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# A Generic One-Pot Route to Acyclic Two-Coordinate Silylenes from Silicon(IV) Precursors: Synthesis and Structural Characterization of a Silylsilylene**

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By comparison with their heavier Group 14 congeners, divalent silicon compounds are typically highly labile species with short lifetimes at ambient temperature.[1] Consequently, the observation by West et al. in 1981 of the transient silylene, $SiMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$), and its subsequent dimerization at 77 K to give the disilene, $Mes_2Si{=}SiMes_2$, represented a breakthrough in the evolution of modern main group chemistry.[2] From that groundbreaking discovery until very recently, only silylene systems stabilized by incorporation into a cyclic framework, or by an augmented coordination number at silicon, had been reported.[3–6] In early 2012, however, near simultaneous reports from our program and that of Power identified acyclic silylene systems that are stable at room temperature and above (Figure 1).[7–9]

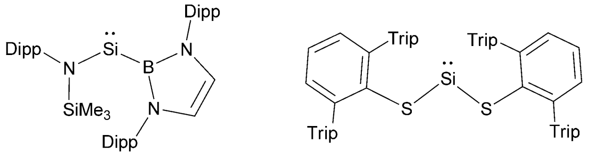
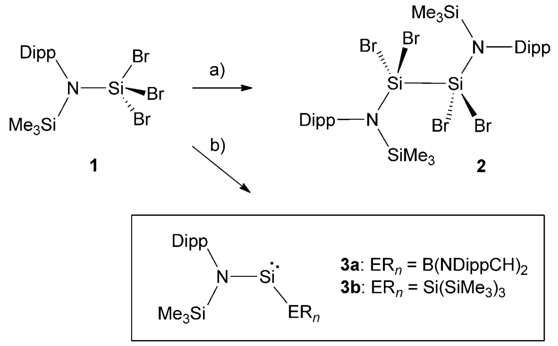


***Figure 1.*** Recently reported acyclic two-coordinate silylenes. Dipp = 2,6-$iPr_2C_6H_3$, Trip = 2,4,6-$iPr_3C_6H_2$.

Both systems exploit the kinetic stabilization imparted by extremely bulky peripheral substituents, a factor which contributes to decomposition temperatures in excess of 130 °C. On the other hand, the contrasting potential of these two compounds for further reactivity is signaled by disparate X-Si-X angles ($\measuredangle$B-Si-N = 109.7(1)°; $\measuredangle$S-Si-S = 90.52(2)°) and HOMO–LUMO gaps (197.2 and 411.0 kJ mol$^{-1}$, respectively).[7,8] Consistently, the unsymmetrical boryl/amido system is uniquely capable of activating E–H bonds (E = H, C) close to room temperature.[7] A convenient synthetic attribute of this compound is its direct formation from the $Si^{IV}$ precursor $Si\{N(SiMe_3)Dipp\}Br_3$ (**1**; Dipp = 2,6-$iPr_2C_6H_3$) and two equivalents of $(thf)_2Li\{B(NDippCH)_2\}$.[10] In effect, the boryllithium reagent accomplishes the dual roles of reducing agent and source of the strongly sigma donating (formally anionic) $[B(NDippCH)_2]^-$ substituent. To better understand this method and its scope for the direct conversion of $Si^{IV}$ halides into acyclic silylenes, we have investigated the reactivity of **1** towards other sterically encumbered anionic main group and transition metal nucleophiles. In doing so we have synthesized the first example of a stable two-coordinate silylsilylene.[11]

Key synthetic steps are outlined in Scheme 1; the synthesis of $Si^{II}$ systems by this route is dependent on the use of an anionic reagent that is not only a good nucleophile, but also 1) sterically bulky and 2) a strong reducing agent. In the absence of sufficient nucleophilicity, as in the case of $KC_8$, dehalogenative coupling occurs to give the disilane **2** (see the Supporting Information). With more nucleophilic, but insufficiently bulky anions, the possibility also exists for simple substitution chemistry to occur at the silicon center, which



***Scheme 1.*** Syntheses of acyclic silylenes **3a** and **3b**. Key reagents: a) $KC_8$ (1.0 equiv), thf, −78 °C to room temperature, ca. 20%; b) $(thf)_2K[Si(SiMe_3)_3]$ (2.0 equiv), hexane, room temperature, 5 min, ca. 50% (for **3b**); see Ref. [7] for **3a**.

