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**Silicon Chemistry**

# A Dimer of Silaisonitrile with Two-Coordinate Silicon Atoms**

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*Dedicated to Professor Raymundo Cea-Olivares on the occasion of his 60th birthday*

Carbenes and silylenes are among the most important reactive intermediates of carbon[1] and silicon.[2,3] These species play key roles in numerous thermal and photochemical reactions and are extremely important in synthetic chemistry.[1–3] The first N-heterocyclic carbene (NHC) that is stable at room temperature was isolated by Arduengo et al. in 1991.[4] The silicon analogue of NHC was reported three years later by West and co-workers[5] as an N-heterocyclic silylene (NHSi) and using the same stabilization concept. Since then, a number of stable carbene[6,7] and silylene[8] compounds have been isolated with various electronic structures and properties. Synthesis and stabilization of the reactive species are not just a simple desire of academic interest to realize highly reactive molecules at normal laboratory conditions; they have also found many useful applications.[7–10] The extraordinary electronic properties of NHCs as strong σ-donor and weak π-acceptor ligands have been shown to bind more strongly with transition metals than classical ligands.[7,9] The unusual stability of transition-metal complexes supported by NHC as ligands has led to a major breakthrough in the second generation of Grubb's catalysts.[10]

The properties of silicon and carbon are rather different from each other although both have the same number of valence electrons. These differences are most pronounced for compounds with low-coordinate silicon and carbon atoms. Among unsaturated compounds, a wide range of carbon compounds are known that are stable, whereas analogous silicon compounds are very limited and quite reactive. The syntheses of stable silicon compounds have been inspired almost exclusively by their relationship with organic congeners. Silicon analogues of alkenes,[11] alkynes,[12] allenes,[13] and other unsaturated organic compounds with a $C{=}X$ ($X = O$ or S) functional group[14,15] have been prepared. The molecular and electronic structures of unsaturated compounds of silicon are very different from those of the corresponding carbon compounds in which s/p hybridization models are valid.[16,17] To understand the physical and chemical properties of unsaturated silicon compounds, additional experimental investigations are required. Further progress and understanding of the field depend on the availability of appropriate stable silicon compounds.

Organic nitriles and isonitriles are very stable, but their silicon analogues are only detected as transient species in a low-temperature argon matrix.[18–20] The first transient silaisonitrile, $HN{=}Si$, was described in 1966 by Ogilvie and Cradock;[19] this species was generated by photolysis of $H_3SiN_3$ in an argon matrix at 4 K. The formation of silaisonitrile[20] was shown by PE and IR spectroscopic studies in an argon matrix. Quantum chemical calculations have shown that silaisonitriles are more stable than silanitriles.[21] This result is in contrast to the carbon analogues.[22] Despite the remarkable theoretical contributions by Apeloig and others[20,21] on the relative stability of silanitrile (RSiN) and silaisonitrile (RNSi), no silaisonitrile or silanitrile has been reported to date that is stable at room temperature.

Very recently, we reported NHC-stabilized dichlorosilaimine[23] $IPr{\cdot}Cl_2Si{=}NAr$ (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene, Ar = 2,6-bis(2,4,6-triisopropylphenyl)-phenyl), which was prepared by the reaction of $IPr{\cdot}SiCl_2$[24] with $ArN_3$. Herein, we present the reduction of dichlorosilaimine **1** with $KC_8$ to afford a dimeric silaisonitrile $(ArNSi{:})_2$ (**3**; Scheme 1). The mechanism for the formation of **3** is unknown. In view of the reluctance of silicon to form compounds with multiple bonds, the formation of **3** is assumed to proceed by the initial formation of the unstable monomeric silaisonitrile **2**. Dimerization of **2** by [2+2] cycloaddition under elimination of two molecules of IPr affords **3** as yellow crystalline blocks in 21 % yield. To the best of our knowledge, an analogous carbon compound is not known.

Treatment of **3** with trimethylsilyl azide ($Me_3SiN_3$) gives the first bis(silaimine) **4** (Scheme 2) with three-coordinate silicon atoms as a colorless crystalline solid in 62 % yield. Formation of **4** confirms the presence of a reactive lone pair of electrons on each of the silicon atoms of **3**.

