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Siloles |*Very Important Paper*|

VIP [2+2+1] Cycloadditions of Bis(dialkylamino)acetylenes with SiI_2(Idip): Syntheses and Reactivity Studies of Unprecedented 2,3,4,5-Tetraamino-1*H*-siloles[**]

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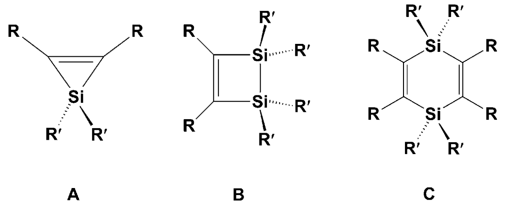
Abstract: A novel method for the synthesis of 1*H*-siloles is presented. It involves a [2+2+1] cycloaddition of the ynediamines $R_2N{-}C{\equiv}C{-}NR_2$ (R = Me, Et) with SiI_2(Idip) (Idip = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) to afford the orange-colored, highly water-sensitive 1,1-diiodo-2,3,4,5-tetraamino-1*H*-siloles $SiI_2\{C_4(NR_2)_4\}$ (**1-I**: R = Me; **2-I** R = Et). Treatment of **2-I** with an excess of $SiBr_4$ afforded after I/Br exchange the 1,1-dibromo-1*H*-silole $SiBr_2\{C_4(NEt_2)_4\}$ (**2-Br**). The 1*H*-siloles **1-I**, **2-I**, and **2-Br** were fully characterized and their molecular structures determined by single-crystal X-ray diffraction. The compounds feature a slightly twisted five-membered silacyclopenta-2,4-diene ring and a double/single C–C bond alternation in the diene fragment. Reaction of **2-I** with the N-heterocyclic carbene IMe_4 (IMe_4 = 1,3,4,5-tetramethylimidazolin-2-ylidene) leads, after displacement of the iodide groups, to the unprecedented diiodide salt $[Si(IMe_4)_2\{C_4(NEt_2)_4\}](I)_2$ (**3**), containing a 1*H*-silole dication with a four-coordinate Si^{IV} center. The crystal structure of **3** reveals similar bonding characteristics for the dicationic 1*H*-silole to those of the neutral 1*H*-siloles **1-I**–**2-Br**. Two-electron reduction of **3** with C_8K affords, after elimination of one IMe_4 group, the thermolabile, carbene-stabilized 1-silacyclopentadien-1-ylidene $Si\{C_4(NEt_2)_4\}(IMe_4)$ (**4**), which was characterized by elemental analysis and ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopies.

Introduction

Low-valent silicon chemistry has witnessed a renaissance following recent studies, which have shown that N-heterocyclic carbenes (NHCs) are very effective bases for the stabilization of unsaturated Si centers in low oxidation states. Appealing examples are the NHC adducts of Si_2,[1] SiX_2 (X = Cl, Br, I),[2] silanones,[3] and Si(Cl)R (R = C_6H_3-2,6-Ar_2 (Ar = C_6H_2-2,4,6-Me_3; C_6H_2-2,4,6-*i*Pr_3); $N(SiMe_3)(C_6H_3$-2,6-*i*Pr_2).[4] Particularly, the Si^{II} compounds SiX_2(Idip) (Idip = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and Si(Cl)R(IMe_4) (IMe_4 = 1,3,4,5-tetramethylimidazolin-2-ylidene) proved to be very valuable building blocks, which enabled the synthesis of new classes of unsaturated silicon compounds, including zwitterionic silylidene complexes, silylidyne complexes, metallosilylenes, and metallosilanones.[5] The electronic structure of SiX_2(Idip) differs considerably from that of dihalosilylenes. As 8VE compounds bearing a lone pair of electrons at silicon, these compounds predominantly react as nucleophiles, as shown by the formation of various transition-metal complexes, in which SiX_2(Idip) act as σ-donor ligands.[6] Reactions of SiX_2(Idip) with strong nucleophiles have also been reported,[5,7] indicating a certain electrophilic character of these compounds, which is, however, much attenuated in comparison to that of dihalosilylenes. Consequently reactions of SiX_2(Idip) with alkynes have so far proved to be sluggish,[8] and only $SiCl_2$(Idip) has been reported to react with diphenylacetylene to give an NHC adduct of a 1,2,3-trisilacyclopent-4-ene.[2a] In contrast, most silylenes are very reactive towards alkynes. Their reactions have been extensively studied and have been shown to give silirenes (silacyclopropenes) (**A**), 1,2-disilacyclobutenes (**B**), or 1,4-disilacyclohexadienes (**C**) depending on the reaction conditions and the substituents in the reactants (Scheme 1).[9a]



Scheme 1. Common products of the reactions of silylenes with alkynes.

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[**] *Idip = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene.*

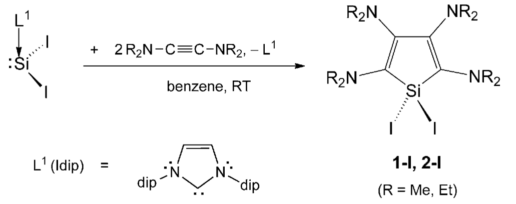
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403108. It contains copies of the ^1H *and* $^{13}C\{^1H\}$ *NMR spectra of* ***1-I**, **2-Br**, and **3**, the* $^{29}Si\{^1H\}$ *NMR spectra of **2-Br** and **4**, and the molecular structure of **1-I**.*

1*H*-Siloles are formed only in traces in these reactions, but are produced in metal-catalyzed reactions of silirenes with alkynes.[9b]

In this work we present a new reaction channel of $SiI_2(Idip)$ with the electron-rich alkynes $R_2NC{\equiv}CNR_2$ (R = Me, Et) leading to unprecedented 2,3,4,5-tetramino-1*H*-siloles, and we report on first reactivity studies of these compounds.

Results and Discussion

Addition of bis(dimethylamino)acetylene to a stirred benzene solution of $SiI_2(Idip)$ was accompanied by an instantaneous color change from yellow to orange to afford a mixture of the 2,3,4,5-tetra(dimethylamino)-1*H*-silole $SiI_2\{C_4(NMe_2)_4\}$ (**1-I**) and Idip (Scheme 2).



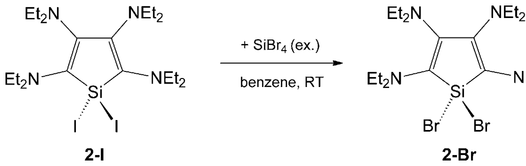
Scheme 2. [2+2+1] cycloaddition of $SiI_2(Idip)$ with the ynediamines $C_2(NR_2)_2$ (dip = 2,6-diisopropylphenyl; two dots have been used to denote a lone pair of electrons).

Rapid work-up was necessary to avoid complete decomposition of the 1*H*-silole **1-I**, leading to a mixture of unidentifiable organic compounds. Decomposition was observed when the reaction mixture was stirred for a longer period of time at ambient temperature (>15 min). Separation of **1-I** from the liberated Idip by fractional crystallization proved difficult due to the similar solubility of the two compounds in common organic solvents. For this reason, one equivalent of SiI_4 was added to the reaction mixture to trap Idip as the much less soluble triiodosilylimidazolium salt $[SiI_3(Idip)]I$, which could be easily separated from **1-I** after extraction of **1-I** with benzene or *n*-hexane. The 1*H*-silole **1-I** was isolated as orange, highly water-sensitive crystals after crystallization from *n*-hexane solution at −60 °C. Compound **1-I** decomposes upon heating at 111 °C to a black mass. The solid deteriorates slowly even at room temperature, but can be stored for weeks at low temperatures (−30 °C).

The analogous diethylamino derivative **2-I** was prepared in a similar manner upon treatment of $SiI_2(Idip)$ with two equivalents of $Et_2N{-}C{\equiv}C{-}NEt_2$ in benzene (Scheme 2). Compound **2-I** was found to be more robust than **1-I**, and no decomposition of **2-I** was observed in solution at ambient temperature upon stirring the reaction mixture for a longer period of time (3 h). Separation of **2-I** from the liberated Idip was achieved after trapping Idip with one equivalent of SiI_4 as described above for **1-I**, or after addition of $(NEt_3H)Cl$ to give the hexane-insoluble imidazolium salt (IdipH)Cl. Compound **2-I** could be easily separated from $[SiI_3(Idip)]I$ or (IdipH)Cl by extraction with *n*-hexane, and was isolated after crystallization at −30 °C as orange, highly water-sensitive crystals, which melt at 85 °C without decomposition.

The fast and selective conversion of $SiI_2(Idip)$ into the [2+2+1] cycloaddition products **1-I** and **2-I** is surprising given the different reactivity pattern of silylenes towards alkynes (see Introduction). It can be attributed to the well-known, high nucleophilicity of the ynediamines $R_2N{-}C{\equiv}C{-}NR_2$. In fact no reaction of $SiX_2(Idip)$ (X = Br, I) was observed with alkynes, such as 3-hexyne, *p*-tolylacetylene, or diphenylacetylene, at ambient temperature.[8] Two pathways may be envisaged for the [2+2+1] cycloaddition of $SiI_2(Idip)$ with $R_2N{-}C{\equiv}C{-}NR_2$. The first one is suggested to involve a substitution of Idip by the ynediamine to give a 1,1-diiodosilacyclopropene intermediate, and the second one a displacement of one iodide group by the ynediamine to give a NHC-stabilized 1-iodosilacyclopropenium salt. Trapping experiments failed so far, the putative intermediates being presumably trapped very fast by the highly nucleophilic ynediamine to give the final product.

