Silicon(II) Coordination Chemistry: N-Heterocyclic Carbene Complexes of Si²⁺ and SiI⁺**
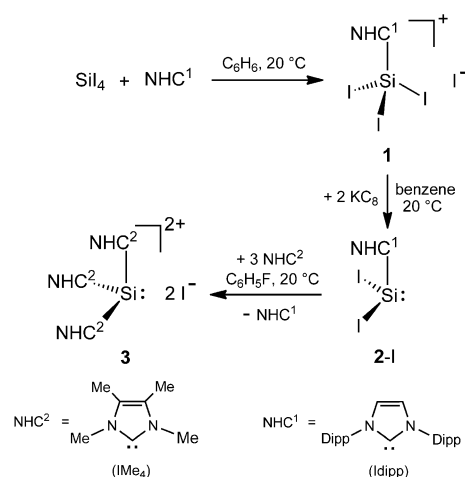
Alexander C. Filippou,* Yury N. Lebedev, Oleg Chernov, Martin Straßmann, and Gregor Schnakenburg

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 $[\{C_{10}H_6\text{-}\alpha,\alpha\text{-}NP(nBu)_3\}SiCl]^+$ stabilized by a chelating bis(iminophosphorane) ligand[7] have been isolated thus far.

Since the first report of the silicon(0) compound $[Si_2(Idipp)_2]$ (Idipp = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) 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 SiX_2 (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

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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 triiodosilyl-imidazolium salt **1** (Scheme 1), which was obtained from the reaction of SiI_4 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(CHCl₃) was determined by single-crystal X-ray crystallography.[13] It resembles that of $[SiBr_3(Idipp)]Br$·3(CH₂Cl₂)[9b] and reveals that the chloroform trissolvate of **1** is composed of well separated $[SiI_3(Idipp)]^+$ 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 SiI_4 (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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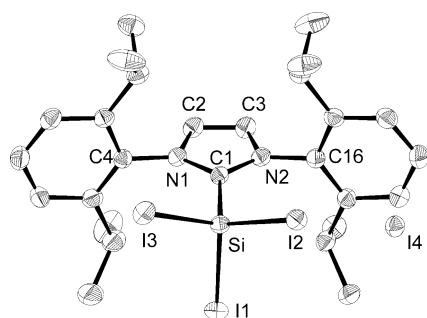*Angew. Chem.* **2013**, *125*, 7112–7116

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 ($\delta = -225.8$ ppm) than that of SiI$_4$ (δ in C$_6$D$_6 = -346.6$ ppm). The same trend was observed for [SiBr$_3$(Idipp)]Br in CD$_2$Cl$_2$ ($\delta = -63.9$ ppm) vs. SiBr$_4$ (δ in C$_6$D$_6 = -90.8$ ppm).[9b] In comparison, the ^{29}Si NMR signal of the neutral pentacoordinate complex [SiCl$_4$(Idipp)][8] appears in CD$_2$Cl$_2$ at considerably higher field ($\delta = -108.9$ ppm) than that of SiCl$_4$ (δ in C$_6$D$_6 = -18.5$ 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 [SiX$_2$-(Idipp)] (X = Cl, Br)[9a,b] and of the germanium analogue [GeI$_2$(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
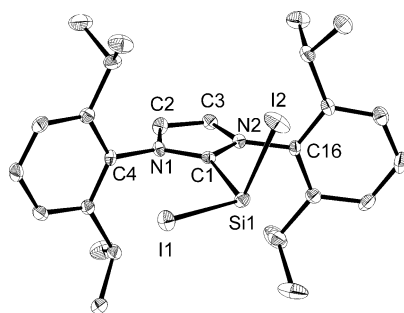

Figure 2. DIAMOND plot of the molecular structure of **2**-I in the solid state. Thermal ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (bond lengths and bond angles of the other two independent molecules of **2**-I are given in 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)°)[24] is slightly smaller than that of [SiBr$_2$(Idipp)] (**2**-Br: DP = 75%; sum of angles at Si = 292.7°)[9b] and [SiCl$_2$(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 (SiI$_4$);[16] 2.453(4) Å (MesSiI$_3$)[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 SiMe$_4$, 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$_2$SiC(NH$_2$)$_2$ (X = H, Me, F, Cl, NH$_2$, 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 H$_2$Si=CH$_2$ at the one end, which features a short Si=C bond (1.704(2) 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-(NCH$_2$tBu)$_2$C$_6$H$_4$) 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 $\Sigma\Delta E_{ST}$ of the carbene and silylene fragments, which is tuned by the substituents.[31,34]

