (average 1.901 Å) in [(Me₂HSi)₂C=C(SiHMe₂)₂] (**16**; Chart 9).^[21] The C16-C17 bond (1.346(2) Å) is a typical C=C double bond (1.34 Å). The C-N bond lengths (C1-N1: 1.333(2), C1-N2: 1.343(2), C24-N3: 1.335(2), C24-N4: 1.343(2) Å) are approximately intermediate between the C=N double and C-N(sp²) single bond lengths. This geometry shows considerable delocalization throughout the N1-C1-N2 and N3-C24-N4 skeletons.

Figure 3. ORTEP drawing of compound **14** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-N1 1.875(1), Si1-N2 1.886(1), Si1-C16 1.905(2), Si2-N3 1.877(1), Si2-N4 1.874(1), Si2-C17 1.927(2), C16-C17 1.346(2), C1-N1 1.333(2), C1-N2 1.343(2), C24-N3 1.335(2), C24-N4 1.343(2); N1-Si1-N2 69.07(6), N1-Si1-C16 95.54(7), N2-Si1-C16 98.48(7), Si1-C16-C17 125.48(13), C16-C17-Si2 118.88(12), N3-Si2-N4 69.34(6), N3-Si2-C17 101.03(6), N4-Si2-C17 99.08(6).

Chart 9. Compounds **15** and **16**.

The reaction of **4** with one or two equivalents of PhC≡CPh in toluene for 2 h afforded [LSi(μ-C₂Ph₂)₂SiL] (**17**; Scheme 4). This suggests that the reaction proceeds through a [LSi{C(Ph)=C(Ph)}SiL] intermediate, which then reacts with another molecule of PhC≡CPh to afford a diradicaloid. The isolation of compound **14** from the reaction of **4** with one equivalent of PhC≡CH further supports the proposed formation of a [LSi{C(Ph)=C(Ph)}SiL] intermediate. The radicals in compound **17** are stabilized by the amidinate ligand and the delocalization within the Si(μ-C₂Ph₂)₂Si six-membered ring (Scheme 5), as confirmed by X-ray crystallography and DFT calculations. Similarly, the reaction of [Ar'GeGeAr'] (Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*Pr₂)₂) with HC≡CSiMe₃ afforded a 1,4-digerma-benzene intermediate with considerable diradical character, which then underwent a cycloaddition with a flanking aryl ring on the terphenyl ligand.^[22] Stable singlet diradicaloid [Ar'Ge(μ-NSiMe₃)₂GeAr'] (**18**; Chart 10) was synthesized by the reaction of [Ar'GeGeAr'] with N₃SiMe₃.^[23] Recently, Ando and co-workers reported that a stable 1,4-disila(Dewar-benzene) **21** (Chart 10) was synthesized successfully by heating a dimethyldisilacyclopropenyl.^[24] Compound **21** underwent a photochemical valence isomerization to a 1,4-disilabenzene intermediate, which was trapped by butadiene to form a [4+2] cycloaddition product.

Scheme 4. Synthesis of **17**.

Scheme 5. Electron delocalization within the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ six-membered ring in compound **17**.

Compound **17** was isolated as a highly air- and moisture-sensitive dark-red crystalline solid in 47.0% yield. It is soluble in CH_2Cl_2 and THF. It is stable in the solid state at room temperature in an inert atmosphere. When crystals of **17** dissolve in $[\text{D}_8]\text{toluene}$, $[\text{D}_6]\text{benzene}$, $[\text{D}_2]\text{dichloromethane}$, $[\text{D}_5]\text{pyridine}$ or $[\text{D}_8]\text{THF}$ at room temperature, the solution decomposes after 1 day to give an unidentified white precipitate. Compound **17** is stable in $[\text{D}_8]1,4\text{-dioxane}$ at room temperature. The ^1H NMR spectrum displays resonances for the amidinate ligand and the phenyl substituents. The ^{29}Si NMR shows a singlet at $\delta = -51.0$ ppm, which is an upfield shift as compared to that of the 1,2-disilabenzene **20** in $[\text{D}_6]\text{benzene}$ ($\delta = 99.2$ ppm)^[26] and silabenzene **19** in $[\text{D}_{12}]\text{cyclohexane}$ ($\delta = 92.5$ ppm).^[25] The ^{29}Si NMR signal lies between the three-coordinate silicon centers in **14** ($\delta = 15.1$ and 29.5 ppm) and the five-coordinate silicon in $[\text{LSiCl}_3]$ ($\delta = -98.6$ ppm).^[15a] The results suggest that compound **17** is a singlet biradicaloid instead of a 1,4-disilabenzene derivative. The UV/Vis spectrum of **17** in CH_2Cl_2 at room temperature shows absorption bands at 431

nm in the visible light region and at 299, 295, 281 and 266 nm in the ultraviolet region. The absorption band of **17** in the visible light region shows a bathochromic shift compared to that of the 1,4-disilabenzene [1,4-Si₂C₄H₆] (**22**; Chart 10) (408, 396, 385, 340, 275 nm) in low-temperature Ar matrices.^[27]

Chart 10. Examples of a biradicaloid, a silabenzene and disilabenzenes.

The molecular structure of **17** is shown in Figure 4. The phenyl rings on the Si(μ-C₂Ph₂)₂Si ring are disordered. The disordered phenyl rings (C17A-C22A) are omitted for clarity. Moreover, in the asymmetric unit, there are two disordered toluene molecules, which were treated by SQUEEZE/PLATON (for details, see Appendix A). Several attempts to obtain more precise structural parameters were unsuccessful.

Figure 4. ORTEP drawing of compound **17** (30% thermal ellipsoids). Hydrogen atoms and the disordered phenyl ring (C17A-C22A) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-C16 1.821(4), Si1-C23 1.819(3), C16-C23A 1.384(5), Si1-N1 1.807(3), Si1-N2 1.819(3), C1-N1 1.339(5), C1-N2 1.339(5); C16-Si1-C23 114.8(2), Si1-C16-C23A 123.4(2), Si1-C23-C16A 121.4(2), N1-Si1-N2 72.3(1), Si1-N1-C1 91.2(2), N1-C1-N2 105.9(3), C1-N2-Si1 90.7(2).

The $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ ring is almost planar (the dihedral angle of Si1A-C23A-C16-Si1: 7.43°) and the sum of the interior angles is 719.2° . The amidinate ligands are bonded in a *N,N'*-chelate fashion to the silicon centers, which display a tetrahedral geometry. Unlike **14**, the Si1 atom in **17** is displaced from the N1-C1-N2 least-squares plane by 0.021 Å. Thus, the Si1-N1-C1-N2 ring is planar and almost perpendicular to the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ ring (dihedral angle: 87.0°). The amidinate phenyl rings are tilted (dihedral angle: 5.98°). The phenyl rings on the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ ring are also tilted and staggered (dihedral angle of C17-C16-C23A-C24A: 35.5° ; for the disordered phenyl ring (C17A-C22A), dihedral angle of C17A-C16-C23A-C24A: 2.67°). According to the theoretical calculations, the tilted phenyl rings provide additional stabilization due to the conjugation between the phenyl rings and the C=C double bonds on the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ ring (section 1.2.3). The C16-C23A bond (1.384(5) Å) is similar to that in benzene (1.39 – 1.40 Å), **19** (1.381(6) – 1.399(6) Å)^[25] and **20** (1.389(6), 1.386(6), 1.452(6) Å).^[26] The C16-C23A bond is longer than the C=C double bond, C16-C17

(1.346(2) Å), in **14**. The Si1-C16 (1.821(4) Å) and Si1-C23 (1.819(3) Å) bond lengths are almost equal to each other and intermediate between the Si-C single (1.87 Å) and double (1.70 Å) bond lengths.^[28] The Si1-C16 and Si1-C23 bonds are significantly shorter than the Si-C single bond **14** (1.905(2), 1.927(2) Å) and the 1,4-disila(Dewar-benzene) **21** (average 1.938 Å).^[24] They are longer than those in **19** (1.765(4), 1.770(4) Å)^[25] and **20** (1.804(4), 1.799(5) Å).^[26] The Si1-Si1A distance (3.343 Å) is significantly longer than the Si-Si bond length (2.248(2) Å) in **21**.^[24] This suggests that there is no Si-Si interaction in **17**. The results suggest that the singlet biradicals are stabilized by the delocalization within the Si(μ -C₂Ph₂)₂Si six-membered ring. The Si-N bonds (average 1.813 Å) in **17** are shorter than those in **14** (average 1.878 Å). The C-N bond lengths (C1-N1(2): 1.339(5) Å) in **17** are approximately intermediate between the C=N double and C-N(sp²) single bond lengths. This geometry shows considerable delocalization throughout the N1-C1-N2 skeleton.

1.2.3. Theoretical Studies of the Amidinate-Stabilized Singlet Delocalized Biradicaloid [LSi(μ -C₂Ph₂)₂SiL] (**17**).

To understand the bonding nature in compound **17**, it was investigated by means of quantum chemical calculations. The theoretical calculations of **17** were performed by means of DFT^[5] B3LYP^[6] with the 6-31G(d) basis set as implemented in the Gaussian 03 program^[8] due to the large molecular structure of **17**. The calculated structural parameters (Si1-C16: 1.813 Å, Si1-N1: 1.910 Å, C16-C23A: 1.432 Å, C1-N1: 1.341 Å; C16-Si1-C23: 114.6°, Si1-C16-C23A: 122.6°, N1-Si1-N2: 68.8°) are in good agreement with the crystallographic data except for the Si1-N1 bond. The 6-31G(d) basis set does not include the diffuse function for electron delocalization, and advanced multiple polarization functions, although there are $\pi_{C=C} \rightarrow \sigma^*_{Si-N}$, $\pi_{C=N} \rightarrow \sigma^*_{Si-C}$, and $p_N \rightarrow \sigma^*_{Si-C}$ donor-acceptor interactions around the Si1-N1 bond. Therefore, the calculated Si1-N1 bond (1.9103 Å) is slightly longer than the

crystallographic data 1.807(3) Å.^[29] Moreover, the calculated dihedral angle of the phenyl rings at the Si(μ -C₂Ph₂)₂Si ring (17.2°) shows deviation from the crystallographic data. This is due to the substantial disorder of the phenyl rings on the Si(μ -C₂Ph₂)₂Si ring in the X-ray structure of **17**.

The energy difference between the singlet and triplet state of **17** was calculated (Figures 5 and 6, respectively). The singlet state of **17** is more stable than the triplet state by 12.2 kcal mol⁻¹. The calculated Si(μ -C₂Ph₂)₂Si ring in the triplet state is not planar (the dihedral angle of Si-C-C-Si: 20.3°), whereas that in the singlet state is almost planar (the dihedral angle of Si-C-C-Si: 4.84°). The results are consistent with the crystallographic data. It is suggested that compound **17** is in singlet state.

Figure 5. Singlet state of compound **17**.

Figure 6. Triplet state of compound **17**.

Figure 7. ORTEP drawing of compound **17** (30% thermal ellipsoids). Hydrogen atoms, the disordered phenyl ring (C17A-C22A), *t*Bu and phenyl ring of the amidinate ligand are omitted for clarity.

The nucleus-independent chemical shift at 1 Å (NICS(1)) above the center of the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ ring in **17** ($\delta = -3.5$ ppm) shows that there is an electron delocalization within the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ six-membered ring.^[30] In contrast, the NICS(1) of benzene ($\delta = -11.2$ ppm) and the simple 1,4-disilabenzene derivative **22** ($\delta = -7.9$ ppm) at the B3LYP/6-31G(d) level shows aromaticity. The natural-bond-orbital (NBO)^[9] analysis (Table 4) shows that the delocalization system of the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$

ring in **17** comprises of the π and π^* orbitals of the C16-C23A and C16A-C23 bonds (total electron occupancy for $\pi = 3.62$; for $\pi^* = 1.18$) and the σ^* orbitals of the Si1-N1, Si1-N2, Si1A-N1A, and Si1A-N2A bonds (total electron occupancy = 0.97). The π orbitals of the C16-C23A and C16A-C23 bonds form π - σ^* hyperconjugation with the σ^* orbitals of the Si-N bonds (second order perturbation stabilizing energy = 5.15 or 4.44 kcal mol⁻¹; Table 5). The results suggest that the radicals are stabilized by the amidinate ligand and the delocalization within the Si(μ -C₂Ph₂)₂Si six-membered ring. Furthermore, Roesky *et al.* reported the absence of EPR signals from compound **17** at elevated temperature. DFT calculations of compound **17** at the UB3LPY/6-311G level show that the HOMO of **17** is doubly occupied, whereas the LUMO has zero electron occupancy.^[31]

Table 4. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of calculated compound **17**.

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Occu-pancy	Wiberg bond index
Si(1)-N(1) (σ)	Si(1)	15.0	sp ^{4.28}	N(1)	85.0	sp ^{2.47}	1.94	0.41
Si(1)-N(1) (σ^*)	Si(1)	85.0	sp ^{4.28}	N(1)	15.0	sp ^{2.47}	0.24	-
Si(1)-C(16) (σ)	Si(1)	25.1	sp ^{2.15}	C(16)	74.9	sp ^{1.95}	1.93	0.94
C(16)-C(23A) (σ)	C(16)	50.0	sp ^{1.83}	C(23A)	50.0	sp ^{1.83}	1.96	1.34
C(16)-C(23A) (π)	C(16)	50.0	p	C(23A)	50.0	p	1.81	-
C(16)-C(23A) (π^*)	C(16)	50.0	p	C(23A)	50.0	p	0.59	-
C(1)-N(1) (σ)	C(1)	39.5	sp ^{2.15}	N(1)	60.5	sp ^{1.89}	1.98	1.39
C(1)-N(1) (π)	C(1)	25.1	p	N(1)	74.9	p	1.95	-

Table 5. The NBO second order perturbation stabilizing energy of calculated compound **17**.

Donor NBO	Acceptor NBO	Energy (kcal mol ⁻¹)	Sum of second order perturbation stabilizing energies/ kcal mol ⁻¹
C(16)-C(23A) (π)	Si(1)-N(1) (σ^*)	5.15	
C(16)-C(23A) (π)	Si(1)-N(2) (σ^*)	4.44	
C(17)-C(18) (π)	C(16)-C(23A) (π^*)	4.92	
C(24A)-C(25A) (π)	C(16)-C(23A) (π^*)	4.92	19.68
C(24)-C(25) (π)	C(16A)-C(23) (π^*)	4.92	
C(17B)-C(18B) (π)	C(16A)-C(23) (π^*)	4.92	

In the calculated structure of **17**, the amidinate phenyl rings are tilted with respect to the Si(μ -C₂Ph₂)₂Si ring (dihedral angle of N-Si-Si-N: 12.4°). The phenyl rings on the Si(μ -C₂Ph₂)₂Si ring are also tilted and staggered. The resulting structure is a stable minimum. When the amidinate phenyl rings and phenyl substituents are perpendicular to the Si(μ -C₂Ph₂)₂Si ring (dihedral angle of the amidinate phenyl rings: 0°, *D*_{2h} symmetry), the resulting structure is less stable than compound **17** by 57.0 kcal mol⁻¹. When the amidinate phenyl rings are tilted and the phenyl substituents are perpendicular to the Si(μ -C₂Ph₂)₂Si ring, the resulting structure is less stable than compound **17** by 35.8 kcal mol⁻¹. When the phenyl rings on the Si(μ -C₂Ph₂)₂Si six-membered ring are tilted, this results in the π orbitals of the phenyl rings forming π - π^* conjugation with the π^* orbitals of the C16-C23A/ C16A-C23 bonds (total second order perturbation stabilizing energy = 19.68 kcal mol⁻¹; Table 5). This conjugation effect provides an additional stabilization in compound **17**.

Since the Si1-N1-C1-N2 ring is planar, this leads to $\pi_{C=N} \rightarrow \sigma^*_{Si-C}$ and $p_N \rightarrow \sigma^*_{Si-C}$ hyperconjugation around the Si-N bonds (the sum of second order perturbation stabilizing energy of $\pi_{C=N} \rightarrow \sigma^*_{Si-C}$ and $p_N \rightarrow \sigma^*_{Si-C} = 4.78$ or 4.65 kcal mol⁻¹). The electronic delocalization ($\pi_{C=N} \rightarrow \sigma^*_{Si-C}$ and $p_N \rightarrow \sigma^*_{Si-C}$) shortens the Si-N bonds,

although **17** has a substantial population in the Si-N σ^* orbitals and steric hindrance arising from the substituents. Similar hyperconjugation is not found in compound **14**, in which the amidinate Si-N-C-N ring is not planar. The calculated Si-N bonds (1.927, 1.924, 1.923, 1.916 Å) in **14** at the B3LYP/6-31G(d) level are longer than those in **17**. The results are consistent with the X-ray data of **14** and **17**, in which the Si-N bonds (average 1.813 Å) in **17** are shorter than those in **14** (average 1.878 Å).

The calculated enthalpies of reaction for compounds **14** and [LSi{C(Ph)=C(Ph)}SiL] show that compound **14** is more stable than [LSi{C(Ph)=C(Ph)}SiL] by 14.5 kcal mol⁻¹ (**14**: $\Delta H^0_{\text{reaction}} = -35.5$ kcal mol⁻¹; [LSi{C(Ph)=C(Ph)}SiL]: $\Delta H^0_{\text{reaction}} = -21.0$ kcal mol⁻¹) in view of thermodynamics. The higher stability of compound **14** means that it may not undergo further reaction with another molecule of PhC≡CH to form a singlet delocalized biradicaloid in the reaction of **4** with PhC≡CH.

Conclusion

DFT calculations and the topological analysis of the electron densities show that the amidinate stabilized silicon(I) dimer [LSi:-Si:L] (**4**; L = PhC(NtBu)₂) comprises a Si^I-Si^I single bond and a lone pair of electrons at each Si atom. With understanding of the bonding nature of **4**, its reactivity was explored. Collectively, the reactivity of **4** with bromine, phenylacetylene and diphenylacetylene resulted in the cleavage of the Si^I-Si^I bond in compound **4**. The reaction of **4** with bromine afforded a stable monomeric bromosilylene [LSiBr] (**8**). It is noteworthy that the lone pair of electrons at the Si^I center in compound **4** did not undergo oxidative addition with bromine.

Additionally, the treatment of **4** with one equivalent of PhC≡CH afforded the *cis*-1,2-disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**14**). On the other hand, the

treatment of **4** with one or two equivalents of $\text{PhC}\equiv\text{CPh}$ afforded $[\text{LSi}(\mu\text{-C}_2\text{Ph}_2)_2\text{SiL}]$ (**17**). Hence, the reactivity of **4** with phenylacetylene suggests that the latter reaction proceeds through a $[\text{LSi}\{\text{C}(\text{Ph})=\text{C}(\text{Ph})\}\text{SiL}]$ intermediate, which then reacts with another molecule of $\text{PhC}\equiv\text{CPh}$ to form compound **17**. X-ray crystallography and DFT calculations show that compound **17** is a singlet delocalized biradicaloid. The singlet biradicals on the silicon centers are stabilized by the amidinate ligands and the delocalization within the $\text{Si}(\mu\text{-C}_2\text{Ph}_2)_2\text{Si}$ six-membered ring.

In conclusion, our initial reactivity studies of the amidinate stabilized silicon(I) dimer $[\text{LSi}:\text{-Si:L}]$ (**4**) show that it can serve as a functionalized silylene in further metathesis reactions. The further reactivities of compound **4**, which resulted in the synthesis of stable heavier group 14 cyclobutadiene analogues and a silyliumylidene cation are described in chapters 2 and 3, respectively.

Experimental Section

General Procedure: All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Toluene was dried over and distilled over Na/K alloy prior to use. Dichloromethane was dried over and distilled over CaH₂ prior to use. [D₆]Benzene and [D₈]1,4-Dioxane were dried over and distilled over K metal prior to use. [LSi:-Si:L] (**4**) was prepared as described in the literature.^[4b] Br₂ and PhC≡CPh were purchased from Aldrich Chemicals and used without further purification. PhC≡CH was purchased from Aldrich Chemicals and distilled prior to reaction. The ¹H, ¹³C and ²⁹Si NMR 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 the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of [LSiBr] (8**).** Br₂ (0.011 mL, 0.210 mmol) was added dropwise to a solution of **4** (0.108 g, 0.210 mmol) in toluene (10 mL) at ambient temperature. The resulting yellow-orange solution was stirred for 2 h. After filtration and concentration of the filtrate, **8** was obtained as pale-yellow crystals. Yield: 0.017 g (11.9 %). M.p. 117 °C; ¹H NMR (395.9 MHz, [D₆]Benzene, 21.0 °C): δ = 1.09 (s, 18H, *t*Bu), 6.81-6.91 ppm (m, 5H, Ph); ¹³C{¹H} NMR (99.55 MHz, [D₆]Benzene, 21.1 °C): δ = 30.89 (*CMe*₃), 53.74 (*CMe*₃), 128.22, 129.38, 129.64, 129.83, 132.59 (Ph), 166.78 ppm (NCN); ²⁹Si{¹H} NMR (78.65 MHz, [D₆]Benzene, 21.2 °C): δ = 18.64 ppm; elemental analysis calcd (%) for C₁₅H₂₃BrN₂Si: C 53.09, H 6.84, N 8.26; found: C 52.87, H 6.63, N 8.05.

Crystal data for 8: [C₁₅H₂₃BrN₂Si]; *M* = 339.35; monoclinic; space group *C2/c*; *a* = 14.2389(11), *b* = 11.1641(8), *c* = 11.9823(9) Å; α = 90, β = 116.280(4), γ = 90°; *V* =

1707.9(2) Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.320 \text{ mg m}^{-3}$; 10372 measured reflections; 2471 independent reflections; 100 refined parameters; $R_1 = 0.0715$, $wR_2 = 0.1862$ ($I > 2\sigma(I)$).

Synthesis of [cis-LSi{C(Ph)=C(H)}SiL] (14). PhC≡CH (22.5 μL, 0.21 mmol) was added dropwise to a solution of **4** (0.11 g, 0.21 mmol) in toluene (16 mL) at ambient temperature and stirred for 2 h. After filtration and concentration of the filtrate, **14** was obtained as yellow crystals Yield: 0.02 g (13.6 %). M.p. 115 °C; ¹H NMR (395.9 MHz, [D₆]Benzene, 21.2 °C): δ = 1.18 (s, 18H, *t*Bu), 1.25 (s, 18H, *t*Bu), 6.89–7.15 (m, 10H, C=C(*H*) & Ph), 7.38–7.43 (m, 3H, Ph), 7.57–7.60 ppm (m, 3H, Ph); ¹³C{¹H} NMR (99.55 MHz, [D₆]Benzene, 21.2 °C): δ = 31.41, 32.01(*CMe*₃), 53.02, 53.18 (*CMe*₃), 124.85, 125.71, 126.08, 128.58, 128.84, 128.91, 129.13, 129.34, 130.57, 130.95, 137.90, 150.39 (Ph), 157.46 ((Ph)C=C(*H*)), 158.54 ((Ph)C=C(*H*)), 171.13, 174.22 ppm (NCN); ²⁹Si{¹H} NMR (78.65 MHz, [D₆]Benzene, 21.2 °C): δ = 15.11, 29.47 ppm; elemental analysis calcd (%) for C₃₈H₅₂N₄Si₂: C 73.50, H 8.45, N 9.03; found: C 73.28, H 8.16, N 8.75.

Crystal data for 14: (C₄₅H₆₀N₄Si₂): $M = 713.15$; triclinic; space group P-1; $a = 10.3544(2)$, $b = 13.7776(3)$, $c = 17.4384(5)$ Å; $\alpha = 111.101(2)$, $\beta = 90.966(2)$, $\gamma = 111.9980(10)^\circ$; $V = 2118.60(9)$ Å³; $Z = 2$; $\rho_{\text{calcd}} = 1.118 \text{ mg m}^{-3}$; 46961 measured reflections; 13055 independent reflections; 473 refined parameters; $R_1 = 0.0509$, $wR_2 = 0.1293$ ($I > 2\sigma(I)$).