Reaction of **2-I** with an excess of $SiBr_4$ in benzene proceeded smoothly at ambient temperature to give, after I/Br exchange, the 1,1-dibromo-1*H*-silole **2-Br**, which, after work-up, was isolated as a highly water-sensitive, orange, low-melting solid (m.p. 54 °C) in 71 % yield (Scheme 3). Interestingly, **2-I** did not react with $SiBr_4$ in *n*-hexane, which indicates a strong influence of the solvent polarity on the I/Br exchange rate of this reaction.



Scheme 3. I/Br exchange reaction of **2-I** with $SiBr_4$.

The molecular structures of **1-I**, **2-I**, and **2-Br** were determined by single-crystal X-ray diffraction analyses (Figure 1). Selected bonding parameters of these compounds are listed in Table 1. All tetraamino-1*H*-siloles feature a slightly twisted silacyclopenta-2,4-diene ring, as evidenced by the dihedral angle of the four-ring carbon carbons C1-C2-C3-C4 (**1-I**: 11.0(14)°; **2-I**: 15.2(2)°; **2-Br**: 16.2(3)°). They also display a C–C double–single bond alternation as shown by the $C_\alpha{-}C_\beta$ and $C_\beta{-}C_\beta$ bond lengths of 1.37 and 1.52 Å, respectively (Table 1).[10] Another common structural feature of the 1*H*-siloles **1-I**, **2-I**, and **2-Br** is the distorted tetrahedral coordination geometry of Si with an acute endocyclic C_α-Si-C_α angle of approximately 96° (Table 1). The Si–C distances (1.827(11)–1.854(2) Å) correspond to those of typical Si–C single bonds, and compare well with those of other structurally characterized 1*H*-siloles.[10] The mean Si–I bond length of **1-I** (2.463 Å) and **2-I** (2.466 Å) is similar to that of SiI_4 (2.432(5) Å),[11] $MesSiI_3$ (2.453 Å),[12] 1,4-diiodo-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene (2.436(2) Å),[13] and other silicon(IV) iodides.[14] Similarly, the mean Si–Br distance of **2-Br** (2.235 Å) compares well with that of other four-coordinate Si^{IV} compounds (2.253 Å).[15]

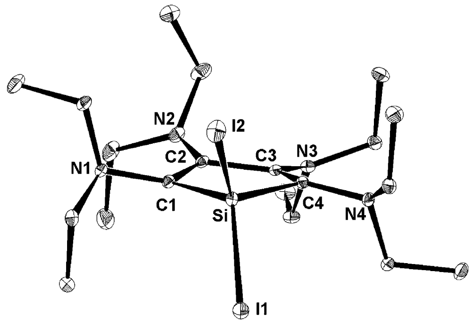


Figure 1. DIAMOND plot of the molecular structure of **2-I**. Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] (bond lengths and angles in square brackets are of **2-Br**): Si–I1 2.4654(5) [Si–Br1 2.2340(6)], Si–I2 2.4672(5) [Si–Br2 2.2363(7)], Si–C1 1.849(2) [1.849(2)], Si–C4 1.854(2) [1.841(2)], C1–C2 1.370(2) [1.365(3)], C2–C3 1.524(2) [1.521(3)], C3–C4 1.370(2) [1.378(3)], C1–N1 1.426(4) [1.422(3)], C2–N2 1.392(2) [1.416(3)], C3–N3 1.402(2) [1.393(3)], C4–N4 1.420(2) [1.422(3)]; I1-Si-I2 104.57(2) [Br1-Si-Br2 104.15(3)], C1-Si-C4 96.58(7) [97.3(1)].

All amino groups in **1-I**, **2-I**, and **2-Br** are rotated out of the five-membered ring, the C_α-bonded amino groups ($C_\alpha = C1,C4$) slightly more than the C_β-bonded amino groups ($C_\beta = C2,C3$). Thereby, the mutual steric repulsion between adjacent amino groups is minimized. Moreover, the amino groups are pyramidal as evidenced by the sum of the bonding angles at the N_α (N1,N4) and N_β (N2,N3) atoms (Table 1). The N_α alkyl substituents are bent away from the neighboring N_β alkyl substituents towards the SiX_2 (X = I, Br) group, and the alkyl substituents at the two N_β atoms are bent away from each other. In combination with the lower pyramidalization of the N_β atoms (Table 1), this alkyl group arrangement minimizes further the steric repulsion especially between the adjacent N_α and N_β amino groups, which are separated by a much shorter C=C bond. The C_{ring}–N bond lengths range from 1.39–1.43 Å and are close to those of C_{sp^2}–N_{sp^3} single bonds.[16] They suggest, in connection with the other parameters presented above, a small π-conjugative interaction of the amino groups with the C=C bonds. This is further confirmed by the ^1H and $^{13}C\{^1H\}$ spectra of **1-I**, **2-I**, and **2-Br** in C_6D_6 at 298 K, which all display a single set of resonances for the N_α- and N_β-bonded alkyl substituents, indicating a rapid rotation of the amino groups about the C_α–N_α and C_β–N_β bonds as well as a rapid inversion of the N_α and N_β atoms on the NMR time scale at ambient temperature (see the Supporting Information). The $^{13}C\{^1H\}$ NMR spectra of **1-I**, **2-I**, and **2-Br** display one diagnostic signal for the C_α ($C^{2,5}$) carbons at $\delta =$ 122.7–124.5 ppm and one for the C_β ($C^{3,4}$) carbons at $\delta =$ 145.5–147.8 ppm, which were assigned by comparing the ^nJ(Si,C) coupling constants (**2-I**: $^1J(Si,C_\alpha) = 71$ Hz, $^2J(Si,C_\beta) =$ 29 Hz) (Table 2).

As observed for other 1*H*-siloles, the relative chemical shifts of the C_α and C_β carbon signals of **1-I**, **2-I**, and **2-Br** are reversed, when compared with those of furans or pyrroles.[17] The ^{29}Si NMR signals of **1-I** (δ in $C_6D_6 = -87.8$ ppm) and **2-I** (δ in $C_6D_6 = -83.5$ ppm) appear at considerably lower field than that of SiI_4 (δ in $C_6D_6 = -346.6$ ppm), and the ^{29}Si NMR signal of **2-Br** (δ in $C_6D_6 = -13.4$ ppm) appears at considerably lower field than that of $SiBr_4$ (δ in $C_6D_6 = -90.8$ ppm). The observed shift of the ^{29}Si NMR signal to lower field upon replacing iodine by bromine substituents in **2-X** (X = I, Br) is a common phenomenon in Si^{IV} chemistry.[18]

Table 2. Selected $^{13}C\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR data of the 1*H*-siloles and **4**.

Comp.	$^{13}C\{^1H\}$ NMR C_α ($C^{2,5}$)	 C_β ($C^{3,4}$)	^{29}Si NMR
1-I[a]	122.7	145.5	−87.8
2-I[a]	124.3 ($^1J(Si,C) = 71$ Hz)	146.7 ($^2J(Si,C) = 29$ Hz)	−83.5
2-Br[a]	124.5	147.8	−13.4
3[b]	122.6 ($^1J(Si,C) = 79$ Hz)	151.3 ($^2J(Si,C) = 23$ Hz)	−29.2
4[a]	153.0 ($^1J(Si,C) = 20$ Hz)	141.9 ($^2J(Si,C) = 8.1$ Hz)	−69.6

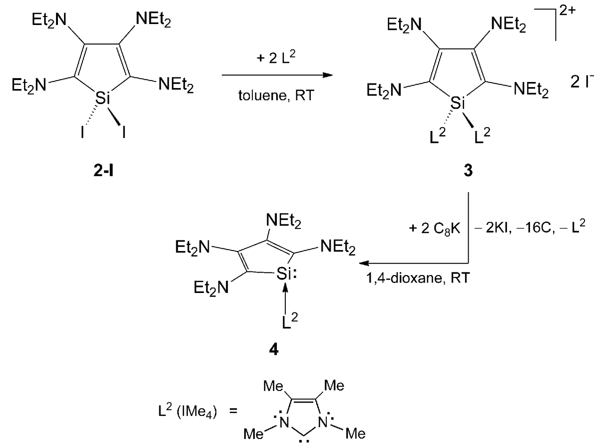
[a] [D$_6$]benzene, 298 K. [b] [D$_2$]dichloromethane, 298 K.

The 1,1-diiodo-1*H*-siloles **1-I** and **2-I** are promising starting materials for further reactivity studies, since they bear two iodide groups, which are good leaving groups and should be easily displaced from silicon. In fact, reaction of **2-I** with two equivalents of the N-heterocyclic carbene IMe_4 (IMe_4 = 1,3,4,5-tetramethylimidazolin-2-ylidene) in toluene was instantaneous, and led, after replacement of both iodide groups, to the iodide salt of the dicationic 1*H*-silole $[Si(IMe_4)_2\{C_4(NEt_2)_4\}]^{2+}$ (**3**$^{2+}$)

Table 1. Selected bond lengths [Å] and angles [°] of the 1*H*-siloles **1-I**, **2-I**, **2-Br**, and **3**·4(CH_2Cl_2).