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Supporting information for this article, including synthetic, spectroscopic, and crystallographic data for compounds **2**, **4**, **5**, **6**, and $\{CpFe(CO)\}_2(\mu\text{-}CO)(\mu\text{-}SiBr\{N(SiMe_3)Dipp\}$, as well as details of the DFT calculations on **3b**, and CIFs for **2**, **3b**, **4**, **5**, **6**, and $\{CpFe(CO)\}_2(\mu\text{-}CO)(\mu\text{-}SiBr\{N(SiMe_3)Dipp\}$, is available on the WWW under http://dx.doi.org/10.1002/anie.201208554.

would consequently remain tetravalent. Thus, although the reaction of **1** with K[CpFe(CO)$_2$] primarily yields the coupling product **2**, a small quantiy of the Fe–Si containing system {CpFe(CO)}$_2$(μ-CO)(μ-SiBr{N(SiMe$_3$)Dipp}), was also isolated (see the Supporting Information).[12] In the case of bulkier nucleophiles, redox properties are important; thus, although **1** is unreactive towards sterically encumbered alkali metal amides, such as Li{N(SiMe$_3$)Dipp} or K{N(SiMe$_3$)$_2$}, it reacts readily with two equivalents of (thf)$_2$Li{B(NDippCH)$_2$} or (thf)$_2$K[Si(SiMe$_3$)$_3$], or three equivalents of K[CPh$_3$], generating BrB(NDippCH)$_2$,[7] BrSi(SiMe$_3$)$_3$, and Gomberg's dimer, respectively.

In the case of K[CPh$_3$], the silicon-containing product is a labile species that gives rise to a $^{29}$Si signal at $\delta_{\text{Si}}=$ 442.6 ppm, in the region characteristic of two-coordinate silylenes ($\delta_{\text{Si}}=439.7$ ppm for Si{B(NDippCH)$_2$}{N(SiMe$_3$)-Dipp}, **3a**).[7] With (thf)$_2$K[Si(SiMe$_3$)$_3$], however, a thermally stable ($T_{\text{d}}=$ ca. 140 °C) purple crystalline material can be isolated, which has been characterized by standard spectroscopic techniques and by single crystal X-ray diffraction (Figure 2).[13] The monomeric structure of the silylene product, Si{Si(SiMe$_3$)$_3$}{N(SiMe$_3$)Dipp} (**3b**), which is implied by $^{29}$Si NMR analysis ($\delta_{\text{Si}}=438$, 467 ppm) is thus confirmed crystallographically. Although the Si–N and Si–Si distances associated with two-coordinate Si(1) (1.720(1) and 2.386(1) Å, respectively) are largely unremarkable,[14] the N(1)-Si(1)-Si(2) angle of 116.91(5)° is significantly wider than the corresponding N-Si-B angle of 109.7(1)° measured for **3a**.[7] This difference is presumably at least partly steric in origin, with the notable buttressing between the amido Dipp substituent and the SiMe$_3$ group centered around Si(5) leading to asymmetry within the Si(SiMe$_3$)$_3$ (hypersilyl) moiety, as manifested by a Si(1)-Si(2)-Si(5) angle of 138.14(3)° vs. 101.32(2) and 92.25(2)° for Si(1)-Si(2)-Si(3/4).

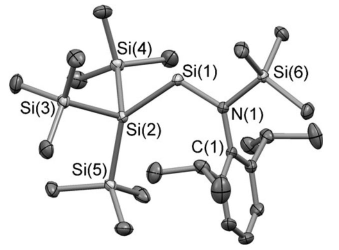


***Figure 2.*** Molecular structure of **3b**. Hydrogen atoms omitted for clarity; thermal elipsoids set at the 35 % probability level. Key bond lengths [Å] and angles [°]: Si(1)–N(1) 1.720(1), Si(1)–Si(2) 2.386(1); N(1)-Si(1)-Si(2) 116.91(5), Si(1)-Si(2)-Si(3) 101.32(2), Si(1)-Si(2)-Si(4) 92.25(2), Si(1)-Si(2)-Si(5) 138.14(3).

