AMIDINATE-STABILIZED SILYLENE-MAIN GROUP ELEMENT COMPLEXES

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

2017

ACKNOWLEDGEMENT

I would like to express my appreciation to those who helped me during my PhD study and the writing of this thesis.

My sincerest thanks go first to Dr Chuek-Wai So, my dear supervisor, for his advice, guidance, support and encouragement to my whole PhD life. Without his patient help, I cannot learn so much with the past four years.

I want to thank my lovely colleagues, Chia Siew Peng, Seow Su Yi Celestine, Khoo Yee Teng Sabrina, Muhammad Luthfi bin Ismail, Leong Bi Xiang, Chia Cher Chiek, Dr Li Yan, Dr Chan Yuk Chi and Dr Rahul Kumar for their kindness when I need help.

I am thankful to Dr Li Yongxin and Dr Rakesh Ganguly for their professional assistance in solving all the crystal structures for me. I am also grateful to Ee-Ling and other SPMS staffs for their technical and academic support.

Last but not least, I want to express great gratitude to my family, they understand and support me all my life. I would also like to show my appreciation to Ms. Cao Jiajia for her support.

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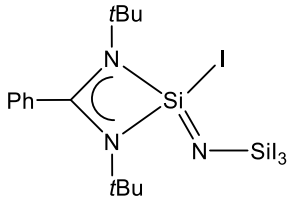
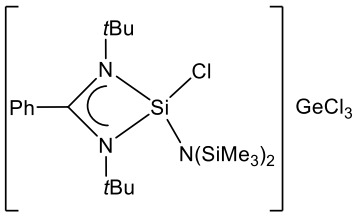
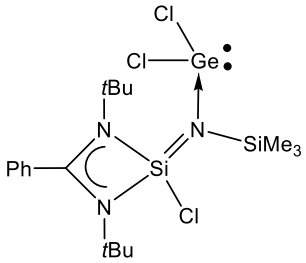
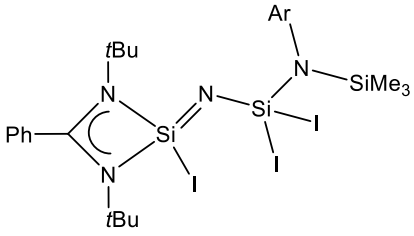
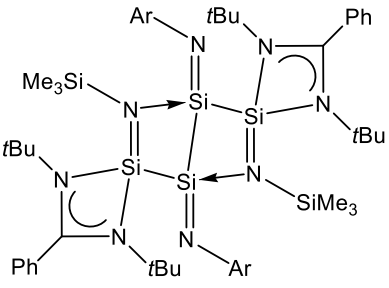
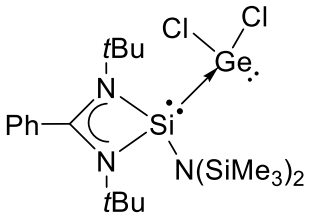
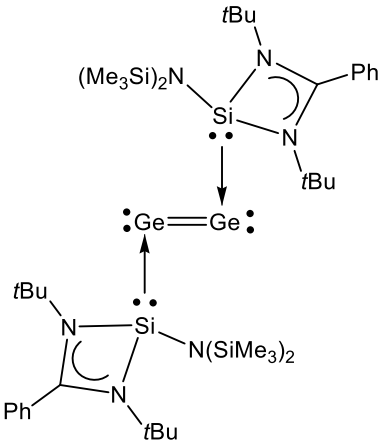
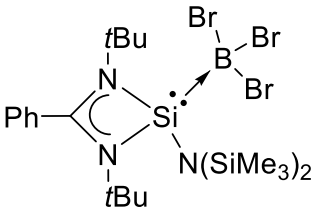
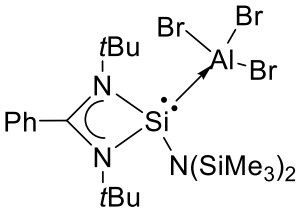
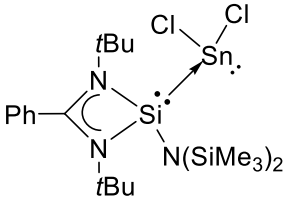
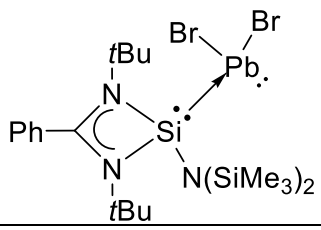
Abbreviations

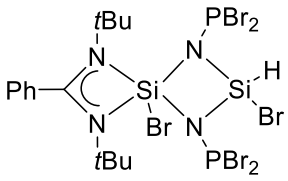
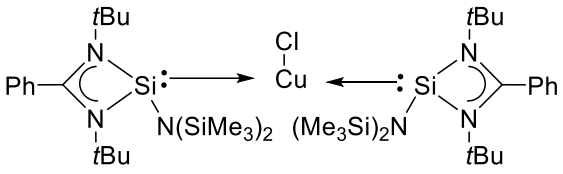
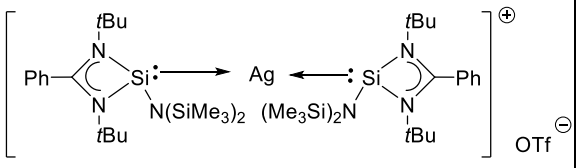
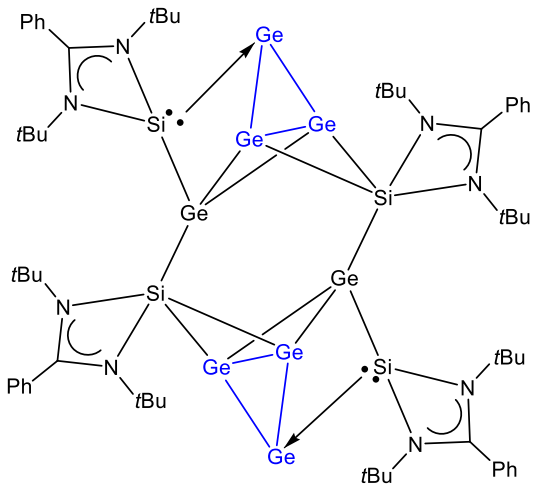
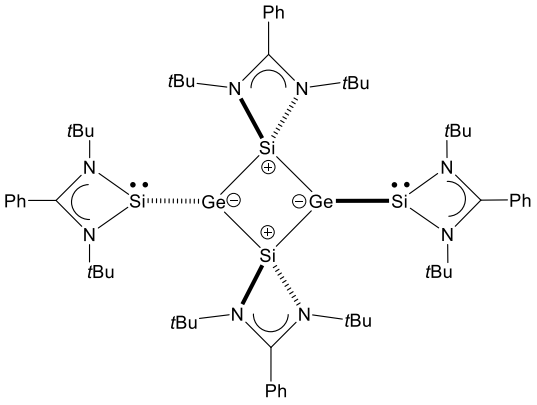
Ar	2, 6-diisopropylphenyl
Br	Broad
Calcd	Calculated
d	Doublet
D	Deuterated
Et	Ethyl
Et_2O	Diethyl Ether
*i*Pr	Isopropyl
IR	Infrared
m	Multiplet
M	Molar (mol dm^{-1})
Mes	2,4,6-trimethylphenyl
M.p.	Melting Point
mL	Milliliter(s)
*n*BuLi	n-butyllithium
Ph	Phenyl
ppm	Parts per Million
*t*Bu	Tert-butyl
t	Triplet
TMS	Trimethylsilyl
THF	Tetrahydrofuran
s	Singlet
sept	Septet
UV-vis	Ultraviolet-visible
Å	Angstrom
°	Degree
°C	Degree Celsius
·	Delta

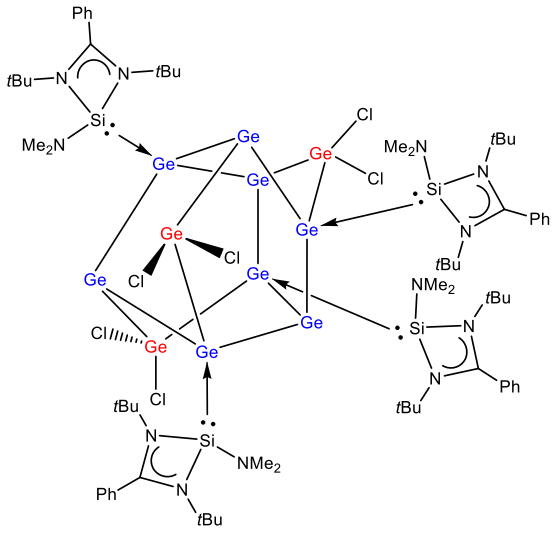
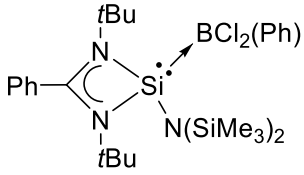
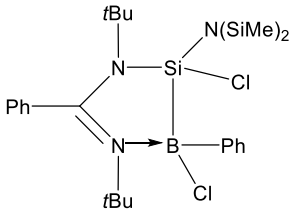
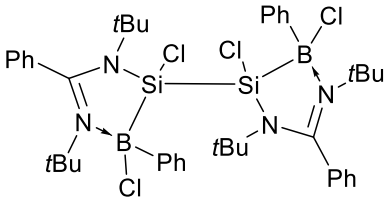
ε	Extinction coefficient
ν	Frequency
%	Percentage
λ_{max}	Wavelength at maximum absorption
cm^{-1}	Wavenumber

List of Synthesized Compounds

Formula	Numbering	Structure
$C_{15}H_{23}I_4N_3Si_2$	**1.2**	
$C_{21}H_{41}Cl_4GeN_3Si_3$	**1.3**	
$C_{18}H_{32}Cl_3GeN_3Si_2$	**1.5**	
$C_{30}H_{49}I_3N_4Si_3$	**1.6**	
$C_{60}H_{98}N_8Si_6$	**1.7**	

$C_{21}H_{41}Cl_2GeN_3Si_3$	**2.2**	
$C_{42}H_{82}Ge_2N_6Si_6$	**2.3**	
$C_{21}H_{41}BBr_3N_3Si_3$	**3.2**	
$C_{21}H_{41}Cl_2SnN_3Si_3$	**3.3**	
$C_{21}H_{41}Cl_2SnN_3Si_3$	**3.4**	
$C_{21}H_{41}PbBr_2N_3Si_3$	**3.5**	

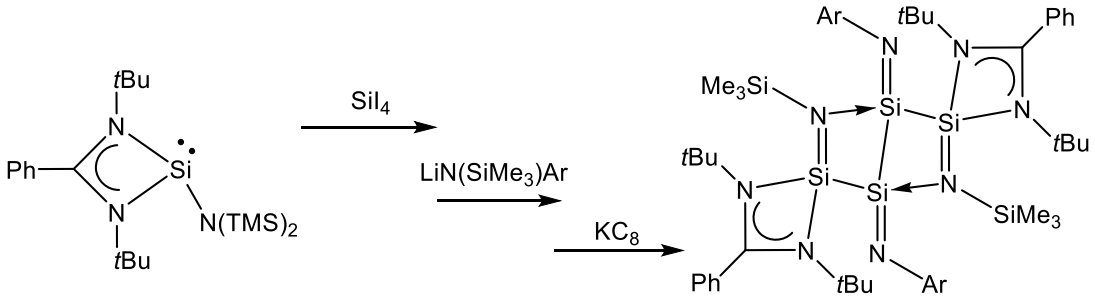
$C_{15}H_{24}Br_6N_4Si_2P_2$	**3.6**	
$C_{42}H_{82}ClCuN_6Si_6$	**3.7**	
$C_{50}H_{90}F_3AgO_3SN_6Si_6$	**3.8**	
$C_{81}H_{116}Ge_8N_8Si_4$	**4.2**	
$C_{74}H_{108}N_8Si_4Ge_2$	**4.4**	

$C_{82}H_{132}N_{12}Si_4Ge_{11}Cl_{16}$	**4.5**	
$C_{21}H_{48}Cl_3BN_2Si$	**5.2**	
$C_{27}H_{46}Cl_2BN_3Si_3$	**5.4**	
$C_{42}H_{56}Cl_4B_2N_4Si_2$	**5.6**	

Abstract

This thesis describes the coordination chemistry of an amidinato amidosilylene and silicon(I) dimer with a series of main-group element and transition metal halides and their further reactivities.

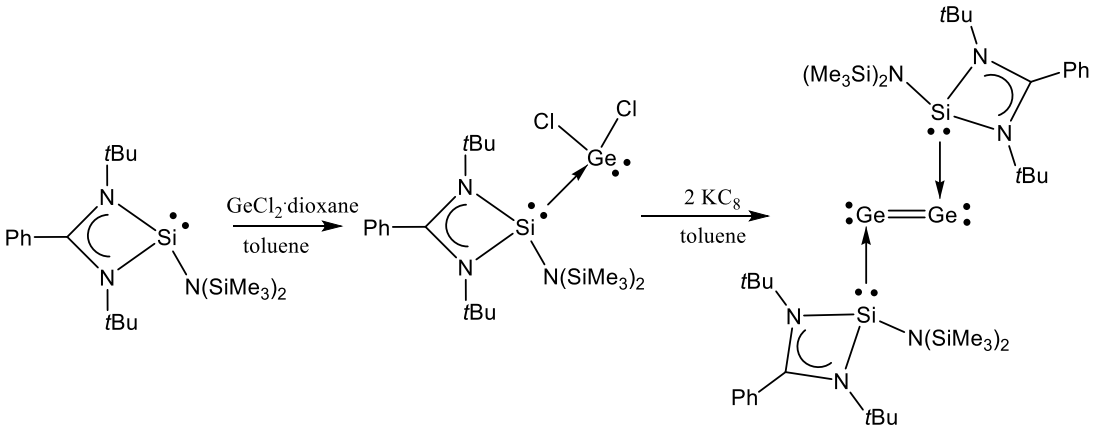
In chapter **1**, the synthesis of an oligo(silanimine) is described. The reaction between the amidinato silylene [LSiN(SiMe$_3$)$_2$] (**1.1**, L = PhCN(*t*Bu)$_2$) and SiI$_4$ in toluene afforded a mixture of the silanimine [LSi(I)NSiI$_3$] (**1.2**), SiMe$_3$I and Si$_2$I$_6$. Compound **1.2** reacted with [LiN(SiMe$_3$)Ar] to form the silanimine [LSi(I)NSiI$_2$N(SiMe$_3$)Ar] (**1.6**, Ar = 2,6-diisopropylphenyl), which was then treated with KC$_8$ to give the base-stabilized tetrasilanetetraimine [LSiN(SiMe$_3$)SiNAr]$_2$ (**1.7**) comprising four conjugated formal silanimine ">Si=N-"units.



1.1 Ar = 2,6-diisopropylphenyl **1.7**

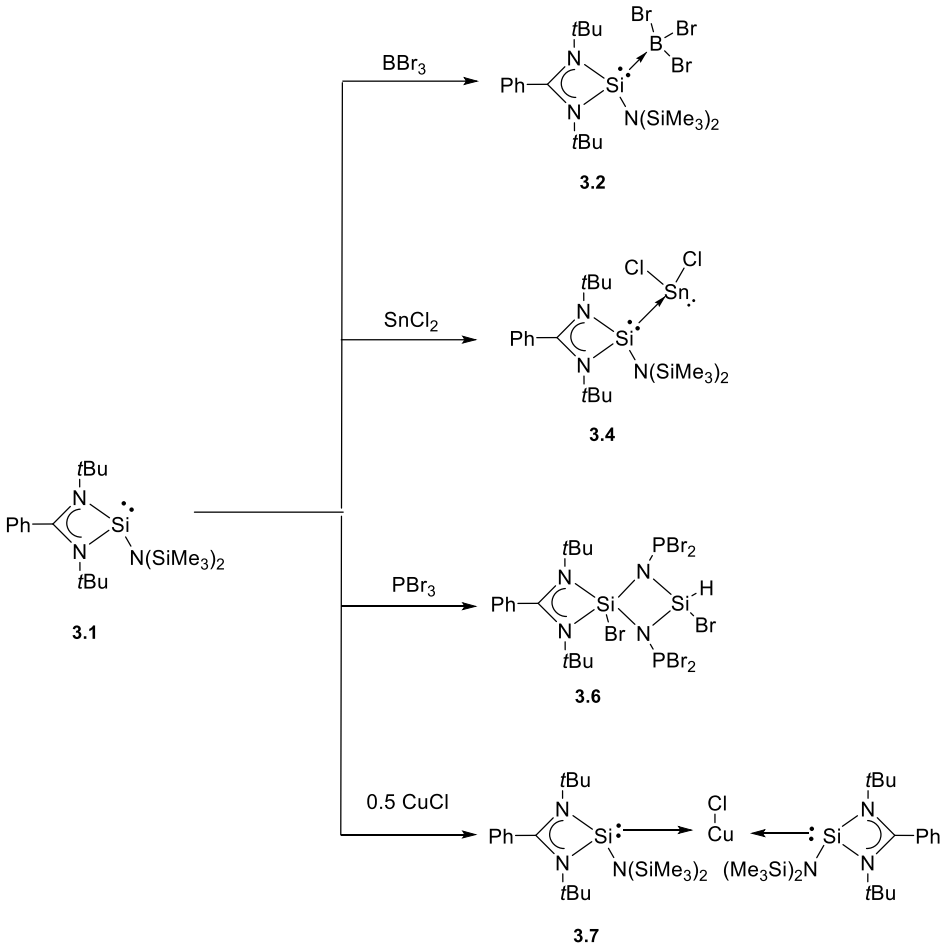
In chapter **2**, the preparation of an N-heterocyclic silylene-stabilized digermanium(0) is described. The treatment of an amidinato silylene

[LSiN(SiMe$_3$)$_2$] (**2.1,** L = PhC(NtBu)$_2$) and GeCl$_2$ formed the Si^{II}–Ge^{II} complex [L{(Me$_3$Si)$_2$N}Si→GeCl$_2$] (**2.2**). Reduction of compound **2.2** with two equivalents of KC$_8$ at ambient temperature formed the N-heterocyclic silylene-stabilized digermanium(0) complex [L{(Me$_3$Si)$_2$N}Si→Ge=Ge←Si{N(SiMe$_3$)$_2$}L] (**2.3**). Theoretical studies, X-ray crystallography and NMR studies reveal conclusively that the singlet digermanium(0) was stabilized by amidinato silylenes with a weak synergic donor–acceptor interaction.

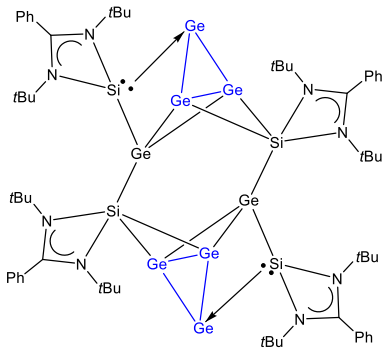


2.1 **2.2** **2.3**

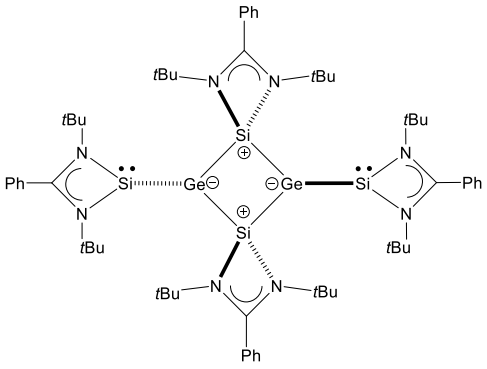
In chapter **3**, the coordination reaction of an amidinato silylene [LSiN(SiMe$_3$)$_2$] (**3.1,** L = PhC(N*t*Bu)$_2$) toward *p*- and *d*-block element halides and pseudohalides is described. The treatment of compound **3.1** and BBr$_3$, AlBr$_3$, SnCl$_2$, PbBr$_2$, CuCl and AgOTf afforded the expected corresponding adducts. However, with PBr$_3$, an unexpected Si$_2$N$_2$ four-membered ring was obtained.



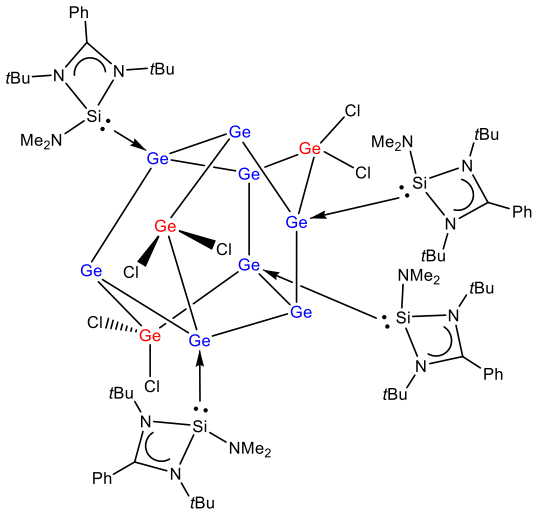
In chapter **4,** the isolation of a trigermanium(0) cluster in the form of an adduct with an amidinate-stabilized bis(silylenyl)germylene is described. The mix of an amidinato silicon(I) dimer [LSi:]$_2$ (**4.1**, L = PhCN(*t*Bu)$_2$), $GeCl_2$ and KC_8 together in a molar ratio of 3 : 4 : 7 afforded a trigermanium moiety in **4.2**. In addition, the isolation of the amidinate-stabilized digermadisilacyclobutadiene [$L_2Ge_2Si_2L'_2$] (**4.4**, L' = LSi) and the trapping of an octagermanium(0) cluster **4.5** by both dichlorogermylene and amidinate-stabilized silylene ligands support the mechanism for the formation of compound **4.2**.



4.2

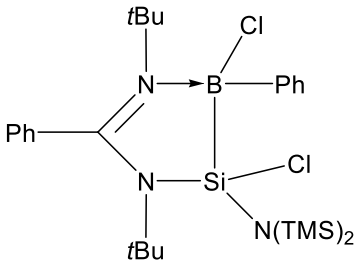


4.4

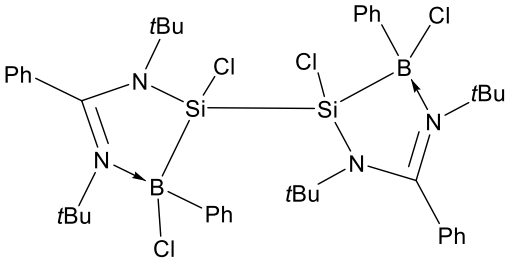


4.5

In chapter **5,** the reactions of the amidinato chlorosilylene, amidosilylene and a silicon(I) dimer with $PhBCl_2$ are described. The amidinato chlorosilylene [LSiCl] (**5.1**, L = PhCN(*t*Bu)$_2$) reacted with $PhBCl_2$ to afford the amidinato silylene-borane adduct **5.2**, while the amidinato silyene [LSi{N(SiMe$_3$)$_2$}] (**5.3**) and amidinato silicon(I) dimer [LSi:]$_2$ (**5.5**) underwent a sequential insertion and ring expansion reaction with $PhBCl_2$ in toluene to form the boron-silicon heterocycle [(μ–κ1:κ1-L)B(Cl)(Ph)Si(Cl){N(SiMe$_3$)$_2$}] (**5.4**) and [(μ–κ1:κ1-L)B(Cl)(Ph)Si(Cl)]$_2$ (**5.6**).


tBu
Cl
N
B
Ph
Ph
N
Si
Cl
N(TMS)2
tBu

5.4


tBu
Ph
Cl
N
Si
Cl
Si
Ph
Cl
B
tBu
N
N
B
tBu
Ph
tBu
N
Cl
tBu
Ph

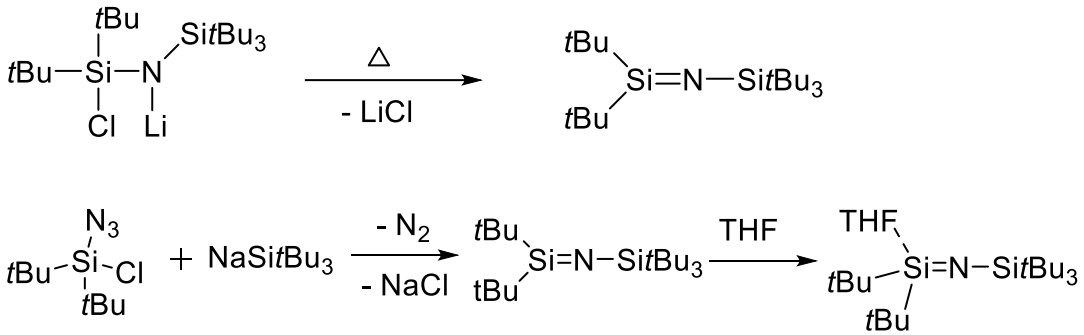
5.6

CHAPTER 1

Donor-Acceptor Stabilized Tetra(silanimine)

1.1 Introduction

The chemistry of multiply-bonded silicon compounds is one of the exciting fields of organosilicon chemistry due to their unprecedented electronic and structural properties.[1] Among these compounds, silanimines are attractive compounds because they are silicon analogues of imine.[2] Using kinetic and/or electronic stabilization, Wiberg et al. synthesized the first stable silanimine [tBu$_2$Si=NSitBu$_3$] by the reaction of the azido-di-*t*butyl-chlorosilane and tri-*t*butyl-silyl sodium.[3] Its THF adduct was also synthesized (**Scheme 1.1**).[4]



Scheme 1.1: The synthesis of the silanimine [tBu$_2$Si=NSitBu$_3$] and its THF adduct

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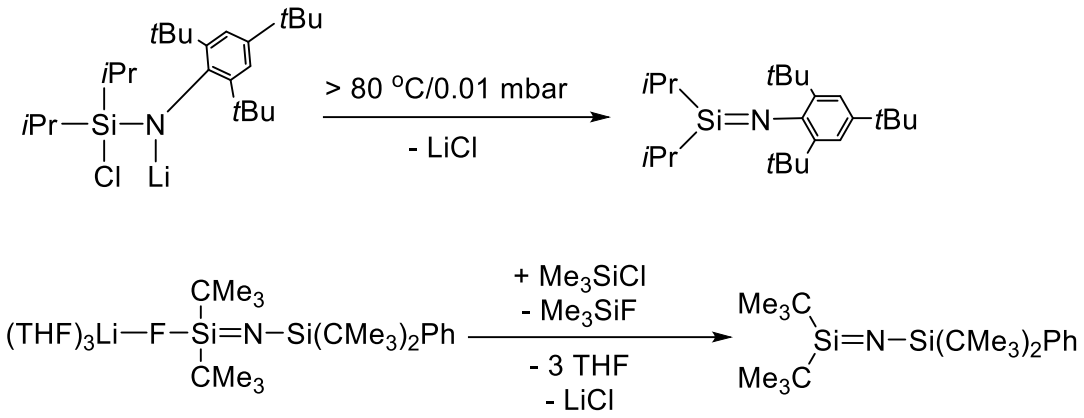
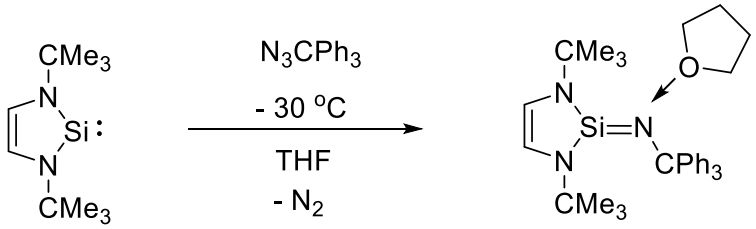
This chapter is taken with permission from Y. L. Shan, B. X. Leong, Y. X. Li, R. Ganguly and C. W. So, *Inorg. Chem*., 2017, **56**, 1609−1615.

Klingebiel et al. also showed that the base-free silanimine [iPr$_2$Si=N(Tip)] (Tip = 2,4,6-iPr$_3$C$_6$H$_2$) can be isolated by the LiCl elimination of the corresponding aminochlorosilane [iPr$_2$Si(Cl)-N(Li)(Tip)] (**Scheme 1.2**).[5]



Scheme 1.2: The synthesis of the base-free silanimine [iPr$_2$Si=N(Tip)]

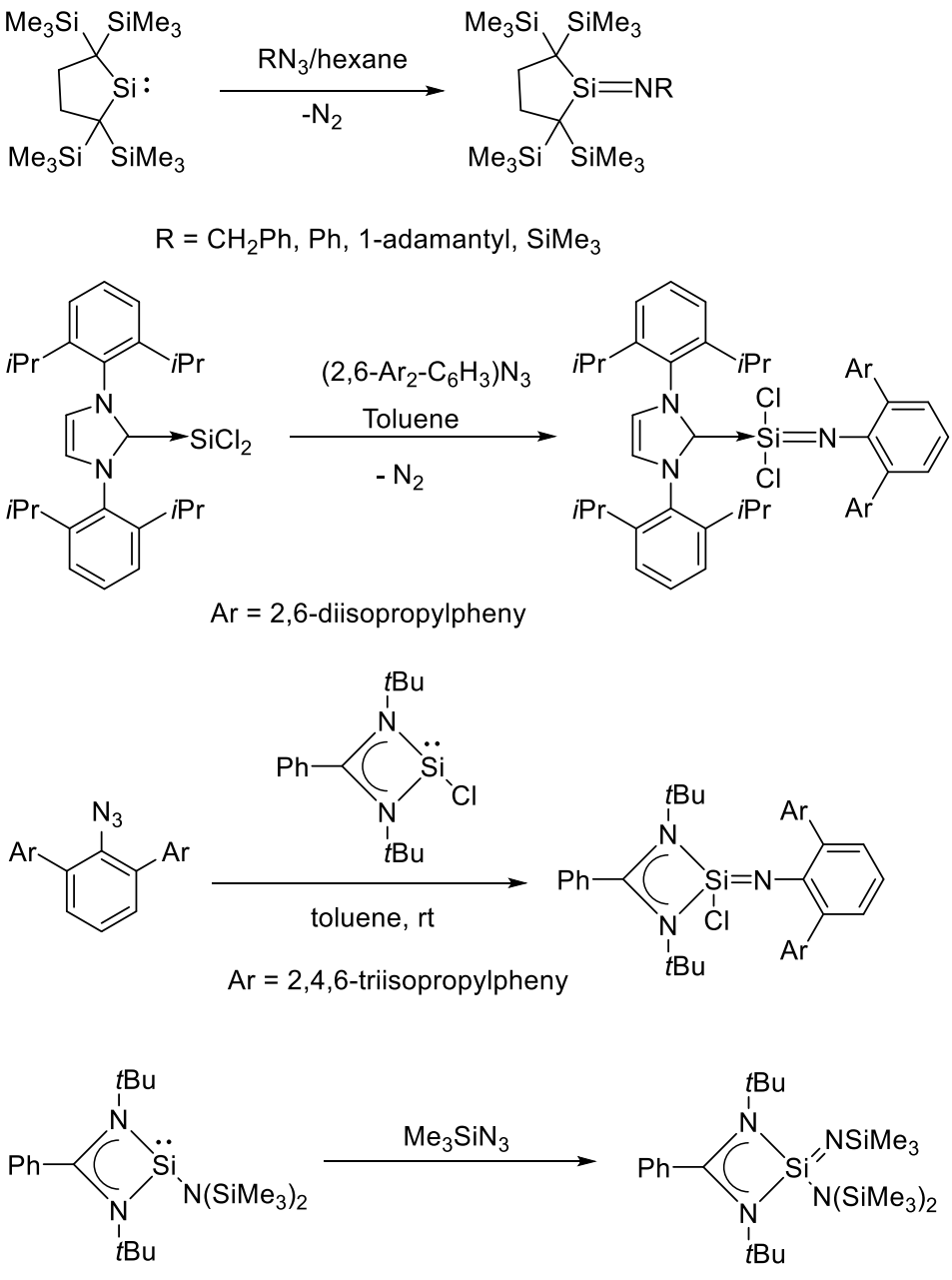
West et al. illustrated another methodology to synthesize the THF-stabilized silanimine [{HC(tBu)N}$_2$Si(THF)=NCPh$_3$] by the oxidation of the silylene [{HC(tBu)N}$_2$Si:] with N$_3$CPh$_3$ (**Scheme 1.3**).[6]



Scheme 1.3: The synthesis of the THF-stabilized silanimine

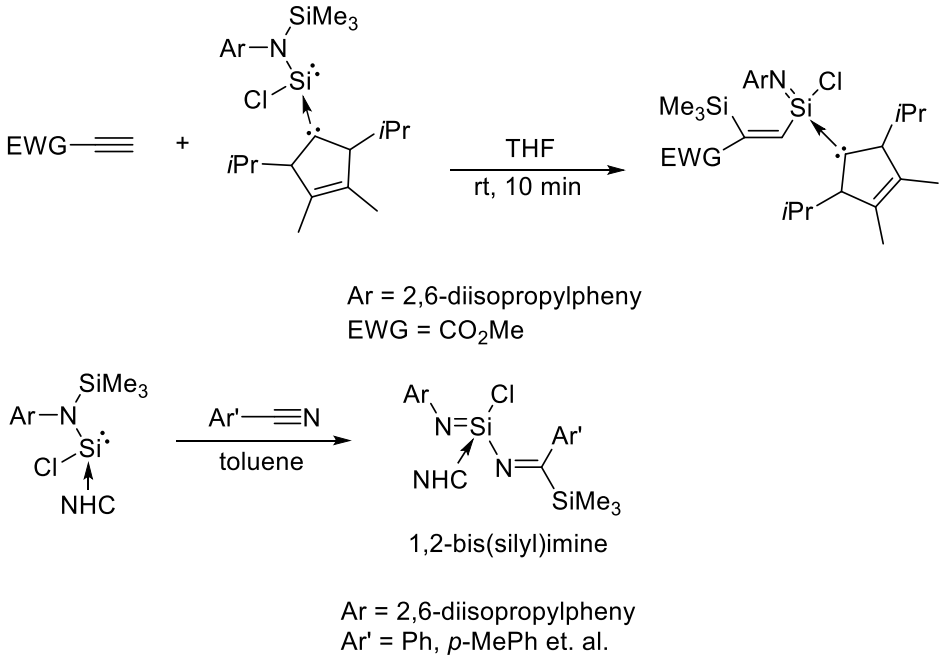
[{HC(tBu)N}$_2$Si(THF)=NCPh$_3$]

Similarly, research groups of Kira and Roesky used a variety of silylenes such as the dialkylsilylene [{$H_2CC(SiMe_3)_2$}$_2$Si:],[7] NHC-dichlorosilylene [$I_{Ar}SiCl_2$] (I_{Ar} = :C{N(Ar)CH}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$, NHC = N-heterocyclic carbene)[8] and amidinato silylene [PhC(N*t*Bu)$_2$SiR] (R = Cl, N(SiMe$_3$)$_2$),[9] to react with organic azide (**Scheme 1.4**).