Comp.	Si–C_α[a]	C_α–C_β[a]	C_β–C_β[a]	Si–X[a]	C_α-Si-C_α[a]	ΣN_α[b]	ΣN_β[b]
1-I	1.827(11)	1.370(14)	1.508(14)	2.455(3)	96.2(5)	343.8	358.3
	1.836(10)	1.350(14)		2.470(3)		343.5	356.5
2-I	1.849(2)	1.370(2)	1.524(2)	2.4654(5)	96.58(7)	341.0	355.2
	1.854(2)	1.370(2)		2.4672(5)		341.8	351.4
2-Br	1.849(2)	1.365(3)	1.521(3)	2.2340(6)	97.3(1)	340.0	348.9
	1.841(2)	1.378(3)		2.2363(7)		339.8	354.1
3[c]	1.862(3)	1.367(4)	1.522(12)	1.898(4)	95.8(3)	350(2)	355(2)

[a] C_α = C1,C4; C_β = C2,C3; X = I1,I2 (for **1-I** and **2-I**), Br1,Br2 (for **2-Br**), C1,C4 (for **3**). [b] ΣN_α and ΣN_β are the sums of the bonding angles at the N_α (N1,N4) and N_β (N2,N3) atoms, respectively. [c] The unweigthed mean values x_u of the individual bonding parameters of the three independent 1*H*-silole dications of **3**·4(CH_2Cl_2) are given; the standard deviations σ of x_u (values in parentheses) were calculated from the equation $\sigma^2 = \Sigma(x_i - x_u)^2/(n^2 - n)$, in which x_i is the respective individual value and n is the total number of individual values.



Scheme 4. Stepwise synthesis of the NHC-stabilized 1-silacyclopentadien-1-ylidene **4** from **2-I** via the 1*H*-silole salt **3** (two dots have been used to denote a lone pair of electrons).

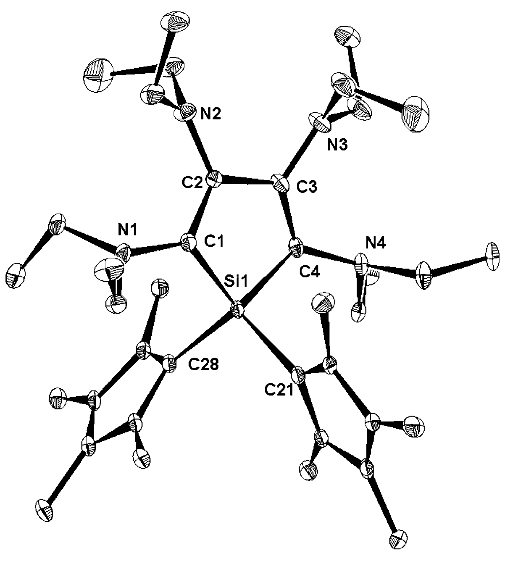


Figure 2. DIAMOND plot of the molecular structure of one of the three independent cations, 3^{2+} in $3\cdot4(CH_2Cl_2)$. Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] (bond lengths and angles in square brackets are of the other two independent cations of 3^{2+} found in the asymmetric unit): Si1–C1 1.865(7) [1.867(6), 1.858(7)], Si1–C4 1.854(6) [1.858(7), 1.870(7)], Si1–C21 1.909(7) [1.898(7), 1.893(6)], Si1–C28 1.894(6) [1.886(7), 1.906(6)], C1–C2 1.378(9) [1.361(10), 1.350(10)], C2–C3 1.511(9) [1.509(10), 1.545(11)], C3–C4 1.368(9) [1.371(9), 1.373(10)], C1–N1 1.390(8) [1.415(9), 1.432(9)], C2–N2 1.391(8) [1.408(8), 1.392(9)], C3–N3 1.382(8) [1.392(9), 1.374(9)], C4–N4 1.417(8) [1.403(9), 1.408(10)], C1-Si-C4 96.3(3) [95.6(3), 95.5(3)], C21-Si1-C28 106.4(3) [107.1(3), 104.1(3)].

(Scheme 4). Salt **3** precipitated out of the solution, and was isolated after crystallization as yellow-orange crystals in 66% yield. The salt is well soluble in CH_2Cl_2, but insoluble in toluene and diethyl ether.

Attempts to stop the reaction of **2-I** with IMe_4 at the mono-substitution step have failed so far. For example, reaction of **2-I** with one equivalent of IMe_4 at −30 °C in toluene afforded, after work-up, a 1:1 mixture of the starting material and **3**. This observation suggests that substitution of the first iodide group in **2-I** by IMe_4 to give the putative ionic intermediate $[SiI\{C_4(NEt_2)_4\}(IMe_4)]^+$ is slower than that in $[SiI\{C_4(NEt_2)_4\}(IMe_4)]^+$ by IMe_4 in the second step leading to the final product.

Compound **3** is the first salt of a dicationic 1*H*-silole to be reported, and to the best of our knowledge an unprecedented dicationic Si^{IV} compound with a tetrahedral coordinated Si center. The crystal structure of $3\cdot4(CH_2Cl_2)$ was determined by single-crystal X-ray diffraction analysis. Three independent pairs of cations/anions with very similar bonding parameters were found in the asymmetric unit. The unweighted mean values of selected bond lengths and angles of 3^{2+} are listed in Table 1 and were used for the discussion below. The molecular structure of one of the three independent cations 3^{2+} is depicted in Figure 2.

The crystal structure of $3\cdot4(CH_2Cl_2)$ shows well-separated 3^{2+} ions and iodide counter anions, the closest Si···I contact (5.49 Å) being much longer than the sum of the van der Waals radii of silicon and iodine of 4.08 Å ($r_w(Si) = 2.10$ Å; $r_w(I) = 1.98$ Å).[19] The 1*H*-silole dication 3^{2+} displays similar bonding parameters to those of the neutral 1*H*-siloles **1-I**, **2-I**, and **2-Br** (Table 1). The slightly twisted silacyclopenta-2,4-diene ring (dihedral angle $(C_\alpha\text{-}C_\beta\text{-}C_\beta\text{-}C_\alpha) = 19(3)°$) in $3\cdot4(CH_2Cl_2)$ contains as in the neutral congeners **1-I–2-Br** a distorted tetrahedral coordinated silicon atom with an acute endocyclic C_α-Si-C_α angle of 95.8(3)° (Table 1). The mean length of the Si–$C_{carbene}$ bonds (1.898(4) Å) is slightly larger than that of the Si–$C_{\alpha(ring)}$ bonds (1.862(3) Å) and approximates those of the silylimidazolium salts $[SiX_3(Idip)]X$ (X = Br: Si–C 1.880(9) Å;[2b] X = I: Si–C 1.911(3) Å[2c]). This comparison indicates that the double positive charge of 3^{2+} is delocalized via strong covalent Si–$C_{carbene}$ single bonds over the IMe_4 groups. Further substantiation of this suggestion is provided by the similar magnitude of the ^1J(Si,C) coupling constants of **3** ($^1J(Si,C_{carbene}) = 72$ Hz; $^1J(Si,C_{\alpha\text{-}(ring)}) = 79$ Hz), which also compare well with those of Si–C_{sp^2} single bonds in silanes (64–70 Hz).[20] In addition, the NMR chemical shift of the $C_{carbene}$ atoms of **3** (δ in $CD_2Cl_2 = 138.8$ ppm) is similar to that of the imidazolium salt $(IMe_4H)Cl$ (δ in $CD_2Cl_2 = 136.9$ ppm),[4a] but differs very much from that of IMe_4 (δ in $C_6D_6 = 212.7$ ppm),[21] indicating that 3^{2+} should be best considered as a bis(imidazolium) salt bridged by a 1-silacyclopenta-dien-1-ylidene group (Figure 3).

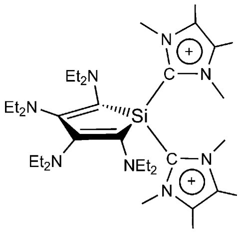


Figure 3. Stereochemical formula of the dication 3^{2+} pointing out its bis-imidazolium salt character.

The $^{13}C\{^1H\}$ NMR spectrum of **3** displays at 298 K one singlet for the $C_{\alpha(ring)}$ ($C^{2,5}$) atoms at $\delta = 122.6$ ppm, one singlet for the C_β ($C^{3,4}$) atoms at $\delta = 151.3$ ppm, but two singlets in each case for the $C^{4,5}$-ring carbons, the $N^{1,3}$-bonded and the $C^{4,5}$-bonded methyl groups of the IMe_4 groups (see Figure 7 in the Supporting Information). In combination with the observed orientation of the IMe_4 groups in the solid-state structure of **3**, the ^{13}C NMR spectrum let us suggest that rotation of the two symmetry-equivalent IMe_4 groups about the Si–$C_{carbene}$ bonds is frozen out at ambient temperature, rendering the two halves of each IMe_4 group chemically inequivalent.