Synthesis of [LSi(μ-C₂Ph₂)₂SiL] (17). A solution of PhC≡CPh (0.073 g, 0.42 mmol) in toluene (1.2 mL) was added dropwise to a solution of **4** (0.11 g, 0.21 mmol) in toluene (16.2 mL) at ambient temperature. After stirring for 2 h, a dark red suspension was formed. Dichloromethane (ca. 10 mL) was added. The resulting solution was filtered and concentrated to obtain dark-red crystals of **17**. After two hours, the mother liquid was filtered; otherwise the dark-red crystals decomposed slowly to give a

yellow precipitate. Yield: 0.103 g (47.0 %). M.p. 153 °C (decomp); ^1H NMR (399.5 MHz, $[\text{D}_8]1,4\text{-dioxane}$, 21.5 °C): δ = 0.981 (s, 36H, *t*Bu), 6.75-6.83 (m, 3H, Ph), 7.21-7.39 (m, 24H, Ph), 7.43-7.49 ppm (m, 3H, Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, $[\text{D}_8]1,4\text{-dioxane}$, 21.7 °C): δ = 31.65 (*CMe*₃), 66.08 (*CMe*₃), 125.20, 128.10, 128.15, 128.29, 128.40, 128.89, 129.44, 130.22, 131.50, 138.80 (Ph), 158.46 ((Ph)*C=C*(Ph)), 181.29 ppm (NCN); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, $[\text{D}_8]1,4\text{-dioxane}$, 21.8 °C): δ = -51.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 266 (19744), 281 (14596), 295 (13047), 299 (13933), 431 nm (2223 mol⁻¹ dm³ cm⁻¹); elemental analysis calcd (%) for $\text{C}_{58}\text{H}_{66}\text{N}_4\text{Si}_2$: C 79.59, H 7.61, N 6.41; found: C 79.32, H 7.51, N 6.24.

Crystal data for 17: $[\text{C}_{72}\text{H}_{82}\text{N}_4\text{Si}_2]$; M = 1059.60; trigonal; space group $P3(1)21$; a = 13.8659(2), b = 13.8659(2), c = 28.2606(6) Å; α = 90, β = 90, γ = 120°; V = 4705.5(1) Å³; Z = 3; ρ_{calcd} = 1.122 mg m⁻³; 29415 measured reflections; 5553 independent reflections; 350 refined parameters; R_1 = 0.0743, wR_2 = 0.2156 ($I > 2\sigma(I)$).

X-ray data collection and structural refinement. Intensity data for compounds **8**, **14** and **17** were collected using a Bruker APEX II diffractometer. The crystals 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 .^[32] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. SQUEEZE/PLATON was employed to treat two highly disordered toluene molecules in the asymmetric unit of **17**. The toluene molecules were removed from the model, but included in the empirical formula. Additional PLATON/SQUEEZE details can be found in Appendix A and the CIF file of **17**. CCDC-752138 (**8**), CCDC-757726 (**14**) and CCDC-757725 (**17**) contain the supplementary crystallographic data for this chapter. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Chapter 2

Stable Heavier Group 14 Cyclobutadiene Analogues

Introduction

Cyclobutadiene (C_4H_4) is the smallest annulene containing conjugated double bonds. The anti-aromaticity and strained geometry account for its high reactivity.^[1] It can be isolated by sequestering it in an unreactive molecular host at room temperature.^[2] The existence of cyclobutadiene in solution is also shown by various trapping reactions to form Diels-Alder adducts.^[3] Moreover, room-temperature-stable cyclobutadiene derivatives, in which the carbon atoms are incorporated with sterically hindered substituents, have been synthesized successfully and structurally characterized.^[4] In contrast, stable heavier group 14 analogues of cyclobutadiene are still rare. Until now, only a handful of examples has been reported and structurally characterized. Power *et al.* reported the synthesis of the 1,2-digermacyclobutadiene (**23**; Chart 11) in which the planar trapezoidal Ge_2C_2 ring comprises a $C=C$ double bond, two $C-Ge$ single bonds and a weak $Ge-Ge$ double bond.^[5] Tamao *et al.* reported the isolation of the tetrasilacyclobutadiene [(EMind) $_4Si_4$] (EMind = 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacen-4-yl) (**24**; Chart 11) in which the planar rhombic Si_4 ring has a charge-separated structure with the $Si-Si$ bond lengths intermediate between typical $Si-Si$ single and double bond lengths. The charge-separated Si_4 ring disfavours 4π electron delocalization, with no observable ring current.^[6] A square planar tetrasilacyclobutadiene was reported to be stabilized as transition-metal complexes (**25** – **28**; Chart 11).^[7] The results illustrate that the geometric and electronic structures of a heavier cyclobutadiene analogue are governed by the heavier group 14 elements and supporting substituents. Therefore, when a cyclobutadiene contains different heavier group 14 elements in the ring skeleton, its geometric and electronic structures are of particular interest from a fundamental point of view.

Chart 11. Examples of heavier group 14 analogues of cyclobutadiene.

It is noteworthy that the abovementioned examples of heavier cyclobutadiene analogues are stabilized by steric effects of bulky substituents that provide kinetic stabilization to the desired resulting structures. However, the synthesis of stable heavier cyclobutadiene analogues containing different heavier group 14 elements is still limited by its synthetic methodology and mode of stabilization. In this chapter, we describe the syntheses and characterizations of the first examples of heavier cyclobutadiene analogues which comprise of heavier group 14 elements in the four-membered skeleton. The cyclobutadiene analogues described herein were synthesized with the use of mild reductants and via straightforward insertion mechanisms.

Results and Discussion

2.1.1. Syntheses of the Amidinate-Stabilized Germatrisilacyclobutadiene Ylides $[\text{L}_3\text{Si}_3\text{GeL}']$ ($\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$; $\text{L}' = \ddot{\text{E}}\text{L}$; $\ddot{\text{E}} = \text{Ge}$ (**29**), Si (**32**)).

The reaction of $[\text{LSi-SiL}]^{[8]}$ (**4**) with one equivalent of $[\text{LGe-GeL}]^{[9]}$ (**7**) in THF at room temperature afforded a mixture of the germatrisilacyclobutadiene ylide $[\text{L}_3\text{Si}_3\text{GeL}']$ (**29**; $\text{L}' = \text{GeL}$) and $[\text{L}_2\text{Ge:}]^{[10]}$ (**30**; Scheme 6). The reaction mixture was filtered and volatiles of the filtrate were removed in vacuo. The crude product was characterized by NMR spectroscopy; the ^1H and ^{13}C NMR spectra show a mixture of compounds **29** and **30**, whereas the ^{29}Si NMR spectrum shows compound **29** only. The crude product was extracted with Et_2O to give **29** as dark-red crystals in 29.9 % yield. Compound **30** was found in the mother liquor, which was confirmed by NMR spectroscopy. However, an attempt to isolate compound **30** by recrystallization from the mother liquor failed. On the basis of experimental results, the mechanism for the formation of **29** and **30** is proposed. The reaction initiates by the lone pair of electrons (LP) at the Si^{I} center in **4** attacking on the Ge^{I} center in **7**, which in turn the amidinate ligand η^1 -coordinates to the Ge^{I} center, to form the intermediate **B** (Scheme 7). Simultaneously, the intermediate $[\text{LSi-GeL}]$ (**A**) is formed by the insertion of the $\text{Ge}^{\text{I}}\text{-Ge}^{\text{I}}$ bond of **7** with the $\text{Si}^{\text{I}}\text{-Si}^{\text{I}}$ bond of **4**. The LP at the Si^{I} center in **A** attacks on the Si^{I} center in **B**, which in turn the amidinate ligand η^1 -coordinates to the Si^{I} center, to form the intermediate **C**. Subsequently, the LP at the Ge^{I} center in **C** attacks on the cationic Si^{I} center to form **29** and **30**.

Scheme 6. Synthesis of **29** and **30**.

Scheme 7. Proposed mechanism for the formation of **29** and **30**.

The existence of the intermediate [LSi-GeL] (**A**) in the mechanism for the formation of **29** and **30** is evidenced by the treatment of [LGeCl]^[9] (**31**) with one equivalent of **4** in THF at room temperature, which afforded a mixture of compounds **29**, **30** and [LSiCl]^[11] (**11**; Scheme 8). Formation of the mixture of **29**, **30** and **11** in a

ratio of 1:1:3 was confirmed by ^1H NMR spectroscopy. The ^{29}Si NMR spectrum showed a mixture of **29** and **11** formed in a ratio of 1:3. Pure compounds **29** and **11** can be isolated by recrystallization. The results show that compound **31** inserts into the $\text{Si}^{\text{I}}\text{-Si}^{\text{I}}$ bond of **4** to form **11** and **A**. However, **A** cannot be observed in the reaction mixture, instead compounds **29** and **30** were found. This suggests that **A** is highly reactive. Moreover, **A** is one of the intermediates in the formation of **29** and **30**.

Scheme 8. Synthesis of **29**, **30** and **11**.

The reaction of **7** with excess **4** (three equivalents) in THF at room temperature afforded the germatrisilacyclobutadiene ylide $[\text{L}_3\text{Si}_3\text{GeL}']$ (**32**; $\text{L}' = \text{SiL}$; Scheme 9).^[12] The reaction mixture was filtered and volatiles of the filtrate were removed in vacuo. The crude product was characterized by NMR spectroscopy. The ^{29}Si NMR spectrum shows the presence of compound **32** and unreacted compound **4**. The ^1H and ^{13}C NMR spectra show a mixture of compounds **30**, **32** and unreacted compound **4**. The crude product was extracted with Et_2O to give **32** as dark-red crystals in 38.8% yield.

Moreover, compound **32** can be synthesized successfully by the reaction of **29** with one equivalent of **4** in THF in 26.9% yield. The results suggest that the reaction of **7** with excess **4** proceeds via the formation of **29**, which then reacts with **4** to form **32**.

Scheme 9. Synthesis of **32**.

Compounds **29** and **32** are soluble in Et₂O, toluene and THF. They are stable in solution and the solid state at room temperature in an inert atmosphere. X-ray crystallography and theoretical calculations show that they are not anti-aromatic and the puckered Si₃Ge four-membered rings in **29** and **32** have a ylide structure and the endocyclic Si-Ge and Si-Si bonds are single bonds (see Sections 2.1.2 and 2.1.3).

Compounds **29** and **32** have been characterized by NMR spectroscopy; the ¹H NMR spectra of **29** and **32** show two sharp singlets (**29**: δ = 1.37 and 1.44 ppm; **32**: δ = 1.47 and 1.50 ppm), which correspond to the *t*Bu substituents of the bidentate amidinate ligands. They also show a broad singlet (**29**: δ = 1.64 – 1.74 ppm; **32**: δ = 1.70 – 1.76 ppm) for the *t*Bu substituents of the monodentate amidinate ligand. The results suggest that the monodentate amidinate ligand is fluxional in solution at room temperature. In this regard, the ¹H NMR spectra of **29** and **32** were acquired at -60 °C, whereupon two singlets (**29**: δ = 1.56 and 2.25 ppm, **32**: δ = 1.56 and 2.25 ppm) were resolved for the non-equivalent *t*Bu substituents of the monodentate amidinate. The

^{29}Si NMR spectra of **29** and **32** show two sharp singlets (**29**: $\delta = -89.0$ and 64.5 ppm; **32**: $\delta = -91.9$ and 63.1 ppm) attributable to the three-coordinate Si2 and four-coordinate Si1 and Si3 centers, respectively. The large difference in chemical shift suggests that there is a ylide structure in the Si_3Ge four-membered rings in **29** and **32**. A similar large difference in chemical shift has been observed in the ^{29}Si solid state NMR spectrum of $[(\text{EMind})_4\text{Si}_4]$ (**24**) ($\delta = -52, -50, 300$ and 308 ppm).^[6] Moreover, the ^{29}Si NMR spectrum of **32** displays a sharp singlet at $\delta = 105.7$ ppm attributable to the exocyclic Si4 center, which shows a downfield shift compared with that of **4** ($\delta = 76.3$ ppm).^[8] The UV/Vis spectrum of **29** in toluene at room temperature shows absorption bands at 469 nm in the visible light region and at 290 and 243 nm in the ultraviolet region. According to the time-dependent density functional theory (TD-DFT) calculations of **29**, the absorption maximum at 469 nm is assigned to the HOMO $\rightarrow$ LUMO+7 transition (see Section 2.1.3). The UV/Vis spectrum of **32** in toluene at room temperature shows absorption bands at 494 and 415 nm in the visible light region and at 335 and 285 nm in the ultraviolet region.

2.1.2. X-ray Crystal Structures of the Amidinate-Stabilized Germatrisilacyclobutadiene Ylides $[\text{L}_3\text{Si}_3\text{GeL}']$ ($\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$; $\text{L}' = \ddot{\text{E}}\text{L}$; $\ddot{\text{E}} = \text{Ge}$ (**29**), Si (**32**)).

The molecular structures of **29** and **32** are shown in Figures 8 and 9, respectively. Compounds **29** and **32** comprise of a puckered Si_3Ge four-membered ring (dihedral angle of $\text{Si}3\text{-Si}2\text{-Si}1\text{-Ge}1$: 10.56° (**29**); 10.23° (**32**)). The amidinate ligands are bonded in a N,N' -chelate fashion to the Si1 and Si3 atoms, which adopt a distorted tetrahedral geometry. The amidinate ligand is η^1 -coordinated to the Si2 atom which displays a distorted trigonal planar geometry (the sum of bond angles around the Si2 atom: 337.00° (**29**), 338.12° (**32**)). The $\text{Ge}1\text{-Si}3$ (**29**: $2.3848(5)$ Å, **32**: $2.3823(5)$ Å) and $\text{Ge}1\text{-Si}1$ (**29**: $2.4098(5)$ Å, **32**: $2.4075(6)$ Å) bonds are comparable

with typical Si-Ge single bonds (2.356(4) – 2.510(2) Å).^[13] The results suggest that the endocyclic Ge-Si bonds in **29** and **32** are single bonds. The Si3-Si2 (**29**: 2.2909(6) Å, **32**: 2.2810(7) Å) and Si2-Si1 (**29**: 2.3024(6) Å, **32**: 2.2960(7) Å) bonds are significantly shorter than the Si^I-Si^I bond (2.413(2) Å) in **4**.^[8] They are longer than the Si=Si double bonds in acyclic neutral disilenes (2.138(2) - 2.2598(18) Å).^[14] The results show that the endocyclic Si-Si bonds are single bonds. Therefore, the puckered Si₃Ge four-membered rings in **29** and **32** have a ylide structure. In contrast, the Si₄ four-membered ring in the tetrasilacyclobutadiene [(EMind)₄Si₄] (**24**) is planar instead of puckered.^[6] The Ge1 atom is bonded with the Ge2 and Si4 atoms of the low valent group 14 metal amidinate substituents in **29** and **32**, respectively. The Ge1 atom adopts a trigonal pyramidal geometry (the sum of bond angles: 286.91° (**29**), 291.24° (**32**)).

In compound **29**, the amidinate ligand is bonded in a *N,N'*-chelate fashion to the Ge2 atom, which adopts a trigonal pyramidal geometry. The sum of bond angles at the Ge2 atom is 253.92°, which is comparable with that of the three-coordinate germanium atoms in compound **7** (266.04°, 267.64°).^[9] This geometry is consistent with a stereoactive lone pair of electrons at the Ge2 atom. The Ge1-Ge2 bond (2.5349(4) Å) is comparable with the Ge^I-Ge^I bond (2.569(5) Å) in **7**.^[9]

In compound **32**, the amidinate ligand is bonded in a *N,N'*-chelate fashion to the Si4 atom, which adopts a distorted trigonal pyramidal geometry. The sum of bond angles at the Si4 atom is 261.33°, which is significantly smaller than that of the three-coordinate silicon atoms in compound **4** (average 282.35°).^[8] This geometry is consistent with a stereoactive lone pair of electrons at the Si4 atom. The Ge1-Si4 bond (2.4778(6) Å) is comparable with typical Si-Ge single bonds (2.356(4) – 2.510(2) Å).^[13]

Figure 8. ORTEP drawing of compound **29** (50% thermal ellipsoids). Hydrogen atoms and a diethylether molecule are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Si2-Si3 2.2909(6), Si1-Si2 2.3024(6), Si1-Ge1 2.4098(5), Ge1-Si3 2.3848(5), Ge1-Ge2 2.5349(4), N5-Si3 1.8715(14), N6-Si3 1.8762(14), N3-Si2 1.8180(15), N1-Si1 1.8718(14), N2-Si1 1.8789(14), Ge2-N7 2.0181(14), Ge2-N8 2.0282(15), C50-N7 1.327(2), C50-N8 1.334(2), C35-N5 1.337(2), C35-N6 1.340(2), C20-N4 1.279(2), C20-N3 1.412(2), C5-N1 1.338(2), C5-N2 1.344(2); Si2-Si3-Ge1 102.36(2), Si1-Si2-Si3 79.21(2), Si2-Si1-Ge1 101.26(2), Si1-Ge1-Si3 75.285(17), Si3-Ge1-Ge2 104.151(15), Si1-Ge1-Ge2 107.475(15), Si3-Si2-N3 123.57(5), Si1-Si2-N3 134.22(5), N7-Ge2-Ge1 95.37(5), N8-Ge2-Ge1 94.29(5), N7-Ge2-N8 64.26(6).

Figure 9. ORTEP drawing of compound **32** (50% thermal ellipsoids). Hydrogen atoms, a diethylether molecule and the disordered phenyl substituent (C6A-C11A) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-Si2 2.2960(7), Si2-Si3 2.2810(7), Ge1-Si1 2.4075(6), Ge1-Si3 2.3823(5), Ge1-Si4 2.4778(6), N1-Si1 1.8670(16), N2-Si1 1.8752(16), N3-Si2 1.8138(17), N5-Si3 1.8694(16), N6-Si3 1.8691(16), N7-Si4 1.8965(17), N8-Si4 1.9024(18), C5-N1 1.337(2), C5-N2 1.342(2), C20-N4 1.278(2), C20-N3 1.408(2), C35-N5 1.336(2), C35-N6 1.340(2), C50-N8 1.334(3), C50-N7 1.338(3); Si2-Si1-Ge1 101.12(2), Si2-Si3-Ge1 102.34(2), Si3-Si2-Si1 79.48(2), Si3-Ge1-Si1 75.302(18), Si1-Si2-N3 134.68(6), Si3-Si2-N3 123.96(6), Si4-Ge1-Si1 109.693(19), Si4-Ge1-Si3 106.248(19), N7-Si4-Ge1 97.17(6), N8-Si4-Ge1 96.19(6), N7-Si4-N8 67.97(7).

2.1.3. Theoretical Studies of Amidinate-Stabilized Germatrisilacyclobutadiene Ylide [L_3Si_3GeL'] (**29**; $L = PhC(NtBu)_2$; $L' = GeL$).

To understand the bonding nature in compounds **29** and **32**, compound **29** was investigated by means of density functional theory calculations.^[15] The optimized geometry of **29** at the B3PW91/6-31+G(d) level (see Appendix B, Figure B4) is in good agreement with the X-ray crystallographic data. The Wiberg bond index (WBI; Table 6)^[16] indicates that the Si-Si (WBI: 1.10) and Si-Ge bonds (WBI: 0.98) in the Si_3Ge four-membered ring are single bonds. The natural-bond-orbital (NBO)^[17] analysis (Table 6) shows that the Si_3Ge four-membered ring has four occupied σ

orbitals for the Si-Si and Si-Ge bonds (electron occupancy: 1.86 for Si1-Si2, 1.87 for Si2-Si3, 1.83 for Si1-Ge1, 1.83 for Si3-Ge1). Moreover, there are lone pair orbitals (LPs) at the Si2 and Ge1 atoms, which are almost pure p orbitals (Si2: $sp^{25.7}$, Ge1: $sp^{82.2}$). The results show that the Si_3Ge four-membered ring has a ylide structure and the Si2-Si and Ge1-Si bonds are single bonds. The electron occupancies of the lone pair orbitals at the Si2 and Ge1 atoms are 1.32 and 1.13, respectively. It is noteworthy that there are 1.78 electrons distributed amongst the Si1-N, Si3-N, Si2-Si and Ge1-Si σ^* orbitals. Moreover, the second order perturbation theory analysis (Table 7) shows that the lone pair orbitals of the Si2 and Ge1 atoms form significant p- σ^* hyperconjugations with the σ^* orbitals of the Si1-N, Si3-N, Si2-Si and Ge1-Si bonds (the sum of second order perturbation stabilizing energies: 38.43 kcal mol⁻¹ for the Si2 LP orbital, 25.16 kcal mol⁻¹ for the Ge1 LP orbital). The results suggest that the lone pair electrons at the Si2 and Ge1 atoms delocalize within the Si_3Ge four-membered ring. The presence of delocalization is also supported by the nucleus-independent chemical shift (NICS).^[18] The NICS (1, same direction as the Ge1-Ge2 bond) ($\delta = -9.83$ ppm) and NICS(-1) ($\delta = -4.66$ ppm) of the Si_3Ge four-membered ring indicate a ring current. The results reveal that there is an electron delocalization within the Si_3Ge four-membered ring. Thus, compound **29** is not anti-aromatic. This is in contrast to the tetrasilacyclobutadiene [(EMind)₄Si₄] (**24**), which is non-aromatic.^[6] The electron delocalization can be illustrated in the HOMO-1 (Figure 10a), which shows the interaction of the lone pair orbitals at the Si2 and Ge1 atoms with the σ^* orbitals of the Si1-N and Si3-N bonds. Although there is an electron delocalization, the NPA charges (Si3: 0.94, Si2: 0.19, Si1: 0.97, Ge1: -0.59; Table 8) show that there is still a considerable charge difference and hence a zwitterionic contribution in the Si_3Ge four-membered ring. The NPA charge of the Si2 atom is higher than expected because the negative charge is pulled towards the N3 atom (NPA: -0.88) by an inductive effect.

The NPA charge of the N3 atom is more negative than other nitrogen atoms (Table 8). A similar charge difference has been observed in the tetrasilacyclobutadiene [(EMind)₄Si₄] (**24**) (NPA charges of the Si atoms: 0.144, 0.167, 0.637, 0.647).^[6]

The NBO analysis also shows that the lone pair electrons at the Ge2 center is high in s character with some directionality ($sp^{0.24}$, occupancy: 1.95; Table 6). The Ge1-Ge2 bond is formed by $sp^{1.95}$ hybrids on the Ge1 atom and p rich hybrids ($sp^{9.12}$) on the Ge2 atom. The Wiberg bond index (WBI)^[16] shows that the Ge1-Ge2 bond (WBI: 0.86) is a single bond.

The HOMO-1 of **29** shows the interaction of the lone pair orbitals at the Si2 and Ge1 atoms with the σ^* orbitals of the Si1-N and Si3-N bonds (Figure 10a). The HOMO involves the Ge1-Ge2 σ bond and the lone pair orbital at the Si2 atom (Figure 10b). The LUMO, LUMO+1 and LUMO+7 (Figures 10c, 10d and 10e, respectively) comprise of the π^* orbitals of the phenyl rings. The time-dependent DFT (TD-DFT) calculations show that the calculated absorption band ($\lambda = 470$ nm, oscillator strength $f = 0.15$) of HOMO $\rightarrow$ LUMO+7 is comparable to the absorption band observed in the UV/Vis spectrum of **29** ($\lambda = 469$ nm). Moreover, the calculations also show two allowed transitions from HOMO-1 $\rightarrow$ LUMO ($\lambda = 481$ nm, $f = 0.04$) and HOMO-1 $\rightarrow$ LUMO+1 ($\lambda = 465$ nm, $f = 0.05$). However, these transitions are calculated to give very weak absorption bands, which could be overlapped by the absorption band observed in the UV/Vis spectrum of **29**.

Table 6. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of calculated compound **29**.

