Ionic Silicon(II) Compounds

Silicon(II) Coordination Chemistry: N-Heterocyclic Carbene Complexes of Si²⁺ and SiI⁺**

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Si²⁺ ions are highly reactive, two-valence-electron species that have been generated in laser-induced plasmas and studied by photoabsorption and microwave spectroscopy.^[1] The ions have also been employed as implants for waveguide fabrication in lithium niobate crystals, which are of great interest for various photonic applications owing to their physical and electro-optical properties.^[2] A possible method of trapping these highly electrophilic ions in the condensed phase, may involve complexation by three strongly basic, neutral ligands (L) to give dications of the general formula $[SiL_3]^{2+}$, in which the silicon center attains a noble gas configuration. However, dicationic silicon(II) complexes are presently unknown, in marked contrast to the few germanium homologues, which were reported some years ago by K. M. Baines et al.^[3] This difference can be explained by the anomalous low electronegativity of silicon versus germanium,^[4] which makes the isolation of silicon(II)-centered dications a highly challenging goal. Even monocationic silicon(II) compounds are very rare, and only the nido-type cluster cation $[(C_5Me_5)Si]^+$, ^[5] the β -diketiminato-substituted cation [HC(CMe)₂(Ndipp)₂Si]⁺ $(dipp = 2,6-diisopropylphenyl)^{[6]}$ and the Si^{II} cation [{C₁₀H₆- α, α -NP(*n*Bu)₃[SiCl]⁺ stabilized by a chelating bis(iminophosphorane) ligand^[7] have been isolated thus far.

Since the first report of the silicon(0) compound [Si₂-(Idipp)₂] (Idipp = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2ylidene) by G. Robinson et al. in 2008,^[8] N-heterocyclic carbenes have been shown to be particularly effective ligands for the stabilization of silicon compounds in unusually low oxidation states. Remarkable examples include NHC adducts of the dihalosilylenes SiX₂ (X = Cl, Br),^[9] which are very valuable precursors in Si^{II} chemistry,^[9c,10] or NHC adducts of the organohalosilylenes RSiCl (R = *m*-terphenyl, (2,6-diisopropylphenyl)(trimethylsilyl)amino),^[11] which paved the way for the preparation of the first complexes featuring metal– silicon triple bonds.^[12] Herein, the exchange of NHC ligands at Si^{II} centers is illustrated for the first time to provide access



Scheme 1. Multistep synthesis of the iodide salt of the dicationic Si^{II} -complex $[Si(IMe_4)_3]^{2+}$ (3) starting from SiI_4 .

to unprecedented dicationic NHC complexes of silicon(II) and NHC adducts of the iodosilyliumylidene cation SiI^+ .

The entry into this chemistry started with the triiodosilylimidazolium salt **1** (Scheme 1), which was obtained from the reaction of SiI₄ with Idipp in toluene and isolated as a yellow, thermally robust solid in 96% yield. Reduction of **1** with potassium graphite (2.3 equiv) in benzene afforded the yellow NHC-diiodosilylene adduct **2**-I in 81% yield (Scheme 1).^[13] Under rigorous exclusion of air, the silicon(II) compound **2**-I is stable in benzene or toluene solution at ambient temperature for several days, and decomposes in the solid state upon heating above 160 °C.

The solid-state structure of $1.3 (\text{CHCl}_3)$ was determined by single-crystal X-ray crystallography.^[13] It resembles that of [SiBr₃(Idipp)]Br·3 (CH₂Cl₂)^[9b] and reveals that the chloroform trissolvate of **1** is composed of well separated [SiI₃-(Idipp)]⁺ cations and iodide counter anions. The shortest Si…I interionic contact of 5.94 Å exceeds by far the sum of the van der Waals radii of silicon and iodine (4.08 Å),^[14] thus excluding any bonding interaction. The mean Si–I bond length of the cation in **1**·3 (CHCl₃) (2.420(8) Å)^[15] compares well with that of SiI₄ (2.432(5) Å)^[16] and the Si–C1 bond (1.911(3) Å) is only slightly longer than a covalent Si–C(sp²) single bond (1.872 Å),^[17] as expected for an imidazolium cation bearing a SiI₃ substituent at the C2 position (Figure 1).^[18]

The ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra confirm the ionic nature of **1** in CDCl₃ solution.^[19] For example, the ²⁹Si{¹H} NMR spectrum of **1** displays a singlet signal at