Compounds **3** and **4** are stable under an inert atmosphere and are soluble in common organic solvents. The molecular structures of **3** and **4** were established by single-crystal X-ray diffraction studies. Refinement of **3** benefited from non-spherical scattering factors of the invariom approach.[25] The $^1H$ and $^{13}C$ NMR spectra of **3** show resonances for terphenyl ($(2,4,6\text{-}i\mathrm{Pr}_3\text{-}C_6H_2)_2C_6H_3$) groups on amino nitrogen atoms.

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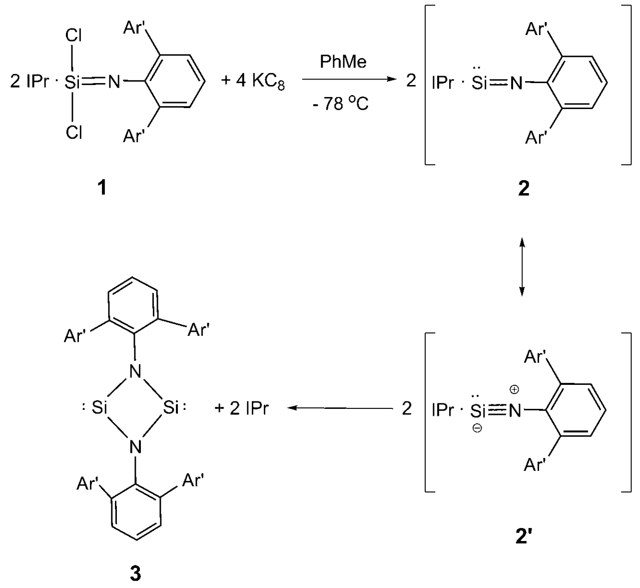
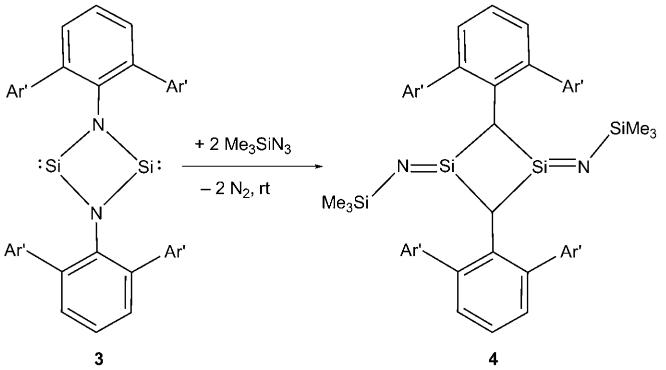


**Scheme 1.** Synthesis of dimeric silaisonitrile **3**. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; Ar′ = 2,4,6-triisopropylphenyl.



**Scheme 2.** Synthesis of bis(silaimine) **4**. Ar′ = 2,4,6-triisopropylphenyl.

Compound **4** exhibits $^{1}$H and $^{13}$C NMR resonances for the $Me_3Si$ groups along with the resonances for terphenyl groups. The $^{29}$Si NMR chemical shift at $\delta = +183.29$ ppm for **3** indicates strong deshielding, as expected for compounds with low-valent silicon atoms. The value is quite far downfield when compared with those of reported NHSi compounds.[5,8] The relatively high downfield shift in the $^{29}$Si NMR spectrum of **3** in comparison to those observed for two-coordinate silicon[5,8] in NHSi compounds may be due to the presence of two silylene moieties in the ring. However, the reason for this strong deshielding is presently unknown. The molecular ion [$M^+$] observed at $m/z$ 1046 in the EI mass spectrum of **3** with the base ion at 1003 [$(M-C_3H_7)^+$] further supports the dimeric nature of **3**. The $^{29}$Si NMR spectrum of **4** exhibits two resonances at $\delta = 2.76$ and $-56.82$ ppm for trimethylsilyl ($SiMe_3$) and silaimine (ArNSi=N) moieties, respectively. The slightly downfield shift in the $^{29}$Si NMR of **4** compared to those of reported compounds[23] may be due to the lower coordination number of silicon in **4**.