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Occu-pancy	Wiberg bond index
Si(3)-Si(2) (σ)	Si(3)	50.8	$sp^{1.83}$	Si(2)	49.2	$sp^{1.74}$	1.87	1.10
Si(3)-Si(2) (σ^*)	Si(3)	49.2	$sp^{1.83}$	Si(2)	50.8	$sp^{1.74}$	0.15	-
Si(2)-Si(1) (σ)	Si(2)	49.2	$sp^{2.14}$	Si(1)	50.8	$sp^{1.85}$	1.86	1.10
Si(2)-Si(1) (σ^*)	Si(2)	50.8	$sp^{2.14}$	Si(1)	49.2	$sp^{1.85}$	0.14	-
Si(1)-Ge(1) (σ)	Si(1)	45.2	$sp^{2.78}$	Ge(1)	54.8	$sp^{2.10}$	1.83	0.98
Si(1)-Ge(1) (σ^*)	Si(1)	54.8	$sp^{2.78}$	Ge(1)	45.2	$sp^{2.10}$	0.24	-
Si(3)-Ge(1) (σ)	Si(3)	44.9	$sp^{2.79}$	Ge(1)	55.1	$sp^{2.02}$	1.83	0.98
Si(3)-Ge(1) (σ^*)	Si(3)	55.1	$sp^{2.79}$	Ge(1)	44.9	$sp^{2.02}$	0.24	-
Si(3)-N(5) (σ)	Si(3)	15.0	$sp^{3.86}$	N(5)	85.0	$sp^{2.26}$	1.94	0.42
Si(3)-N(5) (σ^*)	Si(3)	85.0	$sp^{3.86}$	N(5)	15.0	$sp^{2.26}$	0.25	-
Si(3)-N(6) (σ)	Si(3)	15.1	$sp^{4.34}$	N(6)	84.9	$sp^{2.29}$	1.94	0.41
Si(3)-N(6) (σ^*)	Si(3)	84.9	$sp^{4.34}$	N(6)	15.1	$sp^{2.29}$	0.26	-
Si(2)-N(3) (σ)	Si(2)	18.0	$sp^{2.52}$	N(3)	82.0	$sp^{1.76}$	1.97	0.60
Si(2)-N(3) (σ^*)	Si(2)	82.0	$sp^{2.52}$	N(3)	18.0	$sp^{1.76}$	0.16	-
Si(1)-N(1) (σ)	Si(1)	15.0	$sp^{3.92}$	N(1)	85.1	$sp^{2.27}$	1.94	0.42
Si(1)-N(1) (σ^*)	Si(1)	85.1	$sp^{3.92}$	N(1)	15.0	$sp^{2.27}$	0.25	-
Si(1)-N(2) (σ)	Si(1)	15.2	$sp^{4.21}$	N(2)	84.8	$sp^{2.25}$	1.94	0.42
Si(1)-N(2) (σ^*)	Si(1)	84.8	$sp^{4.21}$	N(2)	15.2	$sp^{2.25}$	0.25	-
Ge(2)-Ge(1) (σ)	Ge(2)	36.7	$sp^{9.12}$	Ge(1)	63.3	$sp^{1.95}$	1.84	0.86
Ge(2)-Ge(1) (σ^*)	Ge(2)	63.3	$sp^{9.12}$	Ge(1)	36.7	$sp^{1.95}$	0.18	-
Si(2) LP	Si(2)	-	$sp^{25.7}$	-	-	-	1.32	-
Ge(1) LP	Ge(1)	-	$sp^{82.2}$	-	-	-	1.13	-
Ge(2) LP	Ge(2)	-	$sp^{0.24}$	-	-	-	1.95	-

Table 7. The NBO second order perturbation stabilizing energy of calculated compound **29**.

Donor NBO	Acceptor NBO	Energy (kcal mol ⁻¹)	Sum of second order perturbation stabilizing energies/ kcal mol ⁻¹
LP(Si(2))	Si(3)-N(5) (σ^*)	5.56	38.43
LP(Si(2))	Si(3)-N(6) (σ^*)	11.87	
LP(Si(2))	Si(1)-N(1) (σ^*)	5.59	
LP(Si(2))	Si(1)-N(2) (σ^*)	10.30	
LP(Si(2))	Si(3)-Ge(1) (σ^*)	2.45	
LP(Si(2))	Si(1)-Ge(1) (σ^*)	2.66	
LP(Ge(1))	Si(3)-N(5) (σ^*)	2.40	25.16
LP(Ge(1))	Si(3)-N(6) (σ^*)	6.69	
LP(Ge(1))	Si(1)-N(1) (σ^*)	2.61	
LP(Ge(1))	Si(1)-N(2) (σ^*)	6.14	
LP(Ge(1))	Si(2)-Si(3) (σ^*)	3.90	
LP(Ge(1))	Si(2)-Si(1) (σ^*)	3.42	

Table 8. The NPA charges of calculated compound **29**.

Atom	NPA Charge	Atom	NPA Charge
Si(3)	0.94	N(5)	-0.78
Si(2)	0.19	N(6)	-0.77
Si(1)	0.97	N(3)	-0.88
Ge(2)	0.65	N(1)	-0.77
Ge(1)	-0.59	N(2)	-0.78

Figure 10. Selected molecular orbitals of compound **29** calculated at the B3PW91/6-31+G(d) level.

- (a) The HOMO-1 representing the interaction of the lone pair orbitals at the Si2 and Ge1 atoms with the σ^* orbitals of the Si1-N and Si3-N bonds. (i) HOMO-1 is viewed from the Si2 atom. (ii) The HOMO-1 viewed from the Si1 atom.

(i)

(ii)

- (b) The HOMO which involves the Ge1-Ge2 σ bond and the lone pair orbital at the Si2 atom.

- (c) The LUMO which comprises the π^* orbitals of the phenyl rings.

(d) The LUMO+1 which comprises the π^* orbitals of the phenyl rings.

(e) The LUMO+7 orbital of a complex molecule, which comprises the π^* orbitals of the phenyl rings.

In view of experimental results and theoretical studies, compounds **29** and **32** are not anti-aromatic. The Si₃Ge four-membered rings in **29** and **32** have a ylide structure and the endocyclic Si-Si and Ge-Si bonds are single bonds. There are lone pair electrons at the Si² and Ge¹ atoms in **29** and **32**, which are stabilized by the electron delocalization within the Si₃Ge four-membered ring (Scheme 10). Similar electron delocalization can be observed in the amidinate-stabilized zwitterionic 2,4-disila-1,3-diphosphacyclobutadiene **33** and tetrasilacyclobutadiene dication **34** (Chart 12).^[19,20] Moreover, in a recent review, Bertrand showed that when a λ⁵-phosphacyclobutadiene contains a phosphorus atom without any p orbitals available for the π system of cyclobutadiene, the four π-electron four-membered heterocycle is not anti-aromatic and features a strong ylide character or interrupted cyclic π delocalization.^[21] This is comparable with compounds **29** and **32**, which have a ylide structure and are not anti-aromatic.

Scheme 10. Electron delocalization within the Si₃Ge four-membered ring.

Chart 12. Electron delocalization in the amidinate-stabilized zwitterionic 2,4-disila-1,3-diphosphacyclobutadiene **33** and tetrasilacyclobutadiene dication **34**.

2.2.1. Synthesis of the Zwitterionic Amidinate-Stabilized Digermadistannacyclobutadiene $[\text{L}_2\text{Ge}_2\text{Sn}_2\text{L}'_2]$ (**36**; $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$; $\text{L}' = \text{GeL}$).

The reaction of $[\text{LGe-GeL}]$ (**7**)^[9] with two equivalents of $[\text{LSnCl}]$ (**35**)^[22] and KC_8 in THF at room temperature afforded a mixture of the zwitterionic amidinate-stabilized digermadistannacyclobutadiene $[\text{L}_2\text{Ge}_2\text{Sn}_2\text{L}'_2]$ (**36**) and the bis(amidinate) stannylene $[\text{L}_2\text{Sn}]$ ^[22] (**37**; Scheme 11), which was confirmed by $^{119}\text{Sn}\{^1\text{H}\}$ and ^1H NMR spectroscopy. The reaction mixture was filtered and Et_2O was added to the filtrate. Concentration of the filtrate afforded compound **36** as a highly air- and moisture-sensitive dark-red crystalline solid in very low yield (5.6 %). Although the mechanism for the formation of **36** and **37** is unknown as yet, on the basis of experimental results, we propose that the reaction appears to proceed through the reduction of $[\text{LSnCl}]$ to form a transient tin(I) radical $[\text{LSn}\cdot]$ or a transient tin(I) dimer $[\text{LSn}]_2$, which undergoes a disproportionation with compound **7** to form **36** and **37**. The evidence for the disproportionation reaction can be illustrated by the reduction of

35 with KC_8 in THF, which afforded **37** and elemental tin.^[23] Moreover, the disproportionation of an organotin(I) dimer $[\text{4-}t\text{Bu-2,6-}\{\text{P}(\text{OiPr})_2=\text{O}\}_2\text{C}_6\text{H}_2\text{Sn:}]_2$ (**38**; Chart 13) to elemental tin and the diorganostannylene $[\{\text{4-}t\text{Bu-2,6-}\{\text{P}(\text{OiPr})_2=\text{O}\}_2\text{C}_6\text{H}_2\}_2\text{Sn:}]$ (**39**) has been demonstrated by Jurkschat *et al.*^[24]

Scheme 11. Synthesis of **36** and **37**.

Chart 13. Disproportionation of organotin(I) dimer **38**.

It is anticipated that compound **36** can be synthesized via a similar insertion mechanism that was proposed for the synthesis of the amidinate-stabilized germatrisilacyclobutadiene ylide **29** (Scheme 8). Hence the reaction of **7** with $[L^{Ar}SnCl]$ (**40**; $L^{Ar} = tBuC(NAr)_2$; $Ar = 2,6-iPr_2C_6H_3$)^[25] was attempted. The reaction of **7** with **40** in THF at room temperature afforded a mixture of **36**, $[L^{Ar}_2Sn:]$ (**41**) and $[LGeCl]$ (**31**; Scheme 12).^[9] After the reaction, volatiles were removed in vacuo and the crude product was characterized by NMR spectroscopy; the 1H NMR spectrum shows a mixture of compounds **36**, **41** and **31**, whereas the $^{119}Sn\{^1H\}$ NMR spectrum shows the presence of compounds **36** and **41**. The crude product was extracted with DME to afford compound **36** in higher yield (16.8 %), as compared with the aforementioned method. However, an attempt to isolate compounds **41** and **31** by recrystallization from the mother liquor failed. In order to verify the formation of **41**, it was synthesized by the reaction of two equivalents of $L^{Ar}Li$ with $SnCl_2$ in Et_2O (Scheme 13) and characterized by X-ray crystallography.^[26] Observation of the same signal ($\delta = -336$ ppm) in the $^{119}Sn\{^1H\}$ spectra of the crude product (from the reaction of **7** with **40**) and pure crystalline form of compound **41** showed that **41** is indeed a side-product of the former reaction. Although the mechanism is unknown as yet, we propose that the reaction proceeds through the insertion of $[L^{Ar}SnCl]$ into the Ge^I-Ge^I bond of **7** to form a transient germanium(I)-tin(I) complex $[LGe-SnL^{Ar}]$, which then undergoes a disproportionation to form **36** and **41**.

Scheme 12. Synthesis of **36**, **41** and **31**.

Scheme 13. Synthesis of **41**.

Compound **36** has been characterized by NMR spectroscopy and X-ray crystallography. It exhibits high solubility in THF, DME and Et₂O, and is sparingly soluble in toluene. It is stable in the solid state at room temperature in an inert atmosphere. When crystals of **36** dissolve in [D₆]Benzene and [D₈]THF at room temperature, the compound decomposes slowly in the deuterated solvents within 2 days to give black solids. In this regard, freshly prepared solution of **36** in [D₈]THF was characterized by NMR spectroscopy. The ¹H NMR spectrum of **36** shows two singlets at δ = 0.96 and 1.40 ppm for the *t*Bu substituents and a multiplet at δ = 7.19 – 7.28 ppm for the phenyl protons of the amidinate ligands. The ¹¹⁹Sn{¹H} NMR

spectrum shows a signal at $\delta = -90.9$ ppm, which lies between that of the 1,3-diaza-2,4-distannacyclobutane-2,4-diyl **42**^[27] ($\delta = -84$ ppm) and the stannyl anion $[n\text{Bu}_3\text{SnLi}(\text{Et}_2\text{O})_3]$ (**43**) ($\delta = -155$ ppm) (Chart 14).^[28] The UV/Vis spectrum of **36** in THF at room temperature shows an absorption band at 508 nm in the visible light region. According to the time-dependent DFT (TD-DFT) calculations of **36**, the absorption maximum at 508 nm is assigned to the HOMO $\rightarrow$ LUMO transition (see section 2.2.5).

Chart 14. 1,3-diaza-2,4-distannacyclobutane-2,4-diyl **42** and the stannyl anion **43**.

2.2.2. Synthesis of the Zwitterionic Amidinate-Stabilized Tetragermacyclobutadiene [L_4Ge_6] (**45**; $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$).

The reaction of **7** with the “onio-substituent transfer” reagent $[4\text{-NMe}_2\text{-C}_5\text{H}_4\text{NSiMe}_3]\text{OTf}$ (**44**)^[29] in THF and 4-dimethylaminopyridine (DMAP)^[30] at room temperature afforded a mixture of the zwitterionic amidinate-stabilized tetragermacyclobutadiene [L_4Ge_6] (**45**), the amidinium triflate $[\text{PhC}(\text{NH}t\text{Bu})_2]\text{OTf}$ (**46**) and $\text{Me}_3\text{SiSiMe}_3$ (**47**; Scheme 14), which was confirmed by NMR spectroscopy and X-ray crystallography. The reaction mixture was filtered and the filtrate was concentrated to afford compound **45** as a highly air- and moisture-sensitive red crystalline solid in 25.8% yield. When volatiles of the reaction mixture were removed in vacuo and the crude product was extracted with toluene, a mixture of red crystals of **45**, colorless crystals of **46**^[31] and crystals of DMAP was afforded after concentration

of the filtrate. The results are in contrast to the reaction of the lighter congener [LSi-SiL] (**4**) with **44**, which afforded the silyliumylidene cation [LSi(DMAP)]OTf supported by an amidinate ligand and DMAP.^[32] Although the mechanism for the formation of **45** is unknown as yet, on the basis of aforementioned experimental results, we propose that the reaction of **7** and **44** proceeds through the oxidation of **7** or the transient germanium(I) radical [LGe•] with **44** to form a Ge^{II} cation intermediate [LGe]OTf and **47**. Subsequently, the highly electrophilic Ge^{II} cation intermediate [LGe]OTf undergoes a disproportionation with **7** to form **45** and **46**. Recently, Driess *et al.* proposed a similar mechanism for the reaction of the amidinate silicon(II) chloride [LSiCl] with Cp*ZrCl₃ (Cp* = C₅Me₅), that it proceeds through the formation of the transient amidinate silicon(II) cation [LSi][Zr₂Cl₇Cp*], which then undergoes a disproportionation with [LSiCl] to form the base-stabilized tetrasilacyclobutadiene dication **34**, LH⁺Cl⁻ and LSiCl₃.^[20]

Scheme 14. Synthesis of **45**, **46** and **47**.

Compound **45** has been characterized by NMR spectroscopy and X-ray crystallography. It is soluble in THF, DME and pyridine. It is stable in the solid state at room temperature in an inert atmosphere. The ^1H NMR and ^{13}C NMR spectra display resonances due to the amidinate ligands. The UV/Vis spectrum of **45** in THF at room temperature shows an absorption band at 524 nm in the visible light region. According to the time-dependent DFT (TD-DFT) calculations of **45**, the absorption maximum at 524 nm is assigned to a mixture of HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+2 transitions (see section 2.2.5).

2.2.3. X-ray Crystal Structure of the Zwitterionic Amidinate-Stabilized Digermadistannacyclobutadiene [$\text{L}_2\text{Ge}_2\text{Sn}_2\text{L}'_2$] (**36**; $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$; $\text{L}' = \text{GeL}$).

The molecular structure of **36** is shown in Figure 11. The Ge_2Sn_2 core is planar and rhombic. The endocyclic Sn1-Ge2-Sn1A and Ge2-Sn1-Ge2A angles are $110.38(2)^\circ$ and $69.62(2)^\circ$, respectively. The sum of the internal bond angles is 360.0° . The results are in contrast to the amidinate-stabilized germatrisilacyclobutadiene ylide **29**, in which the Si_3Ge four-membered ring is puckered. The amidinate ligands are bonded in a N,N' -chelate fashion to the Ge2 and Ge2A atoms, which adopt a distorted tetrahedral geometry. Each endocyclic Sn atom in compound **36** is bonded with a low valent germanium amidinate substituent. The Sn1 and Sn1A atoms adopt a distorted trigonal pyramidal geometry (the sum of bond angles around the Sn atoms: 267.87°). This geometry is consistent with a stereoactive lone pair of electrons on the Sn atoms. The Sn1-Ge2 (2.6863(6) Å) and Sn1-Ge2A (2.6799(6) Å) bonds are longer than the Ge=Sn (2.5065(5) Å) double bond in a stannagermene.^[33] They are comparable with reported Sn-Ge single bonds (2.599(3) – 2.7210(4) Å).^[34] This suggests that the endocyclic Sn-Ge bonds in **36** are single bonds. The results indicate that the Ge_2Sn_2 core has a charge-separated structure, which is also confirmed by theoretical studies (see section 2.2.5). Moreover, the amidinate ligand is bonded in a N,N' -chelate fashion

to the Ge1 and Ge1A atoms, which adopt a trigonal pyramidal geometry. The sum of bond angles at the exocyclic Ge atoms is 245.23° , which is comparable with that of the three-coordinate germanium atoms in **7** (266.04° , 267.64°).^[9] This geometry is consistent with stereoactive lone pair of electrons at the Ge1 and Ge1A atoms. The Ge1-Sn1 bond ($2.7247(7)$ Å) is longer than the endocyclic Sn-Ge bonds and comparable with that in the germylene-stannylene $[\text{HC}(\text{CMeNAr})_2\text{Sn-Ge}\{\text{C}(\text{Me})\text{CHC}(\text{Me})\text{NAr}\}]$ (**48**; Chart 15) ($2.7210(4)$ Å).^[34d]

Figure 11. ORTEP drawing of compound **36** (50% thermal ellipsoids). Disordered phenyl and *t*Bu substituents and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1-Ge1 2.7247(7), Sn1-Ge2 2.6863(6), Sn1-Ge2A 2.6799(6), Ge1-N1 2.026(4), Ge1-N2 2.029(4), Ge2-N3 2.007(4), Ge2-N4 1.981(4); Sn1-Ge2-Sn1A 110.38(2), Ge2-Sn1-Ge2A 69.62(2), Ge1-Sn1-Ge2 99.40(2), Ge1-Sn1-Ge2A 98.85(2), N3-Ge2-N4 66.31(16), N1-Ge1-N2 64.15(16), N1-Ge1-Sn1 90.20(13), N2-Ge1-Sn1 90.88(13).

48: Ar = 2,6-*i*Pr₂C₆H₃

Chart 15. Diorgano germylene-stannylene **48**.

2.2.4. X-ray Crystal Structure of the Zwitterionic Amidinate-Stabilized Tetragermacyclobutadiene [L_4Ge_6] (**45**; $L = PhC(NtBu)_2$).

The molecular structure of **45** is shown in Figure 12. It is isostructural to compound **36**. The Ge_4 core is planar and rhombic. The amidinate ligands are bidentate bonded to the Ge_3 and Ge_{3A} atoms, which adopt a distorted tetrahedral geometry. The Ge_2 and Ge_{2A} atoms are bonded with a low valent germanium amidinate substituent. They adopt a distorted trigonal pyramidal geometry (the sum of bond angles around the Ge atoms: 283.27°). This geometry is consistent with a stereoactive lone pair of electrons on them. The endocyclic Ge-Ge bonds ($2.4577(6)$, $2.4568(6)$ Å) are comparable to Ge-Ge single bonds (average 2.44 Å).^[35] They are also comparable with that of the digermacyclobutadiene **23** ($2.4708(9)$ Å).^[5] The results indicate that the Ge_4 core has a charge-separated structure, which is comparable to **36**. The Ge_1 and Ge_{1A} atoms adopt a trigonal pyramidal geometry (the sum of bond angles around the Ge atoms is 251.26°), which indicate that there are stereoactive lone pairs of electrons on them. The Ge_1 - Ge_2 and Ge_{1A} - Ge_{2A} bonds ($2.5461(6)$ Å) are comparable with that in **7** ($2.569(5)$ Å).^[9] The results imply that these bonds do not have any multiple bond character.

Figure 12. ORTEP drawing of compound **45** (50% thermal ellipsoids). Hydrogen atoms and THF molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Ge2 2.5461(6), Ge2-Ge3 2.4568(6), Ge2-Ge3A 2.4577(6), Ge1-N1 2.020(3), Ge1-N2 2.026(3), Ge3-N3 1.989(3), Ge3-N4 1.976(3); N1-Ge1-N2 64.43(12), N1-Ge1-Ge2 93.68(9), N2-Ge1-Ge2 93.15(9), Ge1-Ge2-Ge3 105.03(2), Ge1-Ge2-Ge3A 106.47(2), Ge3A-Ge2-Ge3 71.77(2), Ge2-Ge3-Ge2A 108.23(2), N3-Ge3-N4 66.16(12).

2.2.5. Theoretical Studies of the Zwitterionic Amidinate-Stabilized Digermadistannacyclobutadiene [$L_2Ge_2Sn_2L'_2$] (**36**; $L = PhC(NtBu)_2$; $L' = GeL$) and Tetragermacyclobutadiene [L_4Ge_6] (**45**).

To understand the bonding nature in compounds **36** and **45**, they were investigated by means of density functional calculations.^[36] The optimized geometries of **36** (UB3PW91/LANL08d for Sn, 6-31+G(d) for Ge and N, and 6-31G(d) for C and H level, see Appendix B, Figure B5) and **45** (UB3PW91/6-31+G(d) level, Figure B6) are in good agreement with the X-ray crystallographic data.

The HOMO of **36** (Figure 13a) and **45** (Figure 14c) comprise of two exocyclic Ge1-E and Ge1A-E σ orbitals (**36**: E = Sn; **45**: E = Ge). The HOMO-1 of **36** and **45** (Figures 13b and 14b, respectively) mainly arise from the combinations of lone pair

orbitals at the three-coordinate E atoms of the Ge₂E₂ ring. The HOMO-1 of **36** also involves the lone pair orbitals at the exocyclic Ge atoms. The HOMO-2 of **36** and **45** (Figures 13c and 14a, respectively) comprise of the endocyclic Ge-E σ orbitals. The LUMO of **36** and **45** (Figures 13d and 14d, respectively) involves (a) the interaction of p orbitals between the four coordinate Ge atoms, (b) the exocyclic Ge-E σ^* orbitals and (c) the π^* orbitals of the phenyl rings. The LUMO+1 of **36** (Figure 13e) comprises π^* orbitals of the phenyl rings and the exocyclic Ge-Sn π orbitals. The LUMO+1 and LUMO+2 of **45** (Figures 14e and 14f, respectively) comprise the π^* orbitals of the phenyl rings. Moreover, the CASSCF(4,6) of **36** and **45** show that they have no biradicaloid character.

The Wiberg bond index (WBI)^[16] indicates that the bond orders of the endocyclic Ge-E bonds (**36**: WBI: 0.90; Table 9; **45**: WBI: 0.99; Table 12) are equal and single bonds. Moreover, the NPA charges of **36** (Ge2: 0.60, Sn1: -0.13; Table 11) and **45** (Ge2, Ge2A: -0.54; Ge3, Ge3A: 0.89; Table 14) show that the Ge₂E₂ four-membered ring has a charge-separated structure. Furthermore, the nucleus-independent chemical shift (NICS)^[18] of **36** [NICS(1): 0.75, 0.96; NICS(0): 4.00] and **45** [NICS(1): -1.10; NICS(0): 2.48] suggest that there is no delocalization of π electrons in the Ge₂E₂ four-membered rings. Thus, compounds **36** and **45** are non-aromatic. The results are in contrast to the amidinate-stabilized germatrisilacyclobutadiene ylide **29** and 2,4-disila-1,3-diphosphacyclobutadiene **33**,^[19] that they exhibit electron delocalization over the four-membered ring skeletons.

The natural-bond-orbital (NBO)^[17] analyses of **36** (Table 9) and **45** (Table 12) also show that the Lewis structures of the Ge₂E₂ rings have four occupied σ orbitals for the endocyclic Ge-E bonds [electron occupancy: 1.80 e (**36**); 1.82 e (**45**)]. Moreover, there are two lone pair orbitals on the three-coordinate E atoms (**36**: sp^{50.9} hybrids; **45**: p orbital), which are stabilized by a geminal hyperconjugation with the

endocyclic and exocyclic Ge-E σ^* orbitals [the sum of second order perturbation stabilizing energies for each lone pair orbital: 417.1 kcal mol⁻¹ (**36**; Table 10); 91.2 kcal mol⁻¹ (**45**; Table 13)].