1*H*-Siloles have been shown to have a low-lying LUMO resulting from the orbital interaction (σ^*–π^* conjugation) between a σ^* orbital of the SiR_2 unit with a π^* orbital of the butadiene moiety.[22] Occupation of this orbital by electrons is therefore expected to weaken the Si–R bonds leading to bond cleavage. In fact, reduction of 1*H*-siloles by alkali metals has been shown to give, after cleavage of the Si–R bonds, monoanions of siloles (silolides (silacyclopentadienides)) or dianions of siloles (silolediides).[23]

In this context, 2e reduction of **3** was an appealing reaction to study. After stirring a mixture of **3** and two equivalents of potassium graphite (C_8K) in 1,4-dioxane for 18 h, the bronze color of C_8K had disappeared. Solvent evaporation followed by extraction with toluene afforded a dark orange extract, which according to ^1H NMR spectroscopy contained a new compound (**4**) and IMe_4 in the molar ratio 1:1. Repeated fractional crystallization from toluene enabled the separation of the two products, and the isolation of **4** as yellow crystals in 49 % yield. Despite numerous attempts no suitable single crystals of **4** could be grown. The obtained crystals had a morphology reminiscent of asbestos fibers but did not diffract. However, the NMR spectra of **4** allowed, in combination with the elemental analysis, the identification of this compound as the IMe_4-stabilized silacyclopentadien-1-ylidene $Si\{C_4(NEt_2)_4\}(IMe_4)$ (Scheme 4). Thus, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** display a single set of signals for the C_α- and C_β-bonded amino groups (Figure 4 and 5). This suggests that **4** has an overall C_s-symmetric structure in solution with the symmetry plane bisecting the silacycle. It also indicates that inversion as well as rotation of all amino groups about their respective C_{ring}–N bonds is fast on the NMR time scale. On the other hand two singlets are observed for the $N^{1,3}$-bonded methyl groups, the $C^{4,5}$-bonded methyl groups and the $C^{4,5}$-ring atoms of the IMe_4 group in **4** (Figure 4 and 5). The signal splitting suggests that the carbene ring plane lies in the symmetry plane of the molecule and that rotation of the IMe_4 group about the Si–$C_{carbene}$ bond is hindered presumably due to the large steric demand of the diethylamino groups. In comparison, free rotation of the IMe_4 group was observed by NMR spectroscopy in the related tetraphenyl derivative $Si(C_4Ph_4)(IMe_4)$, which was obtained upon dehydrochlorination of the 1*H*-silole $SiClH(C_4Ph_4)(IMe_4)$.[24]

The ^{29}Si NMR resonance of **4** ($\delta = -69.6$ ppm) is shifted upfield relative to that of the parent 1*H*-silole **3** ($\delta = -29.2$ ppm) and appears in the region expected for silyl anions.[25] Moreover, the relative position of C_α- and C_β-ring carbon signals is reversed compared with that in the 1*H*-siloles **1-I–3** (Table 2). The $^1J(Si,C_\alpha)$ and $^1J(Si,C_{carbene})$ coupling constants of **4** (20 and 25 Hz, respectively) have similar values, but are considerably smaller than those of the parent 1*H*-silole **3** (79 and 72 Hz, respectively) (Table 2). They approximate the $^1J(Si,C)$ coupling constants of $SiCl(C_6H_3\text{-}2,6\text{-}Mes_2)(IMe_4)$ ($^1J(Si,C_{aryl}) = 48$ Hz; $^1J(Si,C_{carbene}) = 33$ Hz),[4a] and indicate that the Si^{II} center in **4** uses mainly p orbitals for the σ-bonding to its three carbon substituents.

Finally, the $C_{carbene}$ resonance of **4** ($\delta = 168.5$ ppm) is shifted to considerably lower field than that in the parent 1*H*-silole **3** ($\delta = 138.8$ ppm), and appears at a similar position to those of

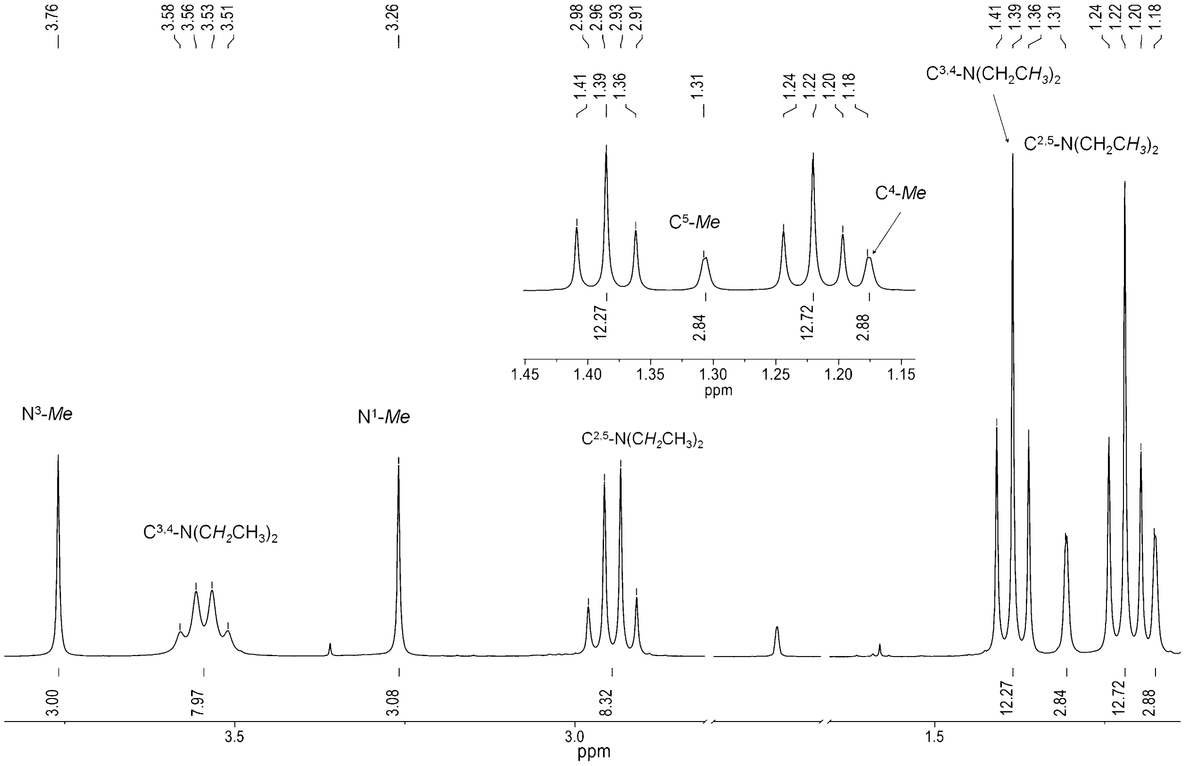


Figure 4. ^1H NMR spectrum of **4** in $[D_6]$benzene at 298 K.

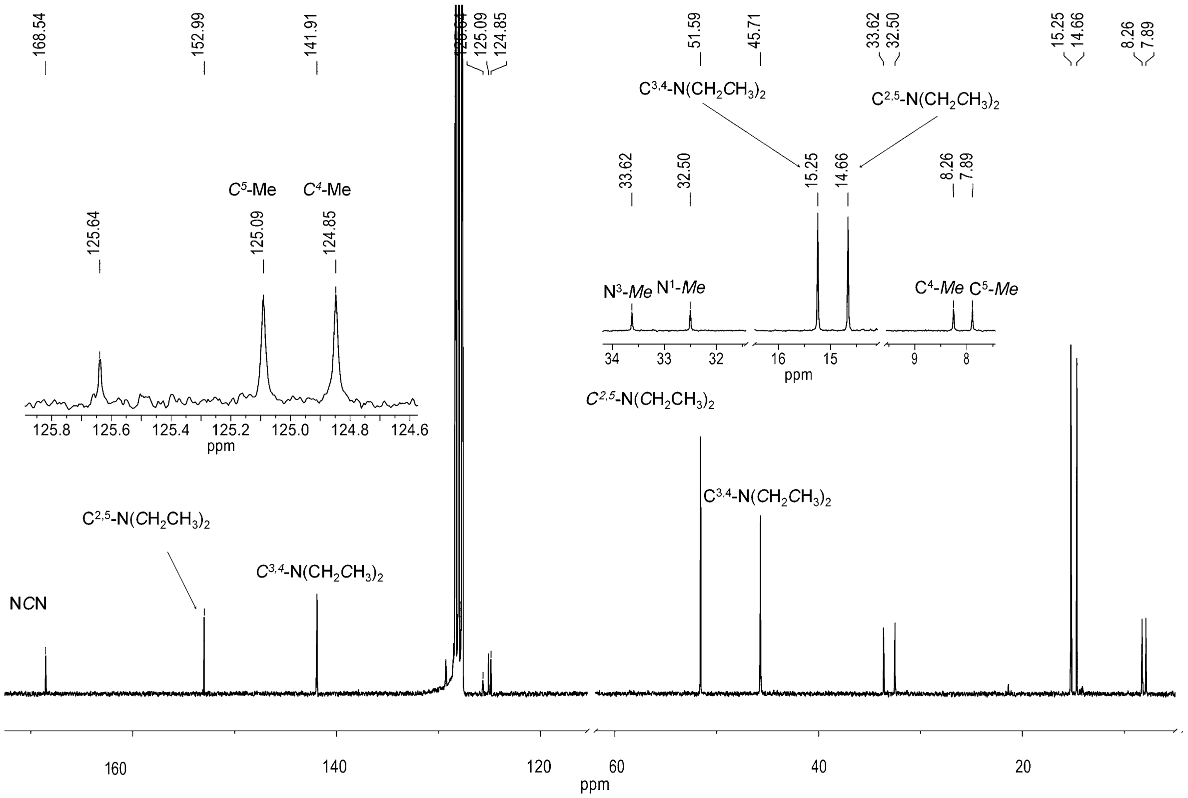


Figure 5. $^{13}C\{^1H\}$ NMR spectrum of **4** in [D$_6$]benzene at 298 K (enlarged sections of the NMR spectrum are shown in the insets).

the NHC-stabilized silylenes SiCl(C$_6$H$_3$-2,6-Mes$_2$)(IMe$_4$) ($\delta =$ 165.2 ppm),[4a] SiBr$_2$(IDip) ($\delta = 164.5$ ppm),[2b] SiI$_2$(IDip) ($\delta =$ 158.4 ppm).[2c] All these NMR parameters clearly indicate a quite different electronic structure of **4**, which can be described either as a NHC-stabilized 1-silacyclopentadien-1-ylidene (**A**) or a zwitterionic silacyclopentadienide (**B**) (Figure 6).