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Figure 1. DIAMOND plot of the structure of the cation of 1.3 CHCl_3 in the solid state. Thermal ellipsoids are set at 30% probability; hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths [Å] and angles [°]: Si–I1 2.439(1), Si–I2 2.410(1), Si–I3 2.412(1), Si–C1 1.911(3), C1–N1 1.371(4), C1–N2 1.352(4), N1–C2 1.370(4), N2–C3 1.373(4), C2–C3 1.352(5); I1-Si-I2 107.99(4), I1-Si-I3 108.16(4), I2-Si-I3 109.33(4), C1-Si-I1 107.5(1), C1-Si-I2 113.6(1), C1-Si-I3 110.1(1), N1-C1-N2 105.4(3).

considerably lower field ($\delta = -225.8 \text{ ppm}$) than that of SiI₄ (δ in C₆D₆ = -346.6 ppm). The same trend was observed for [SiBr₃(Idipp)]Br in CD₂Cl₂ ($\delta = -63.9 \text{ ppm}$) vs. SiBr₄ (δ in C₆D₆ = -90.8 ppm).^[9b] In comparison, the ²⁹Si NMR signal of the neutral pentacoordinate complex [SiCl₄(Idipp)]^[8] appears in CD₂Cl₂ at considerably higher field ($\delta = -108.9 \text{ ppm}$) than that of SiCl₄ (δ in C₆D₆ = -18.5 ppm)^[20] as a result of the higher silicon coordination number.^[21]

Compound 2-I is the first silicon(II) diiodide to be characterized by X-ray crystallography (Figure 2).^[13,22] Its structure closely resembles those of the Si^{II} halides [SiX₂-(Idipp)] (X = Cl, Br)^[9a,b] and of the germanium analogue [GeI₂(IMes)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene),^[23] and features a trigonal pyramidal coordinated silicon center, which indicates the presence of a stereochemically active lone pair of electrons at silicon. The degree



Figure 2. DIAMOND plot of the molecular structure of **2**-1 in the solid state. Thermal ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (bond lengths and bond angles of the other two independent molecules of **2**-1 are given in square brackets): Si1–I1 2.570(1) [2.585(1), 2.563(1)], Si1–I2 2.576(1) [2.578(1), 2.577(1)], Si1–C1 1.997(4) [1.975(4), 1.980(4)], C1–N1 1.362(5) [1.371(5), 1.362(5)], C1–N2 1.363(5) [1.369(5), 1.377(5)], N1–C2 1.388(5) [1.377(5), 1.383(5)], N2–C3 1.373(5) [1.378(5), 1.364(5)], C2–C3 1.339(6) [1.344(6), 1.338(6)]; I1-Si-I2 95.63(4) [96.72(4), 97.16(4)], C1-Si-I1 103.1(1) [104.9(1), 102.8(1)], C1-Si-I2 96.5(1) [97.5(1), 95.6(1)], N1-C1-N2 104.7(3) [103.2(3), 103.7(3)].

of pyramidalization (DP) of **2**-I of 70% (sum of angles at Si = $297(1)^{\circ}$)^[24] is slightly smaller than that of [SiBr₂(Idipp)] (**2**-Br: DP = 75%; sum of angles at Si = 292.7°)^[9b] and [SiCl₂(Idipp)] (**2**-Cl: DP = 78%; sum of angles at Si = 289.7°);^[9a] this trend follows Bent's rule.^[25]

The Si^{II}–I bond length of **2**-I (2.575(3) Å) compares well with that of **4** (2.5591(6) Å) (see below), but is considerably longer than those of Si^{IV} iodides (2.420(8) Å (1); 2.432(5) Å (SiI₄);^[16] 2.453(4) Å (MesSiI₃)^[26]) owing to the lower oxidation state of silicon (+ II) in **2**-I and **4**.