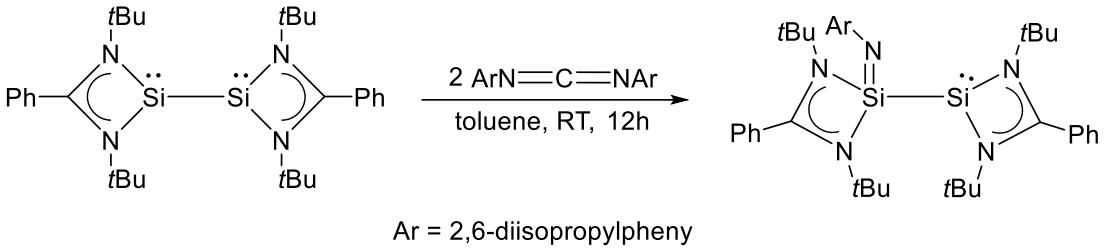
Scheme 1.4: The reaction of silylenes and organic azide

Cui et al. demonstrated that the NHC-silylaminosilylene [Ar(SiMe$_3$)N(Cl)Si(I$_{i\text{PrMe}}$)] (I$_{i\text{PrMe}}$ = :C{N(*i*Pr)C(Me)}$_2$) reacted with alkynes and nitriles, which resulted in silyl migration to form the silanimines [{R(Me$_3$Si)C=C(H)}(Cl)Si(I$_{i\text{PrMe}}$)=NAr] and [{R(Me$_3$Si)C=N}(Cl)Si(I$_{i\text{PrMe}}$)=NAr] (R = supporting substituent), respectively (**Scheme 1.5**).[10]



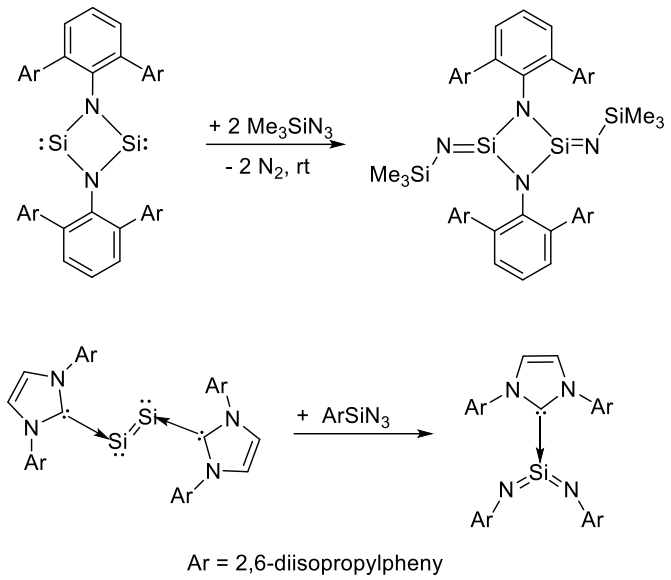
Scheme 1.5: The synthesis of the silanimines [{R(Me$_3$Si)C=C(H)}(Cl)Si(I$_{i\text{PrMe}}$)=NAr] and [{R(Me$_3$Si)C=N}(Cl)Si(I$_{i\text{PrMe}}$)=NAr]

We also reported that the amidinato silicon(I) dimer undergoes an oxidative addition with a transient nitrene to form the silylenylsilanimine [{PhC(N*t*Bu)$_2$}Si(=NAr)-Si{(N*t*Bu)$_2$CPh}] (**Scheme 1.6**).[11]



Scheme 1.6: The synthesis of the silylenylsilanimine [{PhC(N*t*Bu)$_2$}Si(=NAr)-Si{(N*t*Bu)$_2$CPh}]

In the abovementioned examples, a ">Si=N-" unit was formed. There is a handful of compounds containing two ">Si=N-" units. Roesky et al. showed that the dimeric silaisonitrile [2,6-Ar$_2$C$_6$H$_3$NSi:]$_2$[12] reacted with N_3SiMe_3 to form [2,6-Tip$_2$C$_6$H$_3$NSi=SiMe$_3$]$_2$ (**Scheme 1.7**). We also reported the NHC-siladiimide complex [ArNSi(I$_{Ar}$)NAr] by the reaction of the NHC-disilicon complex [I$_{Ar}$Si=SiI$_{Ar}$] with ArN_3 (**Scheme 1.7**).[13] In contrast, a compound containing more than two">Si=N-" units is rare.



Scheme 1.7: The synthesis of the dimeric silaisonitrile [2,6-$Ar_2C_6H_3NSi:]_2$ and the NHC-siladiimide complex [ArNSi(I_{Ar})NAr]

In comparison with silanimine, compounds containing two conjugated heavier silicon-containing double bonds are well-known, for example, the tetrasilabuta-1,3-dienes **A, B, C**,[14-16] conjugated di(silaneselone) [{PhC(N*t*Bu)$_2$}Si(=Se)-Si(=Se){(N*t*Bu)$_2$CPh}] **D**[17] and oligo(p-phenylenedisilenylene)s **E**.[18] Moreover, compounds containing three and four conjugated Si=Si bonds bridged by phenylene substituents **F** were reported by Tamao et al.(Figure **1.1**).[19a] Very recently, Cui et al. showed the formal >C=Si=Si=C< cumulene skeleton being isolated in the form of an adduct with NHCs.[19]

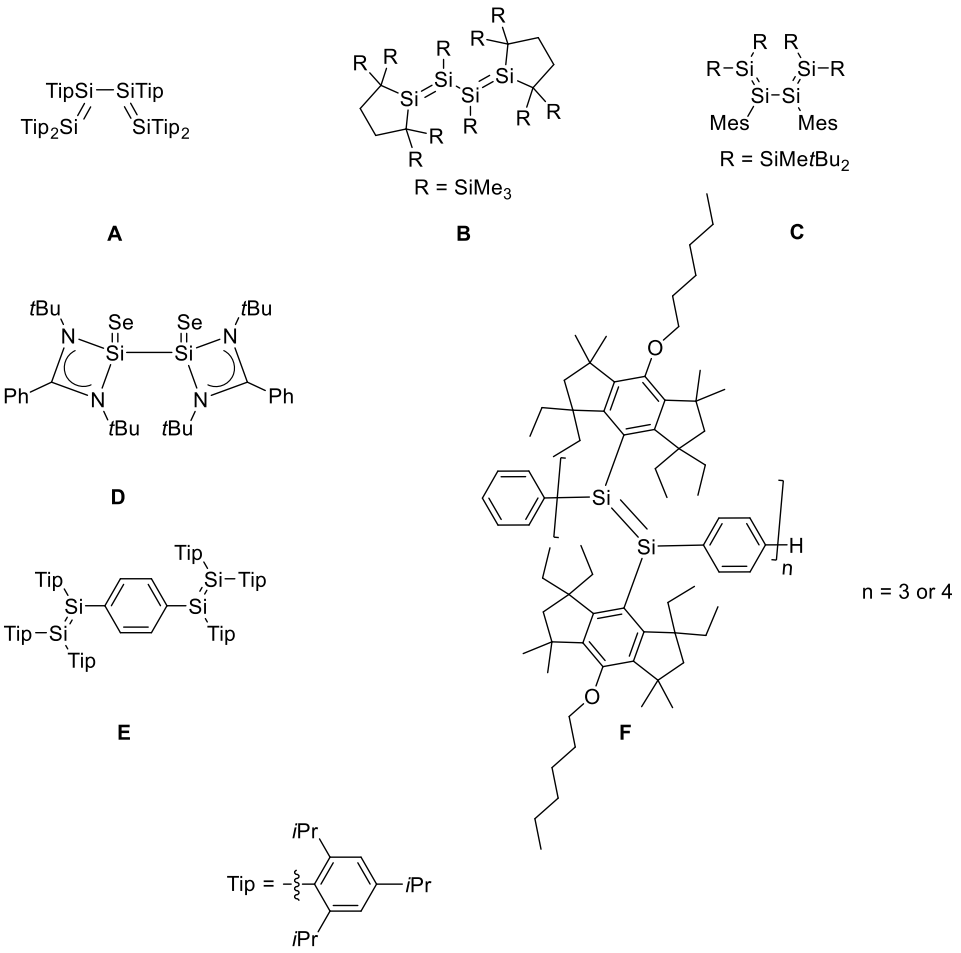


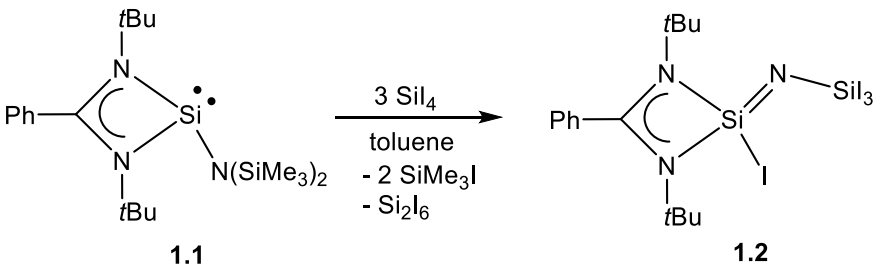
Figure 1.1: The compounds containing two and more conjugated heavier silicon-containing double bonds

In this context, we are interested in investigating whether a conjugated silanimine oligomer $[Si(=NR)]_n$ ($n \geq 3$) can be isolated, although the lighter carbon element has a variety of diimines, triimines and tetraimines. In this chapter, we report the synthesis of a base-stabilized tetrasilanetetraimine, which comprises four conjugated silanimine units, from an amidinato amidosilylene.

1.2 Results and Discussion

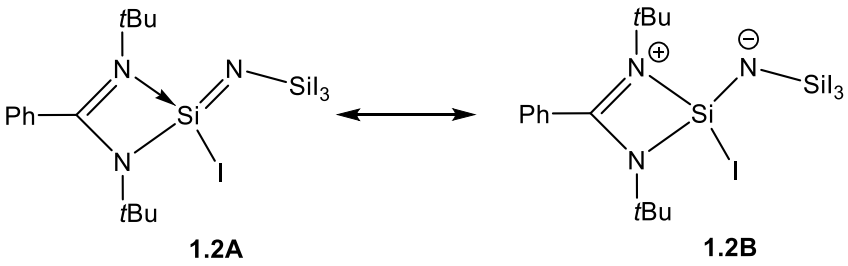
The treatment of the amidinato amidosilylene $[LSiN(SiMe_3)_2]$ (**1.1**, L = $PhCN(tBu)_2$)[20] with SiI_4 in a ratio of 1:1 in toluene afforded a deep purple-green

reaction mixture. It was filtered to remove the insoluble precipitate[21] and the filtrate was analyzed by ^{1}H NMR spectroscopy, which showed a mixture of the silanimine [LSi(I)NSiI$_3$] (**1.2, Scheme 1.8)** and SiMe$_3$I. No starting materials can be found. Volatiles and SiMe$_3$I in the filtrate were removed under reduced pressure to afford compound **1.2**, which was confirmed by ^{1}H NMR spectroscopy. Compound **1.2** can be isolated as colorless crystals (39.6 % yield, based on SiI$_4$), which are suitable for X-ray crystallography and further reactivity, from its concentrated toluene solution. When compound **1.1** was reacted with SiI$_4$ in a ratio of 1:2 or 1:3, an orange-green reaction mixture was afforded. The reaction mixture was filtered to remove the insoluble precipitate,[21] which is significantly less than that in the reaction with the 1:1 ratio of **1.1** and SiI$_4$. The filtrate was analysed by ^{1}H NMR spectroscopy, which showed a mixture of compound **1.2** and SiMe$_3$I. In addition, no starting materials was found. Surprisingly, compound **1.2** cannot be isolated from the concentrated filtrate. Instead colorless crystals of Si$_2$I$_6$ (the 1:2 ratio of **1.1**:SiI$_4$: 64.5 % yield; 1:3 ratio: 76.4 % yield), which are ^{1}H NMR-silent, were afforded. The mother liquor was filtered and the filtrate still showed the presence of compound **1.2** and SiMe$_3$I in the ^{1}H NMR spectrum. In other words, the reaction of **1.1** with SiI$_4$ in a ratio of 1:2 or 1:3 in toluene afforded a mixture of **1.2**, Si$_2$I$_6$ and SiMe$_3$I. However, an attempt to isolate pure compound **1.2** from the mixture by recrystallization failed.



Scheme 1.8: The synthesis of compound **1.2**

Colorless crystals of **1.2** are soluble in toluene and THF. They are stable in solution and the solid state. The ^{1}H NMR spectrum of **1.2** shows a set of resonances due to the *t*Bu, phenyl and $SiMe_3$ protons of the ligands. The ^{29}Si NMR resonance for the L*Si*=N moiety (δ -100 ppm) is comparable with that of the silanimine [LSi(=NAr)Cl] (δ -104.8 ppm),[22] while that for the N-*Si*I_3 fragment (δ -256.7 ppm) is upfield shifted in comparison with that of the N*Si*Me_3 substituent in the donor–free dialkylsilanimine [{$H_2CC(SiMe_3)_2$}$_2$Si=N$SiMe_3$] (δ -15.5 ppm).[7] In addition, compound **1.2** was characterized by X-ray crystallography (**Figure 1.2**). There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. The amidinate ligand is coordinated in a bidentate fashion to the Si1 atom, which adopts a tetrahedral geometry. The Si1-N3 (1.618(7) Å) and Si2-N3 bond lengths (1.610(7) Å) are almost identical, which are intermediate values between the Si-N single bond length (1.695(3) Å) and Si=N double bond length (1.568(3) Å) in [*t*Bu_2Si=N-Si*t*Bu_3].[4] This indicates that compound **1.2** comprises resonance structures as illustrated in **Scheme 1.9**.



Scheme 1.9: Resonance structures of compound **1.2**

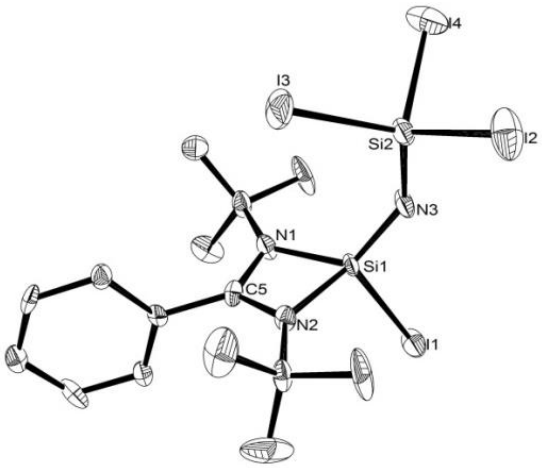
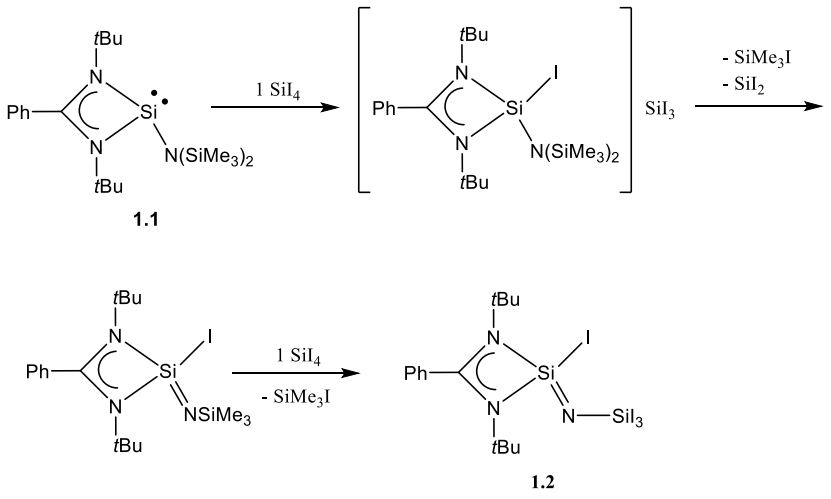


Figure 1.2. Molecular structure of compound **1.2** (ellipsoids set at 50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. One of two independent molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): Si1-N3 1.618(7), Si1-N1 1.793(8), Si1-N2 1.789(8), Si1-I1 2.428(2), Si2-N3 1.610(7), Si1-N3-Si2 139.6(5), N1-Si1-N3 124.8(4), N2-Si1-N3 125.3(4), I1-Si1-N3 111.2(3), N1-Si1-N2 73.5(3).

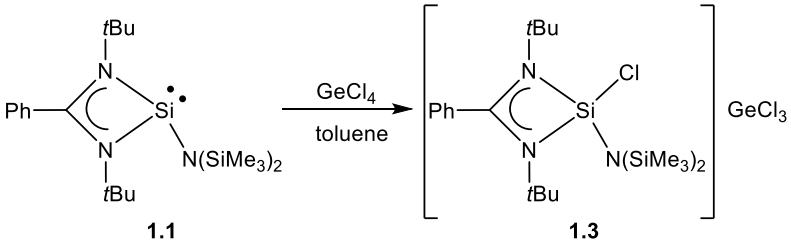
It is proposed that **1.1** reacts with SiI_4 to form a silyl cation intermediate "{LSi(I)N(SiMe$_3$)$_2$}SiI$_3$", which then eliminates $SiMe_3I$ and "SiI_2" to form a silanimine intermediate "LSi(I)NSiMe$_3$". Then, "SiI_2" undergoes a polymerization to form an insoluble poly(silane). In cases of the reactions with the 1:2 or 1:3 ratio of **1.1** and SiI_4, "SiI_2" can also undergo an oxidative addition with SiI_4 to form Si_2I_6. Subsequently, the silanimine intermediate "LSi(I)NSiMe$_3$" undergoes a substitution with another molecule of SiI_4 to form a mixture of **1.2** and $SiMe_3I$ (**Scheme 1.10)**. Based on stoichiometry and proposed reaction mechanism, the reaction of **1.1** and SiI_4 in a ratio of 1:3 should give the highest yield of compound **1.2**. However, the presence of Si_2I_6 in the reaction mixture hinders the isolation of pure compound **1.2** by recrystallization.



Scheme 1.10: The proposed mechanism for the formation of compound **1.2**

The proposed mechanism is verified. The formation of the silyl cation intermediate "{LSi(I)N(SiMe$_3$)$_2$}SiI$_3$" in the reaction of **1.1** with SiI_4 is

evidenced by the reaction of **1.1** with $GeCl_4$ in toluene at room temperature, which afforded the amidinato silyl cation $[LSi(Cl)N(SiMe_3)_2]GeCl_3$ (**1.3**, **Scheme 1.11**) and a mixture of unidentified products. Compound **1.3** was isolated as an air- and moisture-sensitive colorless crystalline solid, which is stable in a glove box under argon gas for a week. However, it is unstable in solution and decomposes in benzene and THF within one day. The ^{29}Si NMR resonances for the LSiCl (δ 31.4 ppm) and $SiMe_3$ (δ 12.1 ppm) moieties in **1.3** are downfield shifted compared with those in **1.1** (LSi: δ -8.07 ppm; $SiMe_3$: δ 2.81, 3.71 ppm). In addition, compound **1.3** was characterized by X-ray crystallography (**Figure 1.3**). There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. The Si-N bonds (Si1-N3: 1.661(3), Si1-N1: 1.777(3), Si1-N2: 1.773(3) Å, Figure 2) are shorter than those in **1.1** ($Si\text{-}N_{amido}$: 1.769(7), $Si\text{-}N_{amidinate}$: 1.8780(10), 1.8776(10) Å). Based on the ^{29}Si NMR resonances and the Si-N bond lengths, compound **1.3** comprises a cationic silicon centre (Si1).



Scheme 1.11: The synthesis of compound **1.3**

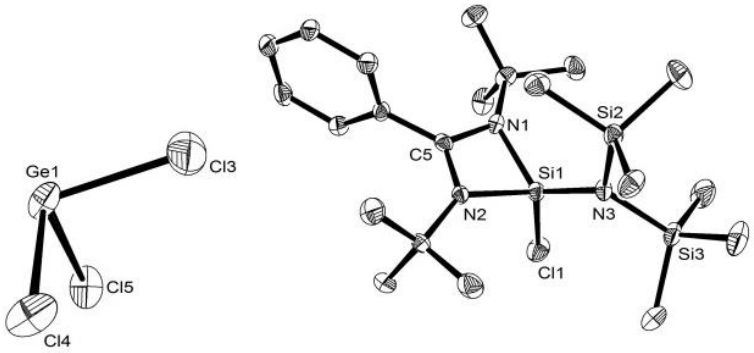
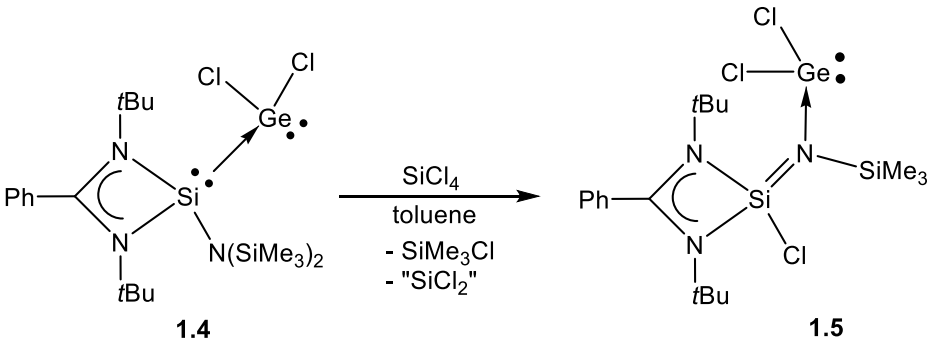


Figure 1.3. Molecular structure of compound **1.3** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. One of two independent molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): Si1-N1 1.777(3), Si1-N2 1.773(3), Si1-N3 1.661(3), Si1-Cl1 2.0199(16), N1-Si1-N2 74.34(15), N1-Si1-N3 123.60(17), N2-Si1-N3 121.32(17), N1-Si1-Cl1 106.78(13), N2-Si1-Cl1 110.19(12), N3-Si1-Cl1 123.60(17).

The proposed mechanism is further verified. The treatment of the amidinato silylene-germylene adduct [L{$(Me_3Si)_2N$}$SiGeCl_2$] (**1.4**)[23] with $SiCl_4$ afforded an orange mixture. It was filtered to remove the insoluble precipitate[21] and the filtrate was analyzed by ^1H NMR spectroscopy, which showed a mixture of the silanimine-germylene adduct [$LSi(Cl)N(GeCl_2)SiMe_3$] (**1.5, Scheme 1.12**) and $SiMe_3Cl$. It is proposed that **1.4** reacts with $SiCl_4$ to form a silyl cation-dichlorogermylene adduct intermediate "{$LSi(Cl)N(GeCl_2)(SiMe_3)_2$}$SiCl_3$", which then eliminates $SiMe_3Cl$ and "$SiCl_2$" to form **1.5**. Then, "$SiCl_2$" undergoes a polymerization to form an insoluble poly(silane). The steric effect of the $GeCl_2$ moiety in **1.5** prevents further substitution of the latter with $SiCl_4$. The formation

of **1.5** suggests the formation of the silanimine intermediate "LSi(I)NSiMe$_3$" in the reaction of **1.1** and SiI$_4$. Pure compound **1.5** was isolated as air- and moisture-sensitive colorless crystals in moderate yield (60.9 %) from the concentrated reaction mixture. The colorless crystals are soluble in toluene and THF. They are stable in solution and the solid state.



Scheme 1.12: The synthesis of compound **1.5**

Compound **1.5** was analysed by NMR spectroscopy. The ^{29}Si NMR resonances attributable to the L*Si*Cl (δ -62.3 ppm) and the N*Si*Me$_3$ moieties (δ 2.88 ppm) are downfield shifted in comparison with that of the L*Si*=N moiety in **1.2** and the N*Si*Me$_3$ substituent in the donor–free dialkylsilanimine [{H$_2$CC(SiMe$_3$)$_2$}$_2$Si=NSiMe$_3$] (δ -15.5 ppm), respectively.[7] Compound **1.5** was analysed by X-ray crystallography. The Si1 atom adopts a tetrahedral geometry in the X-ray crystal structure of **1.5** (**Figure 1.4**). The Si1-N3 (1.644(2) Å) and Si2-N3 (1.762(2) Å) bonds are significantly longer than those of **1.2**, which could be attributable to the steric hindrance of the GeCl$_2$ moiety. The Ge1-N3 bond

(2.031(2) Å) is comparable with that in the dichlorogermylene-benzothiazole adduct (2.092(3) Å, Scheme S1, see the supporting information).[24] It is longer than the Ge-N single bond in the N-heterocyclic germylene (1.859(6), 1.872(6) Å).[25] In addition, the Ge1 atom adopts a distorted trigonal pyramidal geometry (sum of bond angles: 289.5°), which indicates that there is a lone pair of electrons. This suggests that the Ge1-N3 bond is a coordinative covalent bond.

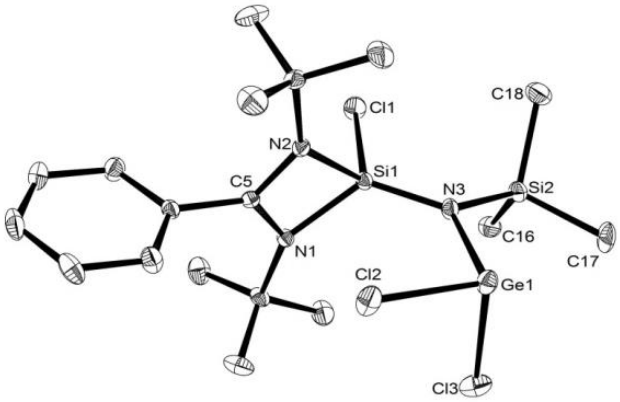
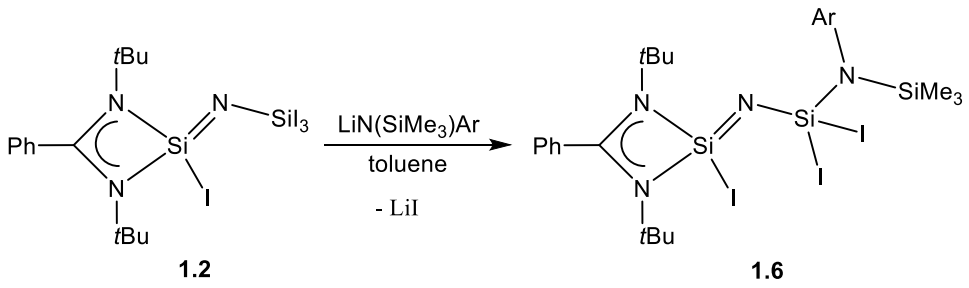


Figure 1.4. Molecular structure of compound **1.5** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-N1 1.778(2), Si1-N2 1.782(2), Si1-N3 1.644(2), Si1-Cl1 2.0586(9), N3-Ge1 2.031(2), Si2-N3 1.762(2), Cl2-Ge1-Cl3 96.02(3), Cl2-Ge1-N3 98.58(6), Cl3-Ge1-N3 94.89(6), Si1-N3-Si2 123.57(12), Si1-N3-Ge1 124.22(12), Si2-N3-Ge1 111.80(11), N1-Si1-N2 74.08(9)

Compound **1.2** was then reacted with the lithium amido compound [$LiN(SiMe_3)Ar$][26] in toluene to form the silanimine [$LSi(I)NSiI_2N(SiMe_3)Ar$] (**1.6, Scheme 1.13**) and LiI. The latter can be removed by simple filtration, while

compound **1.6** was isolated as air- and moisture-sensitive colorless crystals in excellent yield (98.9 %) from the concentrated filtrate. It is soluble in organic solvents such as toluene and THF. Its ^{1}H NMR spectrum shows one set of signals due to the amidinate ligand backbone. It also displays two doublets (δ 1.41, 1.63 ppm) and a septet (δ 4.07 ppm) for the *i*Pr moieties of the Ar substituent. The ^{29}Si NMR resonance (δ -100 ppm) for the L*Si*I moiety is comparable with that of the L*Si*I fragment in **1.2**. In addition, the ^{29}Si NMR signal (δ -139.3 ppm) for the N*Si*I_2N substituent is downfield shifted as compared with that of the N*Si*I_3 unit in **1.2**. The molecular structure of **1.6** is similar to that of **1.2** (**Figure 1.5**), which comprises the tetrahedral Si1 atom, but the Si1-N3-Si2 angle (149.67(14)^{o}) is larger than that in **1.2** (139.6(5)^{o}). The Si1-N3 bond (1.593(2) Å) is shorter than the Si2-N3 bond (1.631(2) Å). The Si1-N3 bond is comparable with that of the amidinato silanimine [LSi(=NAr)Cl] (1.545(2) Å)[22] and the donor-free dialkylsilanimine [{H_2CC(SiMe_3)$_2$}$_2$Si=NR] (R = CH_2Ph, Ph, 1-adamantyl, SiMe_3; 1.5496(14) - 1.5858(9) Å).[7] This indicates that the Si1-N3 bond comprises some double bond character.