Furthermore, the NBO analyses show that the lone pair electrons at the Ge1 and Ge1A atoms in **36** and **45** are high in s character with some directionality (**36**: sp^{0.22}, occupancy: 1.96; **45**: sp^{0.24}, occupancy: 1.95). The WBI shows that the exocyclic Ge(1/1A)-E bonds [WBI: 0.84 (**36**); 0.86 (**45**)] are single bonds.

Table 9. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of calculated compound **36**.

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Occu-pancy	Wiberg bond index
Ge(2)-Sn(1) (σ)	Ge(2)	57.2	$sp^{2.29}$	Sn(1)	42.9	$sp^{2.16}$	1.80	0.90
Ge(2)-Sn(1) (σ^*)	Ge(2)	42.9	$sp^{2.29}$	Sn(1)	57.2	$sp^{2.16}$	0.31	
Ge(2)-Sn(1A) (σ)	Ge(2)	56.4	$sp^{2.38}$	Sn(1A)	43.6	$sp^{2.08}$	1.80	0.90
Ge(2)-Sn(1A) (σ^*)	Ge(2)	43.6	$sp^{2.38}$	Sn(1A)	56.4	$sp^{2.08}$	0.32	
Ge(2A)-Sn(1) (σ)	Ge(2A)	56.4	$sp^{2.38}$	Sn(1)	43.6	$sp^{2.08}$	1.80	0.90
Ge(2A)-Sn(1) (σ^*)	Ge(2A)	43.6	$sp^{2.38}$	Sn(1)	56.4	$sp^{2.08}$	0.32	
Ge(2A)-Sn(1A) (σ)	Ge(2A)	57.2	$sp^{2.29}$	Sn(1A)	42.9	$sp^{2.16}$	1.80	0.90
Ge(2A)-Sn(1A) (σ^*)	Ge(2A)	42.9	$sp^{2.29}$	Sn(1A)	57.2	$sp^{2.16}$	0.31	
Sn(1)-Ge(1) (σ)	Sn(1)	59.4	$sp^{1.93}$	Ge(1)	40.6	$sp^{11.12}$	1.77	0.84
Sn(1)-Ge(1) (σ^*)	Sn(1)	40.6	$sp^{1.93}$	Ge(1)	59.4	$sp^{11.12}$	0.32	
Sn(1A)-Ge(1A) (σ)	Sn(1A)	59.4	$sp^{1.93}$	Ge(1A)	40.6	$sp^{11.12}$	1.77	0.84
Sn(1A)-Ge(1A) (σ^*)	Sn(1A)	40.6	$sp^{1.93}$	Ge(1A)	59.4	$sp^{11.12}$	0.32	
Sn(1) LP	Sn(1)	-	$sp^{50.9}$	-	-	-	1.03	-
Sn(1A) LP	Sn(1A)	-	$sp^{50.9}$	-	-	-	1.03	-
Ge(1) LP	Ge(1)	-	$sp^{0.22}$	-	-	-	1.96	-
Ge(1A) LP	Ge(1A)	-	$sp^{0.22}$	-	-	-	1.96	-

Table 10. The NBO second order perturbation stabilizing energy of calculated compound **36**.

Donor NBO	Acceptor NBO	Energy (kcal mol ⁻¹)	Sum of second order perturbation stabilizing energies/ kcal mol ⁻¹
Sn(1) LP	Sn(1)-Ge(2) (σ^*)	119.7	417.1
Sn(1) LP	Sn(1)-Ge(2A) (σ^*)	122.1	
Sn(1) LP	Sn(1)-Ge(1) (σ^*)	175.3	
Sn(1A) LP	Sn(1A)-Ge(2) (σ^*)	122.1	417.1
Sn(1A) LP	Sn(1A)-Ge(2A) (σ^*)	119.7	
Sn(1A) LP	Sn(1A)-Ge(1A) (σ^*)	175.3	

Table 11. The NPA charges of calculated compound **36**.

Atom	NPA Charge	Atom	NPA Charge
Sn(1)	-0.13	Sn(1A)	-0.13
Ge(2)	0.60	Ge(2A)	0.60
Ge(1)	0.53	Ge(1A)	0.53

Figure 13. Selected molecular orbitals of compound **36** calculated at UB3PW91/LANL08d for Sn, 6-31+G(d) for Ge and N, and 6-31G(d) for C and H level.

(a) The HOMO which comprises the exocyclic Ge-Sn σ orbitals.

(b) The HOMO-1 which involves the lone pair orbitals at the Sn1 and Sn1A atoms. (i) Side-view of the HOMO-1. (ii) Top-view of the HOMO-1.

(i)

(ii)

(c) The HOMO-2 which comprises the endocyclic Ge-Sn σ orbitals.

(d) The LUMO involves (1) the interaction of p orbitals between the Ge2 and Ge2A atoms, (2) the exocyclic Ge-Sn σ^* orbitals and (3) the π^* orbitals of the phenyl rings. (i) Top-view of the LUMO. (ii) Side-view of the LUMO.

(i)
69

(ii)

(e) The LUMO+1 which comprises the exocyclic Ge-Sn π orbitals, endocyclic Ge-Sn σ^* orbitals and the π^* orbitals of the phenyl rings.

Table 12. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of calculated compound **45**.

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Occu-pancy	Wiberg bond index
Ge(1)-Ge(2) (σ)	Ge(1)	35.4	$sp^{8.95}$	Ge(2)	64.6	$sp^{1.58}$	1.84	0.86
Ge(1)-Ge(2) (σ^*)	Ge(1)	64.6	$sp^{8.95}$	Ge(2)	35.4	$sp^{1.58}$	0.21	
Ge(1A)-Ge(2A) (σ)	Ge(1A)	35.4	$sp^{8.95}$	Ge(2A)	64.6	$sp^{1.58}$	1.84	0.86
Ge(1A)-Ge(2A) (σ^*)	Ge(1A)	64.6	$sp^{8.95}$	Ge(2A)	35.4	$sp^{1.58}$	0.21	
Ge(2)-Ge(3) (σ)	Ge(2)	50.7	$sp^{2.32}$	Ge(3)	49.4	$sp^{2.17}$	1.82	0.99
Ge(2)-Ge(3) (σ^*)	Ge(2)	49.4	$sp^{2.32}$	Ge(3)	50.7	$sp^{2.17}$	0.22	
Ge(2)-Ge(3A) (σ)	Ge(2)	51.2	$sp^{2.20}$	Ge(3A)	48.8	$sp^{2.18}$	1.82	0.99
Ge(2)-Ge(3A) (σ^*)	Ge(2)	48.8	$sp^{2.20}$	Ge(3A)	51.2	$sp^{2.18}$	0.23	
Ge(2A)-Ge(3) (σ)	Ge(2A)	51.2	$sp^{2.20}$	Ge(3)	48.8	$sp^{2.18}$	1.82	0.99
Ge(2A)-Ge(3) (σ^*)	Ge(2A)	48.8	$sp^{2.20}$	Ge(3)	51.2	$sp^{2.18}$	0.23	
Ge(2A)-Ge(3A) (σ)	Ge(2A)	50.7	$sp^{2.32}$	Ge(3A)	49.4	$sp^{2.17}$	1.82	0.99
Ge(2A)-Ge(3A) (σ^*)	Ge(2A)	49.4	$sp^{2.32}$	Ge(3A)	50.7	$sp^{2.17}$	0.22	
Ge(1) LP	Ge(1)	-	$sp^{0.24}$	-	-	-	1.95	-
Ge(1A) LP	Ge(1A)	-	$sp^{0.24}$	-	-	-	1.95	-
Ge(2) LP	Ge(2)	-	p	-	-	-	1.20	-
Ge(2A) LP	Ge(2A)	-	p	-	-	-	1.20	-

Table 13. The NBO second order perturbation stabilizing energy of calculated compound **45**.

Donor NBO	Acceptor NBO	Energy (kcal/mol)	Sum of second order perturbation stabilizing energies/ kcal mol ⁻¹
Ge(2) LP	Ge(2)-Ge(3) (σ^*)	27.3	91.2
Ge(2) LP	Ge(2)-Ge(3A) (σ^*)	29.1	
Ge(2) LP	Ge(1)-Ge(2) (σ^*)	34.8	
Ge(2A) LP	Ge(2A)-Ge(3) (σ^*)	29.1	91.2
Ge(2A) LP	Ge(2A)-Ge(3A) (σ^*)	27.3	
Ge(2A) LP	Ge(1A)-Ge(2A) (σ^*)	34.8	

Table 14. The NPA charges of calculated compound **45**.

Atom	NPA Charge	Atom	NPA Charge
Ge(1)	0.65	Ge(1A)	0.65
Ge(2)	-0.54	Ge(2A)	-0.54
Ge(3)	0.89	Ge(3A)	0.89

Figure 14. Selected molecular orbitals of compound **45** calculated at UB3PW91/6-31+G(d) level.

(a) The HOMO-2 which comprises the endocyclic Ge-Ge σ orbitals.

(b) The HOMO-1 which involves the lone pair orbitals at the Ge2 and Ge2A atoms. (i) Side-view of the HOMO-1. (ii) Top-view of the HOMO-1

(i)

(ii)

(c) The HOMO which comprises the exocyclic Ge-Ge σ orbitals.

(d) The LUMO involves (1) the interaction of p orbitals between the Ge3 and Ge3A atoms, (2) the exocyclic Ge-Ge σ^* orbitals, and (3) the π^* orbitals of the phenyl rings.

(e) The LUMO+1 which comprises the π^* orbitals of the phenyl rings.

(f) The LUMO+2 which comprises the π^* orbitals of the phenyl rings.

Overall, the results show that compounds **36** and **45** have a planar rhombic charge-separated Ge₂E₂ ring. Once again, compounds **36** and **45** are non-aromatic and this resonates with Bertrand's deduction that when a λ⁵-phosphacyclobutadiene contains a phosphorus atom without any p orbitals available for the π system of a cyclobutadiene, the 4π electron four-membered heterocycle is not antiaromatic and features a strong ylide character or interrupted cyclic π delocalization.^[21]

Conclusion

The first examples of amidinate-stabilized germatrisilacyclobutadiene ylides [L₃Si₃GeL'] (L = PhC(NtBu)₂; L' = ËL; Ë = Ge (**29**), Si (**32**)) were synthesized successfully by the reaction of [LGe-GeL] (**7**) with one equivalent of [LSi-SiL] (**4**) and with excess of **4** in THF, respectively. Alternatively, **29** can be obtained by the treatment of [LGeCl] (**31**) with one equivalent of **4** in THF. Hence, it is proposed that **29** is formed via an initial insertion reaction of **31** with **4**, which resulted in the bond cleavage of the Si^I-Si^I bond in **4** to afford the intermediate [LSi-GeL]. The latter then undergoes further rearrangement reactions to afford **29** and bis(amidinate) germanium(II) compound [L₂Ge:] (**30**).

On the other hand, the zwitterionic amidinate-stabilized digermadistannacyclobutadiene [L₂Ge₂Sn₂L'₂] (**36**; L' = GeL) was synthesized by the reaction of **7** with one equivalent of [L^{Ar}SnCl] (**40**) in THF. Similar to the formation of **29**, **36** is formed via an initial insertion reaction of **40** with **7**, which resulted in consequential bond cleavage of the Ge^I-Ge^I bond in **7** to form a transient germanium(I)-tin(I) complex [LGe-SnL^{Ar}]. The latter then undergoes a disproportionation to form **36** and bis(amidinate) tin(II) compound [L^{Ar}₂Sn:] (**41**).

Lastly, the zwitterionic amidinate-stabilized tetragermacyclobutadiene [L₄Ge₆] (**45**) was synthesized by reaction of **7** with the "onio-substituent transfer" reagent [4-

NMe₂-C₅H₄NSiMe₃]OTf (**44**) in THF and 4-dimethylaminopyridine (DMAP) at room temperature. It is suggested that **45** is formed via a disproportionation reaction of the Ge^{II} cation intermediate [LGe]OTf with **7**. This postulation is based on the successful synthesis and characterization of its lighter congener, [LSi(DMAP)]OTf by treatment of **4** with **44** in excess DMAP.^[32]

X-ray crystallography and theoretical studies of compounds **29**, **36** and **45** show that the incorporation of different heavier group 14 elements in the four-membered skeleton of a cyclobutadiene yield contrasting geometrical and electronic properties. Compounds **29**, **36** and **45** exhibit charge-separated structures that comprise of single Si-Si, Si-Ge, Ge-Sn, and Ge-Ge bonds, respectively. The Si₃Ge four-membered ring in **29** is puckered, whereas the Ge₂Sn₂ four-membered ring in **36** is planar and rhombic. The Ge₄ four-membered ring in **45** is also planar and rhombic. Although the lone pair electrons at the negatively-charged Si and Ge atoms are delocalized within the Si₃Ge four-membered ring in **29**, there is no delocalization of π electrons in the Ge₂Sn₂ four-membered ring in **36** and the Ge₄ four-membered ring in **45**. Additionally, calculated NICS values suggest that **29** is not anti-aromatic and **36** and **45** are non-aromatic. This is reflective of Bertrand's recent review, where it was shown that when a λ^5 -phosphacyclobutadiene contains a phosphorus atom without any p orbitals available for the π system of a cyclobutadiene, the 4π electron four-membered heterocycle is not anti-aromatic and features a strong ylide character or interrupted cyclic π delocalization.^[21]

Experimental Section

General Procedure: All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Toluene, THF, DME and Et₂O were dried over and distilled over Na/K alloy prior to use. [D₆]Benzene and [D₈]THF were dried over and distilled over K metal prior to use. [D₅]Py was dried over and distilled over CaH₂ prior to use. **4**, **7**, **31**, **35**, **40** and **44** were prepared as described in the literature.^[8, 9, 22, 25, 29] The ¹H, ¹³C, ²⁹Si and ¹¹⁹Sn NMR spectra were recorded on JEOL ECA 400 and Bruker Avance 400 spectrometers. The chemical shifts δ are relative to SiMe₄ for ¹H, ¹³C, and ²⁹Si, and SnMe₄ for ¹¹⁹Sn. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of [L₃Si₃GeL'] (29; L' = GeL). *Method A:* THF (20.8 mL) was added to a mixture of **4** (0.16 g, 0.31 mmol) and **7** (0.19 g, 0.31 mmol) at ambient temperature. The resulting red mixture was stirred overnight. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with Et₂O (50 mL). After filtration and concentration of the filtrate, **29**•Et₂O was obtained as dark-red crystals. Yield: 0.11 g (29.9%).

Method B: THF (17 mL) was added to a mixture of **4** (0.26 g, 0.51 mmol) and **31** (0.17 g, 0.51 mmol) at ambient temperature. The resulting red mixture was stirred overnight. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with Et₂O (50 mL). After filtration and concentration of the filtrate, **29**•Et₂O was obtained as dark-red crystals (0.047 g, 22.5 %). The mother liquor was further concentrated to yield **11** as colourless crystals (0.087 g, 57.8 %). Recrystallisation of **30** by further concentration of mother liquor failed. **29**: M.p. 254 °C. ¹H NMR for **29**•Et₂O (399.5 MHz, [D₆]Benzene, 22.3 °C): δ = 1.08 (t,

6H, Et₂O), 1.37 (s, 18H, *t*Bu), 1.44 (s, 36H, *t*Bu), 1.64-1.74 (br s, 18H, *t*Bu), 3.23 (q, 4H, Et₂O), 6.84-7.74 ppm (m, 20H, Ph); ¹³C{¹H} NMR for **29**•Et₂O (100.5 MHz, [D₆]Benzene, 22.4 °C): δ = 15.32 (Et₂O), 31.83, 32.39, 32.79 (CMe₃), 52.56, 54.46, 55.42 (CMe₃), 65.63 (Et₂O), 126.43, 126.60, 128.63, 129.29, 129.47, 129.96, 130.57, 131.22, 134.00, 137.79, 144.09 (Ph), 155.27, 159.13, 167.37 ppm (NCN); ²⁹Si{¹H} NMR for **29**•Et₂O (79.4 MHz, [D₆]benzene, 22.5 °C): δ = -89.0, 64.5 ppm; ¹H NMR for **29**•Et₂O (395.9 MHz, [D₈]Toluene, -56.1 °C): δ = 1.18 (t, 6H, Et₂O), 1.33 (s, 18H, *t*Bu), 1.43 (s, 36H, *t*Bu), 1.56 (s, 9H, *t*Bu), 2.25 (s, 9H, *t*Bu), 3.21 (q, 4H, Et₂O), 6.74-7.83 ppm (m, 20H, Ph); UV/Vis (toluene): λ_{max} (ε) = 243 (19674), 290 (12151), 469 (4703 mol⁻¹ dm³ cm⁻¹) nm; elemental analysis calcd (%) for C₆₄H₁₀₂Ge₂N₈OSi₃: C 62.54, H 8.36, N 9.12; found: C 62.47, H 8.32, N 9.06.

Crystal data for 29•Et₂O: [C₆₄H₁₀₂Ge₂N₈OSi₃]; *M* = 1228.99; monoclinic; space group *P*2(1)/*c*; *a* = 13.4097(14), *b* = 23.689(3), *c* = 21.754(3) Å; α = 90, β = 97.072(5), γ = 90°; *V* = 6857.9(13) Å³; *Z* = 4; ρ_{calcd} = 1.190 mg m⁻³; 104410 measured reflections; 24127 independent reflections; 729 refined parameters; *R*₁ = 0.0382, *wR*₂ = 0.1001 (*I* > 2σ(*I*)).

Synthesis of [L₃Si₃GeL'] (32; L' = SiL). *Method A*: THF (11.6 mL) was added to a mixture of **4** (0.29 g, 0.55 mmol) and **7** (0.11 g, 0.17 mmol) at ambient temperature. The resulting red mixture was stirred overnight. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with Et₂O (50 mL). After filtration and concentration of the filtrate, **32**•Et₂O was obtained as dark-red crystals. Yield: 0.08 g (38.8%).

Method B: THF (14.4 mL) was added to a mixture of **29** (0.27 g, 0.22 mmol) and **4** (0.11 g, 0.21 mmol) at ambient temperature. The resulting red solution was stirred overnight. Volatiles were removed in vacuo. The residue was extracted with Et₂O (50

mL). After filtration and concentration of the filtrate, **32**•Et₂O was obtained as dark-red crystals. Yield: 0.07 g (26.9%). M.p. 221 °C; ¹H NMR for **32**•Et₂O (395.9 MHz, [D₆]Benzene, 22.4 °C): δ = 1.12 (t, 6H, Et₂O), 1.47 (s, 18H, *t*Bu), 1.50 (s, 36H, *t*Bu), 1.70-1.76 (br s, 18H, *t*Bu), 3.26 (q, 4H, Et₂O), 6.88-7.78 ppm (m, 20H, Ph); ¹³C{¹H} NMR for **32**•Et₂O (100.6 MHz, [D₆]Benzene, 24.6 °C): δ = 15.22 (Et₂O), 31.67, 32.33, 32.38 (*CMe*₃), 52.40, 54.46, 55.29 (*CMe*₃), 65.53 (Et₂O), 126.31, 126.49, 127.02, 127.16, 127.19, 128.50, 129.18, 129.46, 130.02, 130.46, 131.53, 133.99, 135.90, 144.09 (Ph), 147.80, 159.18, 167.20 ppm (NCN); ²⁹Si{¹H} NMR for **32**•Et₂O (79.4 MHz, [D₆]Benzene, 23.0 °C): δ = -91.9, 63.1, 105.7 ppm; ¹H NMR for **32**•Et₂O (395.9 MHz, [D₈]Toluene, -59.9 °C): δ = 1.07 (s, 6H, *t*Bu), 1.18 (t, 6H, Et₂O), 1.28 (s, 3H, *t*Bu), 1.33 (s, 9H, *t*Bu), 1.44 (m, 36H, *t*Bu), 1.56 (s, 9H, *t*Bu), 2.25 (s, 9H, *t*Bu), 3.23 (q, 4H, Et₂O), 6.62-7.85 ppm (m, 20H, Ph); UV/Vis (toluene): λ_{max} (ε) = 285 (7346), 335 (4610), 415 (2808), 494 (3764 mol⁻¹ dm³ cm⁻¹) nm; elemental analysis calcd (%) for C₆₄H₁₀₂GeN₈OSi₄: C 64.89, H 8.68, N 9.46; found: C 64.63, H 8.57, N 9.34.

Crystal data for 32•Et₂O: [C₆₄H₁₀₂GeN₈OSi₄]; *M* = 1184.49; monoclinic; space group *P*2(1)/*c*; *a* = 13.3525(3), *b* = 23.6798(5), *c* = 21.7150(5) Å; α = 90, β = 96.978(10), γ = 90°; *V* = 6815.1(3) Å³; *Z* = 4; ρ_{calcd} = 1.154 mg m⁻³; 132383 measured reflections; 23974 independent reflections; 784 refined parameters; *R*₁ = 0.0446, *wR*₂ = 0.1172 (*I* > 2σ(*I*)).

Synthesis of [L₂Ge₂Sn₂L'₂] (36; L' = GeL). *Method A:* THF (20 mL) was added to a mixture of **7** (0.312 g, 0.513 mmol), **35** (0.398 g, 1.03 mmol) and KC₈ (0.144 g, 1.07 mmol) at ambient temperature. The resulting red mixture was stirred overnight. The insoluble precipitate was filtered off. Et₂O was added to the filtrate. After filtration and concentration of the filtrate, **36** was obtained as dark-red crystals. Yield: 0.021 g (5.6 %).

Method B: THF (10 mL) was added to a mixture of **7** (0.304 g, 0.501 mmol) and **40** (0.287 g, 0.501 mmol) at ambient temperature. The resulting red mixture was stirred overnight. Volatiles were removed in vacuo and the residue was extracted with DME. After filtration and concentration of the filtrate, **36** was obtained as dark-red crystals. Yield: 0.0305 g (16.8 %). M.p. 290 °C (decomp); ^1H NMR (399.5 MHz, $[\text{D}_8]\text{THF}$, 22.2 °C): δ = 0.96 (s, 36H, *t*Bu), 1.40 (s, 36H, *t*Bu), 7.19-7.28 ppm (m, 20H, Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, 23.3 °C): δ = 29.15, 32.91 (*CMe*₃), 51.50, 53.28 (*CMe*₃), 125.83, 128.12, 128.22, 128.70, 128.94, 129.46, 138.23, 141.40 (Ph), 152.93, 153.83 ppm (NCN); $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.1 MHz, THF, 24.7 °C): δ = -90.9 ppm; UV/Vis (THF): λ_{max} (ϵ) = 221 (7884), 241 (6063), 246 (5774), 252 (5594), 258 (5603), 270 (6225), 354 (3867), 508 (1952 mol⁻¹ dm³ cm⁻¹) nm; elemental analysis calcd (%) for C₆₀H₉₂Ge₄N₈Sn₂: C 49.58, H 6.38; N 7.71; found: C 49.24, H 6.32, N 7.43.

Crystal data for 36: [C₆₀H₉₂Ge₄N₈Sn₂]; M = 1453.16; monoclinic; space group $P2(1)/n$; a = 9.2404(4), b = 19.1831(9), c = 18.9287(10) Å; α = 90, β = 99.302(4), γ = 90°; V = 3311.2(3) Å³; Z = 2; ρ_{calcd} = 1.458 mg m⁻³; 48844 measured reflections; 10587 independent reflections; 432 refined parameters; R_1 = 0.0501, wR_2 = 0.1059 ($I > 2\sigma(I)$).