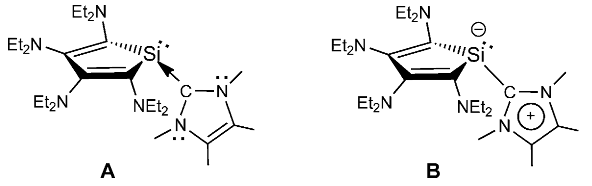


Figure 6. Two ways to view compound **4** as a NHC-stabilized 1-silacyclopentadien-1-ylidene (**A**) or as a zwitterionic silacyclopentadienide (**B**).

Discussion and Outlook

Several methods have been developed for the synthesis of 1*H*-siloles.[17] The most important synthetic methods involve the reaction of 1,4-dilithiobuta-1,3-dienes with halosilanes or Si(OMe)$_4$,[26] and the intramolecular reductive cyclization of bis(phenylethynyl) silanes with lithium naphthalenide leading to 2,5-dilithio-1*H*-siloles, which can be converted into a series of 2,5-difunctionalized 1*H*-siloles.[27] The latter compounds are key building blocks for the synthesis of 1*H*-silole based π-conjugated polymers with interesting photoluminescent and charge carrier properties,[28] making them very promising materials for organic photoelectronic and photovoltaic devices.[29]

In this context, the novel method reported in this work based on the [2+2+1] cycloaddition of SiI$_2$(Idip) with ynediamines may be of particular interest, since it provides access to polyamino-substituted 1*H*-siloles, which are not available by the various methods reported so far for 1*H*-siloles. Moreover, the obtained 2,3,4,5-tetraamino-1*H*-siloles allow further functionalization as shown by the isolation and full characterization of the 1*H* silole salt **3**, an unprecedented dicationic compound of Si^{IV} in a tetrahedral environment. On the other hand 2e-reduction of **3** provides access to the zwitterionic silacyclopentadienide **4**, which belongs to a very rare class of compounds. Prospective studies should clarify whether **4** can be used as a silacyclopentadien-1-ylidene transfer reagent.

Experimental Section

General

All experiments were carried out under an atmosphere of argon using Schlenk or glove-box techniques. The glassware was dried in the oven at approximately 110 °C and heated in vacuo prior to use. The solvents were refluxed over the corresponding drying agent (*n*-hexane: sodium wire/benzophenone/tetraglyme; diethyl ether: sodium wire/benzophenone; benzene: sodium wire/benzophenone; 1,4-dioxane, toluene: sodium wire; dichloromethane: Sicapent followed by Na/Pb alloy), purged several times during reflux with argon and distilled under argon. All solvents except CH$_2$Cl$_2$

were stored in the glove box. CH_2Cl_2 was stored in a Schlenk flask over 4 Å molecular sieves.

SiI_2(Idip),[2c] 1,3,4,5-tetramethyl-imidazolin-2-ylidene (IMe_4),[21] and C_8K[30] were prepared as described in the literature. SiI_4 was prepared from silicon powder and iodine as described in the literature.[31] The obtained crude pink-colored SiI_4 was heated to reflux in toluene with copper powder to remove the excess of iodine, and the resulting mixture filtered to give a light yellow filtrate, from which pure SiI_4 was isolated as a white crystalline solid after crystallization at −30 °C and shown by $^{29}Si\{^1H\}$ NMR spectroscopy to be pure (^{29}Si NMR (59.6 MHz, $[D_6]$benzene, 298 K, ppm): $\delta = -346.6$ (s)). Similarly, $SiBr_4$ was prepared from silicon powder and bromine following the procedure described in reference [32] and isolated after purification as a colorless liquid, which was shown by $^{29}Si\{^1H\}$ NMR spectroscopy to be pure (^{29}Si NMR (59.6 MHz, $[D_6]$benzene, 298 K, ppm): $\delta = -90.8$ (s)). The syntheses of the ynediamines $R_2NC{\equiv}CNR_2$ (R = Me, Et)[33,34] were modified and the ynediamines isolated as colorless, air-sensitive liquids, which were shown by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy to be pure.[35]

The C, H, N analyses were carried out in triplicate for each sample using an Elementar Vario Micro elemental analyzer. The individual C, H, N values did not differ by more than ±0.3%. The mean C, H, N values are given below for each compound. The melting points were determined in duplicate for each sample using a calibrated Büchi melting point apparatus. The samples were sealed in capillary tubes under vacuum and rapidly heated to a temperature approximately 20 K lower than that at which melting or decomposition started. Heating was then continued with a rate of approximately 3 K min^{-1} until the sample melted or decomposed. NMR spectra were recorded on a Bruker Avance DMX-300, DPX-300, DPX-400 NMR or DMX-500 NMR spectrometer in dry deoxygenated $[D_6]$benzene or $[D_2]$dichloromethane. $[D_6]$Benzene was trap-to-trap condensed from sodium powder and $[D_2]$dichloromethane from CaH_2. The ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent relative to tetramethylsilane ($[D_6]$benzene, $\delta_H = 7.15$ ppm and $\delta_C = 128.0$ ppm; $[D_2]$dichloromethane, $\delta_H = 5.32$, $\delta_C = 53.8$ ppm). The ^{29}Si NMR spectra were calibrated against external pure $SiMe_4$. The standard was filled in a capillary, which was sealed-off and introduced in a 5 mm NMR tube containing the corresponding deuterated solvent. The NMR tube was finally vacuum-sealed and used for the calibration. The following abbreviations were used for the forms and multiplicities of the NMR signals: s: singlet, t: triplet, q: quartet, m: multiplet, br: broad. The ^1H and ^{13}C NMR signals of all compounds were assigned by a combination of H,H-COSY, HMQC, HMBC, and DEPT experiments. This allowed in combination with the ^nJ(Si,C) coupling constants an unequivocal assignment of all proton and carbon resonances.

Synthesis

1,1-Diodo-2,3,4,5-tetrakis(dimethylamino)-1*H*-silole, $SiI_2\{C_4(NMe_2)_4\}$ (1-I): Bis(dimethylamino)acetylene (430 mg, 3.83 mmol) was added within 1 min to a yellow solution of SiI_2(Idip) (1.25 g, 1.86 mmol) in benzene (30 mL). After the mixture had been stirred for 1 min at ambient temperature, a solution of SiI_4 (1.00 g, 1.87 mmol) in benzene (20 mL) was added within 30 s. During addition the solution turned orange and formation of a yellow precipitate was observed. The reaction mixture was subsequently stirred for 2 min and then filtered via a cannula. The filtrate was evaporated to dryness in vacuo and the residue was extracted with *n*-hexane (2×10 mL). The extract was filtered, and the filtrate was concentrated in vacuo to approximately 2 mL and stored at −60 °C to afford large orange crystals of **1-I**. Yield 252 mg (0.498 mmol, 27% based on SiI_2(Idip)). Compound **1-I** starts to decompose above 111 °C turning to a black mass. Elemental analysis calcd (%) for $C_{12}H_{24}I_2N_4Si$ (506.24): C 28.47, H 4.78, N 11.07; found: C 28.26, H 5.00, N 10.75%. ^1H NMR (300.1 MHz, $[D_6]$benzene, 298 K, ppm): $\delta = 2.54$ (s, 12 H, $C^{3,4}$-$N(C\mathit{H}_3)_2$), 2.87 ppm (s, 12 H, $C^{2,5}$-$N(C\mathit{H}_3)_2$); $^{13}C\{^1H\}$ NMR (75.47 MHz, $[D_6]$benzene, 298 K, ppm): $\delta = 39.6$ (s, 4C, $C^{3,4}$-$N(\mathit{C}H_3)_2$), 44.8 (s, 4C, $C^{2,5}$-$N(\mathit{C}H_3)_2$), 122.7 (s, 2C, $\mathit{C}^{2,5}$), 145.5 ppm (s, 2C, $\mathit{C}^{3,4}$); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $[D_6]$benzene, 298 K, ppm): $\delta = -87.8$ ppm (s).