1.2 **1.6**

Scheme 1.13: The synthesis of compound **1.6**

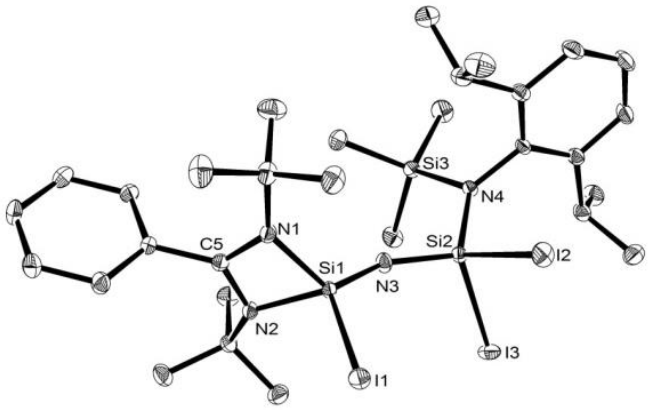
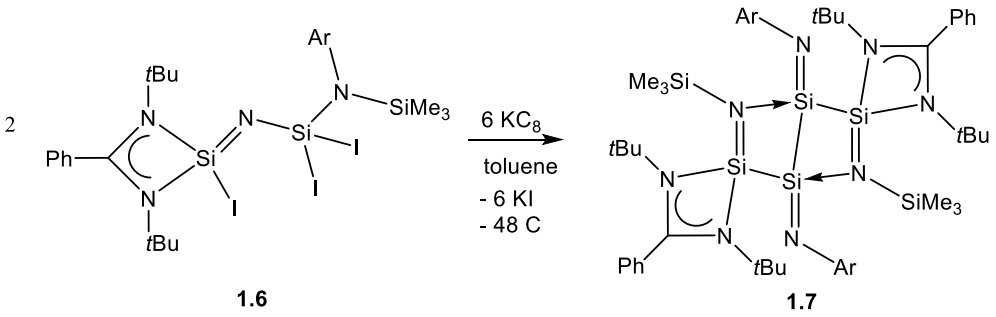


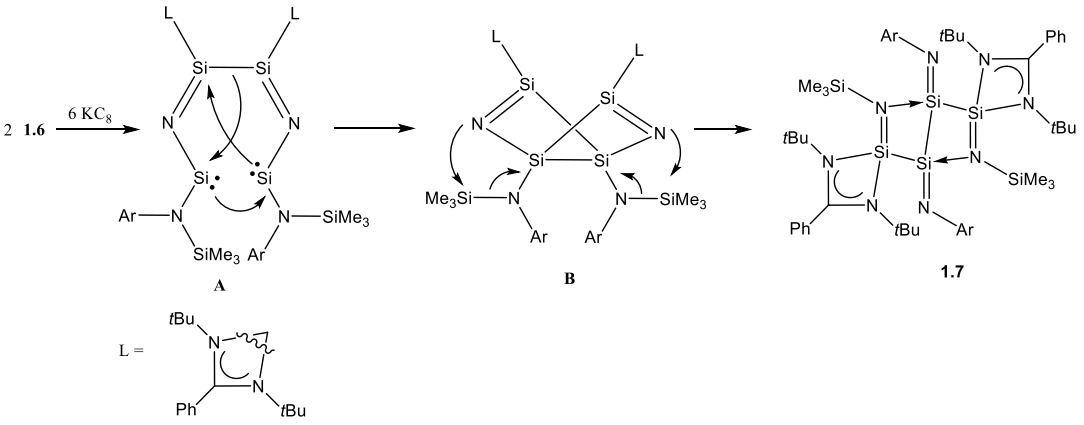
Figure 1.5. Molecular structure of compound **1.6** (ellipsoids set at 50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-I1 2.4497(7), Si1-N1 1.813(2), Si1-N2 1.799(2), Si1-N3 1.593(2), Si2-N3 1.631(2), Si2-N4 1.719(2), Si2-I3 2.5188(7), N1-Si1-N2 73.06(9), N1-Si1-N3 121.26(11), N2-Si1-N3 119.80(10), I1-Si1-N3 118.85(8), Si1-N3-Si2 149.67(14), N3-Si2-N4 111.73(10).

The reaction of **1.6** with three equivalents of KC_8 in toluene afforded the first base-stabilized tetrasilanetetraimine $[LSiN(SiMe_3)SiNAr]_2$ (**1.7**, **Scheme 1.14**), along with KI and graphite as the by-products. The latter can be removed from the reaction mixture by filtration, while compound **7** was isolated as air- and moisture-sensitive red crystals in moderate yield (58.2 %) from the concentrated filtrate. The reaction appears to proceed through the formation of a bis(silanimine) "$LSi\{=N\text{-}:SiN(SiMe_3)(Ar)\}—Si\{=N\text{-}:SiN(SiMe_3)(Ar)\}L$" **A**, which then undergoes a Si-Si bond rearrangement to form a 1,2,4,5-tetrasila-3,6-diaza(Dewar-benzene) intermediate **B**, followed by $SiMe_3$ migrations to form **1.7**

(**Scheme 1.15**). The formation of the 1,2,4,5-tetrasila-3,6-diaza(Dewar-benzene) intermediate **B** could be feasible as the stable 1,4-disila(Dewar-benzene) was able to be synthesized by Ando et al..[27]



Scheme 1.14: The synthesis of compound **1.7**



Scheme 1.15: The proposed mechanism for the formation of compound **1.7**

Compound **1.7** is soluble in toluene and THF. It is stable in solution and the solid state for several months. The ^{1}H NMR spectrum of **1.7** shows a singlet at δ 1.09 ppm for the *t*Bu substituents. It also displays two broad signals at δ 1.17-1.24 and 3.71-3.82 ppm attributable to the *i*Pr substituents. The ^{29}Si NMR signal

for the SiNAr (-13.9 ppm) moiety in **1.7** is comparable with that of the >Si=N moiety in the pyridine-stabilized silanimine [tBu$_2$Si(Py)=NSiMe$_2$Ph] (δ -12.6 ppm).[5b] The ^{29}Si NMR signal attributable to the LSiN moiety (δ -49.1 ppm) in **1.7** shows downfield shift compared with that of the silylenylsilanimine [L*Si*(=NAr)-SiL] (-61.2 ppm).[11]

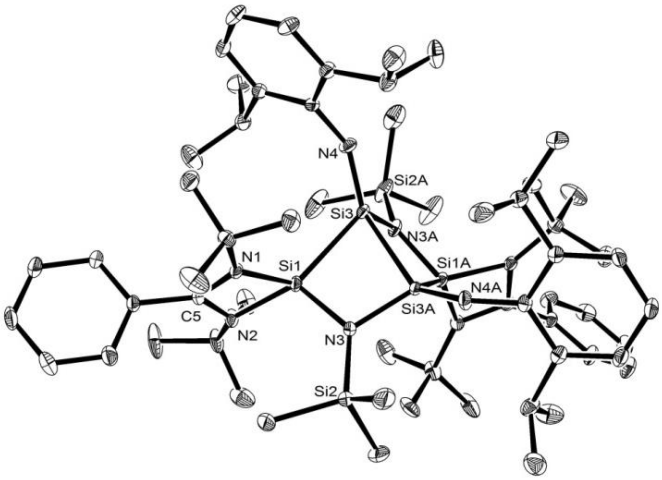
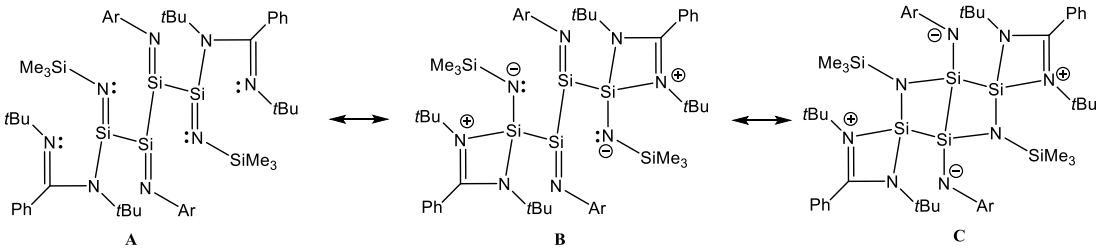


Figure 1.6. Molecular structure of compound **1.7** (ellipsoids set at 25% probability), (Thermal ellipsoids were set at 25% because of clear illustration). Hydrogen atoms, disorder in the tBu substituent and solvent molecules are omitted for clarity. Selected bond length (Å) and angles (°): Si1-Si3 2.405(2), Si3-Si3A 2.413(3), Si1-N3 1.717(4), Si3-N4 1.597(4), Si3A-N3 1.784(4), Si1-Si3-N3A 113.11(16), Si1-Si3-Si3A 70.63(7), Si3-Si3A-N3 90.91(14), Si3A-N3-Si1 105.4(2), N3-Si1-Si3 92.85(15), N4-Si3-Si1 119.75(17), N4-Si3-N3A 114.4(2), N4-Si3-Si3A 140.61(17), N1-Si1-N2 71.89(19).

Compound **1.7** was analysed by X-ray crystallography. The Si1-Si3-N3A-Si1A-Si3A-N3 ring in compound **1.7** comprises an open book conformation in

which the Si1/1A and Si3/3A atoms adopt a tetrahedral geometry **(Figure 1.6**). The Si3-N4, Si1-N3, and Si3A-N3 bond lengths are different from each other. The Si3-N4 bond (1.597(4) Å) is comparable with the Si1-N3 bond in **1.6**, which indicates that it has considerable double bond character. In addition, the Si1-N3 bond length (1.717(4) Å) in **1.7** is an intermediate value between the Si3-N4 bond length in **1.7** and the Si-N single bond length (1.754(5) Å) in the amidinato 1,2-diaza-3,4-disilacyclobutane [LSi(Cl){N(Ph)-N(Ph)}Si{(N*t*Bu)$_2$C(H)Ph}].[28] Moreover, the Si3A-N3 bond (1.784(4) Å) is longer than the Si1-N3 bond in **1.7**, but is shorter than the Si-N dative bonds in the perchlorodisilane.tmeda adduct [{H$_2$C(Me)$_2$N}$_2$SiCl$_3$SiCl$_3$] (2.064(5), 2.113(5) Å).[29] These imply that the Si-N bonds in **1.7** have some double bond characters as it comprises resonance structures as shown in Scheme **1.16**.



Scheme 1.16: Resonance structures of **1.7**

In conclusion, the base-stabilized silanimine [LSi(I)NSiI$_3$] (**1.2**) was synthesized by the reaction of the amidinato amidosilylene [LSiN(SiMe$_3$)$_2$] (**1.1**) with SiI$_4$. The by-products are Si$_2$I$_6$ and SiMe$_3$I. The reaction mechanism for the

formation of **1.2** is evidenced by (a) the synthesis of the amidinato silyl cation [LSi(Cl)N(SiMe$_3$)$_2$]GeCl$_3$ (**1.3**) by treating **1.1** with GeCl$_4$ and (b) the synthesis of the silanimine-germylene adduct [LSi(Cl)N(GeCl$_2$)SiMe$_3$] (**1.5**) by reacting the amidinato silylene-germylene adduct [L{(Me$_3$Si)$_2$N}SiGeCl$_2$] (**1.4**) with SiCl$_4$. Compound **1.2** further reacted with [LiN(SiMe$_3$)Ar] and KC$_8$ to give the base-stabilized tetrasilanetetraimine **1.7**, which comprises four conjugated silanimine units. X-ray crystallography and NMR spectroscopic data show conclusively that the Si-N bonds in **1.7** have some double bond characters. The reactivity of compound **1.7** is currently under investigation.

1.3 Experimental Section

All operations were handled under argon with glovebox and standard schlenk techniques. Solvents were dried by a SPS-Mbraun-800 solvent purification system or by distillation over potassium metal. All the NMR spectra were obtained using the ECA400M JEOL and Advance III 400M spectrometer Bruker. The element analysis and melting point were done in the air. Intensity data for crystal were collected using a Bruker APEX II diffractometer. All 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. 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 calculation.

Synthesis of **1.2**. Toluene (30 mL) was added to a mixture of **1.1** (0.84 g, 2.00 mmol) and SiI_4 (1.07 g, 2.00 mmol) at ambient temperature. The resulting dark purple mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of compound **1.2**. Yield: 0.32 g (39.6 %). Mp: 178.5 °C. Elemental analysis calcd for $C_{15}H_{23}I_4N_3Si_2$: C, 22.27; H, 2.87; N, 5.19. Found: C, 21.95; H, 2.53; N, 4.89. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 1.05 (s, 18H, *t*Bu), 6.48-6.50 (m, 1H, Ph), 6.71-6.86 (m, 4H, Ph) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 30.6 (C*Me*$_3$), 56.1 (*C*Me$_3$), 125.3, 126.5, 129.0, 130.9 (Ph), 176.9 (NCN) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6 25°C): δ = -256.7 (SiI_3), -100.0 (Si(I)=N) ppm.

Crystallographic data for **1.2**: $C_{18.50}H_{27}I_4N_3Si_2$; M = 855.21; monoclinic *P* 1 21/*c* 1; a = 22.2720(16), b = 13.6343(9), c = 19.8421(15) Å; α = 90°, β = 111.712°(3), γ = 90°; V = 5597.8(7) Å^3; Z = 8; ρ_{calcd} = 2.030 mg m^{-3}; 19224 measured reflections; 10775 independent reflections; 498 refined parameters; R_1 = 0.0733, wR_2= 0.1215 ($I > 2\sigma(I)$).

Synthesis of Si_2I_6: Toluene (30 mL) was added to a mixture of **1.1** (0.42 g, 1.00 mmol) and SiI_4 (1.07 g, 2.00 mmol) at ambient temperature. The resulting green mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of Si_2I_6. Yield 0.527 g (64.5%)

Crystallographic data for Si_2I_6: Si_2I_6; M = 855.21; trigonal *R -3*; a = 7.1553(8), b = 7.1553(8), c = 22.226(3) Å; α = 90°, β = 90°, γ = 120°; V = 958.5(3) Å^3; Z = 3; ρ_{calcd} = 4.133 mg m^{-3}; 2843 measured reflections; 620 independent reflections; 13 refined parameters; R_1 = 0.0461, wR_2= 0.1373 ($I > 2\sigma(I)$).

Synthesis of **1.3**: $GeCl_4$ (0.22 g, 1.00 mmol) was added dropwise to the solution of **1.1** (0.42 g, 1.00 mmol) in toluene (30 mL) at ambient temperature. The resulting yellow mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford pale yellow oil. Colorless crystals of compound **1.3** were then afforded at the side of yellow oil overnight. The mother liquor and yellow oil was filtered out. The colorless crystals were then washed by toluene at least 2 times to remove contamination. Yield: 0.16 g (25.2 %). Mp: 214.6 °C (decomposed). Compound **1.3** is highly unstable in solution. Freshly prepared solution of **1.3** is essential for NMR spectroscopy. Elemental analysis for $C_{21}H_{41}Cl_4GeN_3Si_3$: C, 39.79; H, 6.52; N, 6.63. Found: C, 39.38; H, 6.50; N, 6.67. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.17 (s, 9H, $SiMe_3$), 0.38 (s, 9H, $SiMe_3$), 0.98 (s, 18H, *t*Bu), 7.22-7.24 (m, 2H, Ph), 7.35-9.39 (m, 1H, Ph), 7.55-7.64 (m, 2H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.2 ($SiMe_3$), 4.4 ($SiMe_3$), 30.5 (C*Me*$_3$), 57.7 (*C*Me$_3$), 127.1, 128.6, 129.8, 132.7 (Ph), 183.1 (NCN). ^{29}Si{^{1}H} NMR (79.4 MHz, THF-d_8, 25°C): δ = 12.1 ($SiMe_3$), 31.4 (LSiCl) ppm.

Crystallographic data for **1.3**: $C_{21}H_{41}Cl_4GeN_3Si_3$; M = 634.23; monoclinic *P* 1 21/*c* 1; *a* = 18.7105(7), *b* = 21.6514(7), *c* = 16.3484(6) Å; *α* = 90°, *β* = 108.8162(16)°, *γ* = 90°; *V* = 6268.9(4) Å^3; *Z* = 8; ρ_{calcd} = 1.344 mg m^{-3}; 76084 measured reflections; 11555 independent reflections; 601 refined parameters; R_1 = 0.0531, wR_2 = 0.1178 ($I > 2\sigma(I)$).

Synthesis of **1.5**: Toluene (30 mL) was added to a mixture of **1.4** (0.56 g, 1.00 mmol) and $SiCl_4$ (0.17 g, 1.00 mmol) at ambient temperature. The resulting dark orange mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of compound **1.5**. Yield: 0.32 g (60.9 %). Mp: 148.4 °C (decomposed). Elemental analysis calcd for $C_{18}H_{32}Cl_3GeN_3Si_2$: C, 41.15; H, 6.14; N, 8.00. Found: C, 40.87; H, 6.01; N, 7.72. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.53 (s, 9H, $SiMe_3$), 1.21 (s, 18H, *t*Bu), 6.88-6.89 (m, 4H, Ph), 8.41-8.43 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 1.1 ($SiMe_3$), 31.0 (C*Me*$_3$), 55.2 (*C*Me$_3$), 127.3, 127.7, 130.1, 132.6 (Ph), 172.2 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = -62.3 (Si(Cl)=N), 2.9 ($SiMe_3$) ppm.

Crystallographic data for **1.5**: $C_{18}H_{32}Cl_3GeN_3Si_2$; M = 525.58; monoclinic *P* 1 21/*c* 1; *a* = 16.9206(8), *b* = 8.2680(4), *c* = 18.3628(9) Å; *α* = 90°, *β* = 106.236(3)°, *γ* = 90°; *V* = 2466.5(2) Å^3; *Z* = 4; ρ_{calcd} = 1.415 mg m^{-3}; 39499 measured reflections; 9056 independent reflections; 5869 refined parameters; R_1 = 0.0508, wR_2 = 0.1041 ($I > 2\sigma(I)$).

Synthesis of **1.6**: Toluene (30 mL) was added to a mixture of **1.2** (0.81 g, 1.00 mmol) and LiN(SiMe$_3$)Ar·2Et$_2$O (0.26 g, 1.0 mmol) at ambient temperature. The resulting brown mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of **1.6**. Yield: 0.92 g (98.9 %). Mp: 218.4 °C. Elemental analysis calcd for $C_{30}H_{49}I_3N_4Si_3$.¼C_7H_8: C, 40.00; H, 5.39; N, 5.87. Found: C, 39.96; H, 5.98; N, 5.28. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.63 (s, 9H, SiMe$_3$), 1.05 (s, 18H, *t*Bu), 1.41 (d, 6H, CH*Me*$_2$), 1.63 (d, 6H, CH*Me*$_2$), 4.07 (sep, 2H, C*H*Me$_2$), 6.56-6.69 (m, 1H, Ph), 6.75-6.87 (m, 4H, Ph), 7.09-7.13 (m, 3H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 3.4 (SiMe$_3$), 24.7 (CH*Me*$_2$), 27.3 (CH*Me*$_2$), 28.4 (*C*HMe$_2$), 30.7 (C*Me*$_3$), 55.7 (*C*Me$_3$), 127.5, 127.6, 127.7, 128.0, 128.2, 129.0, 142.9, 148.1 (Ph), 166.9 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = -139.3 (Si(NAr)I$_2$), -100.1 (Si(I)=N), 7.5 (SiMe$_3$) ppm.

Crystallographic data for **1.6**: $C_{33.50}H_{53}I_3N_4Si_3$; M = 976.77; triclinic *P* -1; *a* = 9.8334(3), *b* = 12.8781(4), *c* = 17.7755(5) Å; *α* = 107.4942(17)°, *β* = 103.8934(18)°, *γ* = 97.4496(18)°; *V* = 2033.96(11) Å^3; *Z* = 2; ρ_{calcd} = 1.595 mg m^{-3}; 74954 measured reflections; 7733 independent reflections; 426 refined parameters; R_1 = 0.0208, wR_2 = 0.0422 ($I > 2\sigma(I)$).

Synthesis of **1.7**: Toluene (30 mL) was added to a mixture of **1.6** (0.98 g, 1.00 mmol) and KC_8 (0.41 g, 3.0 mmol) at ambient temperature. The resulting red

mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford red crystals of **1.7**. Yield: 0.32 g (58.2 %). Mp: 189.2 °C (decomposed). Elemental analysis calcd for $C_{60}H_{98}N_8Si_6$: C, 65.56; H, 8.98; N, 10.19. Found: C, 65.34; H, 8.72; N, 10.02. ^{1}H NMR (399.5 MHz, THF-d_8, 25°C): δ = 0.40 (s, 18H, $SiMe_3$), 1.09 (s, 36H, *t*Bu), 1.17-1.24 (br, 24H, CH*Me*$_2$), 3.71-3.82 (br, 4H, C*H*Me$_2$), 6.24-7.58 (br, 16H, Ph). ^{13}C{^{1}H} NMR (100.5 MHz, THF-d_8, 25°C): δ = 3.4 ($SiMe_3$), 24.7 (CH*Me*$_2$), 27.3 (CH*Me*$_2$), 28.4 (*C*HMe$_2$), 30.7 (C*Me*$_3$), 55.7 (*C*Me$_3$), 127.5, 127.6, 127.7, 128.0, 128.2, 129.0, 142.9, 148.1 (Ph), 166.9 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, THF-d_8, 25°C): δ = -49.1 (*Si*=N-$SiMe_3$), -13.9 (*Si*=N-Ar), 3.6 (*Si*Me$_3$) ppm.

Crystallographic data for **1.7**: $C_{74}H_{114}N_8Si_6$; M = 1284.27; monoclinic *C* 1 2/*c* 1; a = 19.722(4), b = 13.144(3)(4), c = 30.205(6) Å; α = 90°, β = 100.459(4)°, γ = 90°; V = 7700.0 (3) Å^3; Z = 4; ρ_{calcd} = 1.108 mg m^{-3}; 44318 measured reflections; 7613 independent reflections; 483 refined parameters; R_1 = 0.1055, wR_2 = 0.2143 ($I > 2\sigma(I)$).

1.4 X-ray crystal structures of Si_2I_6

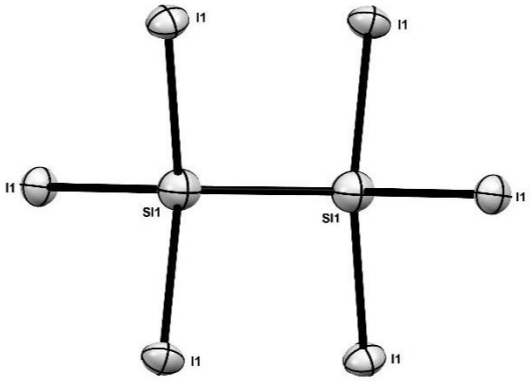


Figure S1. Molecular structure of Si_2I_6 (ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Si1-I1 2.430(9), Si1-Si1 2.328(5), I1-Si1-Si1 107.63(5), I1-Si1-I1 111.25(5).

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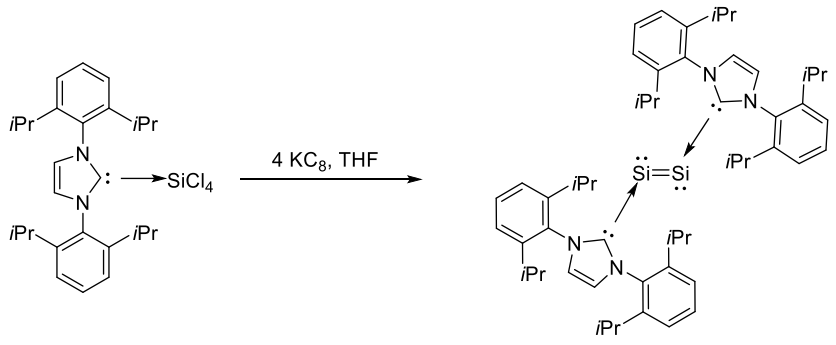
CHAPTER 2

A N-Heterocyclic Silylene-Stabilized Digermanium(0) Complex

2.1 Introdution

The utilization of N-heterocyclic carbenes (NHCs) for the stabilization of group 14 elements in the zero oxidation state has attracted much attention.[1] The most spectacular example of such a complex is [I_{Ar}→Si=Si←I_{Ar}] (I_{Ar} = :C{N(Ar)CH}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), which is considered as a NHC adduct of the singlet disilicon(0) fragment :Si=Si: comprising a Si=Si double bond and a lone pair of electrons on each Si atom. [I_{Ar}→Si=Si←I_{Ar}] can be easily synthesized by the reduction of [I_{Ar}→$SiCl_4$] with KC_8 **(Scheme 2.1)**.[2]

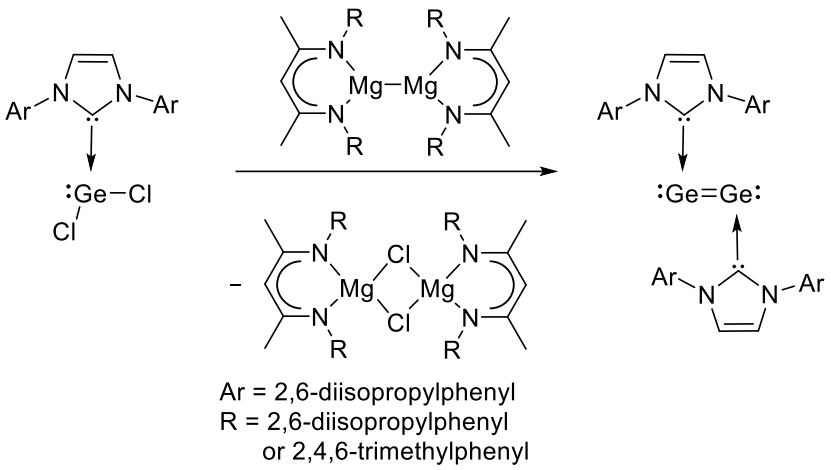


Scheme 2.1: The synthesis of [I_{Ar}→Si=Si←I_{Ar}]

This chapter is taken with permission from Y. L. Shan, W. L. Yim and C. W. So, *Angew. Chem. Int. Ed.*, 2014, **53**, 13155 –13158.