Another consequence of the high degree of steric crowding in **3b** is evident from multinuclear NMR data in [D$_6$]benzene solution. Two sets of signals in approximately 1:1 ratio are observed, resulting from conformers related by restricted rotation about the Si(1)–N(1) bond. Thus, one set of signals is derived from the isomer found in the solid state, in which the Dipp substituent lies *syn* to the hypersilyl group, whereas the other set is due to the corresponding *anti* isomer (a conformation which is analogous to that found in the solid state structure of **3a**). DFT calculations reproduce well the observed pattern of NMR signals for both isomers, and also imply that the energetic difference between these two rotamers is very small (2.7 kJ mol$^{-1}$).

At a more general level, quantum chemical input indicates that the HOMO for **3b** (43.0 % Si(1) 3p, 13.1 % Si(1) 3 s; Figure 3) is separated from the LUMO (70.3 % Si(1) 3p, 9.3 % N 2p) by 192.1 kJ mol$^{-1}$ and that the energetic gap between the singlet ground state and triplet first excited state is 103.7 kJ mol$^{-1}$. These figures are very similar to those determined for **3a** (197.2 and 103.9 kJ mol$^{-1}$, respectively),[7] and consistent with the patterns of reactivity delineated for the borylsilylene system; **3b** also 1) reacts with dihydrogen at room temperature in hexane solution to give the corresponding dihydrosilane **4** (which gives rise to diagnostic new resonances at $\delta_{\text{H}}=5.17$ and $\delta_{\text{Si}}=-35.2$ ppm, $^{1}J_{\text{Si-H}}=$ 195 Hz),[15] and 2) undergoes intramolecular C–H activation in [D$_6$]benzene over a period of 5 days at 80 °C to give silaindoline **5** (Scheme 2, see also the Supporting Information).

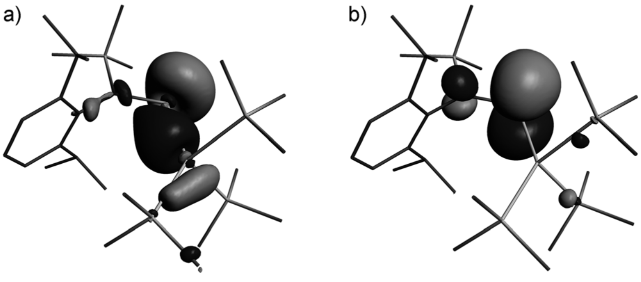
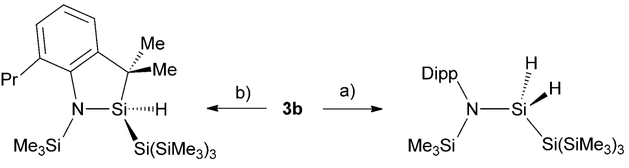


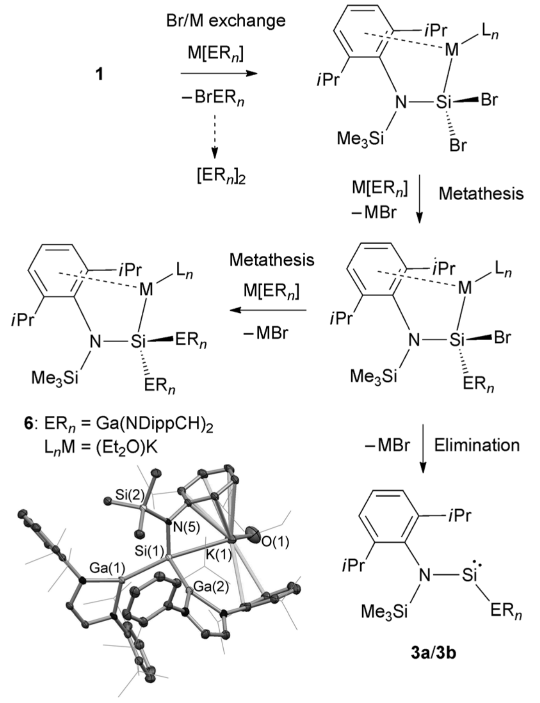
***Figure 3.*** a) HOMO (−4.684 eV) and b) LUMO (−2.693 eV) of silylsilylene **3b**.



**5** **4**

***Scheme 2.*** Activation of H–H and C–H bonds by silylsilylene **3b**. Key reagents and conditions: a) H$_2$ (1 atm), hexane, 20 °C, 2.5 h, > 90 % by NMR spectroscopy (62 % yield of isolated product); b) C$_6$D$_6$, 80 °C, 5 d, ca. 65 % yield (see the Supporting Information for X-ray structures of **4** and **5**).

