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A Donor-Acceptor Stabilized Tetra(silanimine)

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ABSTRACT. The synthesis of an oligo(silanimine) is described. The reaction of the amidinato silylene $[\text{LSiN}(\text{SiMe}_3)_2]$ (**1**, $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$) with SiI_4 in toluene afforded a mixture of the silanimine $[\text{LSi}(\text{I})\text{NSiI}_3]$ (**2**), SiMe_3I and Si_2I_6 . The mechanistic studies showed that **1** reacts with SiI_4 to form the silyl ionic intermediate “ $\{\text{LSi}(\text{I})\text{N}(\text{SiMe}_3)_2\}^+\{\text{SiI}_3\}^-$ ”, which then eliminates SiMe_3I and “ SiI_2 ” to form the silanimine intermediate “ $\text{LSi}(\text{I})\text{NSiMe}_3$ ”. It further undergoes a substitution with another molecule of SiI_4 to form a mixture of **2** and SiMe_3I . In addition, “ SiI_2 ” undergoes an oxidative addition with SiI_4 to form Si_2I_6 . Subsequently, compound **2** reacted with $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ to form the silanimine $[\text{LSi}(\text{I})\text{NSiI}_2\text{N}(\text{SiMe}_3)\text{Ar}]$ (**6**, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$), which then treated with KC_8 to give the donor-acceptor stabilized tetra(silanimine) $[\text{LSiN}(\text{SiMe}_3)\text{SiNAr}]_2$ (**7**). It comprises four formal silanimine “ $>\text{Si}=\text{N}$ ” units, which are linked together. Compounds **2**, **6** and **7** were characterized by NMR spectroscopy and X-ray crystallography.

Introduction

The chemistry of multiple-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 [*t*Bu₂Si=NSi*t*Bu₃] by the reaction of the azido-di-*t*butyl-chlorosilane and tri-*t*butylsilyl sodium.³ Its THF adduct was also synthesized.⁴ Klingebiel et al. also showed that the base-free silanimine [*i*Pr₂Si=N(Tip)] (Tip = 2,4,6-*i*Pr₃C₆H₂) can be isolated by the LiCl elimination of the corresponding aminochlorosilane [*i*Pr₂Si(Cl)-N(Li)(Tip)].⁵ West et al. illustrated another methodology to synthesize the THF-stabilized silanimine [$\{HC(tBu)N\}_2Si(THF)=NCPh_3$] by the oxidation of the silylene [$\{HC(tBu)N\}_2Si:$] with N₃CPh₃.⁶ Similarly, research groups of Kira and Roesky used a variety of silylenes such as the dialkylsilylene [$\{H_2CC(SiMe_3)_2\}_2Si:$],⁷ NHC-dichlorosilylene [$I_{Ar}SiCl_2$] ($I_{Ar} = :C\{N(Ar)CH\}_2$, Ar = 2,6-*i*Pr₂C₆H₃, NHC = N-heterocyclic carbene)⁸ and amidinato silylene [$PhC(NtBu)_2SiR$] (R = Cl, N(SiMe₃)₂),⁹ to react with organic azides to form the corresponding silanimines. Cui et al. demonstrated that the NHC-silylamino silylene [$Ar(SiMe_3)N(Cl)Si(I_{iPrMe})$] ($I_{iPrMe} = :C\{N(iPr)C(Me)\}_2$) reacted with alkynes and nitriles to form the silanimines [$\{R(Me_3Si)C=C(H)\}(Cl)Si(I_{iPrMe})=NAr$] and [$\{R(Me_3Si)C=N\}(Cl)Si(I_{iPrMe})=NAr$] (R = supporting substituent), respectively, through silyl migration mechanisms.¹⁰ We also reported that the amidinato silicon(I) dimer underwent an oxidative addition with a transient nitrene to form the silylenylsilanimine [$\{PhC(NtBu)_2\}Si(=NAr)-Si\{(NtBu)_2CPh\}$].¹¹ In the abovementioned examples, a “>Si=N-“ unit was isolated.