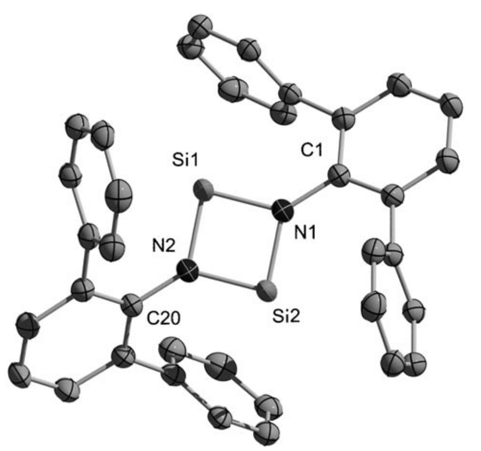


**Figure 1.** Molecular structure of **3**. Ellipsoids set at 50% probability; hydrogen atoms, isopropyl groups, and benzene molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.756(1), Si1–N2 1.754(1), N1–C1 1.408(3), N2–C20 1.408(3); N1-Si1-N2 86.02(6), Si1-N1-Si2 94.02(9), C20-N2-Si1 132.99(5), C1-N1-Si1 133.03(5).

The molecular structure of **3** is shown in Figure 1. Single crystals of **3** were grown from a benzene solution at room temperature. **3** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit of **3** contains half a molecule with one and a half molecules of benzene. Each of the silicon atoms in **3** is two-coordinate and it is the first example of a base-free disilylene.[26] The four-membered $Si_2N_2$ ring in **3** is almost planar. The endocyclic N-Si-N (86.02(6)°) and Si-N-Si (94.02(9)°) angles of the $Si_2N_2$ ring are nearly orthogonal to each other. Bonds to divalent silicon are expected to be longer by $(0.1 \pm 0.02)$ Å in comparison to those of tetravalent silicon.[27] The Si–N bond lengths (av. 1.755(1) Å) in **3** are in agreement with those observed for heterocycles[26] with low-valent silicon. The phenyl rings on the amino nitrogen are almost perpendicular to one another, with a dihedral angle of 83.07°.[28a]

A few silicon compounds with Si=N bonds have been reported; however, most of them are stabilized with a Lewis base.[23,29] Very recently, a base-free monosilaimine was prepared[29] with a terphenyl group on the imine nitrogen atom. Compound **4** is the first example of a base-free bis(silaimine) with two three-coordinate silicon atoms. The molecular structure of **4** is shown in Figure 2. Bis(silaimine) **4** crystallizes in the triclinic space group $P\bar{1}$ with half a molecule of **4** and a molecule of toluene in the asymmetric unit. Each of the silicon atoms in the four-membered $Si_2N_2$ ring of **4** is three-coordinate. As expected for compounds with tetravalent silicon, the endocyclic Si–N bond lengths in **4** (av. 1.724(2) Å) are slightly shorter in comparison to those observed for **3** (av. 1.755(1) Å). The exocyclic Si–N bond lengths (1.564(2) Å) are in agreement with those reported for compounds with silicon–nitrogen double bonds.[23,29] The internal $Si_2N_2$ bond angles are almost the same as those found in **4**. Interestingly, the phenyl rings on the amino nitrogen of the $Si_2N_2$ ring are arranged in the same plane, but perpendicular to the plane of the $Si_2N_2$ ring.[28b]

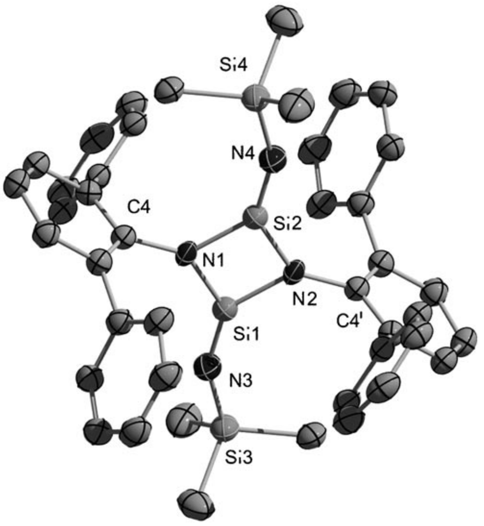


*Figure 2.* Molecular structure of **4**. Ellipsoids set at 50% probability; hydrogen atoms, isopropyl groups, and toluene molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.728(2), Si1–N2 1.720(2), Si1–N3 1.564(2), N3–Si3 1.708(2), N1–C4 1.443(2); N1-Si1-N2 87.31(7), Si1-N1-Si2 94.69(7), C4-N1-Si1 139.99(14), Si1-N3-Si3 153.76(13), N3-Si1-N2 135.05(9).