1,1-Diodo-2,3,4,5-tetrakis(diethylamino)-1*H*-silole, $SiI_2\{C_4(NEt_2)_4\}$ (2-I): Bis(diethylamino)acetylene (0.355 g, 2.11 mmol) was added within 1 min to a solution of SiI_2(Idip) (671 mg, 1.00 mmol) in benzene (4 mL). During addition the solution turned from yellow to orange. After the reaction mixture had been stirred for 10 min, a solution of SiI_4 (0.536 g, 1.00 mmol) in benzene (5 mL) was added dropwise. The resulting suspension was stirred for 5 min, and *n*-hexane (10 mL) were added. The suspension was filtered from a brown sticky material, which was discarded. The dark orange filtrate was evaporated to dryness in vacuo and the residue extracted with *n*-hexane (10 mL). The extract was filtered from some insoluble material, the filtrate was concentrated in vacuo to approximately 2 mL and stored at −30 °C. Large orange crystals of **2-I** were grown, which were separated from the mother liquor by filtration at −30 °C and dried in vacuo at ambient temperature for 3 h. Yield 0.26 g (0.42 mmol, 42% from SiI_2(Idip)). M.p. 85 °C. Elemental analysis calcd (%) for $C_{20}H_{40}I_2N_4Si$ (618.45): C 38.84, H 6.52, N 9.06; found: C 38.39, H 6.31, N 8.85; ^1H NMR (400.1 MHz, $[D_6]$benzene, 298 K): $\delta = 0.95$ (t, ^3J(H,H) = 7.1 Hz, 12 H, $C^{3,4}$-$N(CH_2C\mathit{H}_3)_2$), 1.16 (t, ^3J(H,H) = 7.1 Hz, 12 H, $C^{2,5}$-$N(CH_2C\mathit{H}_3)_2$), 3.17 (q, ^3J(H,H) = 7.1 Hz, 4 H, $C^{3,4}$-$N(C\mathit{H}_2CH_3)_2$), 3.22 ppm (q, ^3J(H,H) = 7.1 Hz, 4 H, $C^{2,5}$-$N(C\mathit{H}_2CH_3)_2$); $^{13}C\{^1H\}$ NMR (75.47 MHz, $[D_6]$benzene, 298 K): $\delta = 13.9$ (s, 4C, $C^{3,4}$-$N(CH_2\mathit{C}H_3)_2$), 15.5 (s, 4C, $C^{2,5}$-$N(CH_2\mathit{C}H_3)_2$), 44.3 (s, 4C, $C^{3,4}$-$N(\mathit{C}H_2CH_3)_2$), 49.7 (s, 4C, $C^{2,5}$-$N(\mathit{C}H_2CH_3)_2$), 124.3 (s, ^1J(Si,C) = 71 Hz, 2C, $\mathit{C}^{2,5}$), 146.7 ppm (s, ^2J(Si,C) = 29 Hz, 2C, $\mathit{C}^{3,4}$); $^{29}Si\{^1H\}$ NMR (59.6 MHz, $[D_6]$benzene, 298 K): $\delta = -83.5$ ppm (s); EI-MS (70 eV): *m/z* (rel. intensity in %) = 618 (100, $[M^+]$), 589 (5, $[M^+-C_2H_5]$), 560 (47, $[M^+-2\,C_2H_5]$), 545 (20, $[M^+-2\,C_2H_5-CH_3]$), 534 (67, $[M^+-2\,C_2H_5-CN]$.

Alternative synthesis of 2-I: Bis(diethylamino)acetylene (350 mg, 2.08 mmol) was added within 1 min to a solution of SiI_2(Idip) (670 mg, 1.00 mmol) in benzene (15 mL). During addition the solution turned orange. The reaction mixture was stirred for 3 h, and the solvent was removed in vacuo. The residue was extracted with *n*-hexane (5 mL) and the extract was filtered. The orange filtrate was evaporated to dryness in vacuo to give 590 mg of a yellow-orange powder, which was shown by ^1H NMR spectroscopy to contain the product **2-I** and Idip in a molar ratio of 10:1.5. The powder was dissolved in THF (10 mL), and $Et_3N{\cdot}HCl$ (16 mg, 0.12 mmol) was added to the solution. The suspension was stirred for 1 h and all volatiles were removed in vacuo. The residue was extracted with *n*-hexane (2×10 mL), and the extract was filtered. The filtrate was concentrated in vacuo to approximately 2 mL and stored at −60 °C for 18 h. Large orange crystals of **2-I** were obtained, which were collected by filtration at −60 °C and dried in vacuo at ambient temperature for 3 h. Yield: 0.27 g (0.44 mmol, 44% from SiI_2(Idip)). The product was shown by ^1H NMR spectroscopy to be pure.

Synthesis of 1,1-dibromo-2,3,4,5-tetrakis(diethylamino)-1*H*-silole, $SiBr_2\{C_4(NEt_2)_4\}$ (2-Br): $SiBr_4$ (1.0 mL, 2.8 g, 8.1 mmol) was added rapidly to a solution of **2-I** (550 mg, 0.889 mmol) in benzene (20 mL). The orange reaction solution was stirred for 20 h at ambient temperature, and all volatiles were removed in vacuo. The residue was extracted with *n*-hexane (2×10 mL), filtered, and the orange filtrate was concentrated in vacuo to approximately 2 mL and stored at −60 °C for 18 h. The formed orange crystals of **2-Br** were collected by filtration at −60 °C and dried in vacuo at ambient temperature for 3 h. Yield: 331 mg (0.631 mmol, 71 % from **2-I**). M.p. 54 °C. Elemental analysis calcd (%) for $C_{20}H_{40}Br_2N_4Si$ (524.45): C 45.80, H 7.69, N 10.69; found: C 45.04, H 7.45, N 10.40 %. ^{1}H NMR (300.1 MHz, [D$_6$]benzene, 298 K): $\delta = 0.95$ (t, ^3J(H,H) = 7.1 Hz, 12 H, C^{3,4}-N(CH$_2$*CH*$_3$)$_2$), 1.15 (t, ^3J(H,H) = 7.1 Hz, 12 H, C^{2,5}-N(CH$_2$*CH*$_3$)$_2$), 3.08 (q, ^3J(H,H) = 7.1 Hz, 8 H, C^{2,5}-N(*CH*$_2$CH$_3$)$_2$), 3.17 ppm (q, ^3J(H,H) = 7.1 Hz, 8 H, C^{3,4}-N(*CH*$_2$CH$_3$)$_2$); ^{13}C{^{1}H} NMR (75.47 MHz, [D$_6$]benzene, 298 K): $\delta = 13.9$ (s, 4C, C^{3,4}-N(CH$_2$CH$_3$)$_2$), 15.1 (s, 4C, C^{2,5}-N(CH$_2$CH$_3$)$_2$), 44.4 (s, 4C, C^{3,4}-N(*CH*$_2$CH$_3$)$_2$), 49.6 (s, 4C, C^{2,5}-N(*CH*$_2$CH$_3$)$_2$), 124.5 (s, 2C, *C*^{2,5}), 147.8 ppm (s, 2C, *C*^{3,4}); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene, 298 K): $\delta = -13.4$ ppm (s).

Synthesis of 1,1-bis(1,3,4,5-tetramethylimidazolin-2-ylidene)-2,3,4,5-tetrakis(diethylamino)-1*H*-silole diiodide, [Si(IMe$_4$)$_2${C$_4$-(NEt$_2$)$_4$}](I)$_2$ (3): An orange solution of **2-I** (1.00 g, 1.62 mmol) in toluene (10 mL) was added to a stirred suspension of IMe$_4$ (400 mg, 3.22 mmol) in toluene (10 mL) at ambient temperature within 1 min. A voluminous, yellow-orange precipitate was rapidly formed. The suspension was stirred for 1 h, filtered off, and dried in vacuo for 30 min at ambient temperature to give a yellow-orange powder. The powder was crystallized from a dichloromethane–diethyl ether mixture (1:2, v/v) at −60 °C to give **3** as yellow-orange crystals. The crystals were collected by filtration at −60 °C and dried in vacuo at ambient temperature for 3 h. Yield: 930 mg (1.07 mmol, 66 %). ^{1}H NMR (300.1 MHz, [D$_2$]dichloromethane, 298 K): $\delta = 0.84$ (s br $w_{1/2} = 28$ Hz, 12 H, C^{2,5}-N(CH$_2$*CH*$_3$)$_2$), 1.07 (t, ^3J(H,H) = 7.1 Hz, 12 H, C^{3,4}-N(CH$_2$*CH*$_3$)$_2$), 2.39 (s, 6 H, 2 × C^4-*Me*, IMe$_4$), 2.42 (s, 6 H, 2 × C^5-*Me*, IMe$_4$), 2.61 (m br, 4 H, C^{2,5}-N(*CH*$_2$CH$_3$)$_2$), 2.76 (m br, 4 H, C^{2,5}-N(*CH*$_2$CH$_3$)$_2$), 3.06 (dq, ^2J(H,H) = 13.5 Hz, ^3J(H,H) = 7.1 Hz, 4 H, C^{3,4}-N(*CH*$_A$H$_B$CH$_3$)$_2$), 3.58 (dq, ^2J(H,H) = 13.5 Hz, ^3J(H,H) = 7.1 Hz, 4 H, C^{3,4}-N(CH$_A$*H*$_B$CH$_3$)$_2$), 3.93 (s, 6 H, 2 × N^1-*Me*, IMe$_4$), 4.03 ppm (s, 6 H, 2 × N^3-*Me*, IMe$_4$); ^{13}C{^{1}H} NMR (75.47 MHz, [D$_2$]dichloromethane, 298 K): $\delta = 10.3$ (s, 2C, 2 × C^5-*Me*, IMe$_4$), 10.7 (s, 2C, 2 × C^4-*Me*, IMe$_4$), 14.1 (s, 4C, C^{3,4}-N(CH$_2$CH$_3$)$_2$), 15.0 (s br, $w_{1/2} = 47$ Hz, 4C, C^{2,5}-N(CH$_2$CH$_3$)$_2$), 35.0 (s, 2C, 2 × N^1-*Me*, IMe$_4$), 39.1 (s, 2C, 2 × N^3-*Me*, IMe$_4$), 44.3 (s br, $w_{1/2} = 68$ Hz, 4C, C^{3,4}-N(*CH*$_2$CH$_3$)$_2$), 50.6 (s br, $w_{1/2} = 51$ Hz, 4C, C^{2,5}-N(*CH*$_2$CH$_3$)$_2$), 122.6 (s, ^1J(Si,C) = 79 Hz, 2C, *C*^{2,5}-N(CH$_2$CH$_3$)$_2$), 133.1 (s, 2C, 2 × *C*^{5}-Me, IMe$_4$), 133.9 (s, 2C, 2 × *C*^{4}-Me, IMe$_4$), 138.8 (s, ^1J(Si,C) = 72 Hz, 2C, 2 × NCN, IMe$_4$), 151.3 ppm (s, ^2J(Si,C) = 23 Hz, 2C, *C*^{3,4}-N(CH$_2$CH$_3$)$_2$); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_2$]dichloromethane, 298 K): $\delta = -29.2$ ppm (s).