There is a handful of compounds containing two “>Si=N-“ units. Roesky et al. showed that the dimeric silaisonitrile $[2,6\text{-Tip}_2\text{C}_6\text{H}_3\text{NSi:}]_2$ ¹² reacted with N_3SiMe_3 to form $[2,6\text{-Tip}_2\text{C}_6\text{H}_3\text{NSi=NSiMe}_3]_2$. We also reported the isolation of the NHC-siladiimide complex $[\text{ArNSi}(\text{I}_{\text{Ar}})\text{NAr}]$ by reacting the NHC-disilicon complex $[\text{I}_{\text{Ar}}\text{Si=SiI}_{\text{Ar}}]$ with ArN_3 .¹³ Moreover, to the best of our knowledge, a compound containing more than two “>Si=N-“ units is unknown.

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

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

Results and Discussion

The treatment of the amidinato amidosilylene $[\text{LSiN}(\text{SiMe}_3)_2]$ (**1**, $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$)²⁰ with SiI_4 in a ratio of 1:1 in toluene afforded a purple-green reaction mixture. It was filtered to remove the insoluble precipitate²¹ and the filtrate was analyzed by ^1H NMR spectroscopy. The spectrum showed a mixture of the silanimine $[\text{LSi}(\text{I})\text{NSiI}_3]$ (**2**, Scheme 1) and SiMe_3I . No starting

materials were found. Volatiles and SiMe_3I in the filtrate were removed under reduced pressure to quantitatively afford compound **2**, which was confirmed by ^1H NMR spectroscopy. Compound **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** 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 lesser than that in the reaction of **1** and SiI_4 in the 1:1 ratio. The filtrate was analysed by ^1H NMR spectroscopy, which showed a mixture of compound **2** and SiMe_3I . In addition, no starting materials were found. Surprisingly, compound **2** cannot be isolated from the concentrated filtrate, instead colorless crystals of Si_2I_6 (Figure S1; **1**: SiI_4 , 1:2 ratio: 64.5 % yield; 1:3 ratio: 76.4 % yield), which are ^1H NMR-silent, were afforded. The mother liquor was filtered and the filtrate still showed the presence of compound **2** and SiMe_3I in the ^1H NMR spectrum. In other words, the reaction of **1** with SiI_4 in a ratio of 1:2 or 1:3 in toluene afforded a mixture of **2**, Si_2I_6 and SiMe_3I . However, an attempt to isolate pure compound **2** from the mixture by recrystallization failed.

Scheme 1. Synthesis of **2**.

Colorless crystals of **2** are soluble in toluene and THF. They are stable in solution and the solid state. The ^1H NMR spectrum of **2** shows a set of resonances due to the *t*Bu and phenyl protons of

the amidinate ligand. The ^{29}Si NMR resonance for the $\text{LSi}=\text{N}$ moiety (δ -100 ppm) is comparable with that of the silanimine $[\text{LSi}(=\text{NAr})\text{Cl}]$ (δ -104.8 ppm),²² while that for the $\text{N}-\text{SiI}_3$ fragment (δ -256.7 ppm) is upfield shifted in comparison with that of the NSiMe_3 substituent in the donor-free dialkylsilanimine $[\{\text{H}_2\text{CC}(\text{SiMe}_3)_2\}_2\text{Si}=\text{NSiMe}_3]$ (δ -15.5 ppm).⁷ In addition, compound **2** was characterized by X-ray crystallography (Figure 1). 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 $[\text{tBu}_2\text{Si}=\text{N}-\text{Si}(\text{tBu})_3]$.⁴ This indicates that compound **2** comprises resonance structures as illustrated in Scheme 2. The large Si1-N3-Si2 bond angle (139.6(5)°) indicates that the hybrids on the N3 atom for σ -bonding are high in s character, which result in better overlapping with the SiI_3 moiety, along with short Si2-N3 bond length.

Scheme 2. Resonance structures of **2**

Figure 1. Molecular structure of compound **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** reacts with SiI_4 to form a silyl ionic intermediate “ $\{\text{LSi}(\text{I})\text{N}(\text{SiMe}_3)_2\}^+ \{\text{SiI}_3\}^-$ ” (**A**, Scheme 3), which then eliminates SiMe_3I and “ SiI_2 ” to form a silanimine intermediate “ $\text{LSi}(\text{I})\text{NSiMe}_3$ ” (**B**). Then, “ SiI_2 ” undergoes a polymerization to form an insoluble poly(silane). In cases of the reactions with the 1:2 and 1:3 ratio of **1** and SiI_4 , “ SiI_2 ” can also undergo an oxidative addition with SiI_4 to form Si_2I_6 . Subsequently, the silanimine intermediate “ $\text{LSi}(\text{I})\text{NSiMe}_3$ ” undergoes a substitution with another molecule of SiI_4 to form a mixture of **2** and SiMe_3I . On the basis of stoichiometry and proposed reaction mechanism, the reaction of **1** and SiI_4 in a ratio of 1:3 should give the highest yield of compound **2**. However, the presence of Si_2I_6 in the reaction mixture hinders the isolation of pure compound **2** by recrystallization.