The Si-C bond length (1.984(7) Å) of 2-I is nearly identical with those of 2-Cl (1.989(3) Å)^[9a] and 2-Br 1.985(4) Å^[9b] and also the Si-C bond dissociation energy of 2-I (121.4 kJ mol⁻¹) compares well with those of 2-Cl (121.4 kJ mol⁻¹) and 2-Br (123.6 kJ mol⁻¹), which suggests the presence of a comparable strong C-Si donor-acceptor single bond in 2-X.^[27] This is verified by the topological analyses of the electron density distributions at the Si-C bond critical points.^[27,28] These analyses further show that the Si-C dative bonds of 2-X have covalent character and are weaker than those of SiMe₄, which provides a rationale for the lower Si-C bond dissociation energies found for 2-X versus those of alkyl silanes (ca. 370 kJ mol⁻¹).^[29] The electronic structure of 2-X compares well with those of the zwitterionic silenes $X_2SiC(NH_2)_2$ (X = H, Me, F, Cl, NH₂, OH), which feature a reversed Si-C bond polarization,^[30] that is best represented by zwitterionic canonical formulas, as depicted for 2-I in Scheme 2.^[31] Compounds 2-X take an intermediate position in the bonding continuum between the planar parent silene H₂Si=CH₂ at the one end, which features a short Si=C bond $(1.704(2) \text{ Å})^{[32]}$ with a large Si-C bond dissociation energy (462 kJ mol⁻¹),^[31a] and the non-planar carbene–silylene adduct [(NN)SiC(NN)] (NN = 1,2-(NCH₂tBu)₂C₆H₄) at the other end, which features a long Si-C single bond (2.162(5) Å) with a very low Si-C bond dissociation energy (13 kJ mol⁻¹).^[33] The position in this bonding continuum depends on the sum of the singlet-triplet gaps $\Sigma \Delta E_{\rm ST}$ of the carbene and silvlene fragments, which is tuned by the substituents.^[31,34]

The ²⁹Si{¹H} NMR spectrum of **2-I** in C₆D₆ solution displays a singlet at a similar position ($\delta = -9.7$ ppm) to those observed in the solid-state ²⁹Si{¹H} NMR-MAS spectrum ($\delta = -5.1$ ppm (1 Si), and -9.2 ppm (2 Si).^[35] This suggests that compound **2-I** has a similar structure in solution and in the solid state. A comparison of the ²⁹Si nucleus chemical shift of **2-I** with that of [SiBr₂(Idipp)] ($\delta =$ 10.9 ppm)^[9b] and [SiCl₂(Idipp)] ($\delta =$ 19.06 ppm)^[9a] reveals the same ²⁹Si nucleus deshielding upon halide substitution (I \rightarrow Br \rightarrow Cl) as observed for Si^{IV} halides.^[36]



Scheme 2. Ylidic canonical structures of **2**-I, $\mathbf{3}^{2+}$ and $\mathbf{4}^+$. Formal charges are shown in circles. L = N-heterocyclic carbene.

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The silicon(II) iodide 2-I is a very promising starting material for the preparation of cationic Si^{II} complexes, since it bears two iodide groups, which are good leaving groups and should be easily displaced from silicon. In fact, addition of 1,3,4,5-tetramethyl-imidazol-2-ylidene (IMe₄; 2.4 equiv) to a solution of 2-I in fluorobenzene rapidly afforded, after replacement of both iodide groups and the Idipp ligand, the iodide salt of the dicationic Si^{II} complex $[Si(IMe_4)]^{2+}$ (3^{2+}), which immediately precipitated out of the reaction solution, and was isolated as a light yellow powder in 79% yield (Scheme 1). Complex salt 3 is only soluble in CH₂Cl₂, in which it slowly decomposes after several hours at ambient temperature. No evidence was found for any intermediates in the reaction of 2-I with IMe4. This suggests that the first step, which probably involves a I-/IMe4 exchange to give the putative intermediate [SiI(IMe₄)(Idipp)]I, is rate determining in the overall reaction sequence ultimately leading to **3**.^[37]

The crystal structure of $3.2 \text{ CD}_2 \text{Cl}_2$ shows well separated 3^{2+} ions and iodide counter anions, the closest Si…I contact (5.88 Å) being much longer than the sum of the van der Waals radii of silicon and iodine (4.08 Å).^[14] The dication 3^{2+} has an almost C_3 symmetric, propeller-like, pyramidal structure (Figure 3), which resembles that of the Ge dication $[Ge(IiPr_2Me_2)_3]^{2+}$.^[3a] The degree of pyramidalization of 3^{2+} (DP = 53%, sum of angles at Si = 312°) is lower than those of $[SiI(IiPr_2Me_2)(Idipp)]^+$ (4⁺) (DP = 65 %, sum of angles at Si = 301.4° ; Figure 4) and 2-I (DP = 70%) and can be rationalized with Bent's rule, according to which silicon uses hybrid orbitals of higher s character for bonding to the less electronegative NHC substituents in 3^{2+} and 4^{+} .^[25] The double positive charge of $\mathbf{3}^{2+}$ is strongly delocalized over the IMe₄ groups, which suggests a strong contribution of the zwitterionic canonical formula depicted in Scheme 2 to the bonding in **3**²⁺.