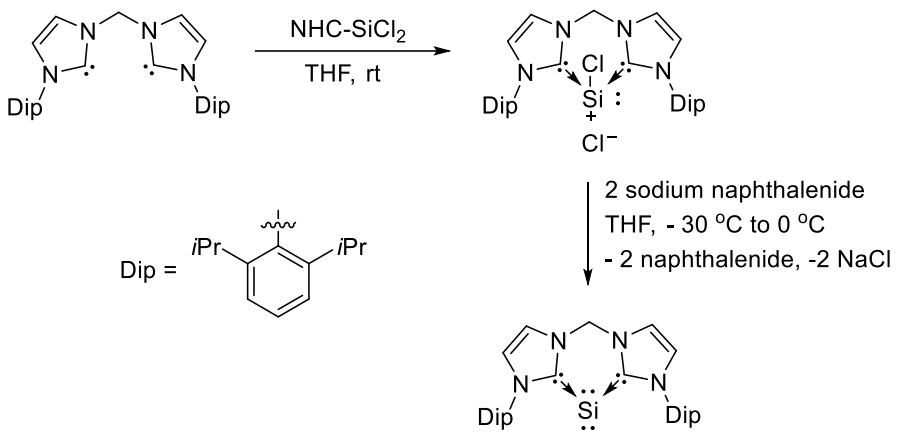
Its unique electronic properties were unraveled by both X-ray crystallography and theoretical studies, which showed that the stability of a NHC adduct of group 14 element(0) can be rationalized purely by the superior σ-donating ability of the NHC.[3] Its reactivities have been studied.[4]

Following this pioneer work, the heavier analogues [I_{Ar}→Ge=Ge←I_{Ar}] (I_{Ar} = :C{N(Ar)CH}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) were synthesized by the reaction of the NHC-stabilized germanium or tin dichloride [I_{Ar}→$GeCl_2$] with the magnesium(I) dimer [HC(CMeNMes)$_2$Mg]$_2$ **(Scheme 2.2)**.[5]

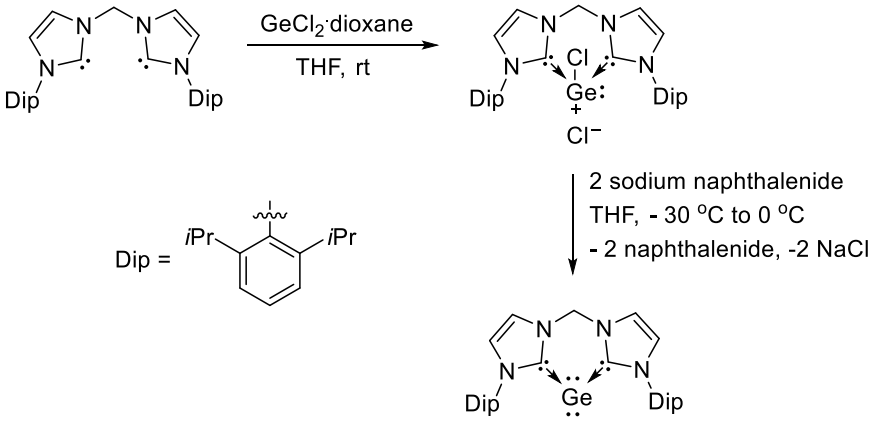


Scheme 2.2: The synthesis of [I_{Ar}→Ge=Ge←I_{Ar}]

The chemistry of group 14 element(0) complex was further extended by modifying the electronic structure of a NHC, which results in the formation of a monoatomic group 14 element(0) complex. The NHC-stabilized silylone and germylone of composition [NHC→E←NHC] were synthesized by the reduction of the bis(NHC)-stabilized silyliumylidene **(Scheme 2.3)** and germyliumylidene cation **(Scheme 2.4)**, in which the E(0) atom retains its valance electrons as two lone pairs.[6]

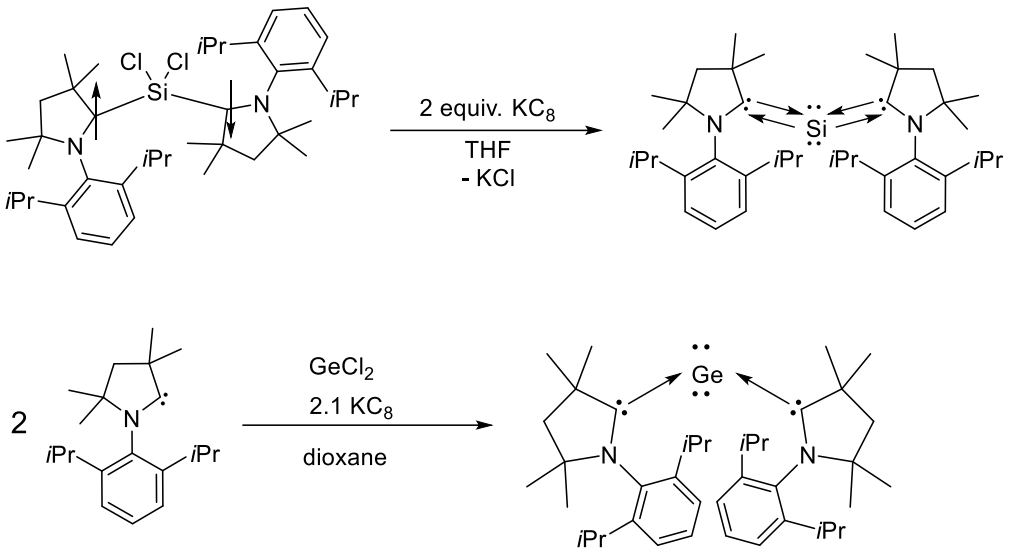


Scheme 2.3: The synthesis of the bis(NHC)-stabilized silylone



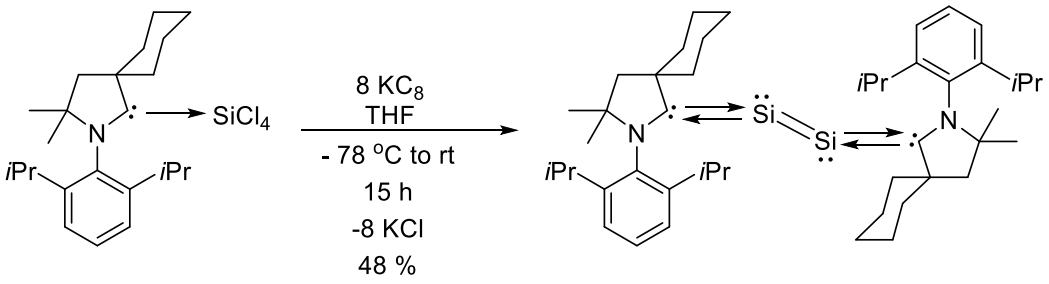
Scheme 2.4: The synthesis of the bis(NHC)-stabilized germylone

When the bis(NHC) was replaced by two enhanced nucleophilic and electrophilic cyclic alkyl amino carbene (cAAC), the resulting silylone and germylone [cAAC⇆E⇄cAAC] (E = Si and Ge) exhibit different electronic properties and possess biradicaloid character **(Scheme 2.5)**.[7]



Scheme 2.5: The synthesis of the cAAC-stabilized silylone and germylone

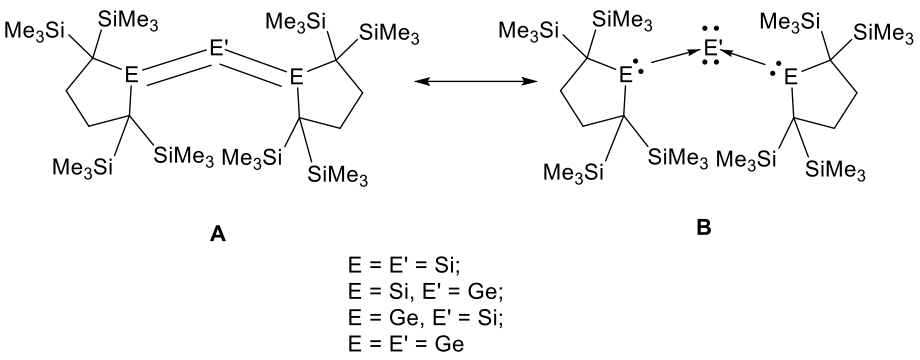
Interestingly, with the aid of a bulkier cAAC, the singlet disilicon(0) complex [cAAC⇆Si=Si⇄cAAC] was afforded **(Scheme 2.6)**.[8]



Scheme 2.6: The synthesis of the cAAC-stabilized singlet disilicon(0)

In sharp contrast to [IPr→E=E←IPr] and [NHC→E←NHC] complexes, the chemical bonding situation in heavier analogues [R_2E:→E←:ER_2] (E = Si, Ge) is open to dispute. Recently, Kira and coworkers synthesized a series of stable heavier allene analogues **A**, which are strongly bent at the central E' atom of the

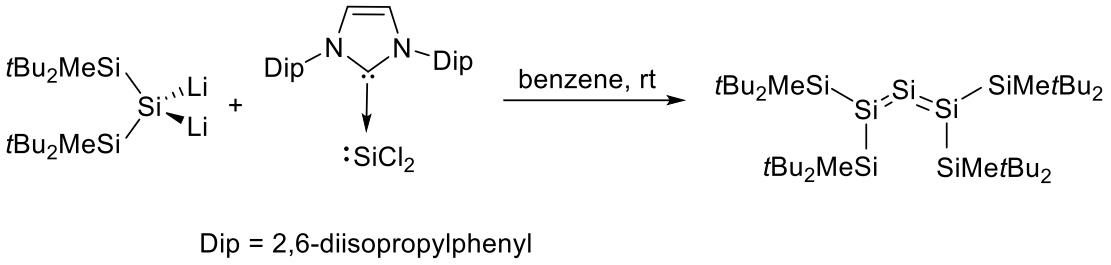
allene skeleton (122 – 137º) and the E=E' bonds have double bond character **(Scheme 2.7)**.



Scheme 2.7: Resonance structure for heavier analogues [$R_2E{:}\rightarrow E\leftarrow{:}ER_2$] (E = Si, Ge) of [NHC→E←NHC] complexes

Their theoretical studies rationalized the strongly bent skeleton in these compounds due to the Jahn-Teller distortion associated with the π-σ* mixing.[9] In contrast, Frenking et al. disputed that the heavier allene analogues should be interpreted as a ylidone **B** stabilized by two silylene or germylene moieties.[10] Further calculations by research groups of Apeloig and Veszprémi showed that the parent trisilaallene $H_2Si{=}Si{=}SiH_2$ has a very complex mixture of isomers which possess different electronic structures such as zwitterionic allylium, trisilacyclopropylidene, etc.[11] These theoretical studies revealed that both structural and electronic properties of heavier allene analogues greatly depend on the substituent effects at the terminal E atoms. In this context, Sekiguchi et al.

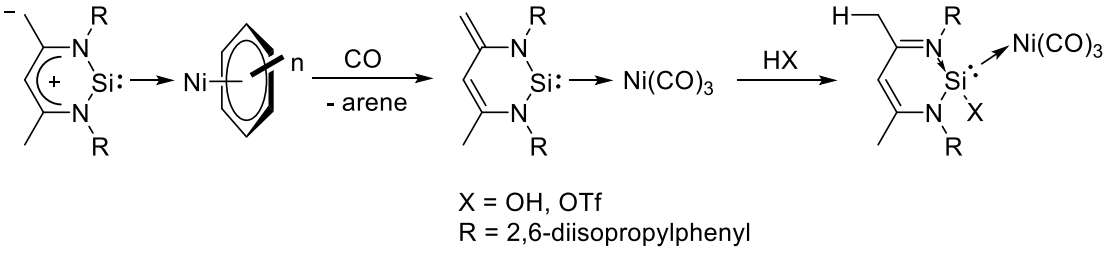
synthesized the trisilaallene [(tBu$_2$MeSi)$_2$Si=Si=Si(SiMetBu$_2$)$_2$] bearing bulkier silyl ligands.[9f] It is slightly bent (164.3°), which greatly influences its electronic properties resulting in different reactivity of regioselective addition compared with that of **A (Scheme 2.8)**.



Scheme 2.8: The synthesis of the trisilaallene [(tBu$_2$MeSi)$_2$Si=Si=Si(SiMetBu$_2$)$_2$]

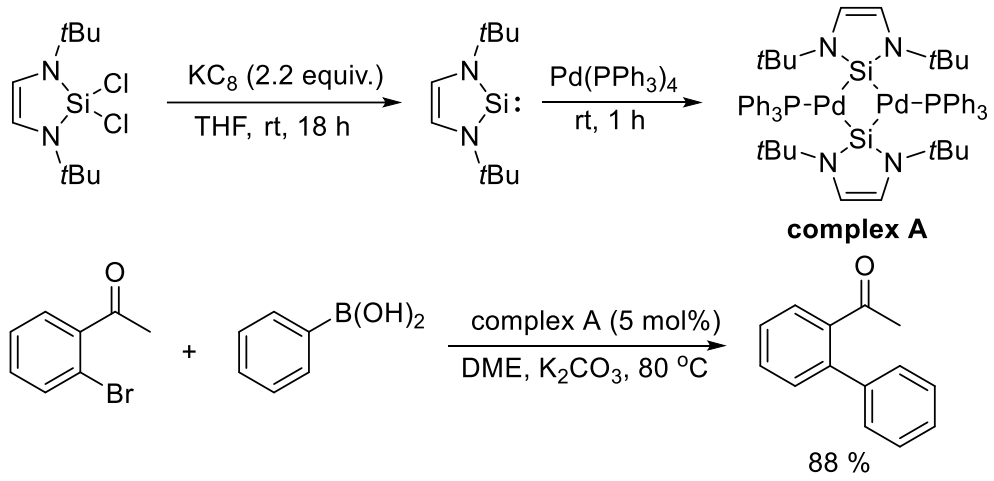
Until now, there is still no solid experimental evidence for the existence of a ylidone **B** stabilized by two silylene or germylene moieties. In other words, the capability of a low valent group 14 carbene analogue (R_2E:) to stabilize a group 14 element(0) fragment is still mysterious.

Recently, N-heterocyclic silylene (NHSi) has been emerging as a prominent ligand class in the coordination chemistry of transition metal in the zero oxidation state **(Scheme 2.9).**[12]



Scheme 2.9: The synthesis of NHSi-stabilized transition metal in the zero oxidation state

The application of transition metal(0)-NHSi complexes toward small molecules activation and catalytic transformations was also investigated **(Scheme 2.10)**.[13-14]

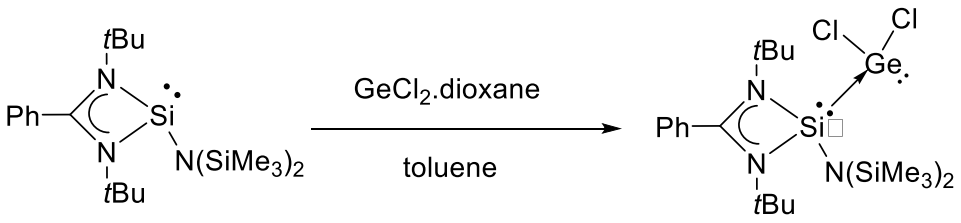


Scheme 2.10: The application of transition metal(0)-NHSi complexes toward catalytic transformations

In parallel with transition metal(0) coordination chemistry, we anticipate that a NHSi is capable of stabilizing main-group elements in the zero oxidation state. In addition, it is highly beneficial to explore whether and how a NHSi stabilizes a group 14 element(0) as the NHSi exhibits different structural and electronic properties compared with those of silylene moieties, "$Si(SiMetBu_2)_2$" and "$Si\{C(SiMe_3)_2CH_2\}_2$", in the heavier allene analogues. Moreover, the resulting group 14 element(0) compound is expected to exhibit different electronic

structures and hence reactivity compared with those of the heavier allene analogues. Thus, a NHSi-stabilized group 14 element(0) complex should be a worthwhile synthetic target not only for the fundamental bonding studies but also for its possible application for small molecules activation. Herein, we report the utilization of an amidinate-stabilized silicon(II) amide [LSiN(SiMe$_3$)$_2$] (L = PhC(N*t*Bu)$_2$) to stabilize a digermanium(0) moiety by a weak synergic donor-acceptor interaction.

2.2 **Results and Discussion**



Scheme 2.11: The synthesis of compound **2.2**

The reaction of the amidinate-stabilized silicon(II) amide [LSiN(SiMe$_3$)$_2$] (**2.1**)[15] with GeCl$_2$·dioxane in toluene afforded the silicon(II)-germanium(II) adduct [L{(Me$_3$Si)$_2$N}Si→GeCl$_2$] (**2.2**, **Scheme 2.11**), which was isolated as an air- and moisture-sensitive colorless crystalline solid in high yield (73 %).[16] Although the coordination chemistry of NHSi toward transition metals and of the NHC-stabilized silylene toward main-group elements were investigated extensively,[9,17] compound **2.2** is the first NHSi adduct of group 14 elements. The

^{1}H NMR spectrum displays one set of resonances due to the amidinate ligand and $SiMe_3$ substituents. The ^{29}Si NMR resonance for the Si^{II} center (δ 2.76 ppm) shows an expected downfield shift compared with that of **2.1** (δ - 8.07 ppm) as the lone pair electrons on the Si^{II} centre are donated to the vacant orbital on the Ge^{II} atom. It also shows a downfield shift compared with that of the NHC/tungsten-stabilized Si^{II}-Ge^{II} adduct [IPrSi(Cl_2)Ge(Cl_2)W($CO)_5$] (δ - 6.1 ppm).[18]

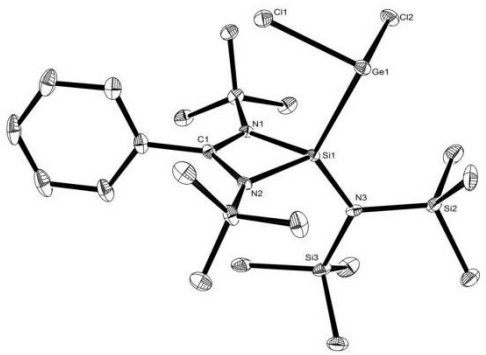
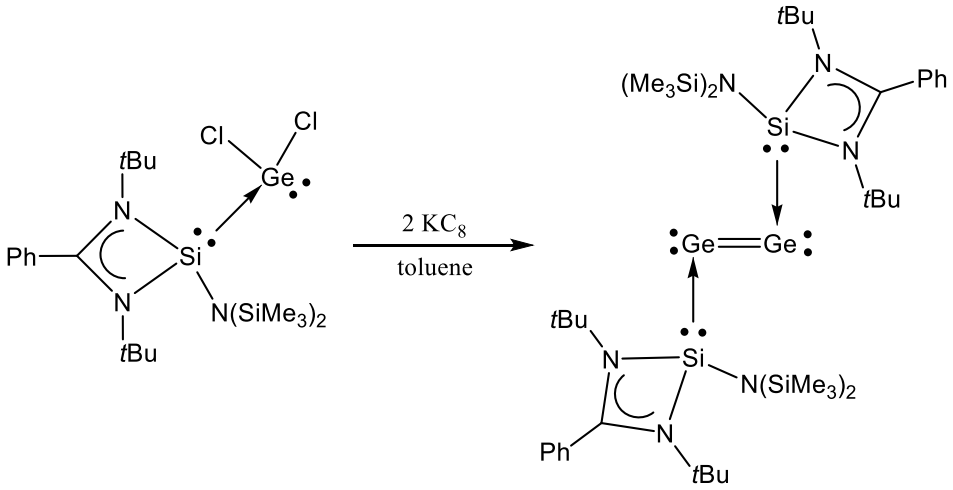


Figure 2.1. Molecular structure of compound **2.2** (ellipsoids set at 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-Ge1 2.5259(13), Si1-N1 1.825(4), Si1-N2 1.823(4), Si1-N3 1.717(5), C1-N1 1.332(7), C1-N2 1.348(7), Cl1-Ge1-Cl2 97.36(6), Cl1-Ge1-Si1 91.53(5), Cl2-Ge1-Si1 92.89(5), N1-Si1-N2 71.93(19), N1-Si1-N3 115.3(2), N2-Si1-N3 114.3(2), Si1-N1-C1 90.7(3), N1-C1-N2 106.1(4), C1-N2-Si1 90.3(3).

The molecular structure of **2.2** (**Figure 2.1**) shows that the amidinate ligand is bidentate coordinated to the Si1 atom. The latter also bonds to the N3 atom of the

amido substituent and the Ge1 atom to adopt a tetrahedral geometry. The Ge1 atom displays a distorted trigonal pyramidal geometry (the sum of bond angles: 281.8°), which indicates that there is a lone pair of electrons on it. The Si1-Ge1 bond (2.5259(13) Å) is significantly longer than typical Si-Ge single bonds (2.40 – 2.45 Å)[19] and that in the NHC/tungsten-stabilized Si^{II}-Ge^{II} adduct [IPrSi(H_2)Ge(H_2)W($CO)_5$] (2.3717(14) Å),[18] which indicates that the Si1-Ge1 bond is a coordinative covalent bond.



2.2 **2.3**

Scheme 2.12: The synthesis of compound **2.3**

Compound **2.2** reacted with two equivalents of KC_8 in toluene at room temperature to afford [L{$(Me_3Si)_2N$}Si→Ge=Ge←Si{$N(SiMe_3)_2$}L] (**2.3**, Scheme 3), which was isolated as an air- and moisture-sensitive dark red crystalline solid in low yield (16 %). The ^{1}H NMR spectrum shows one set of resonances for the amidinate and $N(SiMe_3)_2$ ligands. The ^{29}Si NMR resonance (δ

30.8 ppm) for the Si^{II} center shows a downfield shift compared with that of **2.2**. Similar downfield shift is observed by comparing the ^{13}C NMR resonances for the $C_{carbene}$ atoms in [IPr→Ge=Ge←IPr] (δ 203.3 ppm) and [IPr→$GeCl_2$] (δ 175.3 ppm).[5a]

The molecular structure of **2.3** (Figure **2.2**) shows that the SiGeGeSi skeleton has a trans-bent (Ge1-Ge1A-Si: 91.95(6)°) and planar geometry. Similar trans-bent geometry is observed in [IPr→Ge=Ge←IPr] (C-Ge-Ge: 89.87(8)º).[5a] In addition, the Si1 atom adopts a tetrahedral geometry comparable to that in **2.2**. The Ge1-Ge1A bond (2.3518(16) Å) is comparable with that in [IPr→Ge=Ge←IPr] (2.3490(8) Å) and typical >Ge=Ge< double bonds in digermenes (2.344 Å).[5a] It is noteworthy that the Ge1-Si1 bond (2.406(2) Å) is significantly longer than that in the 2-germadisilaallene (2.2370(7) Å).[12] It is slightly shorter than that in **2.2** and is well within typical Si-Ge single bond lengths (2.40 – 2.45 Å).[19]

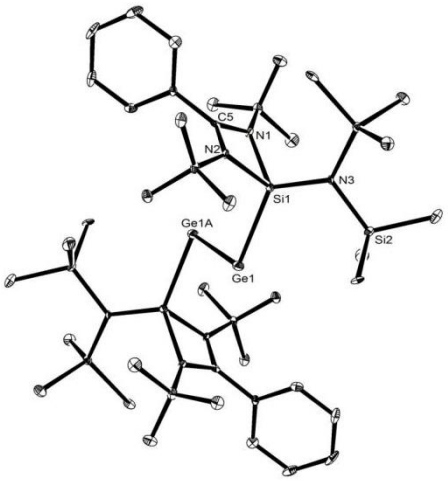
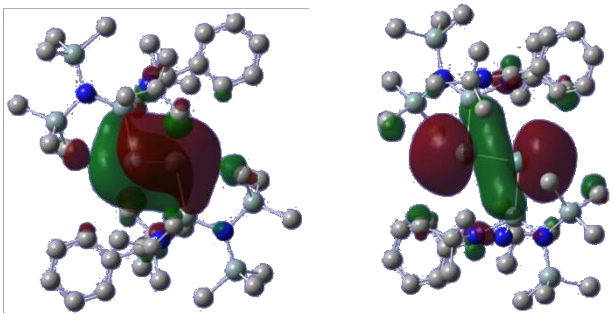


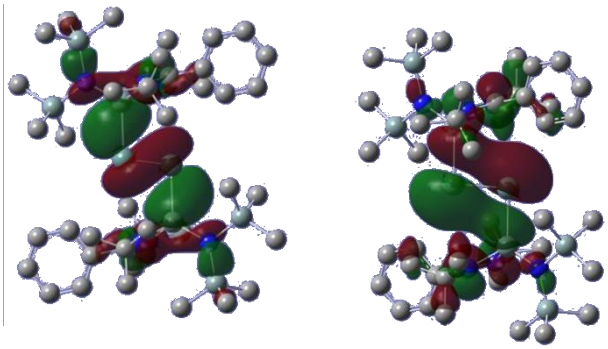
Figure 2.2. Molecular structure of compound **2.3** (ellipsoids set at 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-Ge1A 2.3518(16), Si1-Ge1 2.406(2), Si1-N1 1.859(6), Si1-N2 1.866(5), Si1-N3 1.741(5), C5-N1 1.343(8), C5-N2 1.330(8), Si1-Ge1-Ge1A 91.95(6), N1-Si1-Ge1 123.2(2), N2-Si1-Ge1 108.67(18), N3-Si1-Ge1 121.2(2), N1-Si1-N2 70.2(2), Si1-N1-C5 90.8(4), N1-C5-N2 106.5(5), C5-N2-Si1 90.9(4).

To understand the bonding nature in compound **2.3**, density functional calculations were conducted.[20] The optimized geometry (PBE-vdW-DF level, Table S1, see the theoretical studies) is in good agreement with the X-ray crystallographic data. The HOMO (Figure **2.3**) shows the Ge-Ge π orbital interacting with the empty p orbital on the Si atoms. Such π-back bonding interactions, which are absent in [I_{Ar}→Ge=Ge←I_{Ar}],[5a] are considered to be a key for the stabilization of a NHSi adduct of group 14 element(0) and allowing for its isolation. This also results in shortening the Ge-Si bond, which is consistent with the X-ray crystallographic data. Similar π-back bonding interactions can be observed in the cAAC-stabilized group 14 element(0) complexes.[7-8] The HOMO-1 shows primarily the Ge-Ge σ orbital, while the HOMO-2 shows the donor-acceptor interaction between the lone pair orbitals on the Si atoms and the vacant p orbitals on the Ge atoms. The HOMO-3 displays primarily the lone pair orbitals on the Ge atoms.

Bader analysis was performed, which shows bond critical points (BCPs) with (3,-1) character along the Si-Ge and Ge-Ge bonds. The high ellipticity (ε_{BCP}) and delocalization index (DI) of the Ge1-Ge1A bond (ε_{BCP} = 0.191, DI = 1.679), which are comparable with those of $H_2Ge{=}GeH_2$ (ε_{BCP} = 0.243, DI = 1.821), imply that the Ge1-Ge1A bond has a significant double bond character. In addition, the ellipticity of the Si1-Ge1 bond (ε_{BCP} = 0.073) is intermediate between that of $H_2Si{=}GeH_2$ (ε_{BCP} = 0.623) and $H_3Si\text{-}GeH_3$ ($\varepsilon_{BCP} = 1.19\times10^{-5}$). These suggest that there is a weak π-back bonding from the digermanium(0) :Ge=Ge: to the NHSi, which is consistent with the HOMO. The small $\nabla^2\rho_{BCP}$ (-0.0104 a.u.) and NPA charges (Si: 1.68, Ge: -0.53) also imply a donor-acceptor character of the Si-Ge bonds. It is noteworthy that the electron density of the Si-Ge bonds (ρ_{BCP} = 0.070 a.u.) is smaller than that of $H_3Si\text{-}GeH_3$ (ρ_{BCP} = 0.090) and $H_2Si{=}GeH_2$ (ρ_{BCP} = 0.103), which reveals that the bond strength of the Si⇆Ge donor acceptor interaction in **2.3** is significantly weaker than that of a Si-Ge single bond. The singlet biradicaloid character of **2.3** is ruled out by CASSCF calculations. The oxidation state will further be analyzed by XPS.



(a) HOMO (b) HOMO-1



(c) HOMO-2 (d) HOMO-3

Figure 2.3. Selected molecular orbitals of **2.3**

In conclusion, we have reported the synthesis of the first NHSi adduct of digermanium(0) by a simple procedure. X-ray crystallography and theoretical studies show conclusive ely that a singlet germanium(0) dimer :Ge=Ge: is stabilized by two NHSi ligands. Compared to other base-stabilized (0) compounds, NHSis can stabilize a digermanium(0) moiety by a weak synergic donor-acceptor interaction. Such back-donation abilities of the amidinato silylenes will be examined by reaction of the amidinato silylenes with metal carbonyl compounds in the afuture. These results support Frenking's prediction that the stabilization of a ylidone by low valent heavier group 14 carbene moieties should be possible.

2.3 Experimental Section

All operations were handled under argon with glovebox and standard schlenk techniques. Solvents were dried by a SPS-Mbraun-800 solvent purification

system or by distillation over potassium metal. All the NMR spectra were obtained using the ECA400M JEOL and Advance III 400M spectrometer Bruker. The element analysis and melting point were done in the air. Intensity data for crystal were collected using a Bruker APEX II diffractometer. All 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. 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 calculation

Synthesis of **2.2**. : Toluene (30 mL) was added to a mixture of **2.1**[1] (1.26 g, 3.00 mmol) and $GeCl_2$·dioxane (0.77 g, 3.3 mmol) at room temperature. The resulting dark orange mixture was stirred for 16 hours. The reaction mixture was filtered and the filtrate was concentrated to afford **2.2** as a colorless crystalline solid (yield: 1.24 g, 73.3%). M.p. 171 °C (decomposed); elemental analysis (%) calcd for $C_{21}H_{41}Cl_2GeN_3Si_3$: C 44.77, H 7.28, N 7.46; found: C 44.47, H 7.61, N 7.36; ^{1}H NMR (399.5 MHz, THF-D_8, 25°C): δ = 0.49 (s, 9H, $SiMe_3$), 0.50 (s, 9H, $SiMe_3$), 1.29 (s, 18H, tBu), 7.52-7.54 (m, 4H, Ph), 8.23 (m, 1H, Ph) ppm; ^{13}C{^{1}H} NMR (100.5 MHz, THF-D_8, 25°C): δ = 4.31 ($SiMe_3$), 5.05 ($SiMe_3$), 30.63 (CMe_3), 55.20 (CMe_3), 127.50, 127.91, 128.52, 129.91, 130.99, 132.30 (Ph), 172.53 (NCN) ppm; ^{29}Si{^{1}H} NMR (79.4 MHz, THF-D_8, 25°C):

δ = 2.76 ($SiN(SiMe_3)_2$), 8.66($SiMe_3$), 10.43 ($SiMe_3$).

Crystallographic data for **2.2**: $C_{21}H_{41}Cl_2GeN_3Si_3$; M = 563.33; orthorhombic; P n a 21; a = 17.4534(12), b = 8.8377(6), c = 18.8882(14) Å; α = 90°, β = 90°, γ = 90°; V =2913.5(4) Å3; Z = 4; calcd = 1.284 mg m^{-3}; 46400 measured reflections; 5958 independent reflections; 283 refined parameters; R1 = 0.0380, wR2 = 0.0517 (I > 2σ(I))

Synthesis of **2.3**. : Toluene (30 mL) was added to a mixture of **2.2** (0.56 g, 1.00 mmol) and KC_8 (0.27 g, 2.0 mmol) at room temperature. The resulting dark red mixture was stirred for 16 hours. The reaction mixture was filtered and the filtrate was concentrated to afford **2.3** as a dark red crystalline solid (yield: 0.077 g, 15.6%). M.p. 154 °C (decomposed); ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.57 (s, 9H, $SiMe_3$), 0.74 (s, 9H, $SiMe_3$), 1.48 (s, 18H, tBu), 6.90-7.03 (m, 3H, Ph), 7.36-7.38 (m, 1H, Ph), 8.43-8.45 (m, 1H, Ph) ppm; $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 5.85 ($SiMe_3$), 7.07 ($SiMe_3$), 31.61 (CMe_3), 55.00 (CMe_3), 123.23, 127.12, 127.56, 129.29, 132.21, 132.76 (Ph), 166.9 (NCN) ppm; $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6, 25°C): δ= 2.79 ($SiMe_3$), 6.19 ($SiMe_3$), 30.76 ($SiN(SiMe_3)_2$);UV−vis (THF) λ_{max} (ε) 278 (27400), 290 (48400), 479 (23380) nm(dm^3 mol^{-1} cm^{-1}).

Crystallographic data for **2.3**: $C_{21}H_{41}GeN_3Si_3$; M = 429.43; monoclinic; P 1 21/n 1; a = 11.335(2), b = 17.402(4), c = 14.097(3) Å; α = 90°, β = 103.100(6)°, γ = 90°; V =2708.3(10) Å3; Z = 4; calcd = 1.208 mgm^{-3}; 38006 measured reflections;

4986 independent reflections; 265 refined parameters; R_1 = 0.0577, wR2 = 0.1512 ($I > 2\sigma(I)$).

2.4 Theoretical studies

Starting from the X-ray crystallographic data, the atomic coordinates in the unit cell were fully optimized by planewave DFT calculations[20] using Perdew Burke Ernzerhof (PBE) exchange-correlation functional[21] with the inclusion of van der Waals correction (vdW-DF)[22] as implemented in the Vienna Ab Initio Simulation Package (VASP).[23] Then the electronic structure of isolated molecule of compound **2.3** was further analysed by *ab initio* molecular orbitals calculations using the Gaussian 09 (G09) software package[24] at B3PW91/TZVP level of theory. Natural population analysis (NPA), Bader analysis,[25] and delocalization index (DI)[26] were carried out using G09,[24] AIMPAC[27] and Multiwfn,[28] respectively. Table 1 summarized the optimized parameters of the trans-bent Si-Ge-Ge-Si skeleton in compound **2.3** by periodic DFT calculations. The PBE-vdW-DF calculations show that the Ge-Ge and Si-Ge bond lengths are systematically longer. As shown in the X-ray crystallographic data, the Si-Ge bond is slightly longer than the Ge-Ge bond by 0.054 Å. Such a difference in two bond lengths can be reproduced well at 0.044 Å by computation. In addition, the Ge-Ge-Si bond angle was predicted fairly well at 88.8º with the deviation of 3.2 from the experiment data.

Table 1. Structural parameters in **2.3**

	Ge-Ge (Å)	Si-Ge (Å)	Si-Ge-Ge (°)
Expt	2.3518(16)	2.406(2)	91.95(6)
PBE vdW-DF[a]	2.418	2.462	88.8

[a] VASP calculations with vdW corrections, all atomic positions in the unit cell were relaxed.