Scheme 3. A proposed mechanism for the formation of **2**

The proposed mechanism for the formation of **2** is verified. The formation of the silyl ionic intermediate “ $\{\text{LSi(I)N(SiMe}_3)_2\}^+\{\text{SiI}_3\}^-$ ” in the reaction of **1** with SiI_4 is indicated by the reaction of **1** with GeCl_4 in toluene at room temperature, which afforded the amidinato silylium germanate $[\text{LSi(Cl)N(SiMe}_3)_2]^+[\text{GeCl}_3]^-$ (**3**, Scheme 4) and a mixture of unidentified products. Compound **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 **3** are downfield shifted in comparison with those in **1** (LSi : δ -8.07 ppm; SiMe_3 : δ 2.81, 3.71 ppm). In addition, compound **3** was characterized by X-ray crystallography (Figure 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 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** ($\text{Si-N}_{\text{amido}}$: 1.769(7), $\text{Si-N}_{\text{amidinate}}$: 1.8780(10), 1.8776(10) Å), respectively. On the basis of the ^{29}Si NMR resonances and Si-N bond lengths, compound **3** comprises a cationic silicon centre (Si1).

Scheme 4. Synthesis of **3**.

Figure 2. Molecular structure of compound **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 $[L\{(Me_3Si)_2N\}SiGeCl_2]$ (**4**)²³ with $SiCl_4$ afforded an orange mixture. It was filtered to remove the insoluble precipitate²¹ and the filtrate was analyzed by 1H NMR spectroscopy. The spectrum showed a mixture of the silanimine-germylene adduct $[LSi(Cl)N(GeCl_2)SiMe_3]$ (**5**, Scheme 5) and $SiMe_3Cl$. It is proposed that **4** reacts with $SiCl_4$ to form a silylium-dichlorogermylene silicate intermediate “ $\{LSi(Cl)N(GeCl_2)(SiMe_3)_2\}^+\{SiCl_3\}^-$ ”, which then

eliminates SiMe_3Cl and “ SiCl_2 ” to form **5**. Then, “ SiCl_2 ” undergoes a polymerization to form an insoluble poly(silane). The steric effect of the GeCl_2 moiety in **5** prevents further substitution of the latter with SiCl_4 . The formation of **5** evidences the presence of the silanimine intermediate “ LSi(I)NSiMe_3 ” in the reaction of **1** and SiI_4 . Pure compound **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 5. Synthesis of **5**

Compound **5** was analysed by NMR spectroscopy. The ^{29}Si NMR resonances attributable to the LSiCl (δ -62.3 ppm) and NSiMe_3 moieties (δ 2.88 ppm) are downfield shifted in comparison with that of the $\text{LSi}=\text{N}$ moiety in **2** and the NSiMe_3 substituent in the donor-free dialkylsilanimine [$\{\text{H}_2\text{CC}(\text{SiMe}_3)_2\}_2\text{Si}=\text{NSiMe}_3$] (δ -15.5 ppm), respectively.⁷ Compound **5** was analysed by X-ray crystallography. The Si1 atom adopts a tetrahedral geometry in the X-ray crystal structure of **5** (Figure 3). The Si1-N3 (1.644(2) Å) and Si2-N3 (1.762(2) Å) bonds are significantly longer than those of **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 3. Molecular structure of compound **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 **2** was then reacted with the lithium amido compound $[\text{LiN}(\text{SiMe}_3)\text{Ar}]^{26}$ in toluene to form the silanimine $[\text{LSi}(\text{I})\text{NSiI}_2\text{N}(\text{SiMe}_3)\text{Ar}]$ (**6**, Scheme 6) and LiI. The latter can be removed by simple filtration, while compound **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 ^1H 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 LSiI moiety is comparable with that of the LSiI fragment in **2**. In addition, the ^{29}Si NMR signal (δ -139.3

ppm) for the NSiI_2N substituent is downfield shifted in comparison with that of the NSiI_3 unit in **2**. The molecular structure of **6** is similar to that of **2** (Figure 4), which comprises the tetrahedral Si1 atom, but the Si1-N3-Si2 angle ($149.67(14)^\circ$) is larger than that in **2** ($139.6(5)^\circ$). 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 $[\text{LSi}(=\text{NAr})\text{Cl}]$ ($1.545(2)$ Å)²² and the donor-free dialkylsilanimine $[\{\text{H}_2\text{CC}(\text{SiMe}_3)_2\}_2\text{Si}=\text{NR}]$ ($\text{R} = \text{CH}_2\text{Ph}$, 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.