Synthesis of 1-(1,3,4,5-tetramethylimidazolin-2-ylidene)-2,3,4,5-tetrakis(diethylamino)-silacyclopentadiene-1-ylidene Si(IMe$_4$){C$_4$-(NEt$_2$)$_4$} (4): In a Schlenk tube the 1*H*-silole salt **3** (2.48 g, 2.86 mmol) and C$_8$K (780 mg, 5.77 mmol) were suspended in 1,4-dioxane (50 mL). The suspension was stirred for 18 h. During this time the bronze color of the potassium-graphite had disappeared, and the color of the solution had changed from orange to dark orange. The solvent was removed in vacuo and the residue extracted with toluene (2×30 mL). The extract was filtered from graphite and the filtrate was concentrated in vacuo to approximately 15 mL and stored for 18 h at −30 °C. The crude product was recrystallized three times from toluene to afford compound **4** as yellow crystals. Yield: 680 mg (1.39 mmol, 49 %). M.p. 129 °C. Elemental analysis calcd (%) for $C_{27}H_{52}N_6Si$ (488.83): C 66.34, H 10.72, N 17.20; found: C 66.48, H 11.15, N 16.29 %. ^{1}H NMR (300.1 MHz, [D$_6$]benzene,

Table 3. Crystal data and structure refinement parameters of **1-I**, **2-Br**, **2-I**, and **3**·4(CH$_2$Cl$_2$).

Compound	**1-I**	**2-I**	**2-Br**	**3**·4(CH$_2$Cl$_2$)
empirical formula	$C_{12}H_{24}I_2N_4Si$	$C_{20}H_{40}I_2N_4Si$	$C_{20}H_{40}Br_2N_4Si$	$C_{106}H_{200}Cl_8I_6N_4N_{24}Si_3$
formula weight	506.24	618.45	524.47	2940.17
temperature [K]	123(2)	123(2)	123(2)	123(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
crystal system, space group	triclinic, $P\bar{1}$	monoclinic $P2_1/n$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
unit cell dimensions				
a [Å]	9.3845(4)	10.3605(3)	9.5183(4)	20.269(1)
b [Å]	9.8371(4)	18.1591(4)	10.7177(5)	33.761(2)
c [Å]	11.9831(5)	14.3958(4)	13.8357(4)	21.730(1)
α [°]	100.940(2)	90	77.520(2)	90
β [°]	100.247(2)	107.776(2)	87.776(3)	112.375(2)
γ [°]	117.023(2)	90	67.483(2)	90
volume [Å^3]	922.38(7)	2579.08(12)	1271.52(9)	13 750.1(1)
Z, calculated density [g cm^{-3}]	2, 1.823	4, 1.593	2, 1.370	4, 1.420
absorption coefficient [mm^{-1}]	3.470	2498	3.247	1.587
F(000)	488	1232	544	6000
crystal size [mm]	0.36×0.15×0.10	0.33×0.20×0.17	0.91×0.82×0.24	0.60×0.40×0.08
θ range for data collection	1.82 to 26.00°	2.89 to 28.00°	2.70 to 28.00°	1.18 to 26.00°
limiting indices	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-13 \leq l \leq 14$	$-13 \leq h \leq 13$, $-23 \leq k \leq 23$, $-19 \leq l \leq 19$	$-12 \leq h \leq 12$, $-13 \leq k \leq 14$, $-17 \leq l \leq 18$	$-24 \leq h \leq 25$, $-38 \leq k \leq 41$, $-26 \leq l \leq 26$
reflections collected/unique	15 742/3630 [R(int) = 0.0898]	39 327/6229 [R(int) = 0.0557]	15 498/5942 [R(int) = 0.0483]	164 223/26 984 [R(int) = 0.0476]
completeness to $\theta = 28.00$	99.9 %	99.9 %	96.5 %	99.9 %
absorption correction	semi-empirical from equivalents			
max. and min. transmission	0.91741 and 0.46909	0.7044 and 0.4361	0.5096 and 0.1561	0.8736 and 0.5381
refinement method	full-matrix least-squares on F^2			
data/restraints/parameters	3630/0/182	6229/0/252	5942/0/252	26984/12/1372
goodness-of-fit on F^2	1.155	1.000	1.015	1.048
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0584$, $wR_2 = 0.1594$	$R_1 = 0.0218$, $wR_2 = 0.0485$	$R_1 = 0.0327$, $wR_2 = 0.0751$	$R_1 = 0.0669$, $wR_2 = 0.1790$
R indices (all data)	$R_1 = 0.0669$, $wR_2 = 0.1660$	$R_1 = 0.0279$, $wR_2 = 0.0499$	$R_1 = 0.0498$, $wR_2 = 0.0788$	$R_1 = 0.0872$, $wR_2 = 0.1979$
largest diff. peak and hole [e Å^{-3}]	2.160 and −1.540	0.646 and −0.996	0.525 and −0.785	5.451 and −2.205

298 K): $\delta = 1.18$ (s, 3 H, C^4-*Me*, IMe$_4$), 1.22 (t, ^3J(H,H) = 7.1 Hz, 12 H, C^{2,5}-N(CH$_2$C*H*$_3$)$_2$), 1.31 (s, 3 H, C^5-*Me*, IMe$_4$), 1.39 (t, ^3J(H,H) = 7.0 Hz, 12 H, C^{3,4}-N(CH$_2$C*H*$_3$)$_2$), 2.94 (q, ^3J(H,H) = 7.1 Hz, 8 H, C^{2,5}-N(C*H*$_2$CH$_3$)$_2$), 3.26 (s, 3 H, N^1-*Me*, IMe$_4$), 3.55 (q br, ^3J(H,H) = 7.0 Hz, 4 H, C^{3,4}-N(C*H*$_2$CH$_3$)$_2$), 3.76 ppm (s, 3 H, N^3-*Me*, IMe$_4$); ^{13}C{^{1}H} NMR (75.47 MHz, [D$_6$]benzene, 298 K): $\delta = 7.9$ (s, 1C, C^5-*Me*, IMe$_4$), 8.3 (s, 1C, C^4-*Me*, IMe$_4$), 14.7 (s, 4C, C^{2,5}-N(CH$_2$*C*H$_3$)$_2$), 15.2 (s, 4C, C^{3,4}-N(CH$_2$*C*H$_3$)$_2$), 32.5 (s, 1C, N^1-*Me*, IMe$_4$), 33.6 (s, 1C, N^3-*Me*, IMe$_4$), 45.7 (s, 4C, C^{3,4}-N(*C*H$_2$CH$_3$)$_2$), 51.6 (s, 4C, C^{2,5}-N(*C*H$_2$CH$_3$)$_2$), 124.8 (s, 1C, *C*^{4}-Me, IMe$_4$), 125.1 (s, 1C, *C*^{5}-Me, IMe$_4$), 141.9 (s, ^2J(Si,C) = 8.1 Hz, 2C, *C*^{3,4}-N(CH$_2$CH$_3$)$_2$), 153.0 (s, ^1J(Si,C) = 20 Hz, 2C, *C*^{2,5}-N(CH$_2$CH$_3$)$_2$), 168.5 ppm (s, ^1J(Si,C) = 25 Hz, 1C, NCN, IMe$_4$); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene, 298 K): $\delta = -69.6$ ppm (s).

Crystal structure determination of 1-I, 2-I, 2-Br, and 3·4(CH$_2$Cl$_2$): Single crystals of **1-I** (red blocks), **2-Br** (yellow plates), and **2-I** (orange-yellow blocks) were grown upon slow cooling of *n*-hexane solutions from ambient temperature to −60 °C (Table 3). Orange plates of **3**·4(CH$_2$Cl$_2$) were obtained upon diffusion of diethyl ether into a saturated CH$_2$Cl$_2$ solution at ambient temperature. The data collection of **1-I**, **2-Br**, and **3**·4(CH$_2$Cl$_2$) was performed on a Nonius KappaCCD diffractometer (area detector), and the data collection of **2-Br** on a STOE IPDS-2T diffractometer (area detector). The diffractometers used graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and were equipped with low-temperature devices (Nonius KappaCCD diffractometer: Cryostream 600er series, Oxford Cryosystems, 123 K; STOE IPDS-2T diffractometer: Cryostream 700er series, Oxford Cryosystems). Intensities were measured by fine-slicing ω and ϕ scans and corrected for background, polarization and Lorentz effects. An empirical absorption correction was applied for all data sets. The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system. Hydrogen atoms were included isotropically by using the riding model on the bound carbon atoms. Compound **2-Br** crystallized also in a different modification (**2-Br$_a$**) featuring very similar bonding parameters. This structure is also deposited in the CSD database and is not discussed in this manuscript. The salt **3** crystallized kinetically controlled within a rather large unit cell containing three independent cation/anion pairs of **3** and four dichloromethane molecules in the asymmetric unit. The solvent molecules could be fully located in the difference density map and refined anisotropically applying a soft ISOR restraint at the carbon atoms of the solvent molecules.

CCDC-997162 (**1-I**), CCDC-997163 (**2-I**), CCDC-997164 (**2-Br**), CCDC-997165 (**2-Br$_a$**), and CCDC-997166 (**3**) 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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[1] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069 – 1071.

[2] a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793 – 5796; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683 – 5686; b) A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, *121*, 5797 – 5800; *Angew. Chem. Int. Ed.* **2009**, *48*, 5687 – 5690; c) A. C. Filippou, Y. N. Lebedev, O. Chernov, M. Straßmann, G. Schnakenburg, *Angew. Chem.* **2013**, *125*, 7112 – 7116; *Angew. Chem. Int. Ed.* **2013**, *52*, 6974 – 6978.