The ^{29}Si{^{1}H} NMR spectrum of **2**-I in C$_6$D$_6$ solution displays a singlet at a similar position ($\delta = -9.7$ ppm) to those observed in the solid-state ^{29}Si{^{1}H} 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 ^{29}Si nucleus chemical shift of **2**-I with that of [SiBr$_2$(Idipp)] ($\delta = 10.9$ ppm)[9b] and [SiCl$_2$(Idipp)] ($\delta = 19.06$ ppm)[9a] reveals the same ^{29}Si nucleus deshielding upon halide substitution (I→Br→Cl) as observed for Si^{IV} halides.[36]
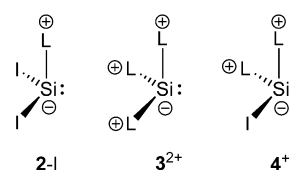
Scheme 2. Ylidic canonical structures of **2**-I, **3**$^{2+}$ and **4**$^+$. Formal charges are shown in circles. L = N-heterocyclic carbene.

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 (IMe$_4$; 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 CH$_2$Cl$_2$, 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 IMe$_4$. This suggests that the first step, which probably involves a I$^-$/IMe$_4$ exchange to give the putative intermediate [SiI(IMe$_4$)(Idipp)]I, is rate determining in the overall reaction sequence ultimately leading to **3**.[37]

The crystal structure of **3**·2 CD$_2$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(I*i*Pr$_2$Me$_2$)$_3$]$^{2+}$.[3a] The degree of pyramidalization of **3**$^{2+}$ (DP = 53%, sum of angles at Si = 312°) is lower than those of [SiI(I*i*Pr$_2$Me$_2$)(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 **3**$^{2+}$ is strongly delocalized over the IMe$_4$ groups, which suggests a strong contribution of the zwitterionic canonical formula depicted in Scheme 2 to the bonding in **3**$^{2+}$.
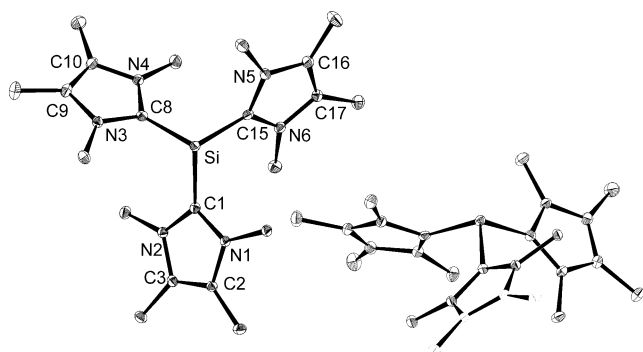

Figure 4. DIAMOND plot of the molecular structure of the cation of **4**·C$_6$H$_5$F in the solid state. Ellipsoids are set at 30% probability; the 2,6-bonded isopropyl substituents of the Idipp ligand, the solvent molecule and the hydrogen atoms, except that (H36) involved in the anagostic interaction 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(C$_6$H$_3$-2,6-Trip$_2$)(IMe$_4$)] (1.963(2) Å)[11a] and [Cp(CO)$_2$Mo=Si(C$_6$H$_3$-2,6-Trip$_2$)(IMe$_4$)] (1.944(1) Å),[12a] and approximate the Si–C$_{aryl}$ single bonds of [SiCl(C$_6$H$_3$-2,6-Trip$_2$)(IMe$_4$)] (1.937(2) Å)[11a] and [Cp(CO)$_2$Mo=Si(C$_6$H$_3$-2,6-Trip$_2$)(IMe$_4$)] (1.920(2) Å).[12a]

The ^{29}Si{^{1}H} NMR spectrum of **3** in CD$_2$Cl$_2$ shows a strongly shielded ^{29}Si 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 ^{13}C{^{1}H} NMR spectrum displays a distinctive signal for the Si-bonded C_{NHC} atom at $\delta = 150.7$ ppm, which is shifted considerably high-field versus that of IMe$_4$ ($\delta = 212.7$ ppm),[38] but appears at a position close to that of the imidazolium salt (IMe$_4$H)Cl ($\delta = 136.9$ ppm).[11a] Finally, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** display a single set of resonances, as expected for three equivalent IMe$_4$ 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 (I*i*Pr$_2$Me$_2$) to a toluene solution of **2**-I at ambient temperature gave, after displacement of only one iodide group, the Si^{II} complex salt [SiI(I*i*Pr$_2$Me$_2$)(Idipp)]I (**4**) [Eq. (1)]. No further reaction of **4** with I*i*Pr$_2$Me$_2$ was observed, even at higher temperature (fluorobenzene, 60°C). Compound **4** was isolated as a yellow, crystalline