Scheme 6. Synthesis of **6**.

Figure 4. Molecular structure of compound **6** (ellipsoids set at 50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): 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 **6** with three equivalents of KC_8 in toluene afforded the first donor-acceptor stabilized tetra(silanimine) $[\text{LSiN}(\text{SiMe}_3)\text{SiNAr}]_2$ (**7**, Scheme 7), along with KI and graphite as 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) “ $\text{LSi}\{\text{=N-:SiN}(\text{SiMe}_3)(\text{Ar})\}\text{—Si}\{\text{=N-:SiN}(\text{SiMe}_3)(\text{Ar})\}\text{L}$ ” **A**, which then undergoes Si-Si bond rearrangements to form a 1,2,4,5-tetrasil-3,6-diaza(Dewar-benzene) intermediate **B**. Subsequently, it undergoes SiMe_3 migrations to form **7** (Scheme 8). The formation of the 1,2,4,5-tetrasil-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 7. Synthesis of **7**

Scheme 8. A proposed mechanism for the formation of **7**

Compound **7** is soluble in toluene and THF. It is stable in solution and the solid state for several months. The ^1H NMR spectrum of **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 (δ -13.9 ppm) moiety in **7** is comparable with that of the $>\text{Si}=\text{N}$ moiety in the pyridine-stabilized silanimine [*t*Bu₂Si(Py)=NSiMe₂Ph] (δ -12.6 ppm).^{5b} The ^{29}Si NMR signal attributable to the LSiN moiety (δ -49.1 ppm) in **7** shows a downfield shift compared with that of the silylenylsilanimine [*L*Si(=NAr)-SiL] (δ -61.2 ppm).¹¹

Figure 5. Molecular structure of compound **7** (ellipsoids set at 25% probability). Hydrogen atoms, disorder in the *t*Bu substituent and solvent molecules are omitted for clarity. Selected bond lengths (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 **7** was analysed by X-ray crystallography. The *R*1 value is large (*R*1 = 0.1055) as red crystals of **7** are not stable during mounting. The Si1-Si3-N3A-Si1A-Si3A-N3 ring in compound **7** comprises an open book conformation in which the Si1/1A and Si3/3A atoms adopt a tetrahedral geometry (Figure 5). 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 **6**, which indicates that it has considerable double bond character. In addition, the Si1-N3 bond length (1.717(4) Å) in **7** is an intermediate value between the Si3-N4 bond length in **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)₂C(H)Ph}].²⁸ Moreover, the Si3A-N3 bond (1.784(4) Å) is longer than the Si1-N3 bond in **7**, but is shorter than the Si-N dative bonds in the

perchlorodisilane.tmeda adduct $[\{H_2C(Me)_2N\}_2SiCl_3SiCl_3]$ (2.064(5), 2.113(5) Å).²⁹ These imply that the Si-N bonds in **7** have some double bond characters as it comprises resonance structures as shown in Scheme 9.

Scheme 9. Resonance structures of **7**

Conclusion

The base-stabilized silanimine $[LSi(I)NSiI_3]$ (**2**) was synthesized by the reaction of the amidinato amidosilylene $[LSiN(SiMe_3)_2]$ (**1**) with SiI_4 . The by-products are Si_2I_6 and $SiMe_3I$. The reaction mechanism for the formation of **2** is evidenced by (a) the synthesis of the silylium germanate $[LSi(Cl)N(SiMe_3)_2]^+[GeCl_3]^-$ (**3**) by treating **1** with $GeCl_4$ and (b) the synthesis of the silanimine-germylene adduct $[LSi(Cl)N(GeCl_2)SiMe_3]$ (**5**) by reacting the amidinato silylene-germylene adduct $[L\{(Me_3Si)_2N\}SiGeCl_2]$ (**4**) with $SiCl_4$. Compound **2** further reacted with $[LiN(SiMe_3)Ar]$ and KC_8 to give the donor-acceptor stabilized tetra(silanimine) **7**. It comprises four silanimine units, which are linked together. X-ray crystallography and NMR spectroscopic data show conclusively that the Si-N bonds in **7** have some double bond characters. The reactivity and theoretical studies of compound **7** are currently under investigation.