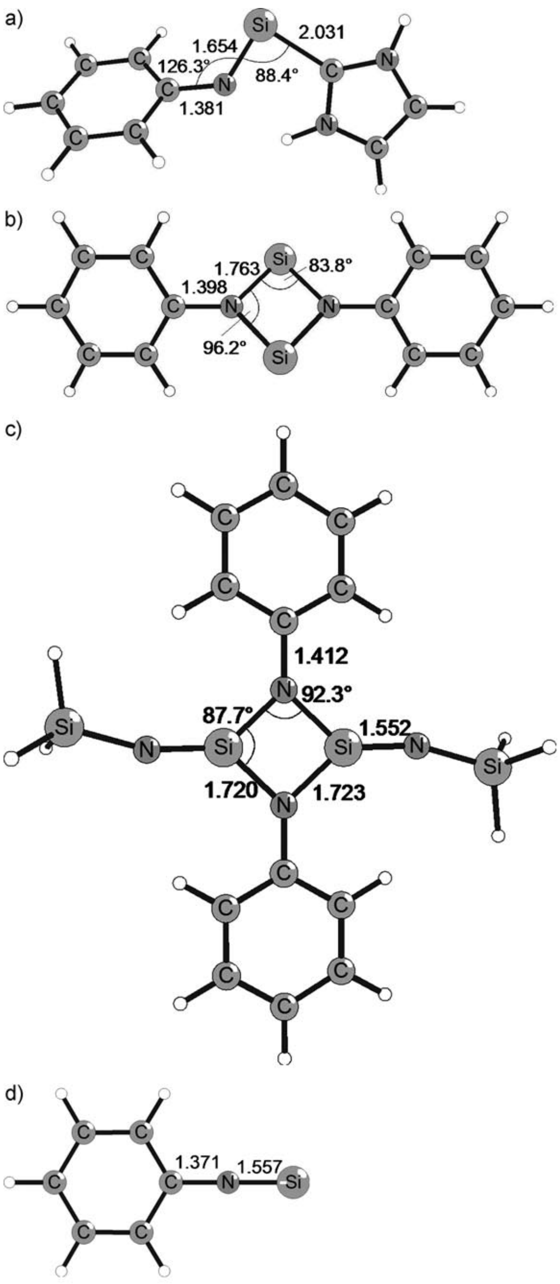


*Figure 3.* Calculated structures (bond lengths [Å], angles [°]) of a) **2M**, b) **3M**, c) **4M**, and d) $C_6H_5NSi$ at M05-2X/TZVPP.

We carried out quantum chemical calculations using density functional theory at the M05-2X/TZVPP level (see the Supporting Information) for the model compounds **2M**, **3M**, and **4M** (Figure 3), where the substituents Ar' are replaced by hydrogen atoms and where the IPr ligand is replaced by 1,3-dimethylimidazol-2-ylidene. We also calculated free phenylsilaisonitrile ($C_6H_5NSi$). Figure 3 shows the optimized geometries and the most important bond lengths and angles. The calculated interatomic distances and angles of **3M** and **4M** are in very good agreement with the experimental values of **3** (Figure 1) and **4** (Figure 2), respectively. Theory and experiment agree that the equidistant Si–N bonds in **3** and **3M** are distorted towards two sets of slightly different Si–N bonds. The elusive phenylisonitrile is predicted with rather short C–N (1.371 Å) and N–Si (1.557 Å) bonds.

The addition of NHC ligand in **2M** slightly elongates the C–N bond (1.381 Å), while the N–Si bond (1.654 Å) is significantly longer than in free $C_6H_5NSi$. The NHC ligand is bonded side-on to the silicon atom in **2M**, which exhibits a rather acute bonding angle of 88.4° (Figure 3). The NBO analysis of $C_6H_5NSi$ and **2M** suggests that free phenylsilaisonitrile has a strongly polarized N–Si triple bond where the σ and the π components are 85.4% (σ bond) and 84.1% and 84.0% (π bond) at the nitrogen end. The partial charge at nitrogen in $C_6H_5NSi$ is −1.16 e, while the silicon atom has a positive charge of +1.05 e. The NHC complex **2M** possesses a N–Si double bond that is also strongly polarized toward the nitrogen atom which carries an electron lone pair. In the latter molecule, 82.9% of the σ bond and 86.1% of the π bond are at the nitrogen end. The partial charges in **2M** are −1.17 e (at N) and +0.86 e (at Si). The calculated charges for the dimer **3M** are −1.33 e (N) and +1.23 e (Si).