Table 2. Selected QTAIM data of E-E bond (E = Si, Ge) at B3PW91/TZVP level of theory

	Delocalization index (DI)	ρ_{BCP} (a.u.)[c]	$\nabla^2\rho_{BCP}$ (a.u.)[d]	ε_{BCP} (λ_1/λ_2)[e]
Compound **2.3**[a]	Ge-Ge: 1.679 Ge-Si: 1.017	Ge-Ge:0.0717 Ge-Si: 0.0701	Ge-Ge:-0.00633 Ge-Si: -0.0104	Ge-Ge: 0.191 Ge-Si: 0.0729
$H_2Ge=GeH_2$[b]	1.821	0.0942	-0.0340	0.243
$H_3Ge\text{-}GeH_3$[b]	1.089	0.0818	-0.0465	1.42×10^{-5}
$H_2Si=GeH_2$[b]	1.835	0.1028	-0.120	0.623
$H_3Si\text{-}GeH_3$[b]	1.065	0.0903	-0.122	1.19×10^{-5}

[a] Geometry optimization was performed at PBE-vdW-DF in the crystalline solid of **2.3**; [b] Geometry optimizations were performed at B3PW91/6-31+G(d,p) level of theory; [c] electronic density at the (3,-1) bond critical point (BCP); [d] Laplacian of electron density at the (3,-1) BCP; [e] ellipticity (ε) at the (3,-1) BCP. λ_1, λ_2 and λ_3 are the eigenvalues of the Laplacian tensor of electron density, with $\lambda_1 < \lambda_2 < \lambda_3$

2.5 References

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CHAPTER 3

Coordination Chemistry of an N-heterocyclic Silylene toward *p*- and *d*-Block Element Halides

3.1 Introdution

N-heterocyclic Carbenes (NHCs) are able to coordinate with *p*- and *d*-block element halides because of the lone pair electrons on the carbenic carbon. In contrast to NHCs, the substitution of one electronegative and π-donating N atom by a less electronegative C atom makes cAACs (Cyclic (alkyl)(amino)carbenes) become both stronger π-acceptors and σ-donors,

along with lower LUMO and higher HOMO energy level. Due to the smaller energy gap between HOMO and LUMO, cAACs display different reactvity in comparison with NHCs.

One decade ago, NHC-BBr_3 was isolated by simply treating NHC with BBr_3 **(Scheme 3.1)**. It was then reduced by potassium graphite in ethereal solvents to form species containing boron-boron single or double bond.[1] Following the pioneering work, Braunschweig and coworkers isolated the NHC-stabilized tetrahalodiborane complex by the reaction of B_2Br_4 and two equivalents of NHC.

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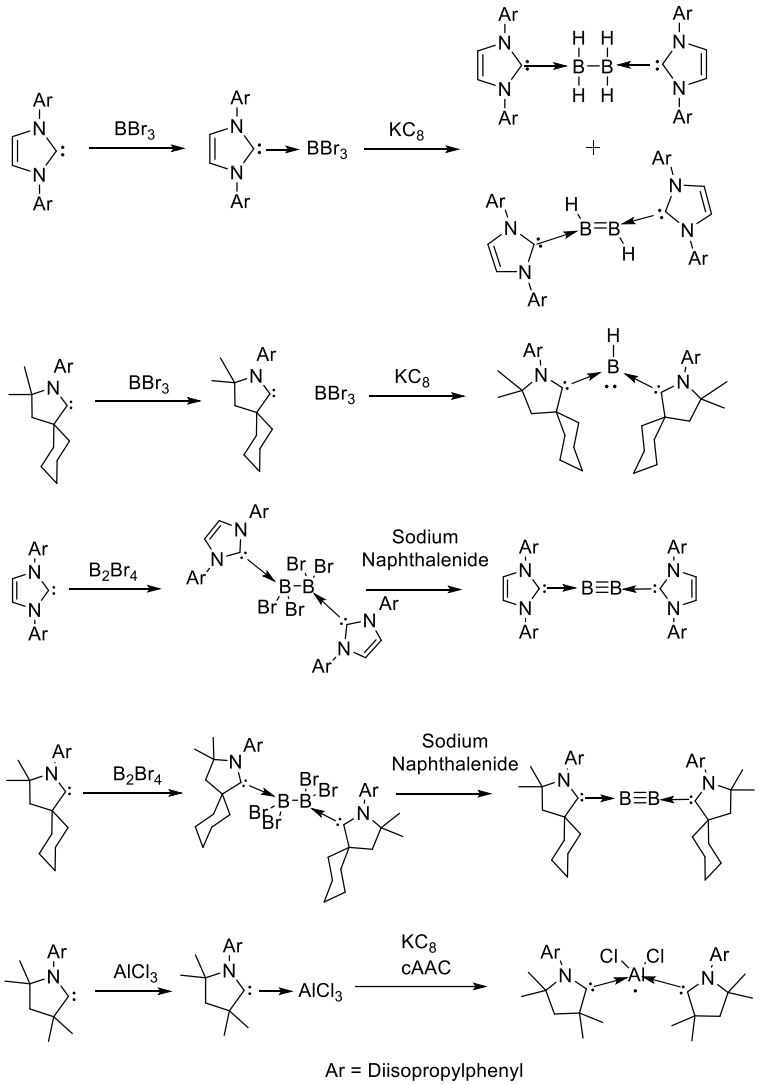
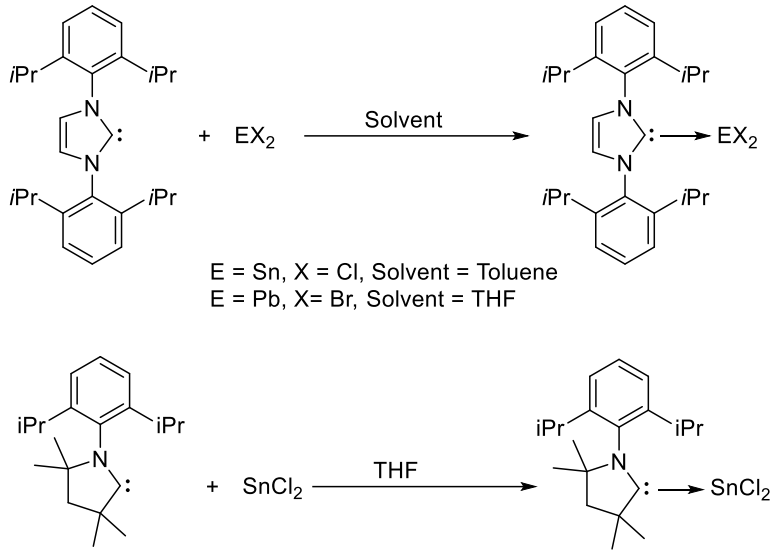
Replacing NHCs by cAACs, the similar adducts cAAC-BBr_3 and cAAC-B_2Br_4-cAAC were also isolated **(Scheme 3.1)**. They were also reduced to form NHC- and cAAC-stabilized low valent boron species.[1] In comparison with boron, cAAC-aluminum trichloride complex was isolated by Roesky et al. very recently. Its reduction with excess KC_8 and cAAC generated a stable cAAC-centered radical in the coordination sphere of aluminum **(Scheme 3.1)**.[1]



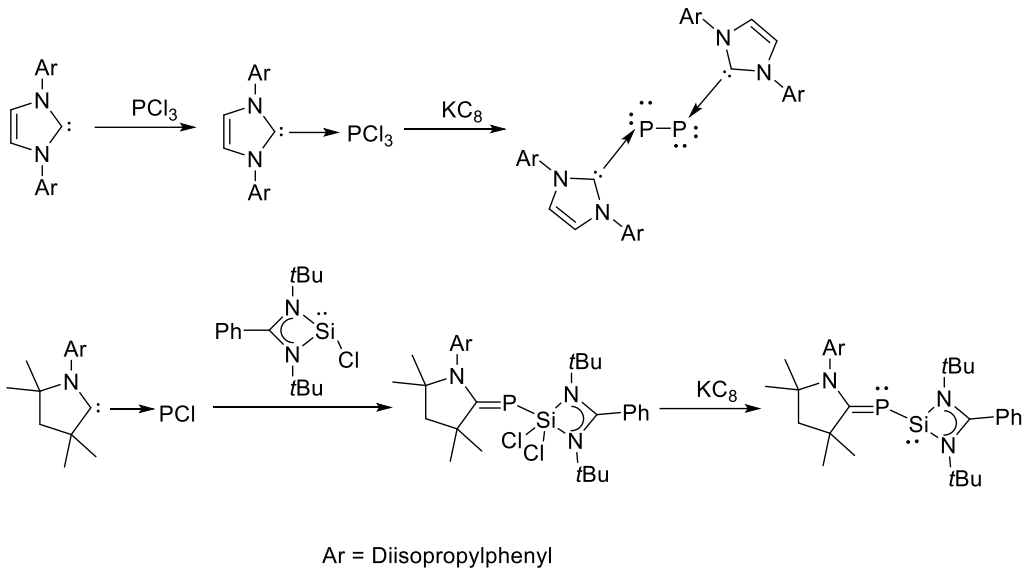
Scheme 3.1: The preparation of NHC- and cAAC- stabilized boron, aluminum compounds

Research groups of Jones and Rivard reported the utilization of NHC to coordinate with $SnCl_2$ and $PbBr_2$ to form the corresponding adducts **(Scheme 3.2)**[2]. In addition, the NHC-$SnCl_2$ was reduced by the magnesium(I) dimer to generate the NHC-stabilized diatomic tin(0) complex, while similar reduction of the lead analogue led to decomposition. When NHC was replaced by cAAC, Roesky et al. successfully prepared the first cAAC-dichlorostannylene complex **(Scheme 3.2)**.[2]



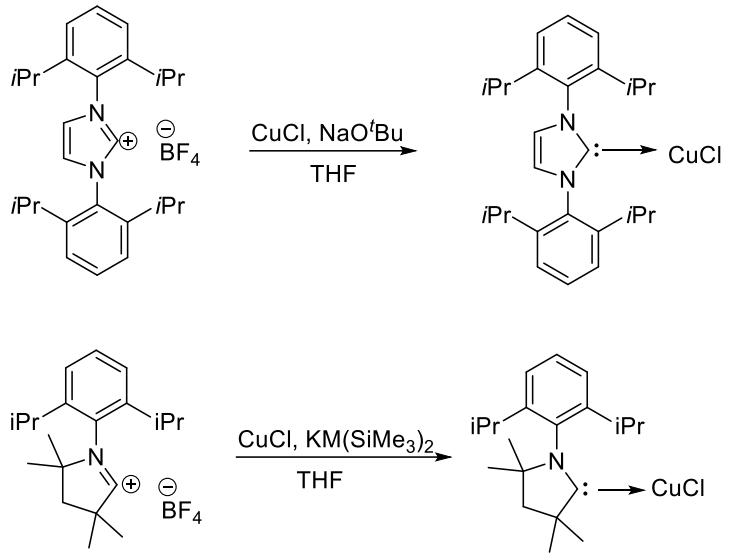
Scheme 3.2: The synthesis of NHC- and cAAC- stabilized tin, lead compounds

The reaction of phosphorus trichloride with NHC was also studied, NHC→PCl_3 was synthesized by treating NHC with PCl_3 **(Scheme 3.3)**, followed by reduction with potassium graphite to afford the NHC-diphosphorus(0) complex [NHC→P-P←NHC] (NHC = :C{N(2,6-diisopropylphenyl)CH}$_2$ or :C{N(2,4,6-trimethylphenyl)CH}$_2$).[3] In contrast, the cAAC-phosphinidene complex [cAAC(PCl)] was synthesized by the reaction of the cAAC with PCl_3. Its reactivity with the amidinato chlorosilylene resulted in an insertion product **(Scheme 3.3)**.[3]

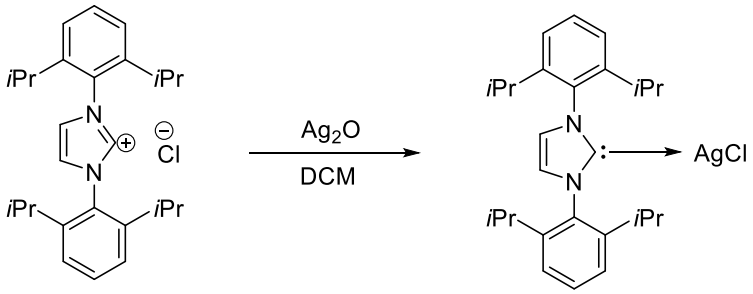


Scheme 3.3: The preparation of NHC- and cAAC-stabilized phosphorous compounds

Apart from the main group element species, both NHCs and cAACs were utilized to coordinate with transition metal species. A series of such compounds were synthesized and some of them were applied as a catalyst in organic transformation.[4] Among NHC- and cAAC-transition metal complexes, cAAC- and NHC-group 11 metal complexes were well studied. The NHC→CuCl complex was obtained with the reaction between an imidazolium salt, sodium tert-butoxide and copper chloride,[5] while the cAAC→CuCl complex was isolated by the reaction between iminium salt, potassium hexamethyldisilazide and copper(I) chloride **(Scheme 3.4)**. In addition, the NHC- or cAAC-silver(I) and gold(I) complexes were synthesized **(Scheme 3.5)**.[6] Moreover, the cAAC-copper(0) and gold(0) complexes were synthesized.[7]



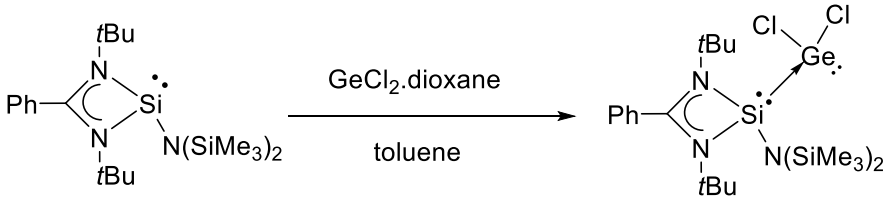
Scheme 3.4: The synthesis of NHC- and cAAC-copper chloride complexes



Scheme 3.5: The synthesis of NHC-silver chloride complex

Stable N-heterocyclic silylenes (NHSis) of composition [L_2Si:] (L = ligand) have attracted much attention in the past two decades due to their unique structures and reactivities.[8] They comprise a lone pair of electrons and vacant p orbital on the low valent silicon atoms. Their electronic structures enable NHSis being both donor and acceptor. As such, it is

capable of being an ancillary ligand and activating small molecules[8]. In recent years, several research groups utilized NHSis to coordinate with transition metal complexes.[9] The resulting complexes were catalytic intermediates or able to catalyse organic transformations.[10-14] In contrast, NHSi-EX_n (E = *p*- or *d*-block element, X = halides) adducts are rare. In the previous chapter, we report the synthesis of the amidinato silylene-germylene adduct [L{$(Me_3Si)_2N$}Si→$GeCl_2$] (L = PhC(N*t*Bu)$_2$) by coordinating the corresponding silylene with $GeCl_2$·dioxane **(Scheme 3.6)**.[15] Herein, we reported more examples of N-heterocyclic silylene-*p*- and *d*-block element halide complexes.

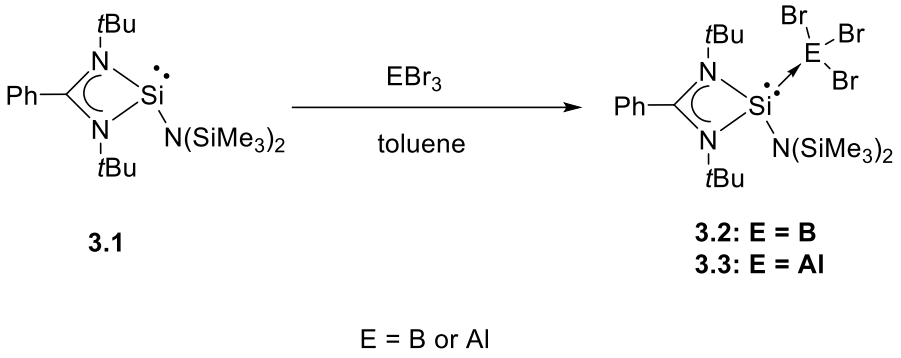


Scheme 3.6: The synthesis of NHSi- stabilized germylene adduct

3.2 Results and Discussion

The stirring of the amidosilylene [LSiN$(SiMe_3)_2$] (**3.1**) with BBr_3 and $AlBr_3$ at ambient temperature in toluene overnight formed pink and yellow suspensions, respectively. The reaction was filtered and concentrated to form the adduct of [L{$(Me_3Si)_2N$}Si→BBr_3] **(3.2)** and [L{$(Me_3Si)_2N$}Si→$AlBr_3$] **(3.3)** in good

yield **(Scheme 3.7)**, respectively. They are moisture- and air- sensitive; stable in THF and toluene; stable as solid in the glovebox. Compound **3.2** can be prepared quantitatively using hexane as the solvent. Both compounds **3.2** and **3.3** were fully characterized by X-ray crystallography and NMR spectra.



3.1

3.2: E = B
3.3: E = Al

E = B or Al

Scheme 3.7: The synthesis of compounds **3.2** and **3.3**

The ^{1}H NMR specta of compounds **3.2** and **3.3** display each set of signals of the amidinate ligands and $SiMe_3$ parts. The ^{29}Si NMR signals of compounds **3.2** (δ 9.5 ppm) and **3.3** (δ 24.2 ppm) are downfield compared to that of compound **3.1**, which indicate the electrons lone pair are donated from the Si centre to the boron and aluminum centers.[1] The ^{29}Si NMR resonances are in the low field area similar to the ^{29}Si NMR signal of the NHSi-BH_3 complexes [{PhC(N*t*Bu)$_2$}(C_5Me_5)Si(BH_3)] (δ 78 ppm) and [{PhC(N*t*Bu)$_2$}SiH(BH_3)] (δ 54.3 ppm).[16] The ^{11}B NMR resonance (δ -13.2 ppm) of compound **3.2** is intermediate between that of the [NHC→BBr_3] (NHC = :C{N(2,6-diisopropylphenyl)CH}$_2$) (δ -16.5 ppm) and [cAAC→BBr_3] (cAAC = :C{C(cy-hexyl)}(CH_2)(CMe_2)NAr, cy-hexyl =

cyclohexyl)) (δ 14.1 ppm). The ^{27}Al NMR signal (δ 88 ppm) of compound **3.3** is in agreement with the bis(amidinato)silylene-triphenylalane adduct [{(Ph)C(N*i*Pr)$_2$}$_2$Si→AlPh$_3$] (δ 134 ppm).[17]

The X-ray structures of compounds **3.2** (**Figure 3.1**) and **3.3** (**Figure 3.2)** show that the Si(II) centers are bonded to atoms N1 and N2 of the amidinate and atom N3 of the amido substituent. They are also coordinated to the boron or aluminum center, which adopts a tetrahedral geometry. The Si-B bond length (2.048(9) Å) is consistent with the NHSi-borane adducts [{PhC(N*t*Bu)$_2$}(H)Si(BH$_3$)] (1.9624(5) Å) and [{(Ph)C(N*i*Pr)$_2$}$_2$Si-BPh$_3$] (2.068(3) Å).[16,17] The Si-Al (2.4881(12) Å) bond length is also comparable with the NHSi-triphenylalane adducts [{PhC(N*i*Pr)$_2$}$_2$SiAlPh$_3$] (2.5293(14)Å).[17] Both the B and Al centers adopt a distorted tetrahedral.

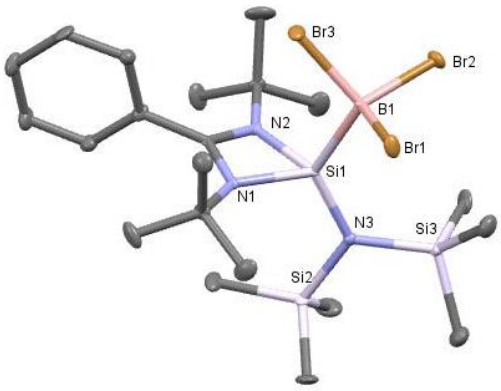


Figure 3.1. X-ray structure of adduct **3.2** (ellipsoids set at 30% probability). Hydrogen atoms are elided: B1-Si1 2.048(9), N1-Si1 1.817(7), Si1-N2 1.817(7), N3-Si1 1.716(7), Br3-B1-Br2 106.5(4), Br3-B1-Br1 107.5(5), Br2-B1-Br1 110.3(4), Br1-B1-

Si1 110.6(4), Br2-B1-Si1 113.2(5), Br3-B1-Si1 108.4(4), B1-Si1-N1 107.1(4), B1-Si1-N2 108.7(4), B1-Si1-N3 124.9(4), N1-Si1-N3 116.7(3), N3-Si1-N2 115.2(4), N2-Si1-N1 72.0(3).

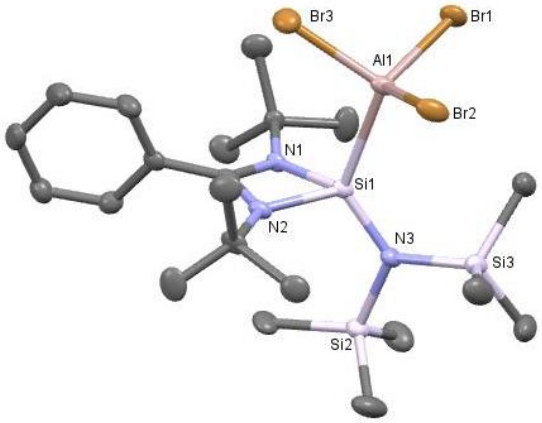
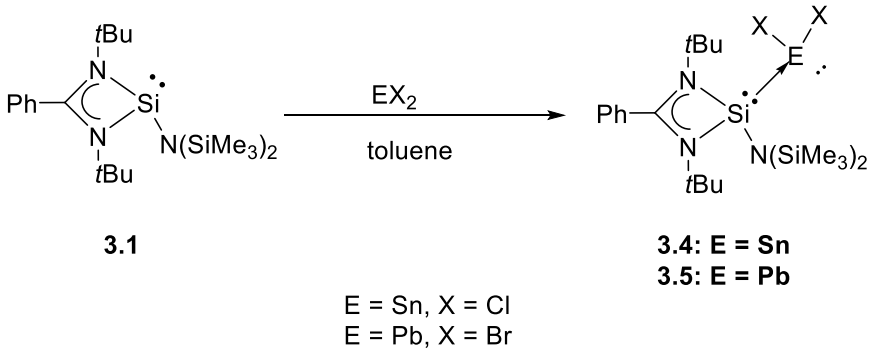


Figure 3.2. X-ray structure of adduct **3.3** (ellipsoids set at 30% probability). Hydrogen atoms are elided: Si1-N2 1.829(2), Al1-Si1 2.4881(12), N1-Si1 1.829(2), N3-Si1 1.710(3), Br3-Al1-Br2 108.42(4), Br3-Al1-Br1 104.75(4), Br2-Al1-Br1 110.01(4), Br1-Al1-Si1 115.54(4), Br2-Al1-Si1 111.92(4), Br3-Al1-Si1 105.63(4), Al1-Si1-N1 106.71(8), Al1-Si1-N2 106.05(8), Al1-Si1-N3 126.79(9), N2-Si1-N1 71.80(10), N3-Si1-N1 116.56(11), N2-Si1-N3 115.54(11).

The reaction of the amidinato silicon(II) amide [LSiN($SiMe_3$)$_2$] (**3.1**) with $SnCl_2$ in toluene at room temperature for 16 hours afforded a brown reaction suspension. It was filtered to remove unreacted $SnCl_2$ and the filtrate was concentrated to afford the amidinato silylene-dichlorostannylene adduct [L{(Me_3Si)$_2$N}$SiSnCl_2$] **(3.4)** as air- and moisture-sensitive colorless crystals in moderate yield **(Scheme 3.8)**. The

colorless crystals are soluble in toluene and THF. They are stable in solution and the solid state. Similar reaction conditions were used in the reaction of **3.1** with $PbBr_2$ to afford the amidinato silylene-dibromoplumbylene adduct $[L\{(Me_3Si)_2N\}SiPbBr_2]$ **(3.5)** as air- and moisture-sensitive colorless crystals in low yield (36.4%), which are soluble in toluene and THF **(Scheme 3.8)**. However, they are not stable in solution and decompose to give black precipitate within two days. Freshly prepared solution of compound **3.4** is essential for NMR spectroscopy. The electronic structures of **3.4** and **3.5** were elucidated by NMR spectroscopy and X-ray crystallography.



Scheme 3.8: The synthesis of compounds **3.4** and **3.5**

The ^{1}H NMR spectra of **3.4** and **3.5** display one set of resonances due to the amidinate ligands and $SiMe_3$ substituents. Their ^{29}Si NMR resonances for the Si(II) atom (**3.4**: δ 25.6 ppm, **3.5**: δ 10.3 ppm) show a downfield shift compared with that of **3.1** (δ - 8.07 ppm) as the lone pair electrons on the Si(II) centres are donated to the vacant orbitals on the Sn(II) and Pb(II)

atoms. The ^{29}Si NMR resonances illustrate the Lewis acidity of the $PbBr_2$ moiety in **3.5** being weaker than the $SnCl_2$ moiety in **3.4**. Similar observation can be found in the ^{13}C NMR signal for the $C_{carbene}$ atom of the NHC-tetrylene adducts [$I_{Ar}EX_2$] (E = Sn, X = Cl, δ 184.2 ppm; E = Pb, X = Br, δ 218.9 ppm),[2] in which the upfield ^{13}C NMR signal of [$I_{Ar}SnCl_2$] indicates $SnCl_2$ being more Lewis acidic than $PbBr_2$. In addition, the ^{29}Si NMR resonances for the Si(II) atom in **3.4** and **3.5** are downfield shifted in comparison with that of the NHC and tungsten-stabilized heavier ethylene analogue [$I_{Ar}Si(H)_2Sn(H)_2W(CO)_5$] (δ -91.1 ppm).[18] Moreover, compound **3.4** has a downfield ^{119}Sn NMR resonance (δ 77.2 ppm) compared with that of the NHC-dichlorostannylene adduct [$I_{Ar}SnCl_2$] (δ -68.7 ppm),[2] which indicates that the amidinato silylene [L{$(Me_3Si)_2N$}Si:] is a weaker Lewis base compared with the N-heterocyclic carbene I_{Ar}. Besides, the ^{119}Sn NMR signal of **3.4** is up-field shifted in comparison with that of the silastannene [(tBu$_2$MeSi)$_2$Si=SnTip$_2$] (+516.7 ppm, Tip = 2,4,6-triisopropylphenyl)[19] and of compounds comprising sp^2 Sn atoms (above +400 ppm).[20] Hence, the ^{119}Sn NMR signals imply that compound **3.4** is not a silastannene. Furthermore, the ^{207}Pb NMR spectrum of **3.5** displays a signal at δ 2866 ppm, which is an intermediate value between those of the base-stabilized low valent lead complexes [Pb{$C(SiMe_3)_2(SiMe_2OMe)$}Cl]$_2$ (δ 4249 ppm)[21] and [2,6-$(HCNAr)_2C_6H_3Pb]_2$ (δ 1684 ppm).[22]

The X-ray crystal structures of **3.4** (**Figures 3.3**) and **3.5** (**Figures 3.4**) show that the amidinate ligands are bidentate coordinated to the Si1 atoms. The latter also coordinate to the N3 atoms of the amido substituents and the E1 (E = Sn, Pb) atoms to adopt a tetrahedral geometry. The E1 atoms display a distorted trigonal pyramidal geometry (the sum of bond angles of Sn: 281.6; Pb: 283.3°), which indicate the presence of a lone pair at the group 14 elements E. The Si1-Sn1 bond (2.7325(18) Å) in **3.4** is significantly longer than typical Si-Sn single bonds (2.60 Å),[8] the Si-Sn bond in the NHC and tungsten-stabilized heavier ethylene analogue [$I_{Ar}Si(H)_2Sn(H)_2W(CO)_5$] (2.5808(5) Å)[18] and the Si=Sn double bond in the silastannene [(tBu$_2$MeSi)$_2$Si=SnTip$_2$] (2.4188(14) Å).[19] Similarly, the Si1-Pb1 bond (2.8051(13) Å) in **3.5** is significantly longer than the Si-Pb single bonds in the tris(trimethylsilyl)silyllead [{(Me$_3$Si)$_3$Si}Pb(Ph)$_2$]$_2$ (2.648(2) Å) and the Si-Pb(II) bond in the bis(hypersilyl)plumbylene [{(Me$_3$Si)$_3$Si}$_2$Pb:] (2.700(3), 2.704(3) Å).[23]

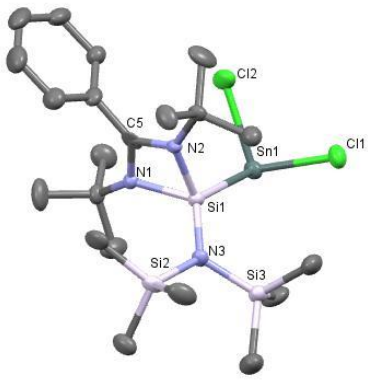


Figure 3.3. Molecular structure of compound **3.4** (ellipsoids set at 50% probability). There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-Sn1 2.7325(18), Si1-N1 1.829(5), Si1-N2 1.818(5), Si1-N3 1.708(5); Cl1-Sn1-Cl2 94.04(7), Cl1-Sn1-Si1 98.57(6), Cl2-Sn1-Si1 88.98(6), Sn1-Si1-N1 100.81(17), Sn1-Si1-N2 114.97(17), Sn1-Si1-N3 125.21(19), N1-Si1-N2 72.4(2), N1-Si1-N3 115.1(3), N2-Si1-N3 114.6(2).

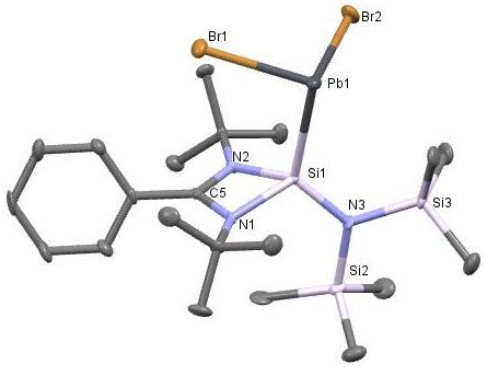


Figure 3.4. Molecular structure of compound **3.5** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-Pb1 2.8051(13), Si1-N1 1.829(4), Si1-N2 1.839(4), Si1-N3 1.707(4); Br1-Pb1-Br2 96.847(18), Br1-Pb1-Si1 93.61(3), Br2-Pb1-Si1 92.85(3), Pb1-Si1-N1 107.62(13), Pb1-Si1-N2 112.69(12), Pb1-Si1-N3 123.32(13), N1-Si1-N2 71.65(17), N1-Si1-N3 113.52(18), N2-Si1-N3 116.13(19).

DFT analyses at the B3PW91/M06-2X level of theory were carried out for compounds **3.4** and **3.5** for understanding the bonding situations between the tetrylenes. A donor-acceptor interaction from the Si(II) centre to the E(II) centre (**3.4**: E = Sn; **3.5**: E = Pb) is shown in the HOMO of each complex (**Figure 3.5 and 3.6**), where it also shows the lone pair orbital on the E(II) (E = Sn, Pb) centre. Accordingly, the NBO analyses show that the Si→E: bonds (**3.4**: E= Sn; **3.5**: E = Pb) are highly polarized (**Table 3.1**) and formed by the overlapping of the sp^2 hybridized lone pair orbitals on the Si(II) atoms (**3.4**: $sp^{2.13}$; **3.5**: $sp^{2.13}$) with the vacant p orbitals on the Sn(II) and Pb(II) atoms, respectively. The lone pair orbitals on the Sn and Pb centres in **3.4** and **3.5** are rich in s-character with some directionality (**3.4**: $sp^{0.17}$; **3.5**: $sp^{0.09}$). In addition, the group charges on the $SnCl_2$ (-0.40 e) and $PbBr_2$ moieties (-0.38 e) in **3.4** and **3.5** indicate a net charge flow from the amidinato silylenes [L{$(Me_3Si)_2N$}Si:] to them. Consequently, the Wiberg bond indices (WBI) show that the Si-E bonds are labile (WBI of **3.4**: 0.70 and **3.5**: 0.68) and their donor-acceptor bond strengths decrease from Sn to Pb. Moreover, the bond dissociation energies (**3.4**: 43.9, **3.5**: 42.0 kcal/mol) of [L{$(Me_3Si)_2N$}$SiEX_2$] into [L{$(Me_3Si)_2N$}Si:] and EX_2 (**3.4**: E = Sn, X = Cl; **3.5**: E = Pb, X = Br) are consistent with the WBI and smaller than the bond dissociation energies of H_3Si-EH_3 into $H_3Si^{\bullet}$ and $H_3E^{\bullet}$ (E = Sn, 68.3 kcal/mol; E = Pb, 62.0 kcal/mol).