Experimental Section

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were dried by MBraun SPS-800. Compounds **1**, **4** and LiN(SiMe₃)Ar·2Et₂O were prepared according to the literatures.^{20, 23, 26} The ¹H, ¹³C, ²⁹Si NMR spectra were recorded on a JEOL ECA 400 and Bruker Advance III 400 spectrometer. The chemical shifts δ are relative to external references SiMe₄ for ¹H, ¹³C, ²⁹Si. Grease was applied on joints and stopcocks during the preparation of the NMR samples of compounds **5** - **7** as their crystals are quite sensitive to moisture. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[LSi(I)NSiI₃] (**2**). Toluene (30 mL) was added to a mixture of **1** (0.84 g, 2.00 mmol) and SiI₄ (1.07 g, 2.00 mmol) at ambient temperature. The resulting purple-green mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of compound **2**. Yield: 0.32 g (39.6 %). Mp: 178.5 °C. Elemental analysis calcd for C₁₅H₂₃I₄N₃Si₂: C, 22.27; H, 2.87; N, 5.19. Found: C, 21.95; H, 2.53; N, 4.89. ¹H NMR (399.5 MHz, C₆D₆, 25°C): δ = 1.05 (s, 18H, *t*Bu), 6.48-6.50 (m, 1H, Ph), 6.71-6.86 (m, 4H, Ph) ppm. ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25°C): δ = 30.6 (CMe₃), 56.1 (CMe₃), 125.3, 126.5, 129.0, 130.9 (Ph), 176.9 (NCN) ppm. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 25°C): δ = -256.7 (SiI₃), -100.0 (Si(I)=N) ppm.

Si₂I₆: Toluene (30 mL) was added to a mixture of **1** (0.42 g, 1.00 mmol) and SiI₄ (1.07 g, 2.00 mmol) at ambient temperature. The resulting orange-green mixture was stirred for 16 hours. It was filtered and the filtrate was concentrated to afford colorless crystals of Si₂I₆. Yield 0.527 g (64.5 %)

[LSi(Cl)N(SiMe₃)₂]GeCl₃ (**3**): GeCl₄ (0.22 g, 1.00 mmol) was added dropwise to the solution of **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 **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 **3** is highly unstable in solution. Freshly prepared solution of **3** is essential for NMR spectroscopy. Elemental analysis for C₂₁H₄₁Cl₄GeN₃Si₃: C, 39.79; H, 6.52; N, 6.63. Found: C, 39.38; H, 6.50; N, 6.67. ¹H NMR (399.5 MHz, C₆D₆, 25°C): δ = 0.17 (s, 9H, SiMe₃), 0.38 (s, 9H, SiMe₃), 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. ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25°C): δ = 4.2 (SiMe₃), 4.4 (SiMe₃), 30.5 (CMe₃), 57.7 (CMe₃), 127.1, 128.6, 129.8, 132.7 (Ph), 183.1 (NCN). ²⁹Si{¹H} NMR (79.4 MHz, THF-*d*₈, 25°C): δ = 12.1 (SiMe₃), 31.4 (LSiCl) ppm.

[LSi(Cl)N(GeCl₂)SiMe₃] (**5**): Toluene (30 mL) was added to a mixture of **4** (0.56 g, 1.00 mmol) and SiCl₄ (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 **5**. Yield: 0.32 g (60.9 %). Mp: 148.4 °C (decomposed). Elemental analysis calcd for C₁₈H₃₂Cl₃GeN₃Si₂: C, 41.15; H, 6.14; N, 8.00. Found: C, 40.87; H, 6.01; N, 7.72. ¹H NMR (399.5 MHz, C₆D₆, 25°C): δ = 0.53 (s, 9H, SiMe₃), 1.21 (s, 18H, *t*Bu), 6.88-6.89 (m, 4H, Ph), 8.41-8.43 (m, 1H, Ph) ppm. ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25°C): δ = 1.1 (SiMe₃), 31.0 (CMe₃), 55.2 (CMe₃), 127.3, 127.7, 130.1, 132.6 (Ph), 172.2 (NCN) ppm. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 25°C): δ = -62.3 (Si(Cl)=N), 2.9 (SiMe₃) ppm.