Synthesis of $[\text{L}^{\text{Ar}}_2\text{Sn}]$ (41**).** *t*BuLi (2.6 mL, 4.42 mmol, 1.7 M in pentane) was added dropwise to a solution of ArN=C=NAr (1.47 g, 4.06 mmol) in Et₂O (27 mL) at -78 °C. The solution was raised to ambient temperature and stirred for 2 h. The solution was then added to a stirred suspension of SnCl₂ (0.385 g, 2.03 mmol) in Et₂O (13.5 mL) at 0 °C. The reaction mixture was raised to ambient temperature and was stirred overnight. The insoluble precipitate was filtered off and the filtrate was concentrated to yield colourless crystals of **41**•Et₂O. Yield: 0.0403 g (19.3 %). M.p.: 207.7 °C; ^1H NMR (399.5 MHz, $[\text{D}_6]\text{Benzene}$, 23.5 °C): δ = 0.42-0.66 (br, 3H, CHMe₂), 0.87 (s, 9H, *t*Bu), 1.09-1.21 (br, 6H, CHMe₂), 1.25-1.34 (br, 18H, CHMe₂), 1.34-1.41 (br, 9H,

CHMe₂), 1.41-1.54 (br, 9H, CHMe₂), 1.59 (s, 9H, *t*Bu), 2.41-2.90 (br, 3H, CHMe₂), 3.37-3.55 (br, 2H, CHMe₂), 3.55-3.74 (br, 4H, CHMe₂), 3.84-4.07 (br, 2H, CHMe₂), 6.86-7.24 ppm (m, 12H, Ph); ¹³C{¹H} NMR (100.6 MHz, [D₆]Benzene, 24.2 °C): δ = 22.41, 22.95, 28.03, 28.24, 28.61 (CHMe₂), 29.08 (CMe₃), 29.60 (CHMe₂), 32.07 (CMe₃), 42.11, 44.32 (CHMe₂), 60.52 (CMe₃), 63.29-64.15 (br, CMe₃), 120.67-121.65 (br, Ph), 123.11 (Ph), 123.23-123.46 (br, Ph), 124.63, 126.24, 140.22 (Ph), 141.83-141.92 (br, Ph), 143.52 (Ph), 145.13-145.82 (br, Ph), 167.26, 180.12 ppm (NCN); ¹¹⁹Sn{¹H} NMR (149.0 MHz, [D₆]Benzene, 22.6 °C): δ = -336.29 ppm; elemental analysis calcd (%) for C₅₈H₈₆N₄Sn: C 72.70, H 9.05, N 5.85; found: C 72.61, H 8.91, N 5.68.

Crystal data for 41•Et₂O: [C₆₂H₉₆N₄OSn]; *M* = 1032.12; monoclinic; space group *P*2(1)/*n*; *a* = 12.2530(12), *b* = 22.722(18), *c* = 20.751(2) Å; α = 90, β = 101.346(4), γ = 90°; *V* = 5664.6(9) Å³; *Z* = 4; ρ_{calcd} = 1.210 mg m⁻³; 74492 measured reflections; 18163 independent reflections; 637 refined parameters; *R*₁ = 0.0320, *wR*₂ = 0.0790 (*I* > 2σ(*I*)).

Synthesis of [L₄Ge₆] (45). A solution of **44** (0.176 g, 0.511 mmol) in THF (2 mL) was added to a stirring solution of **7** (0.309 g, 0.509 mmol) and DMAP (0.128 g, 1.05 mmol) in THF (10 mL) at ambient temperature. The resulting solution was stirred for 12 h. After filtration and concentration of the filtrate, **45** was obtained as red crystals. Yield: 0.0493 g (25.8 %). M.p. 228 °C (decomp); ¹H NMR (395.9 MHz, [D₈]THF, 23.4 °C): δ = 1.16 (s, 72H, *t*Bu), 7.28-7.40 ppm (m, 20H, Ph); ¹³C{¹H} NMR (100.5 MHz, [D₅]Py, 23.6 °C): δ = 32.44, 32.50 (CMe₃), 53.51, 53.84 (CMe₃), 128.42, 129.11, 129.73, 130.38, 130.75, 131.26, 131.97, 137.65 (Ph), 154.95, 158.35 ppm (NCN); UV/Vis (DME): λ_{max} (ε) = 225 (272), 237 (270), 252 (287), 258 (298), 275 (331), 348 (376), 524 (414 mol⁻¹ dm³ cm⁻¹) nm; elemental analysis calcd (%) for C₆₀H₉₂Ge₆N₈: C 52.92, H 6.81, N 8.23; found: C 52.78, H 6.53, N 8.15.

Crystal data for 45•THF: [C₆₈H₁₀₈Ge₆N₈O₂]; *M* = 1505.16; monoclinic; space group *P*2(1)/*c*; *a* = 11.8191(7), *b* = 17.2043(11), *c* = 18.0867(11) Å; $\alpha = 90^\circ$, $\beta = 93.573(3)^\circ$, $\gamma = 90^\circ$; *V* = 3670.6(4) Å³; *Z* = 2; $\rho_{\text{calcd}} = 1.362 \text{ mg m}^{-3}$; 88284 measured reflections; 12224 independent reflections; 391 refined parameters; *R*₁ = 0.0580, *wR*₂ = 0.1399 (*I* > 2 σ (*I*)).

X-ray data collection and structural refinement. Intensity data for compounds **29**, **32**, **36** and **45** were collected using a Bruker APEX II diffractometer. The crystals of **29**•Et₂O, **32**•Et₂O, **36** and **45**•THF 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.^[37] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC-816370 (**29**), CCDC-816371 (**32**), CCDC-904992 (**36**) and CCDC-904994 (**45**) contain the supplementary crystallographic data for this chapter. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Chapter 3

A Silyliumylidene Cation Stabilized by an Amidinate Ligand and 4-Dimethylaminopyridine and its Reactivity

Introduction

Silyliumylidene cation of composition HSi^+ is the simplest form of polyatomic low valent silicon moiety. Since it consists of two vacant orbitals and a lone pair of electrons on the low valent silicon cation, it is Lewis ambiphilic and can possess both electrophilic and nucleophilic characters (Chart 16). By virtue of its diverse electronic structure, silyliumylidene cations can serve to be useful building blocks for the synthesis of novel silicon compounds. However, it is highly reactive and can only be observed in the gas phase under mass spectrometric and astrophysical conditions.^[1] Since the discovery of an *N*-heterocyclic silylene (**49**; Chart 17) by West *et al.*,^[2] the concepts of thermodynamic and/or kinetic stabilization have been applied successfully in the isolation of stable low-valent silicon compounds. Accordingly, stable derivatives of silyliumylidene cation (**50** – **52**), which contain sterically hindered substituents with electron donor moieties, were synthesized.^[3] However, the high synthetic potential of these cations is hampered by the particular stabilization effects of the substituents. In this context, the quest for isolating other types of stable silyliumylidene cation is still very demanding.

Chart 16. Bonding model of HSi^+ .

Chart 17. Compounds **49** – **53**, **33** and **34**.

Recently, amidinate ligands have demonstrated their abilities to stabilize a wide variety of low valent silicon compounds.^[4] They can also stabilize silylium moieties in small ring compounds. Examples include a zwitterionic 2,4-disila-1,3-diphosphacyclobutadiene (**33**),^[5] a five-membered cationic CSi_3P cycle (**53**)^[6] and a tetrasilacyclobutadiene dication (**34**).^[7] Earlier in Chapter 2, we have described the first examples of a germatrisilacyclobutadiene and digermadistannacyclobutadiene, both stabilized by the amidinate ligand.^[8] Based on these results, it seems that amidinate ligands can stabilize a low valent silicon cation. However, in a recent communication regarding the synthesis of the base-stabilized tetrasilacyclobutadiene

dication (**34**),^[7] Driess *et al.* suggest that the singlet amidinate silyliumylidene cation $[\text{LSi:}]^+$ ($\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$) is highly electrophilic. Moreover, the electron deficient silicon atom cannot be shielded from coordination to reactive nucleophilic intermediates. As a result, it undergoes disproportionation to form compound **34**. The results show that the isolation of a singlet amidinate silyliumylidene cation is a formidable challenge.

We anticipate that a singlet amidinate silyliumylidene cation should be a resonance hybrid of the canonical formulas **A** and **B** (Scheme 15). The electronic deficient low-valent silicon atom could be stabilized via coordination to a Lewis base. In Section 3.1 of results and discussion, we describe the synthesis and characterization of the singlet silyliumylidene cation $[\text{LSi}(\text{DMAP})]\text{OTf}$ (**54**), which is stabilized by both amidinate ligand and 4-dimethylaminopyridine (DMAP). Additionally, its theoretical studies are described. The reactivity studies of **54** with amidinate Si^{I} dimer $[\text{LSi-SiL}]$ (**4**), $[\text{K}\{\text{HB}(i\text{Bu})_3\}]$ and elemental sulphur are described in Section 3.2 and the reactivity studies of **54** with $[\text{Rh}(\text{cod})\text{Cl}]_2$ and $\text{W}(\text{CO})_5\text{THF}$ are described in Section 3.3.

Scheme 15. Canonical forms of a singlet amidinate silyliumylidene cation.

Results and Discussion

3.1. Synthesis and Characterization of a Silyliumylidene Cation Stabilized by an Amidinate Ligand and 4-Dimethylaminopyridine.

The reaction of the amidinate Si^{I} dimer $[\text{LSi-SiL}]$ (**4**; $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$)^[9] with one equivalent of “onio-substituent transfer” reagent $[\text{4-NMe}_2\text{-C}_5\text{H}_4\text{NSiMe}_3]\text{OTf}$ ^[10] and two equivalents of DMAP in THF at room temperature afforded $[\text{LSi}(\text{DMAP})]\text{OTf}$ (**54**) in 54% yield (Scheme 16). The by-product is $\text{Me}_3\text{Si-SiMe}_3$, which was confirmed by ^{29}Si and ^1H NMR spectroscopy and mass spectrometry.^[11] On the basis of experimental results, the reaction appears to proceed through the oxidation of **4** or the transient Si^{I} radical $[\text{LSi}\cdot]$ with $[\text{4-NMe}_2\text{-C}_5\text{H}_4\text{NSiMe}_3]\text{OTf}$ to form **54** and $\text{Me}_3\text{Si-SiMe}_3$.

Scheme 16. Synthesis of **54**.

Compound **54** is soluble in THF, CH_2Cl_2 and CHCl_3 . It is stable in the solid state at room temperature in an inert atmosphere. Compound **54** has been characterized by NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **54** display resonances due to the amidinate and DMAP ligands. The ^{19}F NMR spectrum of **54** shows a singlet at $\delta = -78.9$ ppm for the CF_3SO_3^- anion. The ^{29}Si NMR spectrum of **54** exhibits a singlet at $\delta = -82.3$ ppm, which shows an upfield shift compared to that of the three-coordinate amidinate-stabilized silylenes $[\text{LSiX}]$ ($\text{X} = \text{Cl}$: $\delta = 14.6$ ppm; $\text{X} = \text{NMe}_2$: $\delta = -2.62$

ppm).^[12] This can be explained by the strong donor-acceptor interaction between the nitrogen atom of DMAP and the low valent silicon cation, thus reducing the Lewis acidity of the latter. Interestingly, the reactivity studies show that DMAP can be released and hence **54** shows an ambiphilic character (see Section 3.2.1). In addition, the ²⁹Si NMR signal is significantly upfield shifted compared with that of the three-coordinate bis(iminophosphorane) chelate ligand stabilized [SiCl]⁺ (**52**) ($\delta = -3.3$ ppm),^[3c] in which an extensive electronic delocalization is observed. It is also intermediate between that of [HC(CMeNAr)₂Si]⁺ (**51**; Ar = 2,6-*i*Pr₂C₆H₃) ($\delta = 69.3$ ppm) and [η^5 -Cp*Si]⁺ (**50**; Cp* = C₅Me₅) ($\delta = -400.2$ ppm).^[3a,b] The results indicate that the nature of the silicon(II) cation is strongly influenced by the kinetic and electronic stabilization of the ligand.

Compound **54** has been characterized by X-ray crystallography (Figure 15). The SiNCN four-membered ring is puckered. The Si1 cation adopts a distorted trigonal pyramidal geometry (sum of bond angles: 266.1°), which indicates that it is almost non-hybridized and possesses lone pair electrons with high s character. The shortest Si1...F (3.59 Å) distance is longer than the sum of van der Waals radii (3.57 Å), which suggests that the Si1 cation does not have any interaction with the CF₃SO₃⁻ counteranion. The Si-N_{amidinate} (1.8514(18), 1.8625(18) Å) bond lengths are comparable with those in [LSiNMe₂] (1.893(1), 1.905(1) Å).^[12b] The Si1-N3 bond (1.8775(18) Å) is longer than the Si-N_{amide} bond in [LSiNMe₂] (1.724(2) Å).^[12b] It is comparable with that in the DMAP-stabilized silanone derivative [{HC(C{=CH₂}NAr)(CMeNAr)}Si(DMAP)=O] (1.862(2) Å) (Ar = 2,6-*i*Pr₂C₆H₃).^[13]

Figure 15. ORTEP drawing of compound **54** (50% thermal ellipsoids). The disorder in the triflate atoms are omitted for clarity. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-N1 1.8514(18), Si1-N2 1.8625(18), Si1-N3 1.8777(18), C5-N1 1.342(3), C5-N2 1.340(3); N1-Si1-N2 69.91(8), N1-Si1-N3 98.20(8), N2-Si1-N3 97.95(8).

In order to understand the bonding nature of **54**, DFT calculations of $[\text{LSi}(\text{DMAP})]^+$ (**54**⁺, see Appendix C, Figure C1) without a counteranion were performed (M06-2X/6-311+G(2d) for Si and 6-311+G(d,p) for H, C, N level).^[14] The calculated structural parameters are in good agreement with the crystallographic data of **54**. The lone pair orbital at the Si1 atom can be illustrated in the HOMO (Figure 16a). Accordingly, the natural-bond-orbital (NBO)^[15] analysis (Table 15) shows that the lone pair orbital is high in s character ($\text{sp}^{0.37}$, electron occupancy: 1.94 e). Moreover, the natural population analysis (NPA) charges indicate that the silicon atom has a positive charge (+1.16).

Table 15. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of compound **54⁺**.

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Occupancy	Wiberg bond index
Si(1)-N(2) (σ)	Si(1)	13.5	sp ^{9.29}	N(2)	86.5	sp ^{2.55}	1.94	0.48
Si(1)-N(1) (σ)	Si(1)	14.0	sp ^{9.28}	N(1)	86.1	sp ^{2.54}	1.94	0.48
Si(1)-N(3) (σ)	Si(1)	12.1	sp ^{11.3}	N(3)	87.9	sp ^{2.24}	1.95	0.44
Si(1) LP	Si(1)	-	sp ^{0.37}	-	-	-	1.94	-
N(2) LP	N(2)	-	p	-	-	-	1.58	-
N(4) LP	N(4)	-	p	-	-	-	1.64	-

Figure 16. Selected molecular orbitals of compound **54⁺** calculated at M06-2X/6-311+G(2d) for Si and 6-311+G(d,p) for H, C, N level.

(a) The HOMO which involves the lone pair orbital at the Si1 atom.

(b) The LUMO which comprises π^* orbitals of pyridine.

3.2. Reactivity of the Silyliumylidene Cation [LSi(DMAP)]OTf (**54**; L = PhC(N*t*Bu)₂).

The reactivity of **54** was examined with the aim to probe its Lewis ambiphilic nature and to explore its potential as a useful building block for the synthesis of novel silicon compounds. Herein, the reactivity of **54** with the amidinate Si^I dimer [LSi-SiL] (**4**), [K{HB(*i*Bu₃)}] and elemental sulphur are described in sections 3.2.1, 3.2.2 and 3.2.3, respectively.

3.2.1. Reactivity of **54** with the Amidinate Si^I dimer [LSi-SiL] (**4**).

The reaction of **54** with **4** in THF formed the disilylenylsilylium triflate [L'₂(L)Si]OTf (**55**; L' = LSi; 23.3% yield) with the displacement of DMAP (Scheme 17). The reaction appears to proceed through the insertion of **54** into the Si^I-Si^I bond of **4**. Another possible mechanism is that one of the Si^I atoms in **4** acts as a Lewis base to form an adduct with **54**. Compound **55** is the first example of stable silylium cation comprising low-valent silicon substituents, although the chemistry of stable silylium cations has been studied in the past decades.^[16]

Scheme 17. Synthesis of **55**.

Compound **55** is soluble in THF, DME and pyridine. It is stable in the solid state at room temperature in an inert atmosphere. Compound **55** has been characterized by NMR spectroscopy. The ¹H and ¹³C NMR spectra of **55** display resonances due to

the amidinate ligands. The ^{29}Si NMR spectrum of **55** exhibits two singlets at $\delta = 2.96$ and -0.53 ppm for the silylium cation and low-valent silicon atoms, respectively. The ^{29}Si NMR signals are intermediate between the silicon cations ($\delta = 53.4$ ppm) and the three-coordinate low-valent silicon atoms ($\delta = -128.7$ ppm) in the base-stabilized tetrasilacyclobutadiene dication (**34**).^[7]

Compound **55** has been characterized by X-ray crystallography (Figure 17). The Si1 and Si3 atoms adopt a distorted trigonal pyramidal geometry (sum of bond angles of Si1: 281.9° ; Si3: 281.2°), which indicate that they are almost non-hybridized and possess lone pair electrons with high s character. The lone pair electrons on these Si atoms have a gauche-bent conformation. The Si-Si bonds ($2.441(3)$, $2.451(3)$ Å) are comparable with the $\text{Si}^{\text{I}}\text{-Si}^{\text{I}}$ bond ($2.413(2)$ Å) in **4**.^[9] They are longer than those in **34** ($2.321(2)$, $2.331(2)$ Å).^[7] The results indicate that the Si-Si bonds in **55** do not have any multiple bond character. The Si2-N bonds ($1.819(6)$, $1.843(6)$ Å) are shortened compared with those in **54** because the oxidation state of the silicon cation increases from +II to +IV.

Figure 17. ORTEP drawing of compound **55** (50% thermal ellipsoids). The disorder in the triflate atoms are omitted for clarity. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-Si2 2.441(3), Si2-Si3 2.451(3), Si1-N1 1.852(6), Si1-N2 1.864(6), Si2-N3 1.843(6), Si2-N4 1.819(6), Si3-N5 1.865(6), Si3-N6 1.877(6); N1-Si1-N2 69.8(3), N1-Si1-Si2 105.6(2), N2-Si1-Si2 106.5(2), Si1-Si2-Si3 120.41(10), N3-Si2-N4 71.2(2), N5-Si3-N6 69.9(3), N5-Si3-Si2 107.2(2), N6-Si3-Si2 104.1(2).

3.2.2. Reactivity of **54** with [K{HB(*i*Bu)₃}].

Compound **54** is highly electrophilic and is expected to react with a wide range of nucleophilic reagents. As such, the reaction of **54** with [K{HB(*i*Bu)₃}] in THF was performed to afford the silylsilylene [LSiSi(H){(N*t*Bu)₂C(H)Ph}] (**56**)^[17] in 13.4% yield with the displacement of DMAP (Scheme 18). The reaction appears to proceed through the formation of the hydrosilylene intermediate [LSiH], which then reacts with the amidinate ligand of another [LSiH] molecule to form **56**. The synthesis of compound **56** by the reduction of [LSiHCl₂] with 4 equivalents of KC₈ has been previously reported.^[17]

Scheme 18. Synthesis of **56**.

3.2.3. Reactivity of **54** with Elemental Sulphur.

The existence of the lone pair electrons in compound **54** can be illustrated by the reaction of **54** with elemental sulphur in THF to form the base-stabilized silanethionium triflate [LSi(S)DMAP]OTf (**57**) in 30.9% yield (Scheme 19). A similar compound formed by the reaction of **52** with elemental sulphur has been reported by Driess *et al.* very recently.^[3c] Compound **57** is soluble in THF, CH₂Cl₂ and CHCl₃. It is stable in the solid state at room temperature in an inert atmosphere. Compound **57** has been characterized by NMR spectroscopy. The ²⁹Si NMR spectrum of **57** exhibits one singlet at $\delta = -14.09$ ppm, which shows a downfield shift compared with that of **54** ($\delta = -82.3$ ppm). The ²⁹Si NMR signal of **57** is intermediate between the four-coordinate amidinate silanethione complexes **59** (Chart 18; $\delta = -17.5$ ppm) and **58** ($\delta = 1.57$ ppm).^[18a, b] It shows a downfield shift compared with that of five-coordinate amidinate silanethione complex **60** ($\delta = -70.7$ ppm).^[18c]

Scheme 19. Synthesis of **57**.

Chart 18. Examples of silanethione complexes.

Figure 18. ORTEP drawing of compound **57** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-S1 1.9686(10), Si1-N1 1.801(2), Si1-N2 1.800(2), Si1-N3 1.794(2); N1-Si1-N2 73.03(11), N1-Si1-N3 104.46(11), N2-Si1-N3 106.30(11), N1-Si1-S1 124.65(9), N2-Si1-S1 124.91(9), N3-Si1-S1 115.49(8).

Compound **57** has been characterized by X-ray crystallography (Figure 18). The Si1 cation adopts a tetrahedral geometry. The Si1-S1 bond (1.969(10) Å) is comparable with that in the amidinate-silanethione complexes **58** (1.984(8) Å), **59**

(2.079(6) Å) and **60** (2.0193(9) Å).^[18] It is also comparable with those in base-stabilized silanethione complexes **61** and **62** (2.006(1) and 2.013(3) Å, respectively).^[19] The results indicate that the Si1-S1 bond could have double bond character or zwitterionic Si⁺-S⁻ bonding character. The Si-N_{amidinate} (1.800(2), 1.801(2) Å) bond lengths are shorter than those in **54** because the oxidation state of the silicon cation increases from +II to +IV.

3.3. Coordination Chemistry of [LSi(DMAP)]OTf (**54**; L = PhC(NtBu)₂) with Transition-Metals.

Shortly after the isolation of the first stable N-heterocyclic carbene (NHC),^[20] the syntheses of stable silicon analogues (NHSis) and their subsequent reactivities with transition-metals were investigated extensively.^[2, 21, 22] NHSis comprise of a lone pair of electrons and vacant p orbitals on the low valent silicon atom. As a result, they can act as both donor and acceptor ligands and serve as ancillary ligands in transition metal complexes, in which there is a synergy electron transfer between the low-valent silicon atom and the transition metal. Thus, the resulting metal-silicon bonds in transition metal-NHSi complexes are typically shorter than the corresponding single bonds.

Since transition metal-silylene complexes have been postulated as catalytic intermediates,^[23] the application of transition metal-NHSi complexes toward small molecules activation and catalytic transformations has also been investigated recently. For example, [L'Si→Ni(CO)₃] (**63**; Chart 19) (L' = CH{(C=CH₂)NAr}{CMeNAr}); Ar = 2,6-*i*Pr₂C₆H₃) is capable of activating the S-H and N-H bonds of small molecules.^[24] The catalytic activities of transition metal-NHSi complexes include that of [{1,1'-Cp₂Fe(LSi)₂}CoCp] (**64**) (Cp = η⁵-cyclopentadienyl) in the [2+2+2] cyclootrimerization of phenylacetylene and acetonitrile,^[25] and of [(dmpe)₂Fe←Si(H)L]

(**65**; dmpe = 1,2-bis(dimethylphosphino)ethane) as a pre-catalyst in the hydrosilylation of ketones.^[26]

Furthermore, the chemistry of transition metal-NHSi complexes has been extended to the stabilization of otherwise highly reactive silylene species within the coordination sphere of an organometallic fragment. For example, Roesky *et al.* has reported the synthesis and characterization of $[L(F)Si \rightarrow M(CO)_5]$ (**66** - **68**) (M = Cr, Mo, W, respectively) by the reaction of $[L(Cl)Si \rightarrow M(CO)_5]$ with Me_3SnF .^[27] Examples of silicon(II) hydride complexes (**69** and **70**) have also been successfully stabilized by coordination with Cp_2Ti^{II} (Cp = η^5 -cyclopentadienyl) and $Ni(CO)_3$, respectively.^[28]

A silyliumylidene cation of composition $[RSi:]^+$ consists of two vacant orbitals and a lone pair of electrons on the low valent silicon cation. Similarly to NHSi, it could serve as a ligand in a transition metal complex with enhanced π -accepting properties due to its stronger Lewis acidity. However, the coordination chemistry of a silyliumylidene cation toward transition metals is still unknown. This prompted our interest to investigate the reactivity of **54** with transition metals. Herein, we describe the syntheses and characterizations of transition metal-silyliumylidene complexes $[\{L(DMAP)Si\}_2 \{ \mu-Rh(\mu-Cl_2)Rh(cod) \}]OTf_2$ (**71**; cod = 1,5-cyclooctadiene) and $[L(DMAP)Si \rightarrow W(CO)_5]OTf$ (**72**), in Sections 3.3.1 and 3.3.2, respectively.