Figure 3. DIAMOND plot of the molecular structure of the cation of **3**·2 (CD₂Cl₂) in the solid state. Ellipsoids are set at 30% probability; hydrogen atoms and solvent molecules are omitted for clarity. The smaller figure depicts the same structure in a side view that shows the strong pyramidalization of silicon. Selected bond lengths [Å] and angles [°] (corresponding bond lengths and angles of the other two NHC groups are included in squared brackets): Si–C1 1.918(3), Si–C8 1.909(3), Si–C15 1.917(3), C1–N1 1.359(3) [1.356(3), 1.355(3)], C1–N2 1.357(3) [1.352(3), 1.360(3)], N1–C2 1.389(3) [1.384(3), 1.386(3)], N2–C3 1.402(3) [1.388(3), 1.385(3)], C2–C3 1.354(4) [1.360(4), 1.359(4)]; C1-Si-C8 103.9(1), C1-Si-C15 104.7(1), C8-Si-C15 103.4(1), N1-C1-N2 105.1(2) [104.8(2), 104.8(2)].



Figure 4. DIAMOND plot of the molecular structure of the cation of $4 \cdot C_6 H_5 F$ in the solid state. Ellipsoids are set at 30% probability; the 2,6-bonded isopropyl substituents of the Idipp ligand, the solvent molecule and the hydrogen atoms, except that (H36) involved in the anagostic interaction with the silicon center, are omitted for clarity; the anagostic interaction is visualized by a dashed line. Selected bond lengths [Å] and angles [°]: Si–I1 2.5591(6), Si–C1 1.947(2), C1–N1 1.358(3), C1–N2 1.374(3), N1–C2 1.386(3), N2–C3 1.377(3), C2–C3 1.341(3), Si–C28 1.967(2), C28–N3 1.362(3), C28–N4, 1.357(3), N3–C29 1.384(3), N4–C30 1.389(3), C29–C30 1.357(3), N3–C36 1.489(3); C1-Si-I1 103.49(6), C28-Si-I1 98.57(7), C1-Si-C28 99.32(9), N1-C1-N2 104.2(2), N3-C28-N4 105.8(2).

Evidence for this is provided by both the structural and spectroscopic features of 3^{2+} . Thus, the Si–C_{NHC} bonds of 3^{2+} (1.915(3) Å)^[15] are even shorter than that of [SiCl(C₆H₃-2,6-Trip₂)(IMe₄)] (1.963(2) Å)^[11a] and [Cp(CO)₂Mo=Si(C₆H₃-2,6-Trip₂)(IMe₄)] (1.944(1) Å),^[12a] and approximate the Si–C_{aryl} single bonds of [SiCl(C₆H₃-2,6-Trip₂)(IMe₄)] (1.937(2) Å)^[11a] and [Cp(CO)₂Mo=Si(C₆H₃-2,6-Trip₂)(IMe₄)] (1.920(2) Å).^[12a]

The ²⁹Si{¹H} NMR spectrum of **3** in CD₂Cl₂ shows a strongly shielded ²⁹Si NMR signal ($\delta = -89.9$ ppm), which appears at considerably higher field than those of **2**-I ($\delta =$ -9.7 ppm) and **4** ($\delta = -55.3$ ppm). The ¹³C{¹H} NMR spectrum displays a distinctive signal for the Si-bonded $C_{\rm NHC}$ atom at $\delta = 150.7$ ppm, which is shifted considerably high-field versus that of IMe₄ ($\delta = 212.7$ ppm),^[38] but appears at a position close to that of the imidazolium salt (IMe₄H)Cl ($\delta = 136.9$ ppm).^[11a] Finally, the ¹H and ¹³C{¹H} NMR spectra of **3** display a single set of resonances, as expected for three equivalent IMe₄ groups rotating rapidly about the Si–C bonds on the NMR time scale.

Whereas reaction of 2-I with IMe_4 directly afforded the complex salt 3, addition of the sterically more demanding N-heterocyclic carbene 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene ($IiPr_2Me_2$) to a toluene solution of 2-I at ambient temperature gave, after displacement of only one iodide group, the Si^{II} complex salt [SiI($IiPr_2Me_2$)(Idipp)]I (4) [Eq. (1)]. No further reaction of 4 with $IiPr_2Me_2$ was observed, even at higher temperature (fluorobenzene, 60 °C). Compound 4 was isolated as a yellow, crystalline



6976 www.angewandte.org

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Angew. Chem. Int. Ed. 2013, 52, 6974-6978

 C_6H_5F -monosolvate in 84% yield after crystallization from fluorobenzene. Compound **2**-I is moderately soluble in fluorobenzene and THF, and well soluble in dichloromethane, in which it slowly decomposes at ambient temperature.