The theoretically predicted bond dissociation energy (BDE) for the NHC ligand of **2M** is $D_o = 19.7\ \mathrm{kcal\,mol^{-1}}$, which shows that the molecule is a moderately strong donor–acceptor complex.[30] The dimerization energy for the reaction $2\,C_6H_5NSi \rightarrow \mathbf{3M}$ is $-48.9\ \mathrm{kcal\,mol^{-1}}$, which indicates that the formation of **3M** from **2M** that mimics the second reaction step shown in Scheme 1 is energetically favored by 9.5 kcal $\mathrm{mol^{-1}}$.

Figure 4 shows the Laplacian[31] distributions of $C_6H_5NSi$, **2M**, and **3M**, which nicely exhibit the charge concentrations of the electron lone pairs at Si in the three molecules. Figure 4b also shows the charge concentrations of the electron lone pair of nitrogen. The Si–N bonds are strongly polarized towards nitrogen, which becomes visible through the areas of charge concentration at the nitrogen end (solid

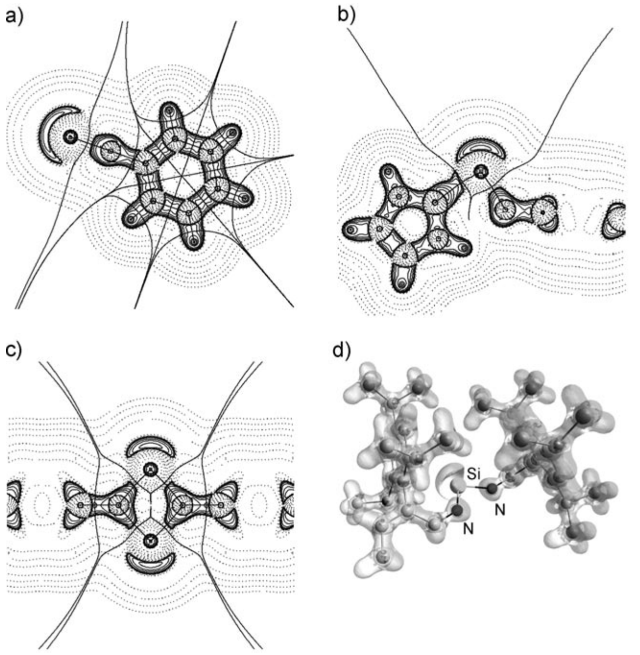


*Figure 4.* a–c) Contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ of $C_6H_5NSi$, **2M**, and **3M**. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). Contours of the Laplacian increase and decrease from zero contour are shown in steps of $\pm 2\times10^n$, $\pm 2\times10^n$, $\pm 2\times10^n$, beginning with $n = -3$ to 3. Solid lines connecting the atomic nuclei are the bond paths; solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane. d) An isosurface of the Laplacian from Invariom refinement with an isosurface value of 0.001 e Å$^5$. Only the asymmetric unit containing half a molecule of **3** is shown.

lines), while there is an area of charge depletion at the silicon end (dotted lines). As in the quantum chemical calculations on model compounds, Invariom refinement[25] of compound **3** also allowed the non-spherical electron density to be evaluated. Figure 4d depicts the Laplacian by means of an isosurface with a value of 0.001 e Å$^5$ for the whole asymmetric unit of **3**. Local charge concentrations around the silicon atoms become visible.

Finally, we calculated the NICS[32] values for the four-membered ring of **3M**, which is formally a 4π-electron antiaromatic system. The theoretical data of NICS(0) = 5.01 and NICS(1) = 0.91 are indeed compatible with an antiaromatic character of the cyclic $N_2Si_2$ moiety.

In summary, a stable dimeric silaisonitrile (**3**) is presented for the first time. Compound **3** is the first base-free disilylene with two-coordinate silicon atoms; and an analogous carbon compound is not known. The formation of silaisonitrile **3** as a dimer and the existence of organic isonitrile or nitrile as monomers seem plausible. Reaction of **3** with trimethylsilyl azide affords the first bis(silaimine) with three-coordinate silicon atoms. Availability of the first silicon analogue of an organic isonitrile as a stable compound will further spark the interest of theoretical and experimental scientists. Quantum chemical calculations of model compounds suggest that the dimerization of the free phenylsilaisonitrile is exoenergetic by 48.9 kcal mol$^{-1}$. The silicon atoms in **3M**, in free $C_6H_5NSi$, and in the complex **2M** carry electron lone pairs.

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[28] a) See Figure F2 in the Supporting Information; b) see Figure F3 in Supporting Information.

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