Chart 19. Examples of transition metal-NHSi complexes.

3.3.1. Reactivity of **54** with [Rh(cod)Cl]₂.

Treatment of 2 equivalents of **54** with [Rh(cod)Cl]₂ in toluene for 60 h afforded [{L(DMAP)Si}₂{μ-Rh(μ-Cl₂)Rh(cod)}]OTf₂ (**71**; Scheme 20). Complex **71** was formed by the displacement of one cod molecule by two silyliumylidene cations **54**. It was crystallized from DME as air- and moisture-sensitive orange crystals in 20.3% yield. It is stable in solution and the solid state at room temperature in an inert atmosphere. Complex **71** has been characterized by elemental analysis, spectroscopic methods and X-ray crystallography.

Scheme 20. Synthesis of **71**.

The ^1H and ^{13}C NMR spectra of **71** display resonances due to the amidinate, DMAP and cod ligand. The ^{13}C NMR spectrum also exhibits a quartet at $\delta = 122.04$ ppm ($^1J_{\text{C-F}} = 324.3$ Hz) for the CF_3SO_3^- anion. The ^{19}F NMR spectrum of **71** shows a singlet at $\delta = -77.77$ ppm for the CF_3SO_3^- anion. The ^{29}Si NMR spectrum of **71** exhibits a doublet at $\delta = 40.54$ ppm ($^1J_{\text{Si-Rh}} = 117.94$ Hz), with coupling to the rhodium atom. This is an expected downfield shift compared with that of compound **54** ($\delta = -82.3$ ppm), as the lone pair electrons of the silicon atoms in **54** are donated to the Rh atom.

The molecular structure of **71** (Figure 19) shows that the Si^{II} atoms are tetracoordinated, each coordinated with two nitrogen atoms of the amidinate ligand, the nitrogen atom of DMAP and the Rh1 atom. The latter adopts an almost square planar geometry (the dihedral angle of $\text{Si}2\text{-Si}1\text{-Cl}1\text{-Rh}1$: 2.90°). The Rh1 atom is bonded to two bridging chloride atoms and the Si1 and Si2 atoms. The Rh1-Cl1 (2.447(3) Å) and Rh1-Cl2 (2.447(16) Å) bonds are slightly elongated compared to the Rh2-Cl bonds (2.357(10), 2.373(14) Å). They are longer than that in $[\text{Rh}(\text{cod})\text{Cl}]_2$ (average Rh-Cl: 2.383 Å).^[29] It is noteworthy that the Rh1-Si1 and Rh1-Si2 bonds (2.184(3) and 2.191(3) Å) are one of the shortest Rh-Si bonds reported. It is significantly shorter than those in two cationic tetrakis(silylene)rhodium(I) complexes

$[\text{Rh}\{\text{Si}[\text{N}(\text{tBu})\text{CH}]_2\}_4]\text{BAr}_\text{F}$ (2.29 Å) and $[\text{Rh}\{\text{Si}[\text{N}(\text{tBu})\text{CH}_2]_2\}_4]\text{BAr}_\text{F}$ (2.32 Å) (BAr_F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate).^[30] Additionally, it is shorter than other Rh-silyl bonds (2.317(1) – 2.380(1) Å) in the literatures.^[31] It is in the range of bridged μ -SiRh₂ complexes (2.054(5) – 2.526(1) Å).^[32] The results indicate that there is significant π -back bonding from Rh1 to the silicon atoms.

Figure 19. ORTEP drawing of complex **71** (50% thermal ellipsoids). Hydrogen atoms, DME molecules and the disorder in cod, phenyl rings and DMAP molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-N1 1.838(10), Si1-N2 1.827(9), Si1-N3 1.848(13), C5-N1 1.379(15), C5-N2 1.332(16), Si1-Rh1 2.184(3), Si2-Rh1 2.191(3), Si2-N5 1.861(8), Si2-N6 1.831(10), Si2-N7 1.854(13), C27-N5 1.310(16), C27-N6 1.351(14), Rh1-Cl1 2.447(3), Rh1-Cl2 2.447(16), Rh2-Cl1 2.357(10), Rh2-Cl2 2.373(14), Rh2-C45 2.12(2), Rh2-C46 2.125(19), Rh2-C49 2.130(18), Rh2-C50 2.105(18), C45-C46 1.451(19), C49-C50 1.441(19); N1-Si1-N2 71.8(4), N1-Si1-N3 97.8(8), N2-Si1-N3 99.4(13), Rh1-Si1-N1 119.5(3), Rh1-Si1-N2 122.8(3), Rh1-Si1-N3 129.5(10), Rh1-Si2-N5 121.4(3), Rh1-Si2-N6 119.7(3), Rh1-Si2-N7 129.5(6), N5-Si2-N6 71.3(4), N5-Si2-N7 98.9(7), N6-Si2-N7 100.1(7), Si1-Rh1-Si2 99.91(11), Si1-Rh1-Cl1 90.50(10), Cl1-Rh1-Cl2 80.9(8), Cl2-Rh1-Si2 89.2(8), Rh1-Cl1-Rh2 88.1(4), Cl1-Rh2-Cl2 84.3(8), Rh2-Cl2-Rh1 87.8(6), C45-Rh2-Cl2 97.5(11), C46-Rh2-Cl2 90.6(8), C49-Rh2-Cl1 93.6(10), C50-Rh2-Cl1 93.9(9), C45-Rh2-C46 40.0(6), C49-Rh2-C50 39.8(6).

3.3.2. Reactivity of **54** with $\text{W(CO)}_5\text{THF}$.

Compound **54** can also displace the THF molecule in $\text{W(CO)}_5\text{THF}$ to afford $[\text{L(DMAP)Si} \rightarrow \text{W(CO)}_5]\text{OTf}$ (**72**; Scheme 21), which was crystallized from toluene as air- and moisture-sensitive pale-yellow crystals in 67.1% yield. It is stable in solution and the solid state at room temperature in an inert atmosphere. Complex **72** has been characterized by elemental analysis, spectroscopic methods and X-ray crystallography.

Scheme 21. Synthesis of **72**.

The ^1H and ^{13}C NMR spectra of **72** display resonances due to the amidinate, DMAP and carbonyl ligands. The ^{13}C NMR spectrum also exhibits a quartet at $\delta = 122.59$ ppm ($^1J_{\text{C-F}} = 322.2$ Hz) for the CF_3SO_3^- anion. The ^{19}F NMR spectrum of **72** shows a singlet at $\delta = -77.71$ ppm for the CF_3SO_3^- anion. The ^{29}Si NMR spectrum of **72** exhibits a singlet at $\delta = 51.61$ ppm. Similarly to complex **71**, this is an expected downfield shift compared with that of compound **54**. Additionally, the ^{29}Si NMR resonance of **72** is the intermediate of $[\text{L(Cl)Si} \rightarrow \text{W(CO)}_5]$ ($\delta = 52.99$ ppm) and $[\text{L(F)Si} \rightarrow \text{W(CO)}_5]$ (**68**; Chart 19) ($\delta = 41.79$ ppm).^[27]

Figure 20. ORTEP drawing of complex **72** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-N1 1.825(4), Si1-N2 1.821(4), Si1-N3 1.839(4), C10-N1 1.341(5), C10-N2 1.336(5), Si1-W1 2.497(1), W1-C1 2.030(5), W1-C2 2.058(5), W1-C3 2.018(5), W1-C4 2.054(5), W1-C5 2.029(5), C1-O1 1.138(5), C2-O2 1.130(6), C3-O3 1.145(6), C4-O4 1.134(5), C5-O5 1.138(5); N1-Si1-N2 71.57(16), N1-Si1-N3 100.09(16), N2-Si1-N3 101.13(16), N1-Si1-W1 124.82(12), N2-Si1-W1 126.26(12), N3-Si1-W1 121.08(13), C1-W1-Si1 91.37(14), C2-W1-Si1 89.30(15), C3-W1-Si1 179.05(13), C4-W1-Si1 90.21(14), C5-W1-Si1 88.58(13), C1-W1-C2 89.78(19), C1-W1-C3 89.54(18), C1-W1-C4 175.96(18), C1-W1-C5 88.29(19), C2-W1-C3 90.4(2), C2-W1-C4 93.96(18), C2-W1-C5 177.10(18), C3-W1-C4 88.89(18), C3-W1-C5 91.70(19).

The molecular structure of **72** (Figure 20) shows that the Si^{II} center is tetracoordinated, which is similar to **71**. The tungsten atom adopts an octahedral geometry, with coordination to one silicon atom and five carbonyl groups. The Si1-W1 bond (2.497(1) Å) is comparable with typical Si-W bonds (2.388(6) – 2.708(3) Å).^[33] The *cis*-CO bond lengths (average 1.135 Å) are comparable to those in W(CO)₆ (1.139 Å),^[34] while the *trans*-CO bond (C3-O3: 1.145(6) Å) is slightly elongated for about 1 pm. The *trans*-W-CO bond (W1-C3: 2.018(5) Å) is also the shortest. These results indicate that the π -accepting ability of **54** is weaker than CO. Moreover, the C3-O3 bond length is between that of [L(F)Si→W(CO)₅] (1.154(3) Å) and [L(Cl)Si→W(CO)₅] (1.139(5) Å).^[27] The results illustrate that the π -accepting ability of the Si^{II} cation in **54** is intermediate between the Si^{II} atoms in [LSiCl] and [LSiF].

Conclusion

The singlet silyliumylidene cation [LSi(DMAP)]OTf (**54**), which is stabilized by both amidinate ligand and DMAP, can be synthesized by a simple procedure. The Lewis ambiphilic nature of **54** has been adequately proven via reactivity studies. Its reactivity towards the amidinate Si^I dimer **4**, which resulted in the formation of the disilylenylsilylium triflate [L'₂(L)Si]OTf (**55**; L' = LSi:) with concomitant displacement of DMAP displayed the nucleophilic nature of **54**. On the other hand, the electrophilic nature of **54** was proven by its reaction with the nucleophilic reagent, [K{HB(*i*Bu)₃}] to form the silylsilylene [LSiSi(H){(N*i*Bu)₂C(H)Ph}] (**56**). Additionally, the high Lewis acidity of **54** was further emphasized by the reactivity of **54** with [Rh(cod)Cl]₂ and W(CO)₅THF, which yielded the first examples of transition metal-silyliumylidene cation complexes **71** and **72**. The reactivity studies of **54** with transition metals also showed that compound **54** can be a two-electron σ donating ligand with good π accepting ability.

Experimental Section

General Procedure: All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF, DME and toluene were dried over and distilled over Na/K alloy prior to use. [D₆]Benzene and [D₈]THF were dried over and distilled over K metal prior to use. [D₁]Chloroform and [D₅]Py were dried over and distilled over CaH₂ prior to use. **4** and [4-NMe₂-C₅H₄NSiMe₃]OTf were prepared as described in the literatures.^[9, 10] [K{HB(*i*Bu)₃}], elemental sulphur, [Rh(cod)Cl]₂ and W(CO)₆ were purchased from Aldrich Chemicals and used without further purification. W(CO)₅THF was prepared by the UV irradiation of W(CO)₆ in THF as described in the literature.^[35] The ¹H, ¹³C, ¹⁹F and ²⁹Si NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H, ¹³C

and ^{29}Si , and CFCl_3 for ^{19}F . The IR spectrum was recorded on a Shimadzu IR Prestige-21 spectrometer in the range of $4000\text{--}40\text{ cm}^{-1}$ as Nujol mulls. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of [LSi(DMAP)]OTf (54**).** A solution of $[4\text{-NMe}_2\text{-C}_5\text{H}_4\text{NSiMe}_3]\text{OTf}$ (0.0735 g, 0.213 mmol) in THF (1 mL) was added to a stirring solution of **4** (0.108 g, 0.208 mmol) and DMAP (0.0518 g, 0.424 mmol) in THF (15 mL) at ambient temperature. The resulting dark-red solution was stirred for 2 h. Volatiles were removed in vacuo and the residue was extracted with toluene. After filtration and concentration of the filtrate, **54** was obtained as colourless crystals. Yield: 0.060 g (54.3 %). M.p. $169.7\text{ }^\circ\text{C}$ (decomp); ^1H NMR (400.2 MHz, $[\text{D}_8]\text{THF}$, $24.8\text{ }^\circ\text{C}$): δ = 1.07 (s, 18H, *t*Bu), 3.22 (s, 6H, *NMe*₂), 7.12–7.55 (m, 7H, Ph & DMAP), 8.37 ppm (d, $^3J_{\text{HH}}$ = 6.44 Hz, 2H, DMAP); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, $24.7\text{ }^\circ\text{C}$): δ = 31.16 (*CMe*₃), 39.61 (*NMe*₂), 54.64 (*CMe*₃), 108.84 (Ph), 121.72 (q, $^1J_{\text{CF}}$ = 321.7 Hz, *CF*₃), 126.16, 128.14, 128.71 (Ph), 128.95 (br, *meta*-*C*_{DMAP}), 129.48, 131.22, 132.46 (*CNMe*₂ & Ph), 146.02 (br, *ortho*-*C*_{DMAP}), 171.63 ppm (NCN); $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, $[\text{D}_8]\text{THF}$, $22.7\text{ }^\circ\text{C}$): δ = -82.27 ppm ; $^{19}\text{F}\{^1\text{H}\}$ NMR (375.94 MHz, $[\text{D}_8]\text{THF}$, $23.2\text{ }^\circ\text{C}$): δ = -78.90 ppm ; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{33}\text{F}_3\text{N}_4\text{O}_3\text{SSi}$: C 52.06, H 6.27, N 10.56; found: C 51.73, H 6.15, N 10.16.

Crystal data for 54: $[\text{C}_{23}\text{H}_{33}\text{F}_3\text{N}_4\text{O}_3\text{SSi}]$; $M = 530.68$; monoclinic; space group *Cc*; $a = 14.0577(6)$, $b = 10.8815(4)$, $c = 18.3062(8)\text{ \AA}$; $\alpha = 90$, $\beta = 102.662(2)$, $\gamma = 90^\circ$; $V = 2732.18(19)\text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.290\text{ mg m}^{-3}$; 18381 measured reflections; 7566 independent reflections; 391 refined parameters; $R_1 = 0.0443$, $wR_2 = 0.0919$ ($I > 2\sigma(I)$).

Synthesis of $[\text{L}'_2(\text{L})\text{Si}]\text{OTf}$ (55**; $\text{L}' = \text{LSi}$).** A solution of **54** (0.107 g, 0.201 mmol) in THF (13.4 mL) was added dropwise to a stirring solution of **4** (0.104 g, 0.201 mmol)

in THF (5 mL) at ambient temperature. The resulting dark-red solution was stirred for 2 h. Volatiles were removed in vacuo and the residue was extracted with DME. After filtration and concentration of the filtrate, **55** was obtained as yellow crystals. Yield: 0.0434 g (23.3 %). M.p. 270.1 °C (decomp); ^1H NMR (399.5 MHz, $[\text{D}_5]\text{Py}$, 23.6 °C): δ = 1.20 (s, 36H, *t*Bu), 1.32 (s, 18H, *t*Bu), 7.35-7.70 ppm (m, 15H, Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, $[\text{D}_5]\text{Py}$, 24.1 °C): δ = 31.41, 31.73 (CMe_3), 53.59, 55.91 (CMe_3), 128.21, 128.30, 128.78, 128.92, 129.20, 129.64, 130.85 (Ph), 132.09 (q, $^1J_{\text{CF}} = 300.95$ Hz, CF_3) 133.11 (Ph), 165.76, 182.92 ppm (NCN); $^{29}\text{Si}\{^1\text{H}\}$ NMR (78.65 MHz, DME, 23.4 °C): δ = -0.53 (LSi:), 2.96 ppm (Si^+); $^{19}\text{F}\{^1\text{H}\}$ NMR (375.94 MHz, $[\text{D}_5]\text{Py}$, 23.7 °C): δ = -77.09 ppm; elemental analysis calcd (%) for $\text{C}_{46}\text{H}_{69}\text{F}_3\text{N}_6\text{O}_3\text{SSi}_3$: C 59.57, H 7.50, N 9.06; found: C 60.77, H 7.92, N 7.67. Attempts to obtain acceptable elemental analysis data for compound **55** failed because of its extreme air sensitivity.

Crystal data for 55: $[\text{C}_{46}\text{H}_{69}\text{F}_3\text{N}_6\text{O}_3\text{SSi}_3]$; $M = 927.40$; monoclinic; space group $P2(1)/n$; $a = 16.0420(13)$, $b = 17.2604(16)$, $c = 18.4942(15)$ Å; $\alpha = 90$, $\beta = 90.112(6)$, $\gamma = 90^\circ$; $V = 5120.9(8)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.203$ mg m⁻³; 40958 measured reflections; 8788 independent reflections; 651 refined parameters; $R_1 = 0.0819$, $wR_2 = 0.1866$ ($I > 2\sigma(I)$).

Synthesis of $[\text{LSiSi(H)}\{(\text{N}t\text{Bu})_2\text{C(H)Ph}\}]$ (56**).** $[\text{K}\{\text{HB}(i\text{Bu})_3\}]$ (0.22 mL, 1M in THF) was added dropwise to a stirring solution of **54** (0.107 g, 0.201 mmol) in THF (13.4 mL) at -78 °C. The resulting orange solution was warmed to ambient temperature and stirred for an additional 2 h. Volatiles were removed in vacuo and the residue was extracted with a mixture of toluene and THF. After filtration and concentration of the filtrate, **56** was obtained as colourless crystals. Yield: 0.0071 g (13.4%). For spectroscopic data of **56**, see reference [17].

Synthesis of $[\text{LSi(S)DMAP}]\text{OTf}$ (57**).** A solution of sulphur (0.0079 g, 0.246 mmol) in THF (1 mL) was added to a stirring solution of **54** (0.111 g, 0.208 mmol) in THF

(13.8 mL) at -78 °C. The reaction mixture was warmed to ambient temperature and stirred for an additional 3 h. The insoluble precipitate was filtered off and the filtrate was concentrated to obtain **57** as colourless crystals. Yield: 0.036 g (30.9 %). M.p. 281.4 °C (decomp); ^1H NMR (399.5 MHz, $[\text{D}_1]\text{Chloroform}$, 23.2 °C): δ = 1.13 (s, 18H, *t*Bu), 3.02 (s, 6H, NMe_2), 6.52 (d, $^3J_{\text{HH}}$ = 6.39 Hz, 1H, *ortho-CH* of DMAP), 7.43 (d, $^3J_{\text{HH}}$ = 7.31 Hz, 2H, *ortho-CH* of Ph), 7.56 (t, $^3J_{\text{HH}}$ = 7.79 Hz, 2H, *meta-CH* of Ph), 7.66 (t, $^3J_{\text{HH}}$ = 7.53 Hz, *para-CH* of Ph), 8.21 (d, $^3J_{\text{HH}}$ = 5.95 Hz, 1H, *ortho-CH* of DMAP), 8.68 ppm (br, 2H, *meta-CH* of DMAP); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_1]\text{Chloroform}$, 24.2 °C): δ = 30.99 (CMe_3), 39.34 (NMe_2), 57.06 (CMe_3), 106.83, 115.84 (Ph & DMAP), 120.60 (q, $^1J_{\text{CF}}$ = 319.14 Hz, CF_3), 127.08, 128.62, 129.74, 132.64, 149.19, 154.71 (Ph & DMAP), 166.83 ppm (NCN); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, $[\text{D}_1]\text{Chloroform}$, 23.6 °C): δ = -14.09 ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (372.5 MHz, $[\text{D}_1]\text{Chloroform}$, 23.4 °C): δ = -79.16 ppm; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{33}\text{F}_3\text{N}_4\text{O}_3\text{S}_2\text{Si}$: C 49.10, H 5.92, N 9.96; found: C 48.87, H 5.63, N 9.74.

Crystal data for 57: $[\text{C}_{23}\text{H}_{33}\text{F}_3\text{N}_4\text{O}_3\text{S}_2\text{Si}]$; M = 562.74; triclinic; space group $P-1$; a = 8.7357(12), b = 10.7468(12), c = 15.909(2) Å; α = 103.952(3), β = 97.110(3), γ = 100.141(6)°; V = 1405.0(3) Å³; Z = 2; ρ_{calcd} = 1.330 mg m⁻³; 22636 measured reflections; 7624 independent reflections; 333 refined parameters; R_1 = 0.0652, wR_2 = 0.1647 ($I > 2\sigma(I)$).

Synthesis of $[\{\text{L}(\text{DMAP})\text{Si}\}_2\{\mu\text{-Rh}(\mu\text{-Cl}_2)\text{Rh}(\text{cod})\}]\text{OTf}_2$ (71**)**. Toluene (16.4 mL) was added to a mixture of **54** (0.174 g, 0.328 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.0819 g, 0.166 mol) at ambient temperature. The reaction mixture was stirred for 60 h. Volatiles were removed in vacuo and the residue was extracted with DME. After filtration and concentration of the filtrate, **71** was obtained as yellow crystals. Yield: 0.0470 g (20.3 %). M.p. 175 °C; ^1H NMR (399.5 MHz, $[\text{D}_6]\text{Benzene}$, 23.9 °C): δ = 1.42 (s, 36H, *t*Bu), 1.44-1.50 (m, 4H, CH_2), 2.13-2.26 (m, 4H, CH_2), 2.75 (s, 12H, NMe_2), 4.40 (s,

4H, =CH), 6.81-6.97 (m, 6H, Ph & DMAP), 7.16-7.23 (m, 2H, Ph & DMAP), 7.54-7.65 (m, 6H, Ph & DMAP), 8.57 ppm (d, $^3J_{\text{HH}} = 6.83$ Hz, 4H, DMAP); $^{13}\text{C}\{^1\text{H}\}$ NMR (99.55 MHz, $[\text{D}_6]\text{Benzene}$, 24.8 °C): $\delta = 30.70$ (CH_2), 31.13 (CMe_3), 39.62 (NMe_2), 55.24 (CMe_3), 78.14 (d, $^1J_{\text{C-Rh}} = 14.30$ Hz, =CH), 109.56 (Ph), 122.04 (q, $^1J_{\text{C-F}} = 324.25$ Hz, CF_3), 128.39, 128.73, 128.85, 130.07, 130.68, 141.86, 156.76 (Ph & DMAP), 176.14 ppm (NCN); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, $[\text{D}_6]\text{Benzene}$, 24.9 °C): $\delta = 40.54$ ppm (d, $^1J_{\text{Si-Rh}} = 117.94$ Hz); $^{19}\text{F}\{^1\text{H}\}$ NMR (375.94 MHz, $[\text{D}_6]\text{Benzene}$, 24.0 °C): $\delta = -77.77$ ppm; elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{70}\text{Cl}_2\text{F}_6\text{N}_8\text{O}_6\text{Rh}_2\text{S}_2\text{Si}_2$: C 44.16, H 4.99, N 7.92; found: C 45.56, H 5.04, N 7.69.

Crystal data for 71•DME: $[\text{C}_{60}\text{H}_{90}\text{Cl}_2\text{F}_6\text{N}_8\text{O}_{10}\text{Rh}_2\text{S}_2\text{Si}_2]$; $M = 1594.42$; monoclinic; space group $P2(1)/c$; $a = 12.5150(6)$, $b = 42.292(3)$, $c = 15.3574(11)$ Å; $\alpha = 90$, $\beta = 112.682(4)$, $\gamma = 90^\circ$; $V = 7499.8(8)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.412$ mg m⁻³; 23172 measured reflections; 23204 independent reflections; 1490 refined parameters; $R_1 = 0.1014$, $wR_2 = 0.2532$ ($I > 2\sigma(I)$).