From a mechanistic perspective, the syntheses of **3a** and **3b** outlined in Scheme 1 implicate the main group anion in both the reduction and metathesis steps. Although a number of observations, such as the lack of reactivity of **1** towards bulky, but less reducing nucleophiles (such as amides), and the fact that systems of the type X$_2$Si{B(NDippCH)$_2$}{N-(SiMe$_3$)Dipp} are stable with respect to B–X reductive elimination,[7] imply that metathesis is not the first mechanistic step, we have sought to confirm that reduction is a viable alternative. Such a mechanism would necessarily involve silylenoid intermediates (Scheme 3); consistent with



***Scheme 3.*** Proposed mechanism for the one-pot formation of acyclic silylenes **3a** and **3b** from **1** through silylenoid intermediates (M = Li or K), and the structure of the digallylsilylenoid **6**. Key bond lengths [Å] and angles [°]: Si(1)–N(5) 1.815(3), Si(1)–Ga(1) 2.438(1), Si(1)–Ga(2) 2.452(1), Si(1)···K(1) 3.470(1); N(5)-Si(1)-Ga(1) 110.3(1), N(5)-Si(1)-Ga(2) 108.8(1), Ga(1)-Si(1)-Ga(2) 91.8(1), K(1)-Si(1)-Ga(1) 152.9(1), K(1)-Si(1)-Ga(2) 99.5(1), K(1)-Si(1)-N(5) 89.3(1).

this proposal, Lee and co-workers have shown that $SiRBr_3$ (where $R = C(SiMe_3)_3$) is susceptible to bromide/lithium exchange in the presence of powerful lithium-containing reductants, to give a silylenoid species, $SiR(Br)_2Li$, which is then amenable to substitution with anionic nucleophiles to give $SiR(Br)Ar(Li)$.[16]

In the current study, the viability of alkali metal silylenoid species can be demonstrated explicitly; the reaction of **1** with $[(Et_2O)K\{Ga(NDippCH)_2\}](OEt_2)$, which is a gallium analogue of $(thf)_2Li\{B(NDippCH)_2\}$,[17] generates the potassium digallylsilylenoid $\{(Et_2O)K\}Si\{Ga(NDippCH)_2\}_2\{N(SiMe_3)Dipp\}$, **6**, together with the Ga–Ga bonded dimer $\{Ga(NDippCH)_2\}_2$ (Scheme 3).[18] Structurally, **6** features a silicon center that is significantly distorted from tetrahedral (∡K-Si-Ga = 152.9(1), 99.5(1)°, ∡K-Si-N = 89.3(1)°), together with a potassium center ligated by a single ether donor and engaged in weak interactions with Si(1) ($d(K\cdots Si) = 3.470(1)$ vs. 3.14 Å for the sum of the respective covalent radii)[19] and with the flanking aryl π systems of the amido and gallyl Dipp substituents, for example, $d(K\cdots C) = 3.156(4)$–$3.287(4)$ for the amido Dipp group. As such, **6** shares key structural features with the alkyltin system $\{(tmeda)K\}Sn\{Ga(NdippCH)_2\}_2\{CH(SiMe_3)_2\}$.[20] These and related tin systems have been prepared from stannylene precursors, and in a similar vein **6** can be formulated as a Lewis base adduct of the putative gallylsilylene $Si\{Ga(NDippCH)_2\}\{N(SiMe_3)Dipp\}$.

Mechanistically, both borylsilylene **3a** and digallylsilylenoid **6** can be regarded as being derived from a common class of bromosilylenoid intermediate of the type $(L_nM)SiBr\{E(NDippCH)_2\}\{N(SiMe_3)Dipp\}$ (E = B or Ga; M = alkali metal). **3a** is thus the product of the subsequent elimination of LiBr, whereas **6** results from an alternative gallyl/bromide metathesis step, presumably made possible by the longer Si–Ga bonds (vs. Si–B) and the consequently reduced steric demands of the gallyl fragment. The weaker donor capabilities of the gallyl (vs. boryl) ligand also provide a rationale for the reduced propensity to eliminate alkali metal halide.[21]