The crystal structure of **4**·PhF reveals the presence of wellseparated trigonal pyramidal Si^{II} monocations [SiI($IiPr_2Me_2$)-(Idipp)]⁺ (**4**⁺) and iodide anions, the shortest interionic Si…I contact being 7.42 Å. The structure of the cation **4**⁺ (Figure 4) resembles those of **2**-I and **3**²⁺.

In contrast to 3, the ¹H and ¹³C NMR spectra of 4 in CD₂Cl₂ show that rotation of both NHC ligands about their respective Si-C_{NHC} bonds is frozen out on the NMR timescale. The stereochemical rigidity of 4 results from the interference of the bulky 2,6-diisopropylphenyl and isopropyl substituents, which locks cation 4^+ in a specific conformation, in which the five-membered rings of the NHC ligands are perpendicularly disposed (dihedral angle of the least squares planes defined by the NHC ring carbon $atoms = 85.7(1)^\circ$). This locked conformation renders all groups in the NHC ligand backbone non-equivalent and leads to a large number of ¹H and ¹³C signals in the NMR spectra of **4**, which were all assigned by 2D NMR spectroscopy.^[13] However, the most intriguing spectroscopic feature of 4 is the doublet signal observed for the ²⁹Si NMR nucleus in the proton-coupled ²⁹Si NMR spectrum at $\delta = -55.3$ ppm (*J*(Si,H) = 10.4 Hz). Selective decoupling of one of two isopropyl methine protons of the I*i*Pr₂Me₂ ligand (septet signal at $\delta = 4.96$ ppm) transformed the ²⁹Si signal into a singlet, and 2D ²⁹Si-¹H correlation spectroscopy revealed a cross-peak with the same isopropyl methine proton.^[13] The observation of ²⁹Si spin coupling to only one isopropyl methine proton of the IiPr₂Me₂ ligand, as well as the magnitude of the ²⁹Si-¹H coupling constant (J = 10.4 Hz), which is even larger than those typically observed for through-bond ³J(Si,H) coupling constants (ca. 5 Hz),^[39] let us exclude a through-bond spin-spin coupling between the silicon and hydrogen nucleus, which are separated by four bonds in 4. Instead, we suggest an unprecedented through-space ²⁹Si-¹H coupling resulting from the close proximity of the two interacting nuclei.^[40] Evidence for this was provided by the solid-state structure of 4, which reveals a close contact of one isopropyl C-H group of IiPr₂Me₂ to silicon leading to a much shorter Si--H distance (2.57(1) Å), than the sum of the van Waals radii of silicon and hydrogen (3.30 Å; Figure 4).^[14] The nature of this interaction was studied by a topological analysis of the electron density.^[28] A bond critical point (BCP) and a bond path could be located between Si and H36, clearly indicating a Si-H-C interaction. The geometrical parameters of this interaction $(d(Si - H)_{calc.} = 2.557 \text{ Å}; d(Si - H)_{exp.} = 2.57(1) \text{ Å};$ \measuredangle (Si···H-C)_{calc.} = 121.0°; \measuredangle (Si···H-C)_{exp.} = 116.6(1)°), as well as the substantial electron density ($\rho_{\rm BCP} = 0.117 \, {\rm e} \, {\rm \AA}^{-3}$), the positive Laplacian ($\bigtriangledown^2 \rho_{BCP} = 0.797 \text{ e} \text{ Å}^{-5}$), and the slightly negative total energy density ($H_{BCP} = -0.0004$ Hartree Å⁻³) at the bond critical point compare well with those found for anagostic M···H-C interactions in transition metal complexes.^[41] NBO second-order perturbation analysis shows a small stabilization energy of 14 kJ mol⁻¹ resulting from the orbital interaction between the silicon lone pair and the antibonding σ^* C–H orbital.^[27] Further proof of the validity of the calculated results was given by the calculated Si–H coupling constant of 9.0 Hz, which compares very well with the experimental value of 10.4 Hz. Compound **4** is thus the first example of an anagostic interaction of a C–H bond with an Si^{II} center.

In conclusion, the isolation and full characterization of **3** and **4**, which can be strikingly viewed as NHC complex salts of Si^{2+} and $[SiI]^+$, highlights the synthetic potential of $[NHC-SiX_2]$ adducts (X = halogen) and opens a new avenue of chemical exploration in Si^{II} chemistry, one in which associative or dissociative substitution of the NHC ligands can provide entry to a series of novel compounds of silicon in low-oxidation states. Moreover, the unprecedented C–H anagostic interaction observed in **4** may serve as a valuable model for intermediates in non-metal-mediated C–H bond activation reactions.

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