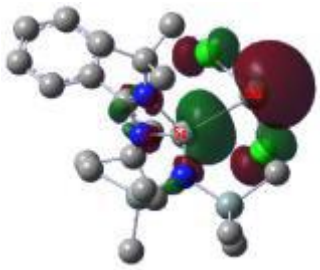


Figure 3.5. HOMO of calculated compound **3.4** showing the donor−acceptor interaction between the Si(II) and Sn(II) centres (isovalue = 0.04).

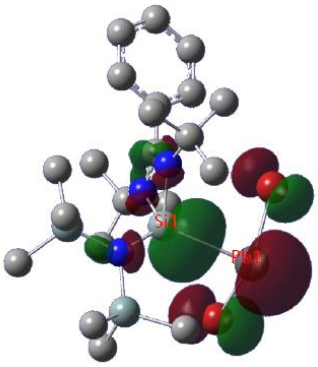


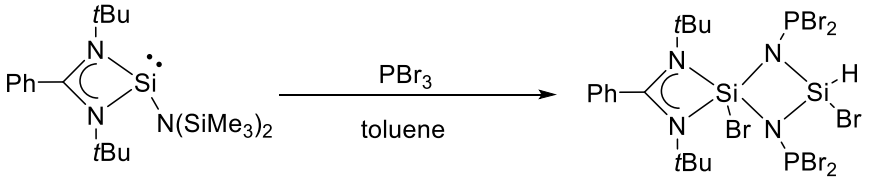
Figure 3.6. HOMO of calculated compound **3.5** showing the donor−acceptor interaction between the Si(II) and Sn(II) centres (isovalue = 0.04)

Table 3.1. NBO analysis of the donor−acceptor Si→E: (E = Sn, Pb) interactions in calculated compounds **3.4** and **3.5**

Bond	Atom	NPA charge	Polarization (%)	s-character (%)	p-character (%)	d-character (%)	Wiberg bond index
Si-Sn: in **3.4**	Si Sn	1.494 0.902	74.17 25.83	31.87 5.76	67.96 93.60	0.17 0.65	0.699
Si-Pb: in **3.5**	Si Pb	1.486 0.869	74.87 25.13	31.87 4.30	67.99 95.50	0.13 0.20	0.678

On the basis of NMR spectroscopic, X-ray crystallographic and theoretical data, the Si-E bonding situation in **3.4** and **3.5** should be described as donor-acceptor single bonds and there are lone pairs of electrons on the Sn and Pb centres.

The reactivity of **3.1** toward trihalophosphane was further investigated. Phosphorus tribromide was dripped to a toluene solution of [LSiN(SiMe$_3$)$_2$] (**3.1**) at ambient temperature. The orange reaction mixtures were stirred overnight and then filtered, compound **3.6** was formed as a colorless crystal upon the removal of solvent (**Scheme 3.9**). Different from the simple carbene adducts [NHC→PCl$_3$] (NHC = :C{N(2,6-diisopropylphenyl)CH}$_2$) and cAAC→PCl (cAAC = :C{CMe$_2$(CH$_2$)(CMe$_2$)NAr),[3] an unexpected Si$_2$N$_2$ four-membered ring was formed in the reaction and the mechanism for its formation is still unkown. Compound **3.6** is moisture- and air- sensitive, but it is stable as solid under argon. It is also stable in solution.



3.1 **3.6**

Scheme 3.9: The synthesis of compound **3.6**

One ^{1}H NMR signal set for the amidinate can be observed in compound **3.6**. The ^{29}Si NMR resonance (δ -122.7 ppm) for the five-coordinate Si centre is comparable to that of $[LSi(Cl)\{N_2CH(SiMe_3)\}]_2$ (δ = −70.2 ppm).[24]

Its x-ray structure is displayed in **Figure 3.7**. The core part of compound **3.6** is the Si_2N_2 unit in which the Si1 atom adopts a geometryof trigonal bipyramidal. The N3 and N2 are in the equatorial orientation with respect to the Si1 atom, while the N4 and N1 are in the axial orientation with respect to the Si1. The bond lengths of Si-N due to the equatorial N atoms are 1.837(4) (Si1-N3) and 1.901(4) Å (Si1-N2). They are longer than the N-Si bond lengths due to the axial N atoms (1.795(4), 1.796(3) Å).[25] The bond lengths of P2-N4 (1.671(4) Å) and P1-N3 (1.665(3) Å) are within the range of P-N single bonds.[26]

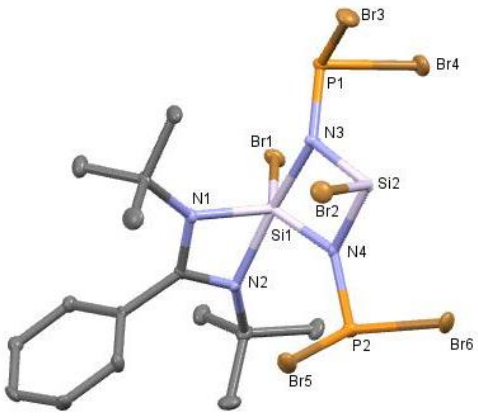
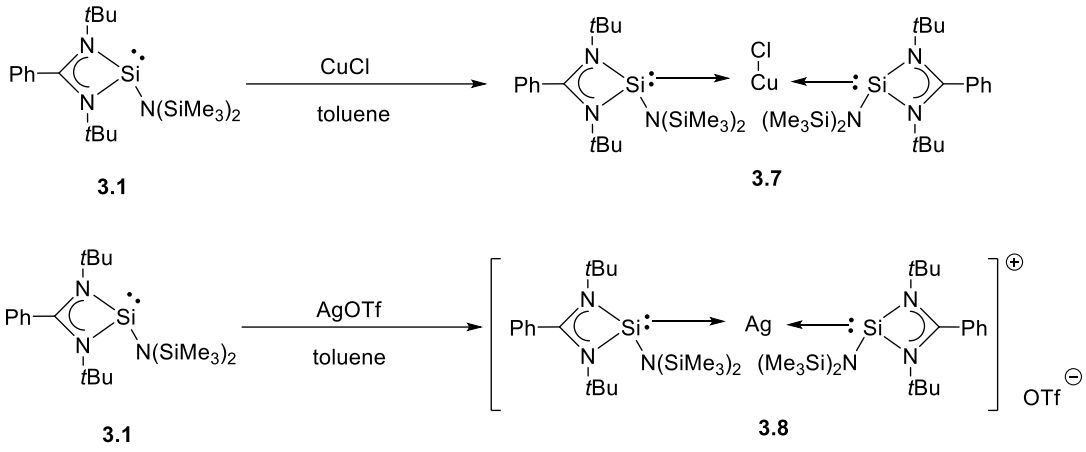


Figure 3.7. X-ray structure of compound **3.6** (ellipsoids set at 50% probability). Hydrogen atoms are elided: Si1-N2 1.901(4), N1-Si1 1.795(4), N4-Si1 1.796(3), Si1-

Br1 2.2592(15), N3-Si1 1.837(4), P1-N3 1.665(3), P2-N4 1.671(4), N4-Si2 1.731(4), N3-Si2 1.700(3); N2-Si1-N1 71.43(16), N1-Si1-Br1 110.84(12), N3-Si1-N4 78.34(16), N3-Si1-Br1 93.64(12), Si1-N3-SI2 98.61(17), Si1-N4-SI2 99.07(17), N3-Si2-N4 83.93(16), Br2-Si2-N3 103.89(14), Si1-N3-P1 128.3(2), Si2-N3-P1 126.5(2), N3-P1-Br3 99.89(13).

The reactivity of **3.1** toward group 11 metals was studied. The reaction between two equivalents of [LSiN(SiMe$_3$)$_2$] **(3.1)** and CuCl at ambient temperature overnight formed the bis(NHSi)-chlorocopper(I) adduct [L{(Me$_3$Si)$_2$N}Si]$_2$CuCl **(3.7)**. It was obtained as a moisture- and air-sensitive colorless crystal (**Scheme 3.10**). Similar product [L{(Me$_3$Si)$_2$N}Si]$_2$Ag$^+$OTf$^-$ **(3.8)** was obtained as colorless crystals by the reaction between AgOTf and two equivalents of compound **3.1** in toluene (**Scheme 3.10**). Complex **3.7** is quite stable in toluene and THF. It can be stored as solid under inert gas. However, complex **3.8** is highly unstable in the solid state and it decomposes to black precipitate within one day. Compound **3.8** is also sensitive to light and free sliver was afforded when exposed to light. Both compounds **3.7** and **3.8** were fully characterized with X-ray crystallography and NMR.



Scheme 3.10: The synthesis of compound **3.7** and **3.8**

The ^{1}H NMR signals of **3.7** and **3.8** display one set of resonances because of the amidinate and $SiMe_3$ substituents. The ^{29}Si NMR signal of the Si(II) centre (δ **3.7**: 9.23, **3.8**: 10.65 ppm) displays a downfield shift in contrast to the ^{29}Si NMR of **3.1** (δ - 8.07 ppm) because of the electrons lone pair of the Si(II) atom transferred to the vacant orbitals of the metal centers. Similar ^{29}Si NMR resonance downfield shift was observed in the reaction of the NHC-disilicon(0) complex [NHC→Si=Si←NHC] (NHC = :C{N(2,6-*i*$Pr_2C_6H_3$)CH}$_2$) with CuCl to afford the NHC-stabilized disilicon-copper(I) chloride complex.[27]

The molecular structures of adducts **3.7** and **3.8** are displayed in Figures **3.8** and **3.9**. In compound **3.7**, the bidentate ligands amidinate are bound to the Si1. The latter also bound to the N3 atoms and Cu atom, which adopt a geometry of tetrahedral. The bond lengths of Cu-Si are 2.320(3) and 2.330(3) Å. They are longer than those(2.243(3), 2.250(3) Å) in [L{$(Me_3Si)_2N$}SiCu(μ-I)]$_2$.[28] The structure of compound **3.8** is resemble to compound **3.7**. The silicon centers adopt a distorted tetrahedral geometry. The bond lengths of Si-Ag are 2.4281(11) and

2.4270(11) Å, which are longer than those (2.337(3), 2.346(3) Å) in $[L\{(Me_3Si)_2N\}SiAg(\mu\text{-}OTf)]_2$, too.[28]

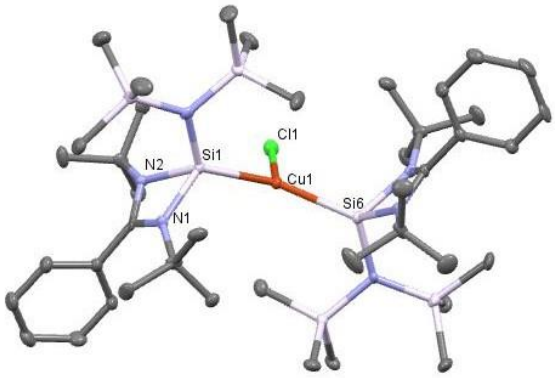


Figure 3.8. X-ray structure of adduct **3.7** (ellipsoids set at 50% probability). Hydrogen atoms are elided: Cu1-Si1 2.320(3), Si6-Cu1 2.330(3) N1-Si1 1.877(7), Si1-N2 1.877(8), N3-Si1 1.758(8); Cl1-Cu1-Si1 107.68(9), Cl1-Cu1-Si6 105.86(9), Si6-Cu1-Si1 146.46(9), Cu1-Si1-N1 119.3(3), N2-Si1-Cu1 114.3(3), Cu1-Si1-N3 123.6(3), N3-Si1-N2 108.6(3), N1-Si1-N3 108.9(4), N2-Si1-N1 69.4(3).

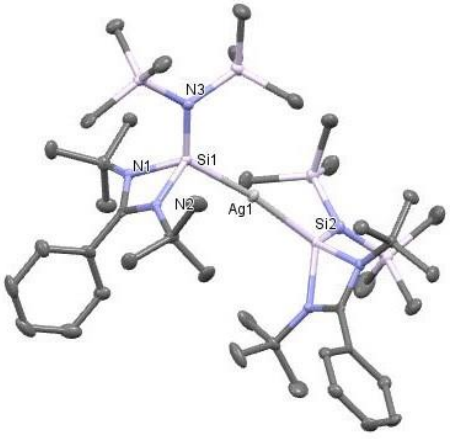


Figure 3.9. X-ray structure of adduct **3.8** (ellipsoids set at 50% probability). Hydrogen atoms are elided: Si1-Ag1 2.4281(11), Si2-Ag1 2.4270(11) N1-Si1 1.844(3), Si1-N2 1.840(3), N3-Si1 1.758(8); Si2-Ag1-Si1 172.01(3), Ag1-Si1-N1 111.91(10), Ag1-Si1-N2 109.46(10), Ag1-Si1-N3 14.54(11), N1-Si1-N2 70.97(13), N1-Si1-N3 114.17(15), N2-Si1-N3 113.40(15).

In conclusion, the amidinato amidosilylene is capable of supporting *p*- and *d*-block element halides. NMR spectroscopy, theoretical studies and X-ray crystallography show that the amidinato amidosilylene donates lone pair eletrons to the *p*- and *d*-block element halides to form adducts in the reactions. However, the reaction between the amidinato amidosilylene and PBr_3 afforded an unexpected compound with a Si_2N_2 four-membered ring.

3.3 Experimental Section

All operations were handled under argon with glovebox and standard schlenk techniques. Solvents were dried by a SPS-Mbraun-800 solvent purification system or by distillation over potassium metal. All the NMR spectra were obtained using the ECA400M JEOL and Advance III 400M spectrometer Bruker. The element analysis and melting point were done in the air. Intensity data for crystal were collected using a Bruker APEX II diffractometer. All 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. 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 calculation.

Synthesis of **3.2**. Method A: BBr_3 (1 ml, 1M in hexane) was dripped slowly to the toluene (30 mL) solution of **3.1** (0.42 g, 1.00 mmol). The resulting pink suspension was stirred overnight at room temperature. It was filtered and concentrated to form colorless crystals as compound **3.2**. Yield: 0.52 g (77.6 %). Method B: BBr_3 (1 ml, 1M in hexane) was dripped slowly to the hexane (30 mL) solution of **3.1** (0.42 g, 1.00 mmol). The resulting white mixture was reacted overnight at room temperature. The suspension was concentrated to 3 ml and then filtered, the white solid was vacuumed for a few hours to afford compound **3.2**. Yield: 0.66g (98.5%). Mp: 178.3 °C (decomposed). ^{1}H NMR (399.5 MHz, *d*-benzene, 25°C): δ = 0.40 (s, 9H, TMS), 0.74 (s, 9H, TMS), 1.27 (s, 18H, *t*Bu), 6.85-6.91 (m, 4H, Ph), 8.13-8.15 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, *d*-benzene, 25°C): δ = 3.5 (TMS), 3.9 (TMS), 35.6 (C*Me*$_3$), 54.5 (*C*Me$_3$), 127.2, 128.4, 129.6, 132.5 (Ph), 175.8 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, *d*-benzene, 25°C): δ = 7.5 (SiMe$_3$), 9.4 (*Si*N(SiMe$_3$)$_2$), 11.3 (SiMe$_3$). ^{119}B{^{1}H} NMR (128.4 MHz, C_6D_6, 25°C): δ = -13.5 ppm.

Crystallographic data for **3.2**: $C_{21}H_{41}N_3Si_3BBr_3$; M = 670.38; monoclinic *P 1 21 1*; *a* = 9.5950(6), *b* = 18.1065(10), *c* = 9.7082(6) Å; *β* = 118.253(3)°; *V* =

1485.69(16) Å^3; Z = 2; ρ_{calcd} = 1.499 mg m^{-3}; 26957 measured reflections; 292 refined parameters; 8719 independent reflections; R_1 = 0.0623, wR_2 = 0.1309 ($I > 2\sigma(I)$).

Synthesis of **3.3**. Toluene (25 mL) was transferred to the mix of **3.1** (0.84 g, 2.00 mmol) and $AlBr_3$ (0.54 g, 2.00 mmol). The brown suspension was stirred overnight at room temperature. It was filtered and concentrated to form a colorless crystal as compound **3.3**. Yield: 0.44 g (64.1 %). Mp: 196.5 °C. Elemental analysis calculated for $C_{21}H_{41}Br_3AlN_3Si_3$: C 36.71; N 6.12; H 5.97. Found: C 36.84; N 6.42; H 6.27. ^{1}H NMR (399.5 MHz, *d*-benzene, 25°C): δ = 0.28 (s, 9H, TMS), 0.64 (s, 9H, TMS), 1.23 (s, 18H, *t*Bu), 6.85-7.15 (m, 4H, Ph), 8.28-8.30 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, *d*-benzene, 25°C): δ = 5.2 (TMS), 5.9 (TMS), 32.5 (C*Me*$_3$), 56.2 (*C*Me$_3$), 126.5, 127.2, 127.8, 133.1 (Ph), 175.8 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, *d*-benzene, 25°C): δ= 8.3 (SiMe$_3$), 11.2 (SiMe$_3$), 24.2 (*Si*N(SiMe$_3$)$_2$). ^{27}Al{^{1}H} NMR (147.6 MHz, *d*-benzene, 25°C): δ = 88.3 ppm.

Crystallographic data for **3.3**: $C_{24.5}H_{45}N_3Si_3AlBr_3$; M = 732.61; monoclinic *P 1 21/n 1*; *a* = 10.0633(4), *b* = 20.1228(7), *c* = 16.5583(6) Å; *β* = 90.6614(15)°; *V* = 3352.9(2) Å^3; Z = 4; ρ_{calcd} = 1.451 mg m^{-3}; 73692 measured reflections; 387 refined parameters; 10730 independent reflections; R_1 = 0.0459, wR_2 = 0.0882 ($I > 2\sigma(I)$).

Synthesis of **3.4**. Toluene (30 mL) was added to a mixture of **1** (1.26 g, 3.00 mmol) and $SnCl_2$ (0.57 g, 3.00 mmol) at ambient temperature. The resulting brown mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of compound **3.4**. Yield: 1.01 g (55.2 %). Mp: 217.5 °C (decomposed). Elemental analysis calcd for $C_{21}H_{41}Cl_2SnN_3Si_3$: C 41.41; H 6.78; N 6.90. Found: C 41.25; H 6.56; N 6.73. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.29 (s, 9H, $SiMe_3$), 0.46 (s, 9H, $SiMe_3$), 1.22 (s, 18H, *t*Bu), 6.87-6.93 (m, 3H, Ph), 7.18-7.20 (m, 1H, Ph), 8.57-8.59 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.7 ($SiMe_3$), 5.7 ($SiMe_3$), 31.2 (C*Me*$_3$), 55.7 (*C*Me$_3$), 127.7, 128.2, 130.6, 133.4 (Ph), 171.9 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = 8.3 ($SiMe_3$), 9.5 ($SiMe_3$), 25.6 (*Si*N(SiMe$_3$)$_2$). ^{119}Sn{^{1}H} NMR (147.6 MHz, C_6D_6, 25°C): δ = 77.2 ppm.

Crystallographic data for **3.4**: $C_{28}H_{49}Cl_2N_3Si_3Sn$; M = 701.56; triclinic *P*-1; a = 10.4822(13) Å, b = 12.7267(14) Å, c = 26.832(3) Å; α =90.404(3)°, β = 90.567(3)°, γ = 102.754(3)°; V = 3490.8(7) Å^3; Z = 4; ρ_{calcd} = 1.334 g cm^{-3}; 58186 measured reflections; 17417 independent reflections; 10669 refined parameters; R_1 = 0.0773, wR_2 = 0.1655 ($I > 2\sigma(I)$).

Synthesis of **3.5**. Toluene (30 mL) was added to a mixture of **1** (1.26 g, 3.00 mmol) and $PbBr_2$ (1.10 g, 3.00 mmol) at ambient temperature. The resulting yellow mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford yellow crystals of compound **3.5**. Yield: 0.86 g (36.4%).

Mp: 143.1 °C (decomposed). Elemental analysis calcd for $C_{21}H_{41}PbBr_2N_3Si_3$: C 32.07; H 5.25; N 5.34. Found: C 31.98; H 5.11; N 5.07. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.28 (s, 9H, $SiMe_3$), 0.35 (s, 9H, $SiMe_3$), 1.24 (s, 18H, *t*Bu), 6.89-6.92 (m, 3H, Ph), 7.18-7.21 (m, 1H, Ph), 8.88-8.89 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.8 ($SiMe_3$), 5.3 ($SiMe_3$), 31.4 (C*Me*$_3$), 55.1 (*C*Me$_3$), 127.7, 129.0, 130.5 136.6 (Ph), 172.2(NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = 9.6 ($SiMe_3$), 9.7 ($SiMe_3$), 10.3 (*Si*N($SiMe_3$)$_2$) ppm. ^{207}Pb{^{1}H} NMR (82.6 MHz, C_6D_6, 25°C): δ = 2866 ppm.

Crystallographic data for **3.5**: $C_{21}H_{41}Br_2N_3PbSi_3$; M = 786.85; monoclinic *P* 1 21/*c* 1; *a* = 11.0430(8) Å, *b* = 17.9127(12) Å, *c* = 15.2372(10) Å; *α* =90°, *β* = 91.423(3)°, *γ* = 90°; *V* = 3013.1(4) Å^3; *Z* = 4; ρ_{calcd} = 1.737 g cm^{-3}; 43279 measured reflections; 7806 independent reflections; 5732 refined parameters; R_1 = 0.0404, wR_2 = 0.0760 ($I > 2\sigma(I)$).

Synthesis of **3.6**. PBr_3 (0.27g 1.00 mmol) was dripped to the toluene solution of **3.1** (0.42 g, 1.00 mmol). The resulting orange suspension was stirred overnight at room temperature. It was filtered and concentrated to form a colorless crystal as compound **3.6**. Yield: 0.19 g (22.4%). Mp: 209.1 °C. ^{1}H NMR (399.5 MHz, *d*-benzene, 25°C): δ = 1.23 (s, 18H, *t*Bu), 5.45 (s, 1H, Si*H*), 6.87-7.02 (m, 4H, Ph), 7.88-7.89 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, *d*-benzene, 25°C): δ = 4.8 ($SiMe_3$), 5.3 ($SiMe_3$), 31.4 (C*Me*$_3$), 55.1 (*C*Me$_3$), 127.7, 129.0, 130.5 136.6

(Ph), 172.2(NCN) ppm. $^{29}Si\{^{1}H\}$ NMR (79.4 MHz, *d*-benzene, 25°C): δ = -122.6 (N_2SiN_2). $^{31}P\{^{1}H\}$ NMR (82.6 MHz, *d*-benzene, 25°C): δ = 175.7 ppm.

Crystallographic data for **3.6**: $C_{15}H_{24}Br_6N_4P_2Si_3$; M = 856.95; triclinic *P -1*; a = 9.6481(3) Å, b = 10.5012(5) Å, c = 13.8120(6) Å; α =78.599(3)°, β = 79.611(3)°, γ = 79.428(3)°; V = 1333.33(10) Å^3; Z = 2; ρ_{calcd} = 2.135 g cm^{-3}; 28995 measured reflections; 268 refined parameters; 7835 independent reflections; R_1 = 0.0373, wR_2 = 0.0957 ($I > 2\sigma(I)$).

Synthesis of **3.7**. Toluene (30 mL) was transferred to the mix of **3.1** (0.84 g, 2.00 mmol) and CuCl (0.10 g, 1.00 mmol). The resulting brown suspension was stirred overnight at room temperature. It was filtered and concentrated to form a colorless crystal as compound **3.7**. Yield: 0.59 g (63.6%). Mp: 205.4 °C. H 9.29. ^{1}H NMR (399.5 MHz, *d*-benzene, 25°C): δ = 0.27 (s, 9H, TMS), 0.44 (s, 9H, TMS), 1.21 (s, 18H, *t*Bu), 6.97-7.15 (m, 4H, Ph), 7.98-8.02 (m, 1H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.5 MHz, *d*-benzene, 25°C): δ = 5.6 (TMS), 6.4 (TMS), 33.5 (CMe_3), 57.3 (CMe_3), 127.3, 128.3, 128.9, 132.9 (Ph), 176.2 (NCN) ppm. $^{29}Si\{^{1}H\}$ NMR (79.4 MHz, *d*-benzene, 25°C): δ = 4.3 ($SiMe_3$), 5.2 ($SiMe_3$), 11.6 ($SiN(SiMe_3)_2$).

Crystallographic data for **3.7**: $C_{42}H_{82}ClCuN_6Si_6$; M = 938.66; triclinic *P 1*; a = 10.2429(10) Å, b = 10.7710(10) Å, c = 13.3173(12) Å; α =89.811(3)°, β = 76.649(3)°, γ = 64.941(3)°; V = 1287.5(2) Å^3; Z = 1; ρ_{calcd} = 1.211 g cm^{-3}; 29098 measured reflections; 529 refined parameters; 13157 independent reflections; R_1 = 0.0633, wR_2 = 0.1989 ($I > 2\sigma(I)$)

Synthesis of **3.8**. Toluene (30 mL) was transferred to the mix of **3.1** (0.84 g, 2.00 mmol) and AgOTf (0.26 g, 1.00 mmol) and the flask was wrapped with aluminum foil. The resulting brown suspension was stirred overnight at room temperature. It was filtered and concentrated to form a colorless crystal as compound **3.8**. Yield: 0.28 g (25.3 %). Mp: 178.3 °C. ^{1}H NMR (399.5 MHz, *d*-benzene, 25°C): δ = 0.31 (s, 9H, TMS), 0.71 (s, 9H, TMS), 1.21 (s, 18H, *t*Bu), 7.02-7.13 (m, 4H, Ph), 7.98-8.03 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, *d*-benzene, 25°C): δ = 4.2 (TMS), 5.1 (TMS), 30.4 (C*Me*$_3$), 53.5 (*C*Me$_3$), 126.9, 128.1, 128.9, 132.8 (Ph), 176.3 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, *d*-benzene, 25°C): δ = 6.3 (SiMe$_3$), 8.3 (SiMe$_3$), 19.8 (*Si*N(SiMe$_3$)$_2$).

Crystallographic data for **3.8**: $C_{50}H_{90}F_3AgO_3SN_6Si_6$; M = 1188.74; monoclinic *P 1 21/n 1*; *a* = 14.7233(3) Å, *b* = 28.7169(9) Å, *c* = 14.8056(4) Å; *β* = 93.5268(9)°; *V* = 6248.1(3) Å^3; *Z* = 4; ρ_{calcd} = 1.264 g cm^{-3}; 88775 measured reflections; 656 refined parameters; 13624 independent reflections; R_1 = 0.0575, wR_2 = 0.1045 ($I > 2\sigma(I)$).

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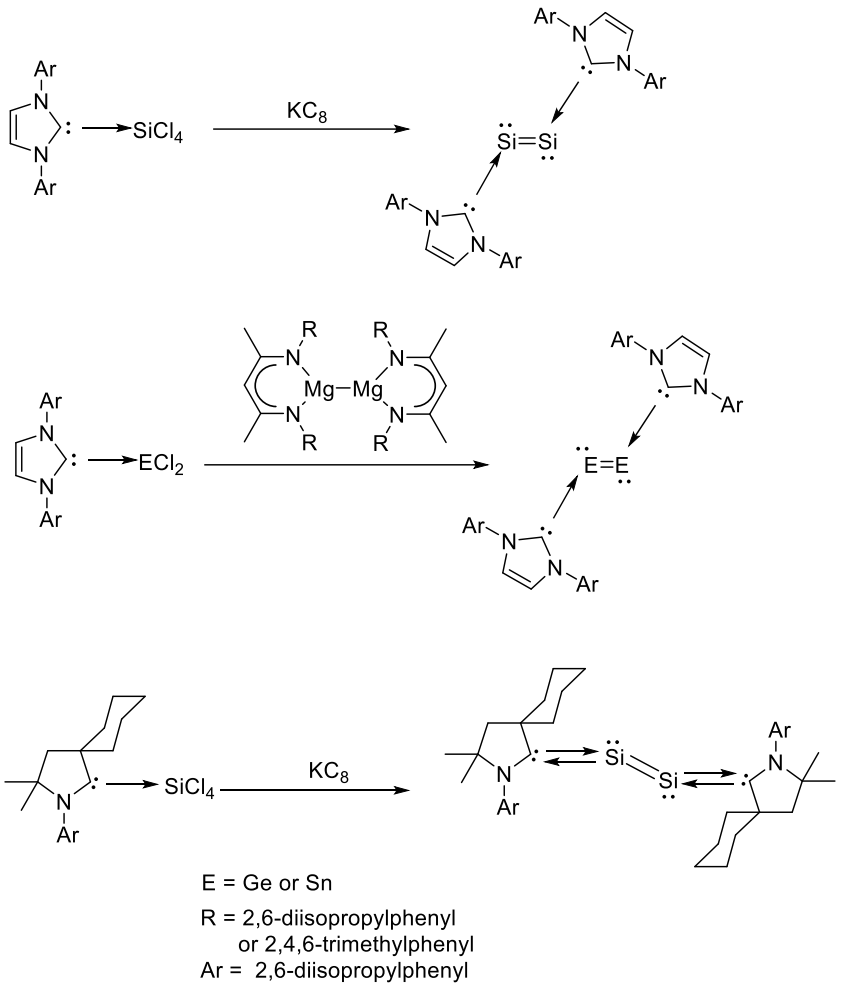
CHAPTER 4

Trapping of Small Germanium(0) Clusters: An Amidinato Bis(silylenyl)germylene-Stabilized Trigermanium(0) Complex

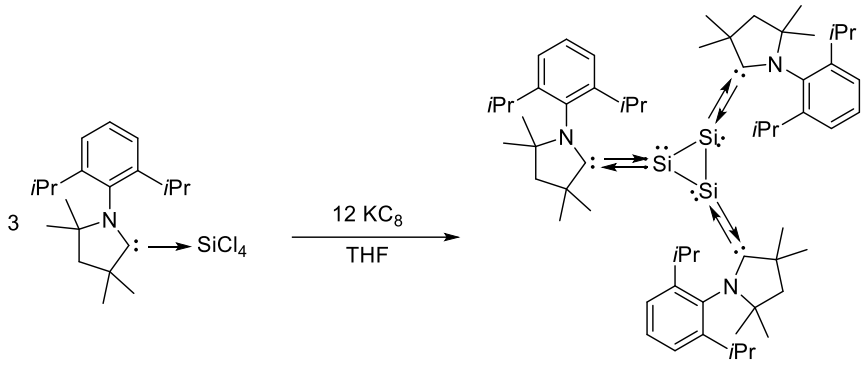
4.1 Introduction

The chemistry of small group 14 element(0) clusters is of fundamental importance as they can be considered as intermediates between the molecular and solid state of group 14 element(0).[1] However, small group 14 element(0) clusters can only be observed in the gas phase by mass spectrometry and high reactivity hampers their isolation.[2] In the past decades, several research groups tackled the difficulties and trap group 14 element(0) clusters with the aid of strong σ-donating N-heterocyclic carbenes (NHCs). Striking examples in diatomic cluster complexes, such as the NHC-disilicon(0),[3] -digermanium(0)[4] and -ditin(0)[5] complexes, [(I_{Ar})E=E(I_{Ar})] (E = Si, Ge, Sn, I_{Ar} = :C{N(Ar)CH}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) and [($cAAC_{Cy}$)Si=Si($cAAC_{Cy}$)] ($cAAC_{Me}$ = :C{C(cy-hexyl)}(CH_2)(CMe_2)NAr, cy-hexyl = cyclohexyl),[6] were synthesized by reacting the corresponding NHC-tetrachlorosilane, -dichlorogermylene and –dichlorostannylene precursors with alkali metal and the β-diketiminato magnesium(I) dimer **(Scheme 4.1)**.