[3] Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562 – 7563.

[4] a) A. C. Filippou, O. Chernov, B. Blom, K. W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866 – 2872; b) H. Cui, C. Cui, *Dalton Trans.* **2011**, *40*, 11937 – 11940.

[5] a) A. C. Filippou, O. Chernov, K. W. Stumpf, G. Schnakenburg, *Angew. Chem.* **2010**, *122*, 3368 – 3372; *Angew. Chem. Int. Ed.* **2010**, *49*, 3296 – 3300; b) A. C. Filippou, O. Chernov, G. Schnakenburg, *Chem. Eur. J.* **2011**, *17*, 13574 – 13583; c) A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev, G. Schnakenburg, *Angew. Chem.* **2014**, *126*, 576 – 581; *Angew. Chem. Int. Ed.* **2014**, *53*, 565 – 570.

[6] R. S. Ghadwal, R. Azhakar, H. W. Roesky, *Acc. Chem. Res.* **2013**, *46*, 444 – 456.

[7] a) Y. Xiong, S. Yao, S. Inoue, E. Irran, M. Driess, *Angew. Chem.* **2012**, *124*, 10221 – 10224; *Angew. Chem. Int. Ed.* **2012**, *51*, 10074 – 10077; b) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepoetter, D. Stalke, *Angew. Chem.* **2013**, *125*, 1845 – 1850; *Angew. Chem. Int. Ed.* **2013**, *52*, 1801 – 1805; c) Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem.* **2013**, *125*, 7287 – 7291; *Angew. Chem. Int. Ed.* **2013**, *52*, 7147 – 7150.

[8] S. Reis, Diplomarbeit, Universität Bonn, **2012**.

[9] a) W. H. Atwell, *Organometallics* **2009**, *28*, 3573 – 3586, and references therein; b) W. S. Palmer, K. A. Woerpel, *Organometallics* **1997**, *16*, 4824 – 4827.

[10] A CSD survey (11.04.2014) of 1*H*-siloles gave 173 hits and mean values of 1.362, 1.500, and 1.870 Å for the C$_\alpha$–C$_\beta$, C$_\beta$–C$_\beta$ and Si–C$_\alpha$ bond lengths, respectively.

[11] M. Kolonits, M. Hargittai, *Struct. Chem.* **1998**, *9*, 349 – 352.

[12] N. Weidemann, G. Schnakenburg, A. C. Filippou, *Z. Anorg. Allg. Chem.* **2009**, *635*, 253 – 259.

[13] J. Yang, I. Guzei, J. G. Verkade, *J. Organomet. Chem.* **2002**, *649*, 276 – 288.

[14] A CSD survey (11.04.2014) of Si–I bonds of four-coordinate silicon centers gave 77 hits and a mean Si–I bond length of 2.489 Å.

[15] According to a CSD survey (11.04.2014, 149 hits) the mean Si–Br bond length of four-coordinate silicon atoms is 2.253 Å.

[16] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, *12*, S1 – S19.

[17] J. Dubac, A. Laporterie, G. Manuel, *Chem. Rev.* **1990**, *90*, 215 – 263.

[18] U. Niemann, H. C. Marsman, *Z. Naturforsch. B* **1975**, *30*, 202 – 206.

[19] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451.

[20] a) G. C. Levy, D. M. White, J. D. Cargioli, *J. Magn. Reson.* **1972**, *8*, 280 – 283; b) A. G. Brook, F. Abdesaken, G. Gutekunst, N. Plavac, *Organometallics* **1982**, *1*, 994 – 998.

[21] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561 – 562.

[22] S. Yamaguchi, K. Tamao, *J. Chem. Soc. Dalton Trans.* **1998**, 3693 – 3702.

[23] a) E. Colomer, R. J. P. Corriu, M. Lheureux, *Chem. Rev.* **1990**, *90*, 265 – 282; b) M. Saito, M. Yoshioka, *Coord. Chem. Rev.* **2005**, *249*, 765 – 780; c) R. West, *Pure Appl. Chem.* **2008**, *80*, 563 – 569.

[24] Y. Gao, J. Zhang, H. Hu, C. Cui, *Organometallics* **2010**, *29*, 3063 – 3065.

[25] A. Sekiguchi, M. Nanjo, C. Kabuto, H. Sakurai, *Organometallics* **1995**, *14*, 2630 – 2632.

[26] a) E. H. Braye, W. Hübel, I. Caplier, *J. Am. Chem. Soc.* **1961**, *83*, 4406 – 4413; b) S. Yamaguchi, R.-Z. Jin, K. Tamao, F. Sato, *J. Org. Chem.* **1998**, *63*, 10060 – 10062; c) S. Yamaguchi, R.-Z. Jin, S. Ohno, K. Tamao, *Organometallics* **1998**, *17*, 5133 – 5138.

[27] a) K. Tamao, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc.* **1994**, *116*, 11715 – 11722; b) S. Yamaguchi, K. Tamao, *J. Organomet. Chem.* **2002**, *653*, 223 – 228; c) J. Braddock-Wilking, Y. Zhang, J. Y. Corey, N. P. Rath, *J. Organomet. Chem.* **2008**, *693*, 1233 – 1242.

[28] a) K. Tamao, S. Yamaguchi, *Pure Appl. Chem.* **1996**, *68*, 139 – 144; b) K. Tamao, S. Yamaguchi, *J. Organomet. Chem.* **2000**, *611*, 5 – 11; c) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1 – 44; d) X. Zhan, S. Barlow, S. R. Marder, *Chem. Commun.* **2009**, 1948 – 1955.

[29] a) S. Yamaguchi, C. Xu, T. Okamoto, *Pure. Appl. Chem.* **2006**, *78*, 721–730; b) S.-C. Lo, P. L. Burn, *Chem. Rev.* **2007**, *107*, 1097–1116; c) J. Chen, Y. Cao, *Acc. Chem. Res.* **2009**, *42*, 1709–1718.

[30] a) K. Fredenhagen, G. Cadenbach, *Z. Anorg. Allg. Chem.* **1926**, *158*, 249–263; b) W. Rüdorff, E. Schulze, *Z. Anorg. Allg. Chem.* **1954**, *277*, 156–171.

[31] *Handbuch der Präparativen Anorganischen Chemie, Vol. 2*, (Ed.: G. Brauer), 3rd ed., Ferdinand Enke Verlag, Stuttgart, **1975**, p. 676–678.

[32] *Handbuch der Präparativen Anorganischen Chemie, Vol. 2*, (Ed.: G. Brauer), 3rd ed., Ferdinand Enke Verlag, Stuttgart, **1975**, p. 671–672.

[33] R. van der Heiden, L. Brandsma, *Synthesis* **1987**, 76–77.

[34] L. Brandsma, *Preparative acetylenic chemistry*, 2nd ed, Elsevier, Amsterdam, **1988**, pp. 185–186.

[35] NMR spectroscopic data of $Me_2NC{\equiv}CNMe_2$: ^1H NMR ([D$_6$]benzene, 298 K, ppm): $\delta = 2.50$ (s, 12 H, 2 × $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 298 K, ppm): $\delta = 45.7$ (s, 2 × $N(CH_3)_2$), 75.3 (s, 2 × C^{alkyne}); NMR spectroscopic data of $Et_2NC{\equiv}CNEt_2$: ^1H NMR ([D$_6$]benzene, 300.1 MHz, 298 K, ppm): $\delta = 1.09$ (t, $^3J(H,H) = 7.1$ Hz, 12 H, 2 × $N(CH_2CH_3)_2$), 2.71 (q, $^3J(H,H) = 7.1$ Hz, 8 H, 2 × $N(CH_2CH_3)_2$); $^{13}C\{^1H\}$-NMR ([D$_6$]benzene, 75.5 MHz, 298 K, ppm): $\delta = 13.2$ (s, 4C, 2 × $N(CH_2CH_3)_2$), 49.9 (s, 4C, 2 × $N(CH_2CH_3)_2$), 74.1 (s, 2 × C^{alkyne}).

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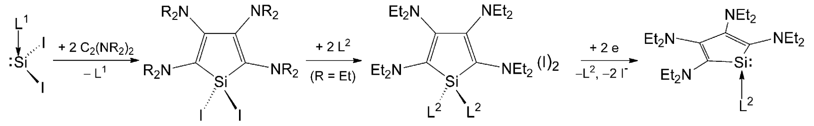
FULL PAPER



1-I, 2-I **3** **4**

2,3,4,5-Tetraamino-1*H*-siloles $SiI_2\{C_4(NR_2)_4\}$ (**1-I**: R = Me; **2-I** R = Et) were synthesized by a [2+2+1] cycloaddition of $R_2N{-}C{\equiv}C{-}NR_2$ (R = Me, Et) with NHC-stabilized SiI_2 (L^1 = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). Reaction of **2-I** with the N-heterocyclic carbene IMe_4 (IMe_4 (L^2) = 1,3,4,5-tetramethyl-imidazolin-2-ylidene) leads to $[Si(IMe_4)_2\{C_4(NEt_2)_4\}](I)_2$ (**3**), containing a 1*H*-silole dication with a four-coordinate Si^{IV} center. Two-electron reduction of **3** with C_8K affords the carbene-stabilized 1-silacyclopentadien-1-ylidene $Si\{C_4(NEt_2)_4\}(IMe_4)$ (**4**).

Siloles

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■■ – ■■

[2+2+1] Cycloadditions of Bis(dialkylamino)acetylenes with SiI_2(Idip): Syntheses and Reactivity Studies of Unprecedented 2,3,4,5-Tetraamino-1*H*-siloles