In summary, we have reported a one-pot, single-step synthesis of a thermally stable acyclic silylsilylene, $Si\{Si(SiMe_3)_3\}\{N(SiMe_3)Dipp\}$ (**3b**), from a $Si^{IV}$ starting material, together with evidence for the formation of alkali metal silylenoid systems under related conditions. Systems of the type $RSi(SiR_3)$ have previously been discussed in the context of their rearrangement to isomeric disilenes, $R_2Si{=}SiR_2$.[22,23] In the current study, no such transformation has been identified for **3b**, which appears to instead undergo C–H activation at elevated temperatures.[24] On the other hand, alternative modes of reactivity have been demonstrated, such as oxidative addition of H–H and C–H bonds, which have ample precedent in d-block chemistry.

## *Experimental Section*

Synthesis of **3b**: A solution of $(thf)_2K[Si(SiMe_3)_3]$ (113 mg, 0.26 mmol) in hexane (4 mL) was added to a solution of **1** (68 mg 0.13 mmol) in hexane (1 mL) at room temperature. The color immediately changed to bright purple and copious precipitate formed. The solution was filtered and stored at −80 °C for 3 d, yielding purple crystals slightly contaminated with $BrSi(SiMe_3)_3$.[25] Slow crystallization from hexanes at room temperature gave X-ray quality crystals of **3b** (35 mg, 0.067 mmol, 51 %). Melting point: decomposing (decolorizing) at 140 °C and above. $^1$H NMR ($C_6D_6$, 293 K): $\delta = 0.30$ (s, 9H+27H, $NSiMe_3$+$SiSiMe_3$), 0.35 (s, 9H, $NSiMe_3$), 0.46 (s, 27H, $SiSiMe_3$), 1.09 (d, $^3J(H,H) = 7.0$ Hz, 6H, $CHMe_2$), 1.17 (d, $^3J(H,H) = 7.0$ Hz, 6H, $CHMe_2$), 1.23 (two overlapping d, 12H, $CHMe_2$), 3.42 and 3.44 (two overlapping sept, $^3J(H,H) = 7.0$ Hz, 4H, $CHMe_2$), 7.06 ppm (br s, 6H, CH of Ar). $^{13}$C NMR ($C_6D_6$, 293 K): $\delta = 3.45$ and 4.11 ($NSiMe_3$), 4.28 and 4.37 ($SiSiMe_3$), 14.35 (hexane $CH_3$), 23.03 (hexane $CH_2$), 23.58, 24.41, 25.29 and 26.24 ($CHMe_2$), 28.58 and 29.07 ($CHMe_2$), 31.94 (hexane $CH_2$), 124.11 and 124.18 (*m*-CH of Ar), 125.16 and 126.16 (*p*-CH of Ar), 142.24 and 145.08 (*o*-C of Ar), 146.12 and 152.31 ppm (*ipso*-C of Ar). $^{29}$Si NMR ($C_6D_6$, 293 K): $\delta = -107.19$ and $-105.89$ ($SiSiMe_3$), $-8.33$ ($SiSiMe_3$), 5.77 and 9.73 ($NSiMe_3$), 438.20 and 467.46 ppm (central Si). Crystallographic data: $C_{24}H_{53}NSi_6$, $M_r$ 524.21, monoclinic, $C2/c$, $a = 22.4461(2)$, $b = 9.6252(1)$, $c = 32.0919(4)$ Å, $\beta = 104.481(1)°$, $V = 6713.1(1)$ Å$^3$, $Z = 8$, $\rho_c = 1.037$ Mg m$^{-3}$, $T = 150$ K, $\lambda = 0.71073$ Å. 25749 reflections collected, 7636 independent [$R(int) = 0.046$], which were used in all calculations. $R_1 = 0.0374$, $wR_2 = 0.0363$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0613$, $wR_2 = 0.0470$ for all unique reflections. Max. and min. residual electron densities 0.34 and $-0.26$ e Å$^{-3}$. CCDC 895809 (**3b**) contains 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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**Keywords:** gallium · reduction · silicon · silylenes · subvalent compounds

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[15] Corresponding values of $\delta_{\mathrm{H}} = 4.56$ ppm and $^{1}J_{\mathrm{SiH}} = 187$ Hz have been measured for $\mathrm{H_2Si\{B(NDippCH)_2\}\{N(SiMe_3)Dipp\}}$, which is the product of the reaction of **3a** with dihydrogen.[7]

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