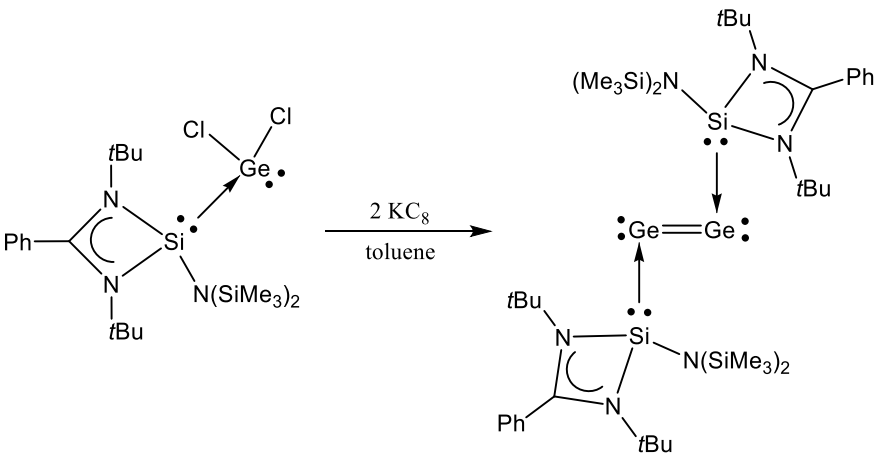
Scheme 4.1: The synthesis of the NHC, cAAC-disilicon(0), -digermanium(0) and -ditin(0)

Moreover, the remarkable trisilicon(0) complex was isolated in the form of an adduct with cAAC, $[(cAAC_{Me})Si]_3$ **(Scheme 4.2)**,[7] which comprises a triangular Si_3 moiety. The interesting structures and electronic properties of these NHC and cAAC-group 14 element(0) cluster complexes enable them to show extraordinary synthetic potential and have beneficial applications in building more complex molecules.[8]



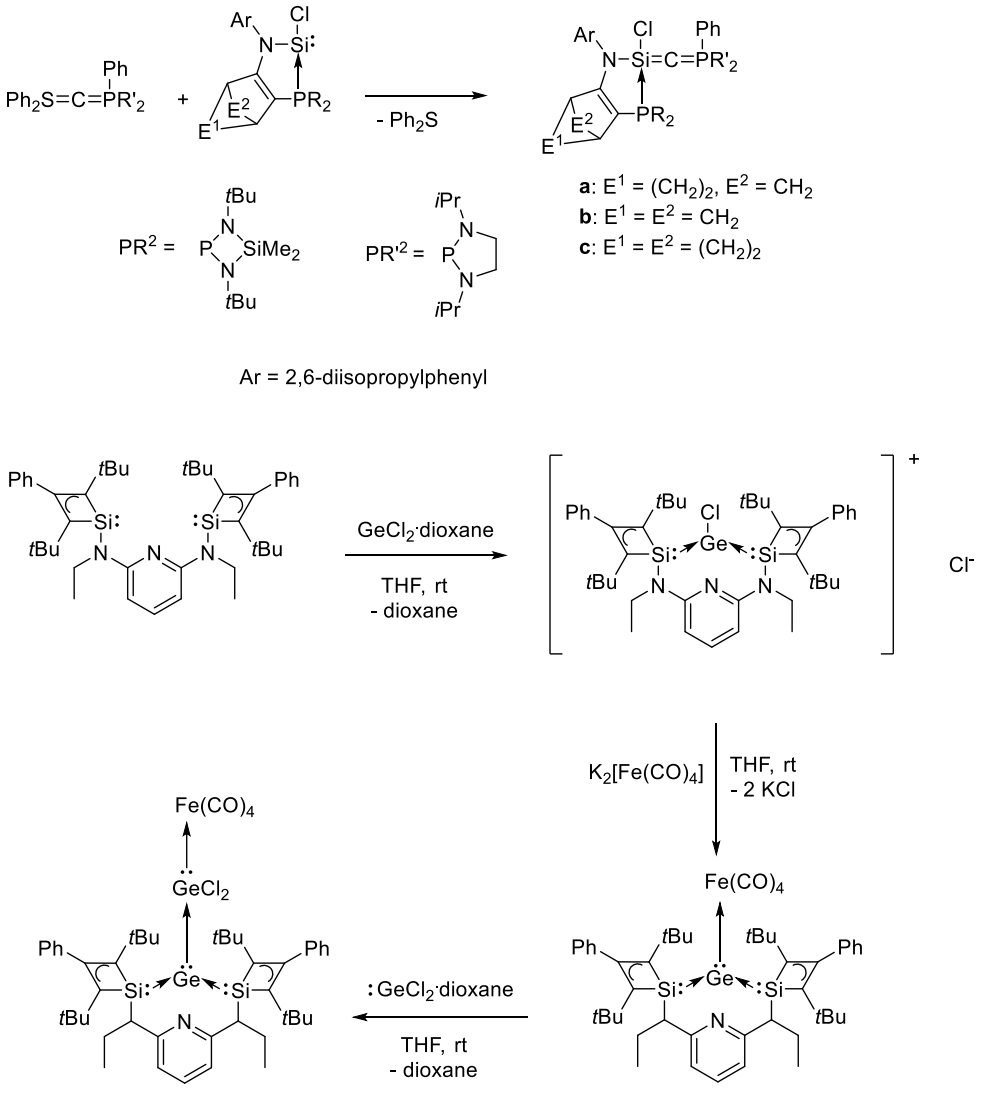
Scheme 4.2: The synthesis of the cAAC-tridisilicon(0)

The above-mentioned examples illustrate that the isolation of small group 14 element(0) clusters required thoughtful design of synthetic strategies and strong σ-donating ligands. Very recently, theoretical studies showed that some of base-stabilized silylenes and germylenes possess stronger σ-donating ability than NHCs,[9] which could be used to stabilize small group 14 element(0) clusters. Such prototypes were then evidenced by our group, we isolated a digermanium(0) cluster in the form of an adduct with base-stabilized silylenes [L{$(Me_3Si)_2N$}Si(Ge=Ge)Si{$N(SiMe_3)_2$}L] (L = $PhC(NtBu)_2$) **(Scheme 4.3)**.[10]



Scheme 4.3: The preparation of the NHSi-digermanium(0)

Besides, a base-stabilized silylene-monoatomic carbon(0)[11] and germanium(0) **(Scheme 4.4)**[12] complex were reported. It is anticipated that other unprecedented small group 14 element(0) clusters could be isolated by rational design of base-stabilized silylene and germylene ligands.

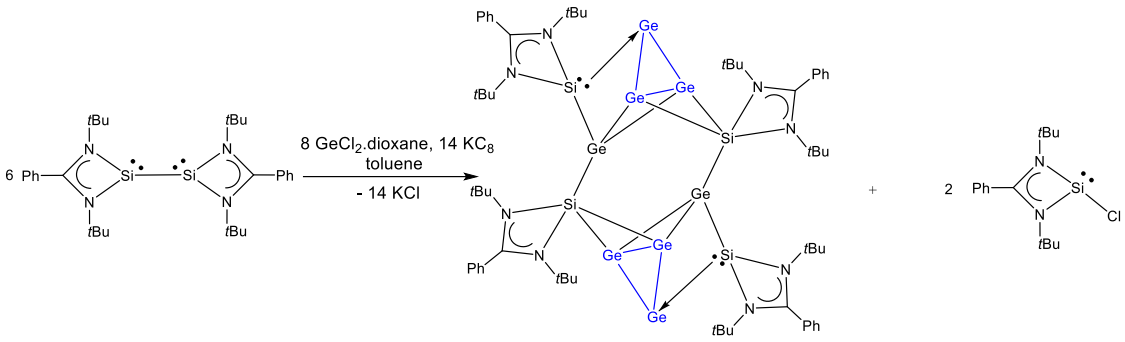


Scheme 4.4: The synthesis of the base-stabilized silylene-monoatomic carbon(0) and germanium(0)

According to recent calculation, amidinato silylene compounds are better ligands than commonly used carbene and phosphine ligands. By changing the substituent bound to the Si center, the properties of amidinato silylene compounds can be tuned to display different activities. Herein, we report the isolation of a trigermanium(0) cluster in the form of an adduct with an amidinate-stabilized bis(silylenyl)germylene. In addition, the trapping of an octagermanium(0) cluster by both dichlorogermylene and amidinate-stabilized silylene ligands is described.

4.2 **Results and Discussion**

The mix of the amidinato silicon(I) dimer $[LSi:]_2$ (**4.1**, L = $PhC(N\textit{t}Bu)_2$), $GeCl_2$ and KC_8 in a molar ratio of 3 : 4 : 7 in toluene overnight formed a dark red suspension (**Scheme 4.5**).[13] The ^1H NMR signals of the resulting mixture revealed that compound **4.1** was fully consumed. The suspension was then filtered and concentrated to afford the first dimeric bis(silylenyl)germylene-trigermanium(0) complex $[\{(LSi)_2Ge\}Ge_3]_2$ (**4.2**) as a red crystalline solid (Yield: 28.7%). The mother liquor was filtered and further concentrated to form the amidinato chlorosilylene [LSiCl] (**4.3**, Yield: 57.4 %),[14] and it was affirmed by X-ray crystallography and NMR studies.



Scheme 4.5: The synthesis of compound **4.2**

Compound **4.2** is the first complex comprising two trigermanium(0) clusters, following a previous report of the only example of the cAAC-trisilicon(0) complex $[(cAAC_{Me})Si]_3$.[7] Compound **4.2** is moisture- and air-sensitive and stable under argon. It can dissolve in THF and toluene. Its ^{1}H NMR spectrum displays a set of signals according to the different amidinate chemical environments. The ^{29}Si NMR signals of δ 9.9 and 26.4 ppm correspond to the bridging and terminal Si donors, respectively. The terminal ^{29}Si NMR signal is consistent with that of the amidinato silylene-digermanium(0) complex $[L\{(Me_3Si)_2N\}Si(Ge{=}Ge)Si\{N(SiMe_3)_2\}L]$ (δ 30.8 ppm),[10] but it is downfield shifted in comparison with the bis(silylenyl)pyridine-germanium(0)-tetracarbonyliron(0) complex $[C_5H_5N\text{-}\{2,6\text{-}(Et)N(L)Si\}_2GeFe(CO)_4]$ (δ −5.92 ppm).[12] The bridging ^{29}Si NMR signal is downfield shifted contrast to that of the tetrahedral Si atom in a $SiGe_2$ three membered ring, such as the 1H-siladigermirene $[(tBu_2MeSi)_2Si\{Ge(SiMetBu_2)\}_2]$ (δ -110.6 ppm)[15] and the hexamesitylsiladigermirane $[Mes_2Si(GeMes_2)_2]$ (δ -35.7 ppm).[16]

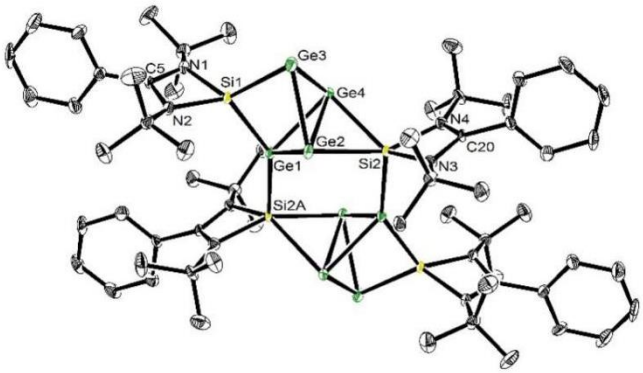


Figure 4.1. X-ray crystal structure of compound **4.2** (50% ellipsoids probability). Hydrogen atoms are elided. Ge2-Ge3 2.5338(7), Ge3-Ge4 2.5335(7), Ge2-Ge4 2.7004(7), Si1-Ge3 2.4012(11), Si2-Ge2 2.5249(12), Si2-Ge4 2.5502(11), Ge1-Ge2 2.4735(7), Ge1-Ge4 2.4810(6), Si1-Ge1 2.3365(12), Ge1-Si2A 2.3856(11); Ge3-Ge2-Ge4 57.794(19), Ge2-Ge3-Ge4 64.403(19), Ge2-Ge4-Ge3 57.803(19), Ge2-Ge1-Ge4 66.055(19), Ge1-Ge2-Ge4 57.106(18), Ge1-Ge4-Ge2 56.839(18), Ge2-Si2-Ge4 64.29(3), Si2-Ge2-Ge4 58.31(3), Si2-Ge4-Ge2 57.40(3), Si1-Ge3-Ge2 75.13(3), Si1-Ge3-Ge4 78.43(3), Si1-Ge1-Si2A 146.20(4).

The molecular structure of **4.2** comprises two planar Ge_3 ring being coordinated with the terminal Si (Si1, Si1A) and bridging Ge (Ge1, Ge1A) and Si (Si2, Si2A) atoms of two bis(silylenyl)germylene ligands. The isosceles triangular Ge_3 skeleton is demonstrated by two almost identical Ge-Ge bond lengths (Ge2-Ge3: 2.5338(7) Å; Ge3-Ge4: 2.5335(7) Å) and GeGeGe bond angles (Ge3-Ge2-Ge4: 57.794(19); Ge2-Ge4-Ge3: 57.803(19)^o), along with long Ge2-Ge4 bond length as the base of the ring (2.7004 Å). This isosceles triangle character resembles theoretical neutra trigermanium(0) cluster with C_{2v} symmetry in a $^1A_1$ ground state, but the latter has a larger apex angle (84.3^o),

shorter leg length (Ge-Ge: 2.324 Å) and longer base length (Ge-Ge: 3.118 Å).[17] Similar deviation in bond lengths and angles were also observed when comparing theoretical anionic trigermanium(0) cluster Ge_3^- (C_{2v} symmetry, $^2A_1$ ground state, apex angle: 66.20, leg lengths: 2.414 Å, base length: 2.636 Å) with the neutral one. This implies that electronic properties of the Ge_3 ring in **4.2** are perturbed by two bis(silylenyl)germylene ligands [LSi—Ge—SiL]. The Ge-Ge bonds (Ge1-Ge2: 2.4735(7), Ge1-Ge4: 2.4810(6) Å), which are formed by the bridging Ge1 donor and Ge_3 ring, are shorter than those of the Ge_3 ring. They are comparable with the Ge^0-Ge^{II} donor-acceptor bond (2.4784(7) Å) in the bis(silylenyl)pyridine-germanium(0)-dichlorogermanium(II)-tetracarbonyliron(0) donor-acceptor complex [C_5H_5N-{2,6-(Et)N(L)Si}$_2$GeGe(Cl)$_2$Fe(CO)$_4$], which comprises a bridging $GeCl_2$ moiety forming donor-acceptor interaction between the germanium(0) and tetracarbonyliron(0) fragments. The Si1-Ge3 bond (2.4012(11) Å), which is formed by the terminal Si1 donor and Ge_3 ring, is longer than those in the bis(silylenyl)pyridine-germanium(0)-tetracarbonyliron(0) [C_5H_5N-{2,6-(Et)N(L)Si}$_2$GeFe(CO)$_4$] (2.3875(6) 2.3729(6) Å),[12] but the Si1-Ge3 bond is comparable with that in the amidinato silylene-digermanium(0) complex [L{(Me$_3$Si)$_2$N}Si(Ge=Ge)Si{N(SiMe$_3$)$_2$}L] (2.406(2) Å).[10] The Si2-Ge bonds (Si2-Ge2: 2.5249(12); Si2-Ge4: 2.5502(11) Å), which are formed by the bridging Si2 donor and Ge3 ring, are comparable with the Si-Ge donor acceptor bond

(2.5259(13) Å) in the amidinato silylene-dichlorogermylene adduct [L{(Me$_3$Si)$_2$N}SiGeCl$_2$].[10]

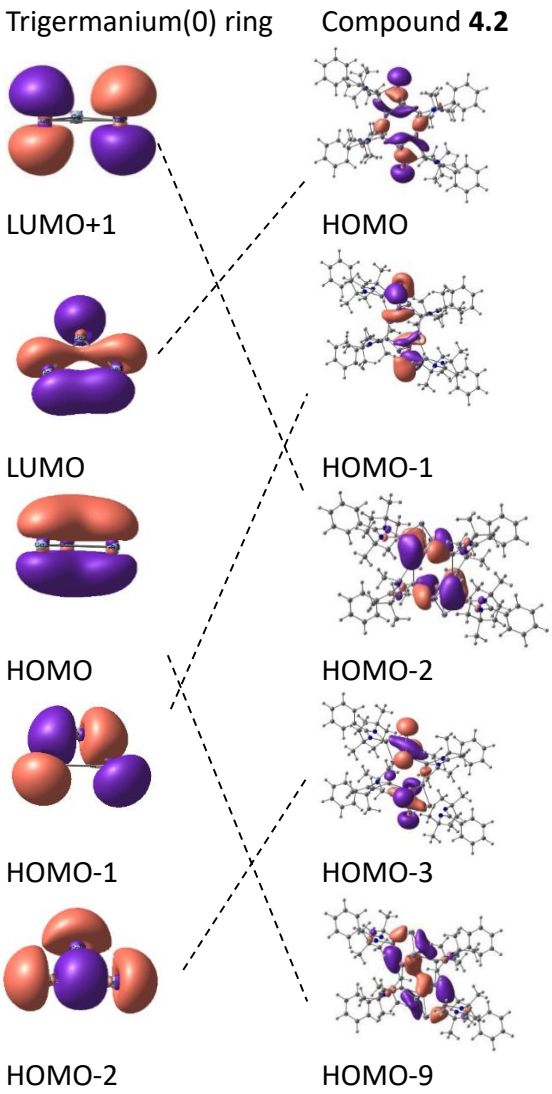
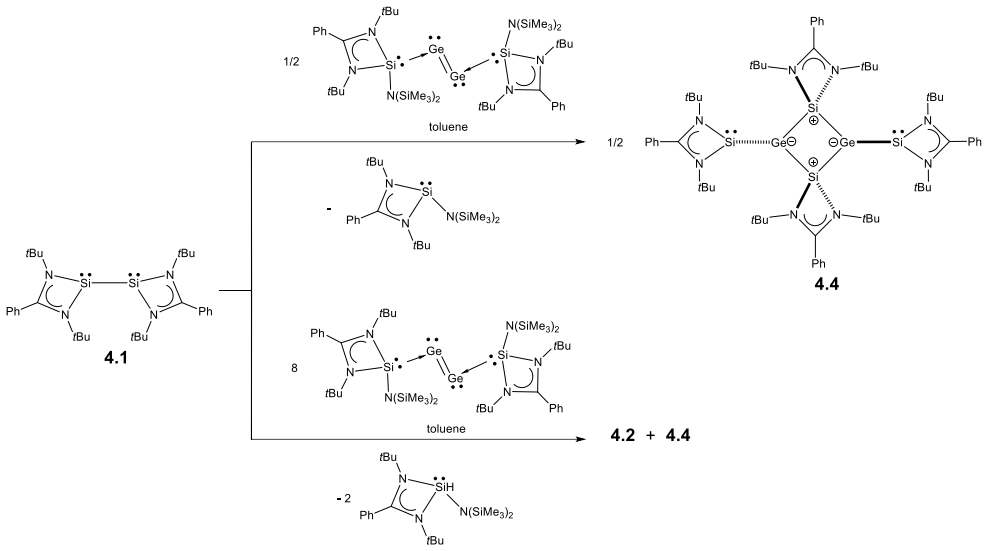


Figure 4.2. MO of free trigermanium(0) ring (left) and MO of trigermanium(0) ring in compound **2** (right)

In support of the experimental observations, DFT calculations of **4.2** were performed at the M06/def2-TZVPP//BP86/def2-SVP level of theory. The HOMO of **4.2** is mainly contributed by the LUMO of the Ge$_3$ ring. The HOMO-1 is the

overlapping of the tangential p orbitals (HOMO-1) of the Ge_3 ring with the empty p orbital on the bridging Ge donor of the [LSi—Ge—SiL] ligands. The HOMO-3 is mainly the radial p orbitals (HOMO-2) of the Ge_3 ring. The HOMO-9 comprises the perpendicular p orbitals (HOMO) of the Ge_3 ring.

The following mechanism for the formation of stable and isolable **4.2** is proposed. Germanium atoms in the reaction mixture were generated by two ways: (1) reduction of $GeCl_2$·dioxane by KC_8; (2) insertion of $GeCl_2$.dioxane into the Si-Si bond of compound **4.1**, along with the formation of compound **4.3**.[18] Subsequently, compound **4.1** reacted with one germanium atom to form an amidinato bis(silylenyl)germylene intermediate "LSi—Ge—SiL", which then trapped three more germanium atoms in the form of a isosceles triangular Ge_3 ring, along with dimerization, to form **4.2**. Once the Ge atom was formed, it was trapped by the ligands. In other word, the Ge atom was consumed by the ligands before becoming the bulk solid. The mechanism for the formation of Ge(0) cluster needs to be verified by DFT calculations which have been started.



Scheme 4.6: The reaction between amidinato silylene-digermanium(0) and amidinato silicon(I) dimer

In support of the proposed reaction mechanism, the feasibility of an amidinato bis(silylenyl)germylene intermediate "LSi—Ge—SiL" and its complexation with germanium(0) atoms are verified by using the amidinato silylene-digermanium(0) complex $[L\{(Me_3Si)_2N\}Si(Ge{=}Ge)Si\{N(SiMe_3)_2\}L]$ as a source of germanium(0) moiety. The reaction of $[L\{(Me_3Si)_2N\}Si(Ge{=}Ge)Si\{N(SiMe_3)_2\}L]$ with two equivalents of compound **4.1** afforded a mixture of the first amidinate-stabilized digermadisilacyclobutadiene $[L_2Ge_2Si_2L'_2]$ (**4.4**; L' = LSi:) and the amidinato silylenes $LSiN(SiMe_3)_2$. When **4.1** was reacted with $[L\{(Me_3Si)_2N\}Si(Ge{=}Ge)Si\{N(SiMe_3)_2\}L]$ in a molar ratio of 1:4 or 1:8, a mixture of compounds **4.2** and **4.4** and $[LSiN(SiMe_3)_2]$ was afforded **(scheme 4.6)**. The results show that the digermanium(0) moiety in

[L{$(Me_3Si)_2N$}Si(Ge=Ge)Si{$N(SiMe_3)_2$}L] inserted into two molecules of **4.1**, along with displacement of $LSiN(SiMe_3)_2$, to form an "LSi—Ge—SiL" intermediate. In the presence of excess digermanium(0) moieties, "LSi—Ge—SiL" was converted to compound **4.2**. Otherwise, it underwent a dimerization to form **4.4**.

Compound **4.4** was obtained as a red crystalline solid from its concentrated toluene solution. The ^{29}Si NMR spectrum displays two signals at δ 6.66 and 31.2 ppm for the four- and three-coordinate Si centres, respectively. The molecular structure shows that the Ge_2Si_2 core is planar and rhombic **(figure 4.3)**. Sum of the internal bond angles is 360°. The bidentate ligands amidinate are coordinated to the Si2 and Si2A, it adopt a distorted tetrahedral geometry. Every endocyclic Ge atom is connected to a low valent silicon amidinate substituent. The Ge1 and Ge1A atoms adopt a geometry of distorted trigonal pyramidal(sum of the bond angles: 294.51°). This geometry is in agreement with a stereoactive lone pair of the Ge atoms. The Ge1-Si2 (2.3852(11) Å) and Ge1-Si2A bond lengths (2.3844(11) Å) are comparable to typical Si-Ge single bond lengths (2.356(4) – 2.510(2) Å).[19] The results indicate that the Ge_2Si_2 core has a zwitterionic structure.[20] Moreover, the bidentate ligand amidinate is bonded to the Si1 and Si1A, and it adopt a trigonal pyramidal geometry (sum of the bond angles: 261.5°). This geometry implies that there is a stereoactive lone pair at the Si1/SiA atoms.

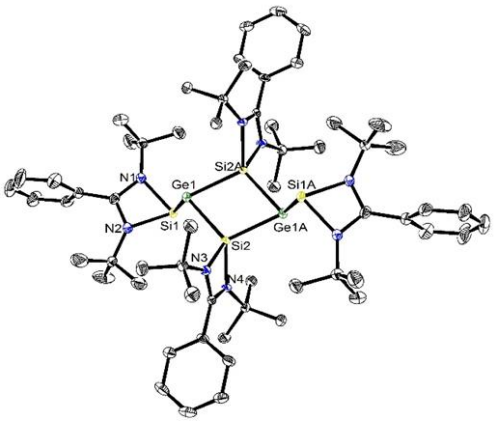
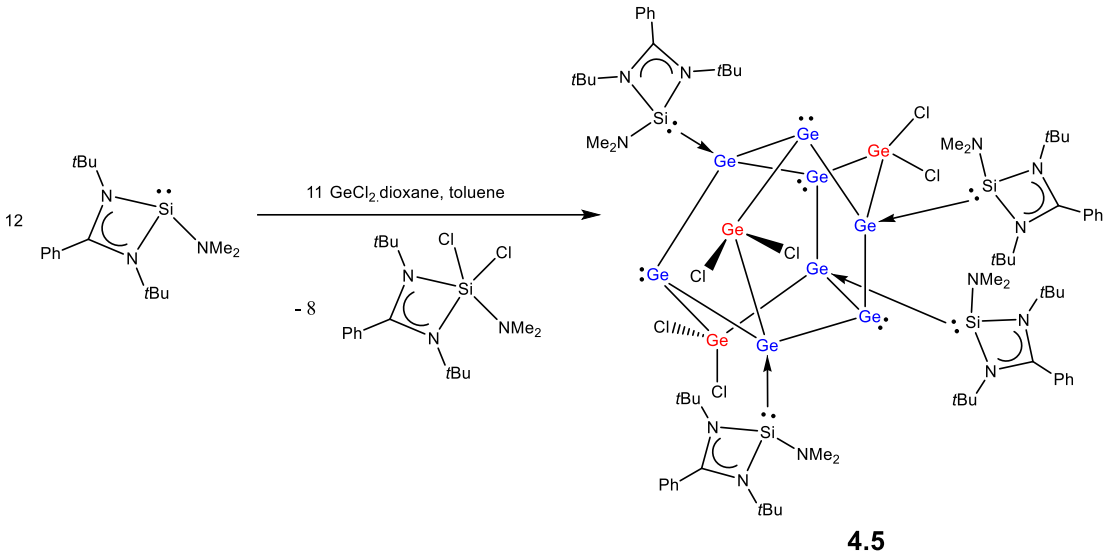


Figure 4.3. X-ray crystal structure of compound **4.4** (50% ellipsoids probability). Hydrogen atoms are elided Ge1-Si2 2.3852(11), Ge1-Si2A 2.3844(11), Ge1-Si1 2.4673(13), Ge1-Si2-Ge1A 106.82(4), Si2A-Ge1-Si2 73.18(4), Si2A-Ge1-Si1 109.50(4), Si2-Ge1-Si1 111.83(4), N1-Si1-N2 68.18(14), N1-Si1-Ge1 97.18(12), N2-Si1-Ge1 96.14(11).

Following complete characterization of **4.2**, its reactivity was preliminarily investigated. It reacted with two equivalents of $GeCl_2$·dioxane and GeI_2 for increasing the size of germanium(0) cluster. However, only [LSiCl] (**4.3**) and [LSiI] were afforded, respectively. It is proposed that $GeCl_2$·dioxane or GeI_2 underwent an insertion reaction with the Si-Ge bonds in **4.2** to form [LSiX] (X = Cl, I) and a pentagermanium(0) cluster, but they cannot coordinate with each other to form a stable amidinato silylene-pentagermanium(0) complex. On the basis of compound **4.2** and the above-mentioned amidinato silylene-germanium(0) complexes,[9,11] it seems that the steric effect and electronic properties of an amidinato low valent silicon donor is critical in coordinating with a germanium(0) cluster and controlling the size of the resulting cluster.

In support of this hypothesis, the amidinato silylene with a less steric dimethylamino substituent [$LSiNMe_2$][21] was utilized to trap a germanium(0) cluster. [$LSiNMe_2$] acted as both reducing agent and Lewis base to react with $GeCl_2$.dioxane in toluene to afford a mixture of the germanium cluster complex [$\{L(Me_2N)Si\}_4(Cl_2Ge)_3(Ge)_8$] (**4.5**) and the amidinato amidodichlorosilane [$LSiCl_2(NMe_2)$], which were isolated as a red and white crystalline solid from the reaction mixture, respectively **(scheme 4.7)**. The yield of **4.5** is only 7.3% because most of the Ge(0) atom deposited out during the reaction. On the basis of its X-ray crystal structure, compound **4.5** can be regarded as an octagermanium(0) cluster coordinated with terminal [$LSiNMe_2$] and bridging $GeCl_2$ ligands. The mechanism for the formation of **4.5** is still unknown. It is proposed that the reaction proceeded through the reduction of $GeCl_2$.dioxane by [$LSiNMe_2$] to form germanium atoms and [$LSiCl_2(NMe_2)$]. Subsequently, eight germanium(0) atoms, which may exist in a polyhedron form on the basis of theoretical studies,[22] are trapped by four [$LSiNMe_2$], and three bridging $GeCl_2$ ligands to form **4.5**.



Scheme 4.7: The synthesis of compound **4.5**

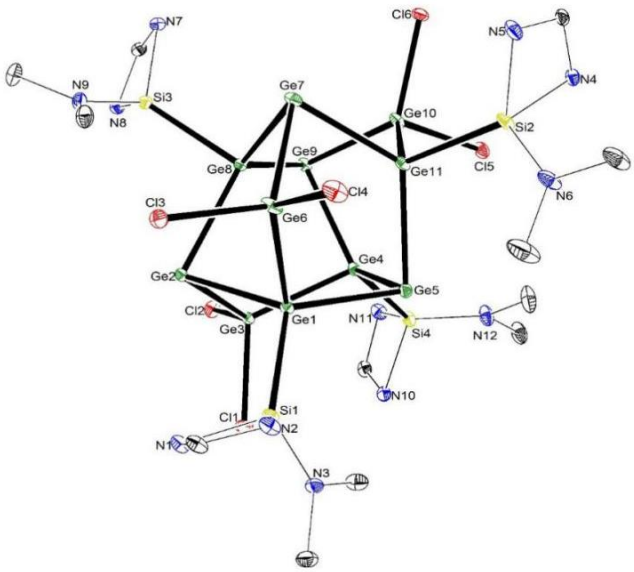


Figure 4.4. X-ray crystal structure of compound **4.5** (20% ellipsoids probability). Hydrogen atoms and phenyl and tBu substituents of amidinate ligands are elided. Ge2-Ge3 2.4678(6), Ge1-Ge2 2.5422(6), Ge3-Ge4 2.4512(6), Ge4-Ge5 2.5473(6), Ge1-Ge6 2.4574(6), Ge6-Ge7

2.4828(6), Ge2-Ge8 2.5728(6), Ge4-Ge9 2.5525(6), Ge5-Ge11 2.5592(6), Ge8-Ge9 2.5572(6), Ge7-Ge8 2.5696(6), Ge9-Ge10 2.4694(6), Ge10-Ge11 2.4575(6), Si1-Ge1 2.3903(11), Si2-Ge11 2.3949(12), Si3-Ge8 2.3894(11), Si4-Ge4 2.3929(12); Ge1-Ge2-Ge3 81.598(18), Ge1-Ge2-Ge8 86.712(18), Ge3-Ge2-Ge8 85.731(18), Ge1-Ge5-Ge4 90.664(18), Ge11-Ge5-Ge1 90.984(19), Ge11-Ge5-Ge4 90.512(18), Ge6-Ge7-Ge8 87.040(19), Ge6-Ge7-Ge11 82.42(2), Ge8-Ge7-Ge11 86.473(18), Ge8-Ge9-Ge10 87.534(19), Ge4-Ge9-Ge8 86.028(18), Ge4-Ge9-Ge10 80.645(18).