[LSi(I)NSiI₂N(SiMe₃)Ar] (**6**): Toluene (30 mL) was added to a mixture of **2** (0.81 g, 1.00 mmol) and LiN(SiMe₃)Ar·2Et₂O (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 **6**. Yield: 0.92 g (98.9 %). Mp: 218.4 °C. Elemental analysis calcd for C₃₀H₄₉I₃N₄Si₃·¼C₇H₈: C, 40.00; H, 5.39; N, 5.87. Found: C, 39.96; H, 5.98; N, 5.28. ¹H NMR (399.5 MHz, C₆D₆, 25°C): δ = 0.63 (s, 9H, SiMe₃), 1.05 (s, 18H, *t*Bu), 1.41 (d, 6H, CHMe₂), 1.63 (d, 6H, CHMe₂), 4.07 (sep, 2H, CHMe₂), 6.56-6.69 (m, 1H, Ph), 6.75-6.87 (m, 4H, Ph), 7.09-7.13 (m, 3H, Ph) ppm. ¹³C{¹H} NMR (100.5 MHz, C₆D₆, 25°C): δ = 3.4 (SiMe₃), 24.7 (CHMe₂), 27.3 (CHMe₂), 28.4 (CHMe₂), 30.7 (CMe₃), 55.7 (CMe₃), 127.5, 127.6, 127.7, 128.0, 128.2, 129.0, 142.9, 148.1 (Ph), 166.9 (NCN) ppm. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 25°C): δ = -139.3 (Si(NAr)I₂), -100.1 (Si(I)=N), 7.5 (SiMe₃) ppm.

[LSiN(SiMe₃)SiNAr]₂ (**7**): Toluene (30 mL) was added to a mixture of **6** (0.98 g, 1.00 mmol) and KC₈ (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 **7**. Yield: 0.32 g (58.2 %). Mp: 189.2 °C (decomposed). Elemental analysis calcd for C₆₀H₉₈N₈Si₆: C, 65.56; H, 8.98; N, 10.19. Found: C, 65.34; H, 8.72; N, 10.02. ¹H NMR (399.5 MHz, THF-*d*₈, 25°C): δ = 0.40 (s, 18H, SiMe₃), 1.09 (s, 36H, *t*Bu), 1.17-1.24 (br, 24H, CHMe₂), 3.71-3.82 (br, 4H, CHMe₂), 6.24-7.58 (br, 16H, Ph). ¹³C{¹H} NMR (100.5 MHz, THF-*d*₈, 25°C): δ = 3.4 (SiMe₃), 24.7 (CHMe₂), 27.3 (CHMe₂), 28.4 (CHMe₂), 30.7 (CMe₃), 55.7 (CMe₃), 127.5, 127.6, 127.7, 128.0, 128.2, 129.0, 142.9, 148.1 (Ph), 166.9 (NCN) ppm. ²⁹Si{¹H} NMR (79.4 MHz, THF-*d*₈, 25°C): δ = -49.1 (*Si*=N-SiMe₃), -13.9 (*Si*=N-Ar), 3.6 (*Si*Me₃) ppm.

X-ray data collection and structural refinement. Intensity data for compounds **2 - 3** and **5 – 7** were collected using a Bruker APEX II diffractometer. The crystals of **2 - 3** and **5 – 7** 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 .³⁰ 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.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publication website.

X-ray data for compounds **2 - 3** and **5 – 7** (CIF)

Selected spectra, X-ray crystal structure of Si₂I₆, Scheme S1 for the molecular structure of the dichlorogermylene-benzothiazole adduct, Table S1 giving selected X-ray crystallographic data of compounds **2 - 3** and **5 – 7** (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y.-L.S. synthesized compounds **2** - **3** and **5** – **7**. Y.L. and R.G. performed X-ray crystallography.

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SYNOPSIS

The amidinato amidosilylene **1** reacted with SiI_4 , $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ and KC_8 to give the **donor-acceptor stabilized** tetra(silanimine) **7**. It comprises **four silanimine units linked together** in which the Si-N bonds have some double bond characters.