Synthesis of $[\text{L}(\text{DMAP})\text{Si} \rightarrow \text{W}(\text{CO})_5]\text{OTf}$ (72). A solution of $\text{W}(\text{CO})_5\text{THF}$ (32 mL, 0.320 mmol) was added to a stirring solution of **54** (0.170 g, 0.320 mmol) in THF (16 mL) at ambient temperature. The resulting yellow reaction solution was stirred for 3 days. Volatiles were removed in vacuo and the residue was extracted with toluene. After filtration and concentration of the filtrate, **72** was obtained as pale-yellow crystals. Yield: 0.184 g (67.1 %). M.p. 237 °C; ^1H NMR (395.9 MHz, $[\text{D}_6]\text{Benzene}$, 24.3 °C): $\delta = 1.05$ (s, 18H, *t*Bu), 2.46 (s, 12H, NMe_2), 6.84-6.89 (m, 3H, Ph & DMAP), 6.99-7.03 (m, 2H, Ph & DMAP), 7.52 (t, $^3J_{\text{HH}} = 8.16$ Hz, 1H, Ph), 8.50 (d, $^3J_{\text{HH}} = 7.68$ Hz, 2H, DMAP), 8.96 ppm (d, $^3J_{\text{HH}} = 7.72$ Hz, 1H, DMAP); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_6]\text{Benzene}$, 24.9 °C): $\delta = 30.73$ (CMe_3), 39.54 (NMe_2), 55.63 (CMe_3), 109.01 (Ph), 122.59 (q, $^1J_{\text{C-F}} = 322.2$ Hz, CF_3), 127.28, 127.55, 129.40, 129.69, 131.63,

143.54, 157.42 (Ph & DMAP), 178.38 (NCN), 196.87, 198.02 ppm (CO); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, $[\text{D}_6]\text{Benzene}$, 24.8 °C): $\delta = 51.61$ ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (372.50 MHz, $[\text{D}_6]\text{Benzene}$, 24.3 °C): $\delta = -77.71$ ppm; FT-IR (Nujol, cm^{-1}): wave number 1921 (br), 1991 (s), 2070 (s); elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{33}\text{F}_3\text{N}_4\text{O}_8\text{SSiW}$: C 39.35, H 3.89, N 6.56; found: C 38.38, H 4.13, N 6.32.

Crystal data for 72: $[\text{C}_{28}\text{H}_{33}\text{F}_3\text{N}_4\text{O}_8\text{SSiW}]$; $M = 854.58$; monoclinic; space group $P2(1)/c$; $a = 12.6859(7)$, $b = 20.4319(12)$, $c = 13.4535(7)$ Å; $\alpha = 90$, $\beta = 94.956(2)$, $\gamma = 90^\circ$; $V = 3474.1(3)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.634$ mg m⁻³; 37418 measured reflections; 11120 independent reflections; 423 refined parameters; $R_1 = 0.0367$, $wR_2 = 0.836$ ($I > 2\sigma(I)$).

X-ray data collection and structural refinement. Intensity data for compounds **54**, **55**, **57**, **71** and **72** were collected using a Bruker APEX II diffractometer. The crystals 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 .^[36] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. The restraints and constraints for solving disordered triflate moieties in compounds **54** and **55** are described in Appendix C. CCDC-901880 (**54**), CCDC-901879 (**55**), CCDC-901878 (**57**), CCDC-941821 (**71**) and CCDC-941822 (**72**) contain the supplementary crystallographic data for this chapter. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Chapter 4

Synthesis of a Base-Stabilized Germanium(I) Dimer and Germlydenide Anion

Introduction

Stable heavier group 14 alkyne analogues of composition REER (R = bulky or silyl ligand; E = Si, Ge, Sn, Pb) have attracted much attention because of their unique bonding and reactivities.^[1] These complexes can be synthesized via kinetic stabilization provided by sterically bulky substituents at the heavier group 14 elements. The X-ray crystal structures of heavier group 14 alkyne analogues show that they have a *trans*-bent and planar geometry in which the R–E–E angle decreases from silicon to lead. Theoretical studies of simple derivatives [MeEEMe] (E = Si, Ge, Sn, Pb) show that a disilyne and digermynes show a multiple-bonded structure [REER] (**M'**; Chart 20), while a distannynes and diplumbyne has a single-bonded structure [R $\ddot{E}$ - $\ddot{E}$ R] (**S'**; Chart 20). The *trans*-bending angles are related to a larger extent of the in-plane- π bonding.^[2] In addition, the bond order of the E–E multiple bond decreases from ca. 2.4–2.6 at silicon to 1 at lead.^[1a, 2] However, recent time dependent-density functional theory (TD-DFT) calculations and UV/Vis spectroscopy studies showed that the tin [Ar'SnSnAr'] (Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*Pr₂)₂) and lead alkyne analogues [Ar*PbPbAr*] (Ar* = C₆H₃-2,6-(C₆H₂-2,4,6-*i*Pr₃)₂), still adopt the multiple-bonded structure **M'** in solution.^[3] In addition, the reactivity of stable disilynes, digermynes and distannynes has been investigated considerably.^[1d, 4] For example, they can undergo one- and two-electron reductions to give the radical anions [REER]^{•-} and the doubly reduced species [REER]²⁻, respectively.^[1f, 5] A comparison of their structural data with those of the heavier alkyne analogues can provide insight into the E-E bonding.

Chart 20. Multiple-bonded M' and single-bonded S' structures.

$R^1 = t\text{Bu}$; $R^2 = \text{Ph}$; $E = \text{Si}$ (4), Ge (7)

73: $R^1 = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$; $R^2 = t\text{Bu}$; $E = \text{Ge}$

74: $R^1 = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$; $R^2 = \text{N}i\text{Pr}$; $E = \text{Ge}$

75 - 77: $R^1 = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$; $R^2 = 4\text{-}t\text{BuC}_6\text{H}_4$; $E = \text{Si} - \text{Sn}$

78: $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$

79

80: $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$

81: $R^3 = t\text{Bu}$; $E = \text{Sn}$

82: $R^3 = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$; $E = \text{Pb}$

83

6: $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$

38

Chart 21. Examples of base-stabilized heavier group 14 element(I) dimers.

Recently, a series of base-stabilized group 14 element(I) dimers $[\text{L}\ddot{\text{E}}-\ddot{\text{E}}\text{L}]$ ($E = \text{Si}, \text{Ge}, \text{Sn}$ and Pb ; $L = \text{amidinate, guanidinate, } \beta\text{-diketiminate, N-functionalized aryl, P-functionalized amide}$) were synthesized (Chart 21).^[6] They comprise of a $\ddot{\text{E}}-\ddot{\text{E}}$ single bond and a lone pair of electrons at each E atom. In this respect, they represent the

singly-bonded structure of the heavier alkyne analogues and are considered as base-stabilized heavier alkyne analogues. Similarly, the reactivity of base-stabilized group 14 element(I) dimers has been studied extensively.^[6b, c, g, 7] One of which includes the reduction by alkali metals or KC₈. Very recently, stable germylidenide, stannylide and plumbylidenide anions (**84** – **86**; Chart 22) supported by the 2,6-diiminophenyl ligand were synthesized by the reduction of the corresponding group 14 element(I) dimers.^[6e, p, q] Other examples, **87** and **88** (Chart 22), whereby the alkali metal cations are η^5 -coordinated to the planar C₃NGe rings were synthesized by Driess and Jones *et al.*^[8] The molecular structure of **85** is similar to that of **87** and **88**, in which the potassium counter-cation is also η^5 -coordinated to the planar heterocyclic ring. Moreover, the negative charge at the Sn and Pb atoms in **85** and **86**, is stabilized by an electron delocalization in the low-valent tin and lead heterocycles, respectively. On the other hand, the K atom in compound **84** is η^1 -coordinated with the low-valent Ge atom and the negative charge on Ge atom is stabilized by an electron delocalization in the germanium heterocycle. These results suggest that different heavier group 14 elements and supporting substituents might yield contrasting geometric and electronic structures in an ylidenide anion. Moreover, the heavier group 14 analogues of ylidenide anions may serve as useful building blocks for the synthesis of novel heavier group 14-containing complexes.

Chart 22. Examples of heavier group 14 element ylidenide anions.

Although 2-imino-5,6-methylenedioxyphenyl (L^1) has been used as a stabilizing ligand for complexes comprising of titanium, zirconium, niobium and tantalum (Chart 23),^[9] it has not been utilized for the stabilization of heavier group 14 main-group metals. Hence, this prompted our interest to explore the effectiveness of L^1 as an ancillary ligand for the isolation of a novel germanium(I) dimer and its reduction reactions. In this chapter, the synthesis and characterization of a 2-imino-5,6-methylenedioxyphenyl (L^1) stabilized Ge^I dimer and its reduction with potassium graphite to afford the corresponding germylidenide anion are described.

Chart 23. Examples of group IV and V metal complexes stabilized by 2-imino-5,6-methylenedioxyphenyl ligands.

Results and Discussion

4.1. Synthesis of the 2-Imino-5,6-methylenedioxyphenyl (L^1) Stabilized Germanium(II) Chloride [$L^1\text{GeCl}$] (**94**).

The reaction of [$L^1\text{Li}$] (**93**)^[9b] with $\text{GeCl}_2\cdot\text{dioxane}$ in Et_2O at 0°C afforded [$L^1\text{GeCl}$] (**94**; Scheme 22). Compound **94** was isolated as an air- and moisture-sensitive yellow crystalline solid in 56.4 % yield. It is soluble in Et_2O , THF and toluene. Compound **94** is stable in the solid state at room temperature in an inert atmosphere. It has been characterized by NMR spectroscopy. The ^1H NMR spectrum of **94** displays one set of signals due to the 2-imino-5,6-methylenedioxyphenyl ligand. It is noteworthy that the $-\text{OCH}_2\text{O}-$ protons are non-equivalent and display an AB quartet at $\delta = 5.18$ and 5.27 ppm. The signal for the $\text{MeC}=\text{N}$ protons ($\delta = 1.68$ ppm) shows an upfield shift compared to that of **93** ($\delta = 1.90$ ppm).^[9b]

Scheme 22. Synthesis of **94**.

Compound **94** has been characterized by X-ray crystallography (Figure 21). In the asymmetric unit of **94**, there are two independent molecules with slightly different bond lengths and angles. Only one of them is discussed here for clarity. The L^1 ligand is bonded in a C,N -chelate fashion to the Ge1 atom. The Ge atom adopts a distorted trigonal pyramidal geometry. The sum of the bond angles at the Ge1 atom is 268.76° . It is comparable with that of the 2,6-diiminophenyl stabilized Ge^{II} chloride **95**^[6e] (267.40°) and $[(\text{Mamx})\text{GeCl}]$ (270.25°) (**96**; $\text{Mamx} = 2,4\text{-}i\text{Bu}_2\text{-6-}[(N,N\text{-}$

dimethylamino)methyl]phenyl; Chart 24).^[10] The geometry at the Ge1 atom in **94** indicates that the Ge1 atom is almost nonhybridized and possesses lone pair electrons with high s character. The Ge1-C1 (1.992(3) Å) and Ge1-N1 (2.054(2) Å) are comparable with those in **96** (Ge-C, 2.0156(14) Å, Ge-N, 2.0936(13) Å).^[10]

Chart 24. Examples of organo-germanium(II) chloride compounds **95** and **96**.

Figure 21. ORTEP drawing of **94** (50% thermal ellipsoids). In the asymmetric unit of **94**, there are two independent molecules with slightly different bond lengths and angles. Only one of them is shown for clarity. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Cl1 2.3024(8), Ge1-C1 1.992(3), Ge1-N1 2.054(2), C1-C7 1.423(4), C7-C8 1.460(4), N1-C8 1.301(3); C1-Ge1-N1 80.40(11), C1-Ge1-Cl1 93.98(8), N1-Ge1-Cl1 94.38(7), Ge1-C1-C7 113.6(2), C1-C7-C8 114.3(2), C7-C8-N1 115.7(3), C8-N1-Ge1 115.50(18).

4.2. Synthesis of the 2-Imino-5,6-methylenedioxyphenyl (L^1) Stabilized Germanium(I) Dimer [$L^1\text{Ge-Ge}L^1$] (**97**).

The reaction of [$L^1\text{GeCl}$] (**94**) with KC_8 in THF at room temperature afforded the 2-imino-5,6-methylenedioxyphenyl (L^1) stabilized germanium(I) dimer [$L^1\text{Ge-Ge}L^1$] (**97**; Scheme 23) in 70.5 % yield. Recently, the Ge^{I} radical

[HC{C(*t*Bu)NAr}₂Ge•] (Ar = 2,6-*i*Pr₂C₆H₃) was synthesized by the reduction of the corresponding chlorogermylene with Na(C₁₀H₈) in THF.^[11] The results imply that compound **97** is formed via the dimerization of a Ge^I radical intermediate. Compound **97** was isolated as an air- and moisture-sensitive red crystalline solid. It is soluble in THF, Et₂O and toluene. Compound **97** is stable in the solid state at room temperature in an inert atmosphere. It has been characterized by NMR spectroscopy. The ¹H NMR spectrum of **97** shows one set of signals due to the 2-imino-5,6-methylenedioxyphenyl ligand. The signal for the *Me*C=N protons (δ = 1.97 ppm) shows a downfield shift compared with that of **94** (δ = 1.68 ppm). The UV/Vis spectrum of **97** in THF shows three absorption bands at 475, 506 and 659 nm in the visible-light region. It is comparable with that observed in the UV/Vis spectrum of **80**, which also shows three absorption bands at 438, 586 and 702 nm.^[6e] The results imply that the Ge-Ge bond in **97** has little π character.

Scheme 23. Synthesis of **97**.

Compound **97** has been characterized by X-ray crystallography (Figure 22). Similar to the amidinate-stabilized germanium(I) dimer [PhC(N*t*Bu)₂Ge]₂ (**7**)^[6j] and **80**^[6e], it comprises of a gauche-bent structure. On the other hand, the more sterically hindered germanium(I) dimer [*t*BuC(NAr)₂Ge]₂ (**73**) shows a *trans*-bent structure.^[6h] The Ge atoms in **97** adopt a trigonal pyramidal geometry with the sum of bond angles around the Ge1 and Ge2 atoms being 279.44° and 278.29°, respectively. This indicates

that there are stereoactive lone pairs of electrons on the Ge atoms. The Ge1-Ge2 bond (2.5685(5) Å) is comparable with that of **80**, **7** and **73** (2.5059(5), 2.569(5) and 2.6380(8) Å, respectively).^[6e, j, h] The results imply that the Ge-Ge bond in **97** does not have any multiple-bond character. The Ge-C (1.968(4) and 1.954(4) Å) bonds and Ge-N (2.022(3) and 2.017(3) Å) bonds are slightly shorter than that in compound **94**.

Figure 22. ORTEP drawing of **97** (50% thermal ellipsoids). Hydrogen atoms and *iPr* substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Ge2 2.5685(5), Ge1-N1 2.022(3), Ge1-C1 1.968(4), C1-C7 1.436(5), C7-C8 1.437(5), C8-N1 1.310(5), Ge2-N2 2.017(3), Ge2-C22 1.954(4), C22-C28 1.434(5), C28-C29 1.447(5), C29-N2 1.321(4); C1-Ge1-N1 80.95(14), C1-Ge1-Ge2 101.50(10), N1-Ge1-Ge2 96.99(8), Ge1-C1-C7 113.2(3), C1-C7-C8 114.1(3), C7-C8-N1 115.5(3), C8-N1-Ge1 115.5(2), C22-Ge2-N2 80.87(14), C22-Ge2-Ge1 98.22(11), N2-Ge2-Ge1 99.20(9), Ge2-C22-C28 114.3(3), C22-C28-C29 113.3(3), C28-C29-N2 114.9(3), C29-N2-Ge2 115.5(2).

4.3. Reaction of [L¹Ge-GeL¹] with KC₈: Synthesis of 2-Imino-5,6-methylenedioxyphenyl (L¹) Stabilized Germalidenide Anion [L¹GeK] (**98**).

The reaction of [L¹Ge-GeL¹] (**97**) with excess KC₈ (2.7 equiv) in THF for 2 days resulted in cleavage of the Ge^I-Ge^I bond in **97** to afford the germalidenide anion [L¹GeK] (**98**; Scheme 24) in 21.0 % yield. The result is in contrast to the reduction of the heavier alkyne analogue [Ar'SnSnAr'] [Ar' = 2,6-C₆H₃-(2,6-*i*Pr₂C₆H₃)₂] with

potassium, whereby the doubly reduced species $K_2[Ar'SnSnAr']$ was formed.^[1f] Moreover, the reduction of the amidinate-stabilized Ge^I dimer $[tBuC(NAr)_2Ge]_2$ (**73**) led to decomposition to give elemental germanium and $[tBuC(NAr)_2K]$.^[6h]

Scheme 24. Synthesis of **98** by treatment of **97** with excess KC_8 .

Power *et al.* showed that the radical anions $[REER]^{\bullet-}$ and the doubly reduced species $[REER]^{2-}$ (E = Ge, Sn; R = terphenyl substituent) were synthesized by the reaction of the corresponding heavier chlorocarbene analogues $[RECl]$ with excess alkali metal.^[12] In this regard, the reaction of **94** with excess KC_8 (3.5 equiv) in THF was performed to afford compound **98** in 43.5 % yield (Scheme 25). The reaction appears to proceed through the formation of **97**, which then reacts with two molecules of KC_8 to form **98**. This reaction mechanism is similar to that of 2,6-diiminophenyl-stabilized germylidenide, stannylidenide and plumbylidenide anions (**84** – **86**).^[6e, p, q] However, the synthesis of **87** and **88**, which were formed from the treatment of $[HC\{C(R)N(Ar)\}GeCl]$ (R = Me, *t*Bu; Ar = 2,6-*i*Pr₂C₆H₃) with 2 equiv of alkali metal, involved a mechanism that proceeds through several reductive processes and ring contraction.^[8]

Scheme 25. Synthesis of **98** by treatment of **94** with excess KC_8 .

Compound **98** was isolated as a highly air- and moisture-sensitive red crystalline solid. It is stable in ethereal solvents and in the solid state. However, it is unstable in toluene and benzene, which was confirmed by NMR spectroscopy. Thus, the spectroscopic analysis of **98** can only be performed in $[\text{D}_8]\text{THF}$. The ^1H NMR spectrum shows one set of signals due to the 2-imino-5,6-methylenedioxyphenyl ligand. The signal for the $\text{MeC}=\text{N}$ protons ($\delta = 2.12$ ppm) shows a downfield shift compared to that of **94** ($\delta = 1.68$ ppm), indicating that there is electron delocalization in the GeC_3N five-membered ring. Therefore, the negative charge at the germanium center in compound **98** is stabilized by electron delocalization in the germanium heterocycle (Scheme 26).

Scheme 26. Electron delocalization in the GeC_3N ring in compound **98**.

Figure 23. Molecular structure of compound **98** (20% thermal ellipsoids): (a) perspective view of the molecule and (b) its polymeric form. Hydrogen atoms and disordered solvent molecule(s) are omitted for clarity in Figures 23a and 23b. Ar substituents are also omitted for clarity in Figure 23b.

(a)

(b) Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Ge1-K1 3.5252(17), Ge1-C1 1.919(6), C1-C7 1.464(9), C7-C8 1.375(9), C8-N1 1.377(8), Ge1-N1 1.916(5), O1-K1 2.991(5), O4-K1 2.865(5), O6-K1 2.723(4), Ge2-K1 3.5357(19); N1-Ge1-K1 126.69(15), C1-Ge1-K1 68.54(18), N1-Ge1-C1 82.4(2), Ge1-C1-C7 112.9(5), C1-C7-C8 114.1(6), C7-C8-N1 113.7(6), C8-N1-Ge1 116.9(4), O1-K1-Ge1 64.64(9).

Compound **98** was crystallized in a polymeric form from Et₂O and was characterized fully by X-ray crystallography (Figure 23). In the monomeric form of compound **98** (Figure 23a), the K1 atom is η^1 -coordinated with the Ge1 atom of the GeC₃N ring. The coordination sphere on the K1 atom is further supplemented by an η^2 -interaction of the phenyl ring at C1 and C2, the O1 atom of the –OCH₂O– substituent, and the O3 atom of the disordered Et₂O molecule (Figure 23a). This leads to the K1 atom displacing from the GeCCCN plane by 2.358 Å. Overall, this is similar to that of the 2,6-diiminophenyl-stabilized germylidenide anion **84**, where the K atom is also η^1 -coordinated with the Ge atom of the GeC₃N ring.^[6e] On the other hand, it is different from **87** and **88**, which comprise of a η^5 -coordinated alkali-metal center.^[8] The Ge1-K1 bond (3.5252(17) Å) is comparable with those in **84** (3.3560(9) Å).^[6e] The GeC₃N ring is puckered (dihedral angle of C7-C1-Ge1-N1: 1.41°). This is in contrast to **84**, **87** and **88**, where the germanium heterocycles are planar.^[6e, 8]

The bond lengths of the GeC₃N ring in **98** (Ge1-N1: 1.916(5), C8-N1: 1.377(8), C7-C8: 1.375(9), C1-C7: 1.464(9), Ge1-C1: 1.919(6) Å) suggest that there is an appreciable electron delocalization in the GeC₃N five-membered ring compared with those of **94** (Ge1-N1: 2.054(2), C8-N1: 1.301(3), C7-C8: 1.460(4), C1-C7: 1.423(4), Ge1-C1: 2.3024(8) Å). Moreover, they are comparable with that of **84**.^[6e] In addition, the electrostatic interaction of the K1 atom with the oxygen O4, O6 atoms and the Ge2 atom of the adjacent germylidenide molecules leads to a polymeric form (Figure 23b). In the asymmetric unit (Figure 24), there is solvent disordering at the K atoms. The K2 and K4 atoms are coordinated with either a THF or Et₂O molecule. However, attempts to resolve the solvent disordering in the asymmetric unit of compound **98** failed because it can only be synthesized in THF and crystallized in Et₂O. As a result, the THF and Et₂O molecules compete for the coordination sphere of the potassium atoms.

The ^1H NMR spectrum of the crude product shows the presence of two THF molecules.

Figure 24. The asymmetric unit of compound **98** (20% thermal ellipsoids). Hydrogen atoms and disordered Et_2O molecules at the K1 and K3 atoms are omitted for clarity. Ar substituents are also omitted for clarity. The K2 atom and K4 atoms coordinate with either a THF or Et_2O molecule.

Conclusion

In conclusion, the Ge^{I} dimer $[\text{L}^1\text{Ge}-\text{GeL}^1]$ (**97**) which is supported by a 2-imino-5,6-methylenedioxyphenyl ligand (L^1) was synthesized by the reaction of the germanium(II) chloride $[\text{L}^1\text{GeCl}]$ (**94**) with one equivalent of KC_8 . The germylidenide anion $[\text{L}^1\text{GeK}]$ (**98**) was synthesized by the reaction of **97** with excess KC_8 . Alternatively, **98** can also be obtained from the reduction of **94** with excess KC_8 . The crystallographic and spectroscopic data of compound **98** show that the potassium atom is η^1 -coordinated with the low-valent germanium center. Moreover, the negative charge at the germanium center in compound **98** is stabilized by the electron delocalization in the germanium heterocycle.

Experimental Section

General Procedure: All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF and Et₂O were dried over and distilled over Na/K alloy prior to use. [D₆]Benzene and [D₈]THF were dried over and distilled over K metal prior to use. **93** was prepared as described in the literature.^[9b] The ¹H and ¹³C spectra were recorded on JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C. The IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer in the range of 4000-40 cm⁻¹ as Nujol mulls. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of [L¹GeCl] (94**).** A solution of L¹Li (**93**) (0.68 g, 2.06 mmol) in Et₂O (57 mL) was added dropwise to a stirring suspension of GeCl₂·dioxane (0.48 g, 2.06 mmol) in Et₂O (4.7 mL) at 0°C. The reaction mixture was raised to ambient temperature and stirred additionally for 15 h. The precipitate was filtered and the filtrate was concentrated to afford yellow crystals of **94**. Yield: 0.50 g (56.4 %). M.p. 207 °C; ¹H NMR (395.9 MHz, [D₆]Benzene, 23.3 °C): δ = 0.84 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 0.91 (d, ³J_{HH} = 7.2 Hz, 3H, CH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂), 1.43 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂), 1.68 (s, 3H, CH₃), 2.64 (sept, ³J_{HH} = 6.8 Hz, 1H, CH(CH₃)₂), 3.21 (sept, ³J_{HH} = 6.8 Hz, 1H, CH(CH₃)₂), 5.18 (AB q, ¹J_{HH} = 3.2 Hz, 1H, OCH₂O), 5.27 (AB q, ¹J_{HH} = 3.2 Hz, 1H, OCH₂O), 6.53 (d, ³J_{HH} = 8.2 Hz, 1H, Ph), 6.83 (d, ³J_{HH} = 8.2 Hz, 1H, Ph), 6.99-7.01 (m, 1H, Ph), 7.10-7.13 ppm (m, 2H, Ph); ¹³C{¹H} NMR (100.6 MHz, [D₆]Benzene, 24.0 °C): δ = 17.18, 24.08, 24.22, 25.23 (CH(CH₃)₂), 28.24, 29.15 (CH(CH₃)₂), 101.33, 107.48, 124.03, 124.81, 125.23, 135.36, 138.08, 141.12, 143.15, 145.22 (Ar/Ph), 150.73 (CH₃), 151.11 (OCH₂O), 178.88 ppm (C=NAr); UV/Vis (THF): $\lambda_{\text{max}}(\epsilon)$ = 217 (7326), 254 (2297), 260 (1809), 348 nm

(2409 dm³ mol⁻¹cm⁻¹); IR (Nujol, cm⁻¹): 2953s, 2922s, 2853s, 1549m, 1445m, 1435m, 1377w, 1362w, 1316m, 1256m, 1152w, 1128w, 1096w, 1043m, 935w, 887w, 802w, 777w; elemental analysis calcd (%) for C₂₁H₂₄ClGeNO₂: C 58.59, H 5.62, N 3.25; found: C 58.21, H 5.43, N, 3.19.