Compound **4.5** was characterized by X-ray crystallography and NMR studies. The ^{29}Si NMR signal (δ -2.48 ppm) shows an upfield shifted contrast to that of bis(silylenyl)pyridine-germanium(0)-dichlorogermanium(II)-tetracarbonyliron(0) donor-acceptor complex [C_5H_5N-{2,6-(Et)N(L)Si}$_2$GeGe(Cl)$_2$Fe(CO)$_4$] (δ 2.14 ppm). The molecular structure of **4.5** shows that there are three different germanium environments (**figure 4.4**): (1) L(Me_2N)Si-coordinated Ge atoms (Ge1, Ge4, Ge8, Ge11); (2) $GeCl_2$ fragments (Ge3, Ge6, G10) and (3) naked germanium atoms (Ge2, Ge5, Ge7 Ge9). It is noteworthy that the naked germanium atoms adopt a distorted trigonal pyramidal geometry (sum of bond angles, Ge2: 254.041; Ge5: 272.16; Ge7: 255.933; Ge9: 254.207°), which indicate the presence of a stereoactive electrons lone pair. The Ge-Ge(3/6/10) bonds (2.4512(6) - 2.4828(6) Å), which are formed by the germanium atoms (Ge3/6/10) of $GeCl_2$ fragments, are comparable with those (2.4735(7), 2.4810(6) Å) formed between the bridging Ge donor and Ge_3 rings in

compound **4.2**. They are shorter than the rest of Ge-Ge bonds (2.5422(6) - 2.5728(6) Å) in **5**. The latter are comparable with Ge-Ge bonds in metalloid germanium clusters.[23] The Si-Ge bonds (Si1-Ge1: 2.3903(11); Si2-Ge11: 2.3949(12); Si3-Ge8: 2.3894(11); Si4-Ge4: 2.3929(12) Å) are comparable with those of the $Si_{terminal}$-Ge donor-acceptor interaction in **4.2**.

In conclusion, the first isosceles triangular trigermanium(0) ring was isolated in the form of an adduct with amidinato bis(silylenyl)germylene ligands. In addition, the octagermanium(0) cluster was also afforded in the form of an adduct with the amidinato silylene and dichlorogermylene ligands.

4.3 Experimental Section

All operations were handled under argon with glovebox and standard schlenk techniques. Solvents were dried by a SPS-Mbraun-800 solvent purification system or by distillation over potassium metal. All the NMR spectra were obtained using the ECA400M JEOL and Advance III 400M spectrometer Bruker. The element analysis and melting point were done in the air. Intensity data for crystal were collected using a Bruker APEX II diffractometer. All 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. 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 calculation

Synthesis of **4.2**. Toluene (30 mL) was transferred to a mix of amidinato silicon(I) dimer [LSi:]$_2$ (0.16 g, 0.30 mmol), $GeCl_2$ (0.09 g, 0.40 mmol) and KC_8 (0.09 g, 0.70 mmol). The resulting red mixture was stirred overnight at room temperature. It was filtered and concentrated to form red crystals as compound **4.2**. Yield: 0.034 g (7.3%). Mp: 113.8 °C (decomposed). ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 1.22 (s, 18H, *t*Bu), 1.43 (s, 18H, *t*Bu), 6.66-7.02 (m, 10H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 30.6, 32.2 (C*Me*$_3$), 54.7, 57.2 (*C*Me$_3$), 126.4, 126.8, 172.8, 128.3, 129.0, 130.8, 132.9, 133.2 (Ph), 175.4, 178.9 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = 9.9 (LSi), 26.4 (LSi).

Crystallographic data for **4.2**: $C_{81}H_{116}Ge_8N_8Si_4$; M = 1894.89; triclinic P -1; *a* = 12.07180(10) Å, *b* = 13.99550(10) Å, *c* = 14.92650(10) Å; α =113.6632(5)°, *β* = 96.9458(6)°, *γ* = 102.2063(6)°; *V* = 2197.13(3) Å^3; *Z* = 1; ρ_{calcd} = 1.432 g cm^{-3}; 29249 measured reflections; 411 refined parameters; 6375 independent reflections; R_1 = 0.0571, wR_2 = 0.1567 ($I > 2\sigma(I)$).

Synthesis of **4.4**. Toluene (30 mL) was added to a mixture of LSiGe=GeSiL (0.19 g, 0.20 mmol) and LSiSiL (0.11 g, 0.2 mmol). The resulting red mixture was stirred overnight at room temperature. It was filtered and concentrated to form red crystals as compound **4.4**. Yield: 0.054 g (40.1 %). Mp: 124.3 °C (decomposed). ^{1}H NMR (399.5 MHz, D_8-THF, 25°C): δ = 0.19 (s, 9H, *t*Bu), 0.29

(s, 9H, *t*Bu), 1.18 (s, 18H, *t*Bu), 7.23-7.24 (m, 5H, Ph), 7.26-7.41 (m, 5H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 33.4, 36.4 (C*Me*$_3$), 52.1, 54.2 (*C*Me$_3$), 126.9, 128.1, 128.8, 129.3, 129.8, 131.1, 131.8, 133.0 (Ph), 173.1, 175.4 (NCN) ppm. $^{29}Si\{^{1}H\}$ NMR (79.4 MHz, C_6D_6, 25°C): δ = 6.66 (LSi), 31.2 (LSiGe).

Crystallographic data for **4.4**: $C_{74}H_{108}N_8Si_4Ge_2$; M = 1367.22; monoclinic *P*1 21; *a* = 11.8909(17) Å, *b* = 17.158(2) Å, *c* = 18.316(2) Å; *β* = 91.698(4)°; *V* = 3490.8(7) Å^3; *Z* = 2; ρ_{calcd} = 1.216 g cm^{-3}; 56423 measured reflections; 411 refined parameters; 8889 independent reflections; R_1 = 0.0560, wR_2 = 0.1486 ($I > 2\sigma(I)$).

Synthesis of **4.5**. Toluene (30 mL) was transferred to a mixture of LSiSiL (0.26 g, 0.50 mmol), $GeCl_2$ (0.12 g, 0.50 mmol) and KC_8 (0.27, 1.0 mmol). The resulting red mixture was reacted overnight at room temperature. It was filtered and concentrated to form red crystals as compound **4.5**. Yield: 0.034 g (7.3%). Mp: 176.4 °C (decomposed). ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 1.17 (s, 18H, *t*Bu), 2.66 (s, 6H, N*Me*$_2$), 6.66-7.02 (m, 5H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 30.2 (C*Me*$_3$), 55.0 (*C*Me$_3$), 65.4 (NMe$_2$), 127.2, 127.9, 129.0, 130.2, 133.9 (Ph), 178.0 (NCN) ppm. $^{29}Si\{^{1}H\}$ NMR (79.4 MHz, C_6D_6, 25°C): δ = -2.48 (LSi) ppm.

Crystallographic data for **4.5**: $C_{82}H_{132}N_{12}Si_4Ge_{11}Cl_{16}$; M = 2409.54; monoclinic *C2/c*; *a* = 28.790(2) Å, *b* = 16.3629(12) Å, *c* = 45.127(3) Å;, *β* = 90.6314(8)°; *V*

= 21258(3) Å^3; Z = 8; ρ_{calcd} = 1.506 g cm^{-3}; 100430 measured reflections; 1316 refined parameters; 23045 independent reflections; R_1 = 0.0432, wR_2 = 0.1005 ($I > 2\sigma(I)$).

4.4 References

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CHAPTER 5

The Sequential Insertion and Ring Expansion of an Amidinato Silylene and Silicon(I) Dimer with Boranes

5.1 Introduction

Applications of N-heterocyclic carbenes (NHCs) have grown rapidly, since their isolation and characterization.[1] Their adhibition in both transition metal and main group element chemistry, especially, utilizing as ligands in homogeneous catalysis[2] and in stabilizing main group elements in the oxidation state of 0,[3] are now well established. Although NHCs are generally treated as stable spectator ligands, they are not innocent in all reactions and can themselves undergo unanticipated C-N, C-H and C-C reactions at the metal centre.[4] Recently, ring expansion reactions of NHCs with beryllium **(I)**,[5] boron **(II, III)**[6] and silicon

hydrides **(IV)**[7] were reported **(Figure 5.1)**. In each compound, two hydrides migrate from the main group element centre to the $C_{carbene}$ atom of the NHC forming an endocyclic CH_2 part, along with an insertion of the main-group atom in a C-N bond of the carbene to form a six-membered heterocycle. The mechanisms were also studied by theoretical studies.[8] In addition, similar ring expansion chemistry between NHCs and diboranes **(V, VI)** were observed **(Figure 5.1)**.[9]

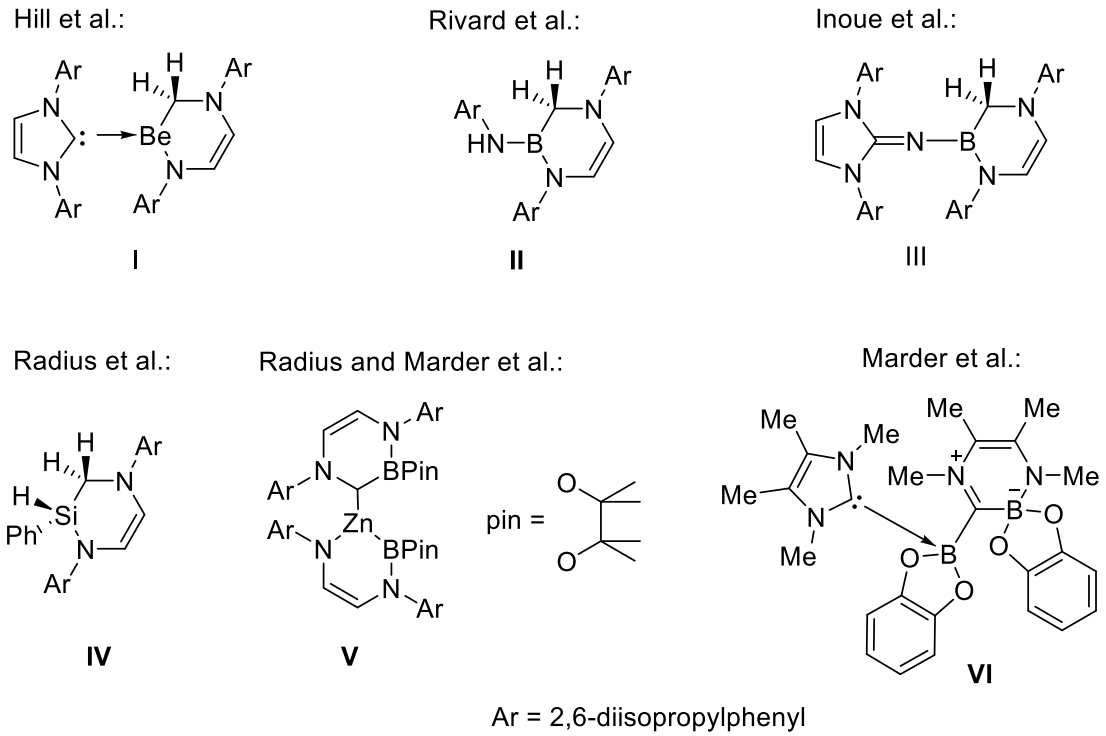
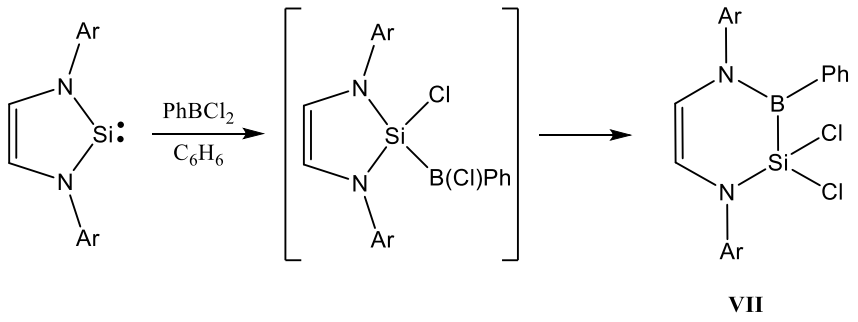


Figure 5.1. NHC-ring expansion products I –VI by the reaction of :C{N(Ar)CH}$_2$ and :C{N(Me)C(Me)}$_2$ with beryllium, boron and silicon hydrides and diboranes.

The heavier analogue, N-heterocyclic silylene NHSi, can exhibit ring expansion reaction, but only one example was reported. In 2016, Braunschweig

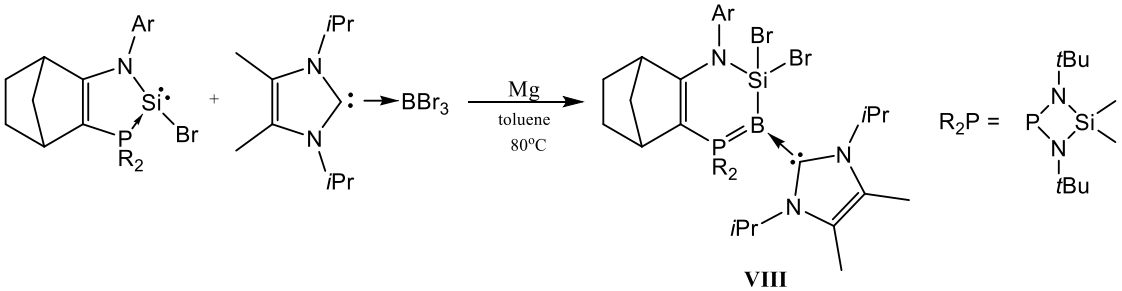
et al. reported that the N-heterocyclic silylene [{HCN(Ar)}$_2$Si:] (Ar = 2,6-$Me_2C_6H_3$) reacted with $PhBX_2$ (X = Cl, Br) to form an oxidative addition intermediate [{HCN(Ar)}$_2$Si(X)B(X)Ph], which then underwent a ring expansion reaction to form the six-membered boron-silicon heterocycle **(Scheme 5.1)**.[10]



VII

Scheme 5.1: The ring expansion reaction of NHSi and $PhBCl_2$

Very recently, Baceiredo and Kato et al. reported an analogous ring expansion with the reaction between the N-heterocyclic bromosilylene and NHC-BBr_3 and Mg to afford the stable cyclic silylborylidene–phosphorene **(Scheme 5.2)**.[11]

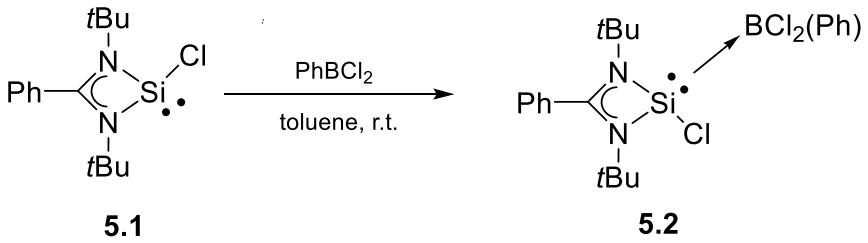


VIII

Scheme 5.2: The ring expansion reaction of N-heterocyclic bromosilylene with NHC-BBr_3 and Mg

Several research groups show that a variety of N-heterocyclic silylenes supported by amidinate ligands were utilized as spectator ligands in homogeneous catalysis.[12] We were interested in investigating whether an amidinato silylene and silicon(I) dimer can undergo a sequential insertion and ring expansion reaction, similar to the abovementioned N-heterocyclic carbene. Herein, we report the reactivity of an amidinato amidosilylene and silicon(I) dimer toward $PhBCl_2$.

5.2 Results and Discussion



5.1 **5.2**

Scheme 5.3: The synthesis of compound **5.2**

Adding $PhBCl_2$ to a toluene solution of the amidinato chlorosilylene [LSiCl] (**5.1**, L = $PhCN(tBu)_2$) afforded a light orange reaction suspension. It was stirred overnight and filtered. The filtrate was concentrated to form the amidinato silylene-borane adduct [L(Cl)$SiBCl_2$(Ph)] (**5.2**) as an moisture- and air-sensitive colorless crystal **(Scheme 5.3)**. The molecular structure of **5.2** shows that the Si1 center is bound to the B centre of $PhBCl_2$, which adopts a tetrahedral geometry **(Figure 5.2)**. The Si1-B1 bond length (2.039(3)Å) is in line with the amidinato

silylene-borane adducts such as [L{$(Me_3Si)_2N$}$SiBBr_3$] (2.048(9)Å) and [{PhC(N*i*Pr)$_2$}$_2$$SiBPh_3$] (2.068(3)Å), which indicate that it is a coordinative covalent bond. In comparison with starting material **5.1**, the ^{29}Si NMR signal of product **5.2** is downfield shifted, which indicates the lone pair electrons on the silicon center being donated to the boron atom.

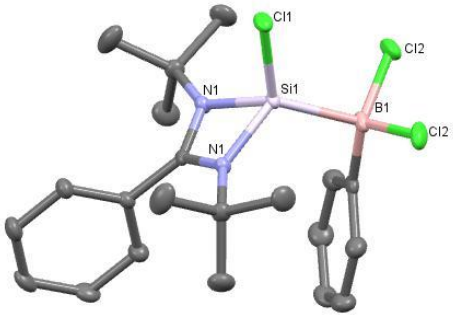
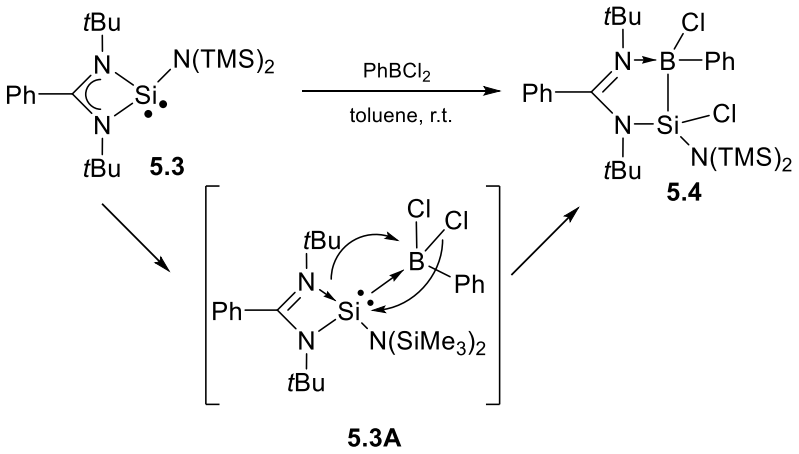


Figure 5.2. X-ray structure of adduct **5.2** (ellipsoids set at 30% probability). Hydrogen atoms are elided: Si1-B1 2.039(3), N1-Si1 1.8037(13), Si1-N1' 1.8037(13), Si1-Cl1 2.0445(8), Cl2-B1-Cl2' 108.48(12), Cl2-B1-C12 113.20(10), Cl2'-B1-C12 113.20(10), Cl2-B1-Si1 107.82(9), Cl2'-B1-Si1 107.82(9), C12-B1-Si1 106.05(14), B1-Si1-N1 118.91(7), B1-Si1-N1' 118.91(7), B1-Si1-Cl1 119.48(4), N1-Si1-Cl1 108.75(5), N1'-Si1-Cl1 108.75(5), N1-Si1-N1' 72.96(8).

In contrast, when the Cl substituent was replaced by the amido $N(SiMe_3)_2$ substituent, the amidinato amidosilyene [LSi{$N(SiMe_3)_2$}] (**5.3**) underwent a sequential insertion and ring expansion reaction with $PhBCl_2$ in toluene to form

the boron-silicon heterocycle [(μ–κ1:κ1-L)B(Cl)(Ph)Si(Cl){N(SiMe$_3$)$_2$}] (**5.4**), which was isolated as an moisture- and air- sensitive colorless crystals. The formation of different products of compound **5.2** and **5.4** is due to the fact that the less electronegative Cl substituent enhances the nucleophilicity of the Si centre and hence the stability of compound **5.2**. On the basis of the formation of **5.2**, this reaction is proposed to proceeds through a silylene-borane adduct intermediate "L{(Me$_3$Si)$_2$N}SiBCl$_2$(Ph)" **5.3A**, which then undergoes a B-Cl bond insertion with the Si^{II} centre, along with coordination of the amidinate part to the boron centre to afford **5.4 (Scheme 5.4)**.

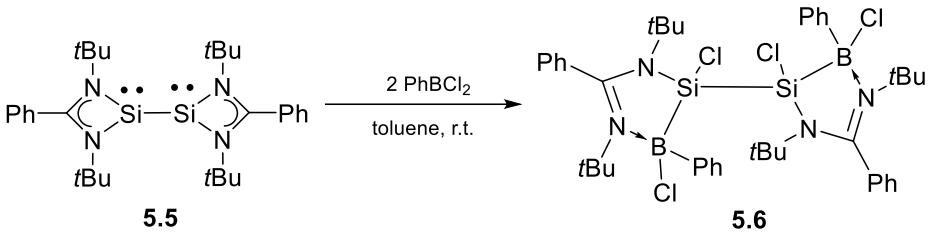


Scheme 5.4: The synthesis of compound **5.4** through intermediate **5.3A**

Compound **5.4** can dissolve in toluene and THF and stable in the solid state in the glovebox. It was characterized using NMR spectroscopy. The proton NMR spectrum displays two signals for the *t*Bu substituents (δ 1.21, 1.23 ppm), which indicate two different N environments. The ^{11}B NMR signal (δ 5.3 ppm) is in

agreement with that of base-stabilized silylboranes such as [I_{iPrMe}B(pin)$SiPh_3$] (δ 6.5 ppm, I_{iPrMe} = :C{N(*i*Pr)CMe}$_2$).[13] All attempts to obtain a ^{29}Si NMR spectrum were unsuccessful due to the dynamic processes and the adjacent quadrupolar boron atom.

Similar ring expansion was observed in the reaction of the amidinato silicon(I) dimer [LSi:]$_2$ (**5.5**) with two equivalents of $PhBCl_2$ in toluene to form the bis(boron-silicon heterocycle) **5.6**, which was isolated as an moisture- and air-sensitive colorless crystalline solid. It is stable in both solution state and solid state under inert gas. It was characterized by NMR spectroscopy and X-ray crystallography. The ^{1}H NMR spectrum displays two signals for the *t*Bu substituents (δ 1.24, 1.25 ppm), which indicate two different N environments. Its ^{11}B NMR signal (δ 7.11 ppm) is similar to that of **5.4**. Similar to compound **5.4**, the ^{29}Si NMR signal of **5.6** cannot be observed. The molecular structure of **5.6** shows that it has a gauche-bent geometry, similar to compound **5.5**. The Si and B atoms adopt a tetrahedral geometry. The Si-Si bond length (2.3725(19) Å) is shorter than that of compound **5.5** (2.413(2) Å). The B-N bond lengths (1.579(7), 1.581(7) Å) are comparable with those of the quanidinato boranes such as [(Ph_2N)CN(Mes)BCl_2] (1.559(3), 1.566(3) Å). The B-Si bond lengths (1.998(6), 1.999(6) Å) are shorter than that of the stabilized silylborane [C_5H_5NB(Br)$_2$Si*t*Bu$_3$] (2.116 Å).[14]



5.5 **5.6**

Scheme 5.5: The synthesis of compound **5.6**

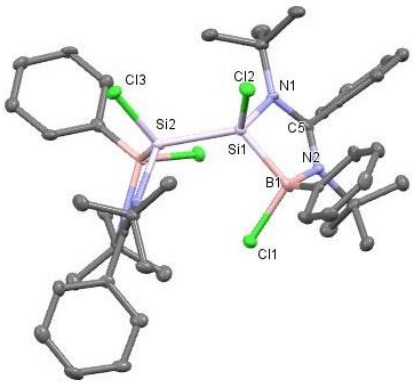


Figure 5.4. X-ray structure of compound **5.6** (ellipsoids set at 30% probability). Hydrogen atoms are elided: Si1-B1 1.998(6), Si1-N1 1.805(4), B1-N2 1.582(7), Si1-Cl2 2.0939(18), Si1-Si2 2.3725(19), Cl1-B1 1.915(6), N1-C5 1.365(6), N2-C5 1.337(6), Cl2-B1-Cl2 108.48(12), Si1-B1-N2 99.7(3), Si1-B1-Cl1 106.9(3), N2-B1-Cl1 111.0(4), N1-Si1-B1 91.9(2), N1-Si1-Cl2 107.44(14), B1-Si1-Cl2 112.66(18), N1-Si-Si2 113.39(14), B1-Si1-Si2 118.54(18), Cl2-Si-Si2 110.10(17).

In conclusion, the amidinato chlorosilylene [LSiCl] (**5.1**, L = PhCN(*t*Bu)$_2$) reacted with PhBCl$_2$ to afford the amidinato silylene-borane adduct **5.2**, while the amidinato amidosilyene [LSi{N(SiMe$_3$)$_2$}] (**5.3**) and amidinato silicon(I) dimer [LSi:]$_2$ (**5.5**) underwent a sequential insertion and ring expansion reaction with

$PhBCl_2$ in toluene to form the boron-silicon heterocycle [(μ–κ1:κ1-L)B(Cl)(Ph)Si(Cl){$N(SiMe_3)_2$}] (**5.4**) and [(μ–κ1:κ1-L)B(Cl)(Ph)Si(Cl)]$_2$ (**5.6**).

5.3 Experimental Section

All operations were handled under argon with glovebox and standard schlenk techniques. Solvents were dried by a SPS-Mbraun-800 solvent purification system or by distillation over potassium metal. All the NMR spectra were obtained using the ECA400M JEOL and Advance III 400M spectrometer Bruker. The element analysis and melting point were done in the air. Intensity data for crystal were collected using a Bruker APEX II diffractometer. All 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. 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.

Synthesis of **5.2**: $PhBCl_2$ (0.16 g, 1.00 mmol) was dripped to a solution of **5.1** (0.30 g, 1.00 mmol) in toluene (30 mL). The resulting pale yellow mixture was stirred overnight at room temperature. It was filtered and concentrated to afford compound **5.2** as colorless crystals. Yield: 0.34 g (75.2 %). Mp: 230.2 °C (decomposed). ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 1.06 (s, 18H, *t*Bu), 7.22-

7.24 (m, 2H, Ph), 7.35-9.39 (m, 1H, Ph), 7.55-7.64 (m, 2H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 30.5 (C*Me*$_3$), 57.7 (*C*Me$_3$), 127.1, 128.6, 129.8, 132.7 (Ph), 183.1 (NCN). $^{11}B\{^{1}H\}$ NMR (79.4 MHz, C_6D_6, 25°C): δ = 20.3 ppm. $^{29}Si(^{1}H)$ NMR can not been obtained because of the quadrupolar coupling with B (I = 3/2).

Crystallographic data for **5.2**: $C_{21}H_{48}Cl_3BN_2Si$; M = 453.70; orthorhombic *P n m a*; *a* = 18.0195(10), *b* = 10.5725(6), *c* = 12.0146(5) Å; *β* = 90°; *V* = 2288.9(2) Å^3; *Z* = 4; ρ_{calcd} = 1.317 mg m^{-3}; 19975 measured reflections; 148 refined parameters; 3879 independent reflections; R_1 = 0.0433, wR_2 = 0.0998 ($I > 2\sigma(I)$).

Synthesis of **5.4**: $PhBCl_2$ (0.16 g, 1.00 mmol) was dripped to the solution of **5.3** (0.42g, 1.00 mmol) in toluene (30 mL). The resulting yellow mixture was stirred overnight at room temperature. It was filtered and concentrated to afford compound **5.4** as colorless crystals. Yield: 0.22 g (36.6 %). Mp: 250.7 °C (decomposed). ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.64 (s, 18H, TMS), 1.21 (s, 18H, *t*Bu), 1.23 (s, 18H, *t*Bu), 6.92-7.14 (m, 9H, Ph), 7.87-7.94 (m, 1H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.2 (TMS), 30.9, 32.9 (C*Me*$_3$), 53.4, 56.8 (*C*Me$_3$), 127.0, 127.7, 128.2, 128.9, 129.5, 129.9, 133.2, 133.3 (Ph), 180.1, 182.8 (NCN). $^{11}B\{^{1}H\}$ NMR (79.4 MHz, C_6D_6, 25°C): δ = 5.37 ppm. $^{29}Si(^{1}H)$ NMR can not been obtained because of the quadrupolar coupling with B (I = 3/2).

Synthesis of **5.6**: $PhBCl_2$ (0.32 g, 1.00 mmol) was dripped to the solution of **5.5** (0.52g, 1.00 mmol) in toluene (30 mL). The resulting yellow mixture was stirred overnight at room temperature. It was filtered and concentrated to afford compound **5.6** as colorless crystals. Yield: 0.42 g (50.6 %). Mp: 214.2 °C (decomposed). ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 1.24 (s, 18H, *t*Bu), 1.25 (s, 18H, *t*Bu), 6.79-6.84 (m, 2H, Ph), 6.88-6.97 (m, 4H, Ph), 7.06 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H, Ph), 7.23-7.28 (m, 2H, Ph), 7.48-7.54 (m, 4H, Ph), 7.62 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H, Ph), 7.90 (d, $^{3}J_{H-H}$ = 7.3 Hz, 2H, Ph), 8.21 (d, $^{3}J_{H-H}$ = 7.3 Hz, 2H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.5 MHz, C_6D_6, 25°C): δ = 33.10, 35.08 (CMe_3), 60.80, 65.56 (CMe_3), 125.73, 126.83, 127.07, 127.28, 130.73, 131.29, 131.99, 132.32, 132.98, 134.26 (Ph), 178.46 (NCN). $^{11}B\{^{1}H\}$ NMR (79.4 MHz, C6D6, 25°C): δ = 7.11 ppm. $^{29}Si(^{1}H)$ NMR can not been obtained because of the quadrupolar coupling with B (I = 3/2).

Crystallographic data for **5.6**: $C_{42}H_{56}Cl_4B_2N_4Si_2$; M = 836.50; monoclinic *P* 1 21/*c* 1; *a* = 12.3743(16), *b* = 18.678(2), *c* = 18.680(2) Å; *β* = 92.004(7)°; *V* = 4314.8(9) $Å^3$; *Z* = 4; ρ_{calcd} = 1.288 mg m^{-3}; 72325 measured reflections; 499 refined parameters; 7793 independent reflections; R_1 = 0.0729, wR_2 = 0.1659 ($I > 2\sigma(I)$)

5.4 References

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