Figure 3. DIAMOND plot of the molecular structure of the cation of **3**·2 (CD$_2$Cl$_2$) 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)].
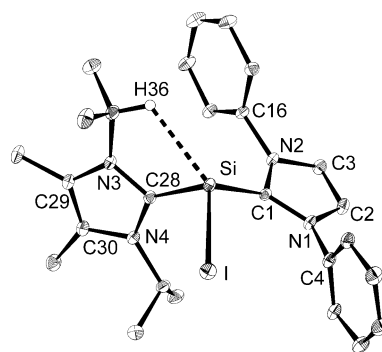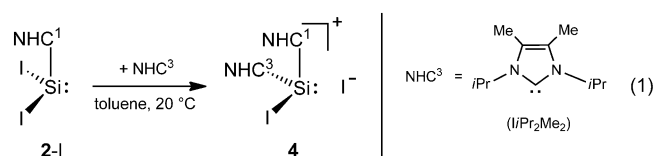

$$\text{(1)}$$

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 well-separated 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 ^{13}C NMR spectra of **4** in CD_2Cl_2 show that rotation of both NHC ligands about their respective Si−C_{NHC} bonds is frozen out on the NMR time-scale. 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)°). This locked conformation renders all groups in the NHC ligand backbone non-equivalent and leads to a large number of ^1H and ^{13}C 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 ^{29}Si NMR nucleus in the proton-coupled ^{29}Si NMR spectrum at $\delta = -55.3$ ppm ($J(Si,H) = 10.4$ Hz). Selective decoupling of one of two isopropyl methine protons of the $IiPr_2Me_2$ ligand (septet signal at $\delta = 4.96$ ppm) transformed the ^{29}Si signal into a singlet, and 2D ^{29}Si−^1H correlation spectroscopy revealed a cross-peak with the same isopropyl methine proton.[13] The observation of ^{29}Si spin coupling to only one isopropyl methine proton of the $IiPr_2Me_2$ ligand, as well as the magnitude of the ^{29}Si-^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 ^{29}Si−^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 $IiPr_2Me_2$ 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 ($d(Si···H)_{calc.} = 2.557$ Å; $d(Si···H)_{exp.} = 2.57(1)$ Å; $\angle(Si···H$-$C)_{calc.} = 121.0°$; $\angle(Si···H$-$C)_{exp.} = 116.6(1)°$), as well as the substantial electron density ($\rho_{BCP} = 0.117$ e Å^{-3}), the positive Laplacian ($\nabla^2\rho_{BCP} = 0.797$ e 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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[13] The Supporting Information contains the syntheses, analytical, and spectroscopic data of compounds **1**–**4**, as well as selected NMR spectra for compounds **1**–**4** and crystallographic data for **1**·3(CHCl$_3$), **2**-I, **3**·2(CD$_2$Cl$_2$) and **4**·C$_6$H$_5$F. CCDC 924156 (**1**·3(CHCl$_3$)), 924157 (**2**-I), 924158 (**3**·2(CD$_2$Cl$_2$)) and 924159 (**4**·C$_6$H$_5$F) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] Alternatively, [SiI$_3$(Idipp)]$^+$ can be regarded as a donor-acceptor complex of Idipp with the triiodosilylium ion SiI$_3^+$. However, the following findings are less supportive of this view, which implies the presence of a Si–C dative bond in [SiI$_3$(Idipp)]$^+$, and instead suggest the presence of a covalent Si–C bond (see the Supporting Information): The NBO charges of the SiI$_3$ ($q = +0.53e$) and Idipp fragment ($q = +0.47e$) have similar values; also, the ZPVE corrected energy required for the Si–C bond homolysis to give the fragments SiI$_3$ and Idipp$^+$ (BDE$_{hom.} = 315.4$ kJ mol^{-1}) is similar to that required for the Si–C bond heterolysis to give the fragments SiI$_3^+$ and Idipp (BDE$_{het.} = 330.9$ kJ mol^{-1}); furthermore, the Si–C bond dissociation energy of [SiI$_3$(Idipp)]$^+$ compares well with those of typical Si–C covalent bonds (BDE ca. 370 kJ mol^{-1})$^{[29]}$ and is considerably higher than those of Si–C dative bonds as found in **2**-X (BDE ca. 120 kJ mol^{-1}). For studies of donor–acceptor (dative) bonds, see: a) A. Haaland, *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992; b) V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, *116*, 8741; c) H. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1994**, *116*, 7429.

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