Crystal data for 94: [C₂₁H₂₄ClGeNO₂]; *M* = 430.45; monoclinic; space group *P*2(1)/*c*; *a* = 14.9469(3), *b* = 15.6737(3), *c* = 18.6069(4) Å; *α* = 90, *β* = 112.249(10), *γ* = 90°; *V* = 4034.55(14) Å³; *Z* = 8; *ρ*_{calcd} = 1.417 mg m⁻³; 57560 measured reflections; 11670 independent reflections; 479 refined parameters; *R*₁ = 0.0432, *wR*₂ = 0.1042 (*I* > 2σ(*I*)).

Synthesis of [L¹Ge-GeL¹] (97). THF (14.2 mL) was added to a mixture of **94** (0.91 g, 2.12 mmol) and KC₈ (0.32 g, 2.37 mmol) at ambient temperature. The resulting green reaction mixture was stirred overnight. The solvent was then removed in vacuo and the residue was extracted with Et₂O (50 mL). The insoluble precipitate was filtered off, and the green filtrate was concentrated to yield red crystals of **97**. Yield: 0.59 g (70.5 %). M.p. 243 °C; ¹H NMR (395.9 MHz, [D₆]Benzene, 23.3 °C): δ = 0.89 (br, 6H, CH(CH₃)₂), 1.12 (br, 6H, CH(CH₃)₂), 1.22 (br, 6H, CH(CH₃)₂), 1.47 (br, 6H, CH(CH₃)₂), 1.97 (s, 6H, CH₃), 2.60 (br, 2H, CH(CH₃)₂), 3.41 (br, 2H, CH(CH₃)₂), 5.17 (br, 2H, OCH₂O), 5.28 (br, 2H, OCH₂O), 6.67 (d, ³*J*_{HH} = 8.2 Hz, 2H, Ph), 7.09 (br, 3H, Ph), 7.18-7.21 ppm (m, 5H, Ph); ¹³C{¹H} NMR (100.5 MHz, [D₆]Benzene, 23.0 °C): δ = 17.55, 23.90, 25.14, 25.48 (CH(CH₃)₂), 28.31 (CH(CH₃)₂), 100.26, 105.47, 123.75, 124.06, 134.09, 140.97, 142.96, 144.61 (Ar/Ph), 148.95 (CH₃), 160.00 (OCH₂O), 166.90 ppm (C=NAr); UV/Vis (THF): λ_{max}(ε) = 217 (14210), 253 (6816), 259 (6681), 261 (6370), 295 (5136), 347 (4280), 475 (477), 506 (756), 659 nm (4357 dm³ mol⁻¹cm⁻¹); IR (Nujol, cm⁻¹): 2953s, 2922s, 2853s, 1607w, 1493w, 1456s, 1377s, 1337w, 1319w, 1304w, 1258m, 1192w, 1177w, 1142w, 1113m, 1094m, 1043m, 1018m, 986w, 935w, 874w, 849w, 800m, 777w, 737w, 721w, 704w, 642w; elemental analysis calcd (%) for C₄₂H₄₈Ge₂N₂O₄: C 63.83, H 6.13, N, 3.55; found: C 63.67, H 5.92, N 3.31.

Crystal data for 97: [C₄₂H₄₈Ge₂N₂O₄]; *M* = 790.00; monoclinic; space group *P*2(1)/*c*; *a* = 12.1121(4), *b* = 15.1482(6), *c* = 22.2158(9) Å; $\alpha = 90^\circ$, $\beta = 110.586(2)^\circ$, $\gamma = 90^\circ$; *V* = 3815.8(3) Å³; *Z* = 4; $\rho_{\text{calcd}} = 1.375 \text{ mg m}^{-3}$; 48879 measured reflections; 7786 independent reflections; 461 refined parameters; *R*₁ = 0.0417, *wR*₂ = 0.1024 (*I* > 2σ(*I*)).

Synthesis of [L¹GeK] (98). *Method A*: THF (20 mL) was added to a mixture of **97** (0.59 g, 0.75 mmol) and excess KC₈ (0.27 g, 2.02 mmol) at ambient temperature. The resulting red reaction mixture was stirred for 2 days. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with Et₂O (30 mL). After filtration and concentration of the filtrate, **98** was afforded as red crystals. Yield: 0.16 g (21.0 %).

Method B: THF (31 mL) was added to a mixture of **94** (1.30 g, 3.03 mmol) and excess KC₈ (1.43 g, 10.6 mmol) at ambient temperature. The resulting red reaction mixture was stirred overnight. The insoluble precipitate was filtered off. Volatiles of the filtrate were removed in vacuo. The residue was extracted with Et₂O (50 mL). After filtration and concentration of the filtrate, **98** was afforded as red crystals. Yield: 0.67 g (43.5 %).

M.p. 380 °C; ¹H NMR (400.1 MHz, [D₈]THF, 23.3 °C): δ = 1.03 (d, ³*J*_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.12 (d, ³*J*_{HH} = 7.0 Hz, 6H, CH(CH₃)₂), 2.12 (s, 3H, CH₃), 2.65 (sept, ³*J*_{HH} = 6.8 Hz, 2H, CH(CH₃)₂), 5.72 (s, 2H, OCH₂O), 6.31 (d, ³*J*_{HH} = 8.7 Hz, 1H, Ph), 7.04-7.07 ppm (m, 4H, Ph); ¹³C{¹H} NMR (100.6 MHz, [D₈]THF, 23.3 °C): δ = 15.71, 23.83 (CH(CH₃)₂), 27.05, 27.86 (CH(CH₃)₂), 98.18, 104.07, 119.73, 122.50, 125.25, 128.24, 128.55, 130.18, 145.41 (Ph/Ar), 147.49 (CH₃), 148.06 (OCH₂O), 155.93 ppm (C=NAr); UV/Vis (THF): λ_{max}(ε) = 220 (2591), 252 (1945), 254 (1955), 261 (1800), 268 (1663), 297 (1227), 328 (1174), 505 (120), 662 nm (510 dm³ mol⁻¹cm⁻¹); IR (Nujol, cm⁻¹): 2940s, 2909s, 2855s, 1609w, 1460s, 1377m, 1339w, 1246w, 1196w,

1096w, 1026w, 926w, 777w, 721w; elemental analysis calcd (%) for $C_{21}H_{24}GeKNO_2$: C 58.08, H 5.57, N 3.23; found: C 56.86, H 4.13, N 2.52. Attempts to obtain acceptable elemental analysis data for compound **98** failed due to its extreme air sensitivity.

Crystal data for 98: $[C_{100}H_{134.45}Ge_4K_4N_4O_{12}]$; $M = 2031.33$; monoclinic; space group $P2(1)/n$; $a = 15.8408(6)$, $b = 26.3835(8)$, $c = 25.1989(9)$ Å; $\alpha = 90$, $\beta = 95.867(2)$, $\gamma = 90^\circ$; $V = 10476.4(6)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.288$ mg m⁻³; 129898 measured reflections; 19228 independent reflections; 1333 refined parameters; $R_1 = 0.0585$, $wR_2 = 0.1374$ ($I > 2\sigma(I)$).

X-ray data collection and structural refinement. Intensity data for compounds **94**, **97**, **98** were collected using a Bruker APEX II diffractometer. The crystals of **94**, **97** and **98** 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 .^[13] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. CCDC-875955 (**94**), CCDC-875956 (**97**) and CCDC-875959 (**98**) contain the supplementary crystallographic data for this chapter. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Future Developments

The reactivity of the amidinate-stabilized germatrisilacyclobutadiene ylides $[L_3Si_3GeL']$ ($L = PhC(NtBu)_2$; $L' = \ddot{E}L$; $\ddot{E} = Ge$ (**29**), Si (**32**)), zwitterionic digermadistannacyclobutadiene $[L_2Ge_2Sn_2L'_2]$ (**36**; $L' = GeL$) and tetragermacyclobutadiene $[L_4Ge_6]$ (**45**) is worthy of further investigation. Although a square planar tetrasilacyclobutadiene was reported to be stabilized as transition-metal complexes^[1], examples of transition-metal complexes which comprise of small ring compounds of different heavier group 14 elements have not been reported. In other words, compounds **29**, **32**, **36** and **45** could serve as a new class of η^4 π -ligands for transition-metal complexes (Schemes 27 and 28). In addition, it will be worthwhile to explore a synthetic methodology for the isolation of a base-stabilized tetrastannacyclobutadiene $[L_4Sn_6]$ (**99**; Chart 25). In this regard, a suitable precursor might be the amidinate-stabilized tin(I) dimer $[(R^2C(NR^1)_2Sn)_2]$ (**77**; $R^1 = 2,6$ - $iPr_2C_6H_3$; $R^2 = 4$ - $tBuC_6H_4$; Chart 21), as $[(PhC(NtBu)_2Sn)_2]$ is synthetically inaccessible as yet.^[2]

Scheme 27. Proposed reactivity of compounds **29** and **32** with transition-metals.

Scheme 28. Proposed reactivity of **36** and **45** with transition-metals.

Chart 25. Proposed base-stabilized tetrastannacylcobutadiene **99**.

Complexes **71** and **72** are the first examples of transition metal-silyliumylidene complexes. Its potential as a catalyst can be further investigated. For example, complex **71** can serve as a pre-catalyst in the hydrosilylation of alkynes.^[3] Furthermore, the Si^{II} atom in compound **54** can be further functionalized. This may be feasible via treatment of **54** with stronger nucleophiles like PMe_3 and $\text{PH}(t\text{Bu})_2$, which may possibly displace the coordinating DMAP (Scheme 29).

Scheme 29. Proposed reactivity of **54**.

Lastly, compound **98** can serve to be a useful building block for the synthesis of novel heavier group 14 compounds. This can be done so via salt-elimination reactions (Scheme 30).

Scheme 30. Proposed reactivity of **98**.

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ACADEMIC PUBLICATIONS

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Appendix A

Supplementary Information of Chapter 1

Explanation for alerts A in the CIF check file of compound **17**.

Alert level A

CHEMW03 ALERT 2A ALERT: The ratio of given/ expected molecular weight as calculated from the _atom_site* data lies outside the range 0.90 < > 1.10

From the CIF: _cell_formula_units_Z = 3

From the CIF: _chemical_formula_weight = 1059.60.

TEST: Calculate formula weight from _atom_site_*

Atom	Mass	Num	Sum
C	12.01	58.00	696.64
H	1.01	66.00	66.53
N	14.01	4.00	56.03
Si	28.09	2.00	56.17

Calculated formula weight = 875.37

Response: PLATON/SQUEEZE was used to treat two badly disordered toluene molecules in the asymmetric unit. These were removed from the model, but included in the empirical formula.

Additional PLATON/SQUEEZE details appear above in _refine_special_details.

PLAT316 ALERT 2 A Too many H on C in C=N Moiety in Main Residue C1.

Response: There is no H on C1.

PLAT602 ALERT 2 A VERY LARGE Solvent Accessible VOID(S) in Structure!

Response: PLATON/SQUEEZE was used to treat two badly disordered toluene molecules in the asymmetric unit. These were removed from the model, but included in the empirical formula.

Additional PLATON/SQUEEZE details appear above in _refine_special_details .

PLAT043 ALERT 1 A Check Reported Molecular Weight = 1059.60.

Response: PLATON/SQUEEZE was used to treat two badly disordered toluene molecules in the

asymmetric unit. These were removed from the model, but included in the empirical formula.

Additional PLATON/SQUEEZE details appear above in _refine_special_details .

Appendix B

Supplementary Information of Chapter 2

1. Experimental section.
2. Figure B1. X-ray Crystal Structure of **30**.
3. Figure B2. X-ray Crystal Structure of **41**.
4. Figure B3. X-ray Crystal Structure of **46**.
5. Theoretical calculations of **29**.
6. Figure B4. Calculated compound **29** at the B3PW91/6-31+G(d) level.
7. Theoretical studies of **36** and **45**.
8. Figure B5. Calculated compound **36** at the UB3PW91/LANL08d for Sn, 6-31+G(d) for Ge and N, and 6-31G(d) for C and H level.
9. Figure B6. Calculated compound **45** at the UB3PW91/6-31+G(d) level.
10. References

1. Experimental section.

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Et₂O, hexane, THF, DME and toluene were dried over and distilled over Na/K alloy prior to use. [D₆]Benzene and [D₈]THF was dried over and distilled over K metal prior to use. GeCl₂·dioxane, PhLi and *t*BuN=C=N*t*Bu were purchased from Aldrich Chemicals and used without further purification. The ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C, and CFCl₃ for ¹⁹F. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of [L₂Ge] (30). PhLi (1.6 mL, 3.3 mmol, 2.0 M in dibutylether) was added to a solution of *t*BuN=C=N*t*Bu (0.58 mL, 3.0 mmol) in Et₂O (17.6 mL) at -78 °C. The solution was raised to ambient temperature and stirred for 6 h. The solution was then added to a stirred suspension of GeCl₂·dioxane (0.35 g, 1.5 mmol) in Et₂O (9 mL) at 0 °C. The reaction mixture was raised to ambient temperature and was stirred overnight. The insoluble precipitate was filtered off and volatiles of the filtrate were removed in vacuo. The residue was extracted with hexane. The extract was kept at -30 °C to afford colourless crystals of **30**. Yield: 0.15 g (18.7%). M.p.: 128 °C; ¹H NMR (395.9 MHz, [D₆]benzene, 22.3 °C): δ = 1.37 (s, 36H, *t*Bu), 7.00-7.28 ppm (m, 10H, Ph); ¹³C{¹H} NMR (100.6 MHz, [D₆]benzene, 22.4 °C): δ = 32.64 (CMe₃), 54.38 (CMe₃), 126.92, 128.30, 129.63 (Ph), 163.37 ppm (NCN); elemental analysis calcd (%) for C₃₀H₄₆GeN₄: C 67.31, H 8.66, N 10.47; found: C 67.05, H 8.26, N 10.15.

Crystal data for 30: [C₃₀H₄₆GeN₄]; *M* = 535.30; monoclinic; space group *P*2(1)/*c*; *a* = 15.3244(10), *b* = 16.5770(9), *c* = 11.6965(7) Å; α = 90, β = 92.921(2), γ = 90°; *V* = 2967.4(3) Å³; *Z* = 4; ρ_{calcd} = 1.198 mg m⁻³; 27082 measured reflections; 9049 independent reflections; 328 refined parameters; *R*₁ = 0.0455, *wR*₂ = 0.1016 (*I* > 2 σ (*I*)).

Isolation of [PhC(NH*t*Bu)₂]OTf (46). The procedure to synthesize **45** was repeated. After stirring the reaction mixture for 12 h, volatiles were removed in vacuo. The residue was extracted with toluene. After filtration and concentration of the filtrate, a mixture of red crystals of **45** (minor product), colorless crystals of **46** and DMAP was obtained. A mixture of colorless crystals of **46** and DMAP was obtained by recrystallization in DME. With reference to the NMR spectrum of DMAP, the NMR resonances of **46** can be identified. ¹H NMR (399.5 MHz, [D₈]THF, 23.7 °C): δ = 0.86-1.51 (br, 18H, *t*Bu), 7.41-7.63 ppm (br, 5H, Ph); ¹³C NMR (100.6 MHz, [D₈]THF, 25.3 °C): δ = 29.72-32.13 (br, CMe₃), 121.82 (q, CF₃, ¹*J*_{CF} = 324.39 Hz), 129.76-130.89 (br, Ph), 155.07 ppm (NCN); ¹⁹F{¹H} NMR (375.94 MHz, [D₈]THF, 23.7 °C): δ = -79.22 ppm. An attempt to isolate pure **46** by recrystallization failed. Therefore the chemical yield, melting point and elemental analysis of **46** cannot be obtained.

Crystal data for 46: [C₁₆H₂₅F₃N₂O₃S]; *M* = 382.44; orthorhombic; space group *P*na2(1); *a* = 11.7341(5), *b* = 13.5487(7), *c* = 12.0085(6) Å; α = 90, β = 90, γ = 90°; *V* = 1909.13(16) Å³; *Z* = 4; ρ_{calcd} = 1.331 mg m⁻³; 33315 measured reflections; 6092 independent reflections; 299 refined parameters; *R*₁ = 0.0415, *wR*₂ = 0.0935 (*I* > 2 σ (*I*)).

X-ray data collection and structural refinement. Intensity data for compounds **30**, **41** and **46** were collected using a Bruker APEX II diffractometer. The crystals of **30**, **41**·Et₂O and **46** were measured at 103(2) K. The structure was solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on *F*².^[6] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned

appropriate isotopic thermal parameters and included in the structure-factor calculations. CCDC-832880 (**30**), CCDC-904993 (**41**) and CCDC-904995 (**46**) contain the supplementary crystallographic data for this chapter. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2. Figure B1. X-ray Crystal Structure of **30**.

Hydrogen atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Ge1-N1 2.0161(19), Ge1-N2 2.0993(18), Ge1-N3 1.9415(19), C1-N1 1.335(3), C1-N2 1.339(3), C16-N3 1.391(3), C16-N4 1.291(3); N1-Ge1-N2 63.92(7), C1-N1-Ge1 93.69(13), N1-C1-N2 109.17(19), C1-N2-Ge1 89.94(14), N1-Ge1-N3 103.67(8), N2-Ge1-N3 104.81(7).

3. Figure B2. X-ray Crystal Structure of **41** (50% thermal ellipsoids).

Hydrogen atoms and Et_2O molecule are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Sn1-N1 2.2412(13), Sn1-N2 2.3699(13), Sn1-N3 2.3680(12), Sn1-N4 2.2550(12); N1-Sn1-N2 57.28(4), N1-Sn1-N3 102.28(4), N3-Sn1-N4 57.26(4), N2-Sn1-N4 103.37(5).

4. Figure B3. X-ray Crystal Structure of **46** (50% thermal ellipsoids).

Selected bond lengths [Å] and angles [°]: C7-N1 1.322(2), C7-N2 1.320(2); N1-C7-N2 123.42(15).

5. Theoretical calculations of **29**.

In order to understand the bonding nature, compound **29** (Figure B4) was investigated using DFT^[1] B3PW91^[2] method with the 6-31+G(d) basis set and natural-bond-orbital (NBO)^[3] analysis. All calculations were carried out using the Gaussian 03 packages^[4] and the NBO analyses were performed using the NBO 5.9 program.^[5] The optimized geometry of **29** is in good agreement with the X-ray crystallographic data of **29**•Et₂O.

6. Figure B4. Calculated compound **29** at the B3PW91/6-31+G(d) level.

Selected bond lengths [Å], angles [°] and dihedral angles [°]: Si3-Si2 2.305, Si2-Si1 2.318, Si1-Ge1 2.413, Ge1-Si3 2.404, Ge2-Ge1 2.505, Si3-N5 1.885, Si3-N6 1.904, Si2-N3 1.828; Si3-Si2-Si1 78.86, Si2-Si1-Ge1 101.96, Si1-Ge1-Si3 75.14, Ge1-Si3-Si2 102.63, Si1-Si2-N3 131.43, Si3-Si2-N3 125.70, Ge2-Ge1-Si1 109.28, Ge2-Ge1-Si3 109.82, Si3-Si2-Si1-Ge1 9.20.

7. Theoretical studies of **36** and **45**.

In order to understand the bonding nature, compound **36** (Figure B5) was investigated using DFT^[1] UB3PW91^[2] method with the LANL08d for Sn, 6-31+G(d) for Ge and N, and 6-31G(d) for C and H basis set and natural-bond-orbital (NBO)^[3] analysis. Compound **45** (Figure B6) was investigated using DFT UB3PW91 method with the 6-31+G(d) basis set. All calculations were carried out using the Gaussian 09 packages^[4] and the NBO analyses were performed using the NBO 5.9 program.^[5] The optimized geometries of **36** and **45** are in good agreement with their X-ray crystallographic data.

8. Figure B5. Calculated compound **36** at the UB3PW91/LANL08d for Sn, 6-31+G(d) for Ge and N, and 6-31G(d) for C and H level.

Selected bond lengths [Å] and angles [°]: Sn1-Ge1 2.781, Sn1-Ge2 2.714, Sn1-Ge2A 2.711, Ge1-N1 2.038, Ge1-N2 2.039, Ge2-N3 2.021, Ge2-N4 2.021; Sn1-Ge2-Sn1A 109.66, Ge2-Sn1-Ge2A 70.34, Ge1-Sn1-Ge2 103.55, Ge1-Sn1-Ge2A 104.80, N3-Ge2-N4 65.15, N1-Ge1-N2 64.14, N1-Ge1-Sn1 92.43, N2-Ge1-Sn1 91.79.

9. Figure B6. Calculated compound **45** at the UB3PW91/6-31+G(d) level.

Selected bond lengths [Å] and angles [°]: Ge1-Ge2 2.4872, Ge2-Ge3 2.4351, Ge2-Ge3A 2.4318, Ge1-N1 2.0055, Ge1-N2 2.0031, Ge3-N3 1.9723, Ge3-N4 1.9760, N1-Ge1-N2 64.94; N1-Ge1-Ge2 86.57, N2-Ge1-Ge2 85.43, Ge1-Ge2-Ge3 110.95, Ge1-Ge2-Ge3A 110.91, Ge3A-Ge2-Ge3 70.29, Ge2-Ge3-Ge2A 109.71, N3-Ge3-N4 66.32.

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Appendix C

Supplementary Information of Chapter 3

1. X-ray structural refinement.
2. Theoretical studies of compound **54**⁺.
3. Figure C1. Compound **54**⁺ with selected bond lengths and angles.
4. References

1. X-ray structural refinement

(a) The disordering in compound **54** was solved with the following restraints and constraint:

eadp s1 s1a

DELU S1A > C23

SIMU 0.02 S1A > C23

ISOR 0.02 S1A > C23

(b) The disordering in compound **55** was solved with the following restraints:

simu 0.02 c46 > S1a

isor 0.02 c46 > S1a

delu c46 > S1a

sadi c46 f1 c46 f2 c46 f3

sadi s1 f1 s1 f2 s1 f3

sadi s1 o1 s1 o2 s1 o3

sadi c46 o1 c46 o2 c46 o3

sadi f1 f2 f2 f3 f3 f1

sadi o1 o2 o2 o3 o3 o1

same (before c46a > S1a)

2. Theoretical studies

In order to understand the bonding nature, compound **54**⁺ (Figure C1) was investigated using DFT^[1] M06-2X^[2] method with the 6-311+G(2d) for Si and 6-311+G(d,p) for H, C, N basis set and natural-bond-orbital (NBO)^[3] analysis. All calculations were carried out using the Gaussian 09 packages^[4] and the NBO analyses were performed using the NBO 5.9 program.^[5] The optimized geometry of **54**⁺ is in good agreement with the X-ray crystallographic data of **54**.

3. Figure C1. Compound **54**⁺ with selected bond lengths and angles.

Selected bond lengths [Å] and angles [°]: Si1-N1 1.860, Si1-N2 1.860, Si1-N3 1.907, C5-N1 1.340, C5-N2 1.340; N1-Si1-N2 70.03, N1-Si1-N3 96.75, N2-Si1-N3 96.76.

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Appendix D

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Chapter 1

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Chapter 2

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Chapter 3

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Chapter 4

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