Silanes

An Isolable Radical Anion and Dianion of a Cyclotetrasilane: Synthesis and Structure of $[\mathrm{Si}\{1,2\text{-}(\mathrm{NEt})_2\mathrm{C}_6\mathrm{H}_4\}]_4^{-\bullet}$ and $[\mathrm{Si}\{1,2\text{-}(\mathrm{NEt})_2\mathrm{C}_6\mathrm{H}_4\}]_4^{2-}$**

Barbara Gehrhus, Peter B. Hitchcock, and Lihong Zhang*

The stability of isolable N-heterocyclic silylenes[1,2] has its origin in a significant π delocalization in the five-membered ring of Si[N(*t*Bu)CHCHN*t*Bu] (**A**)[3] or the benzo-annulated $\mathrm{Si}[1,2\text{-}(\mathrm{NCH_2}t\mathrm{Bu})_2\mathrm{C_6H_4}]$ (**B**)[4] with incorporation of the formally empty silicon out-of-plane p orbital.[5,6] In contrast, the silylene $\mathrm{Si}[\mathrm{N}(t\mathrm{Bu})\text{-}\mathrm{CH_2CH_2N}t\mathrm{Bu}]$ (**C**),[7] which lacks π delocalization is only marginally stable and converts into its stable tetramer.[8] But how important is the steric protection provided by the bulky *t*Bu or $\mathrm{CH_2}t\mathrm{Bu}$ groups in the stable silylenes **A** and **B**, respectively, and what effect will a reduction of the size of the substituent at the nitrogen atom have on the stability of a two-coordinate silicon species? Herein we report 1) the reduction of the $\mathrm{Cl_2Si}[1,2\text{-}(\mathrm{NR})_2\mathrm{C_6H_4}]$ (R = Et; **3**) analogue of the silylene precursor of **B** ($\mathrm{R} = \mathrm{CH_2}t\mathrm{Bu}$) with potassium, 2) the synthesis of the first isolable and structurally characterized radical anion of a cyclotetrasilane, $[\mathrm{Si}\{1,2\text{-}(\mathrm{NEt})_2\mathrm{C_6H_4}\}]_4^{-\bullet}$, and 3) its dianion $[\mathrm{Si}\{1,2\text{-}(\mathrm{NEt})_2\mathrm{C_6H_4}\}]_4^{2-}$.

Reduction of $\mathrm{Cl_2Si}[1,2\text{-}(\mathrm{NEt})_2\mathrm{C_6H_4}]$ (**3**)[9] with potassium in THF at ambient temperature afforded a product mixture of the potassium salt of the radical anion $\mathbf{1}^{-\bullet}$ and the dianion $\mathbf{2}^{2-}$ (Scheme 1). Complex **1** could be isolated from the mixture as green crystals at −25 °C whereas the orange complex **2** was crystallized from DME.

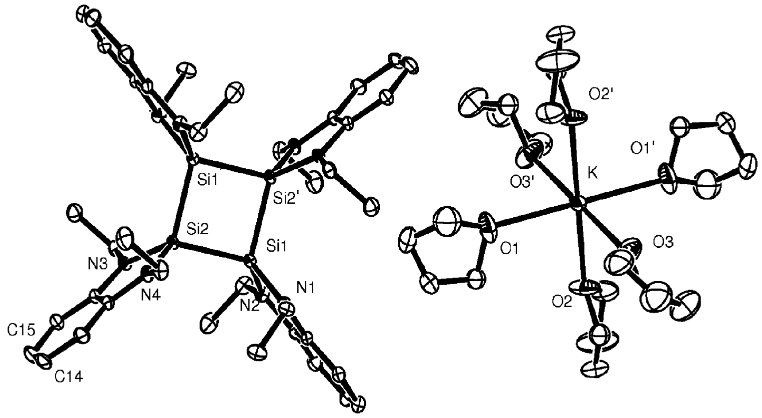
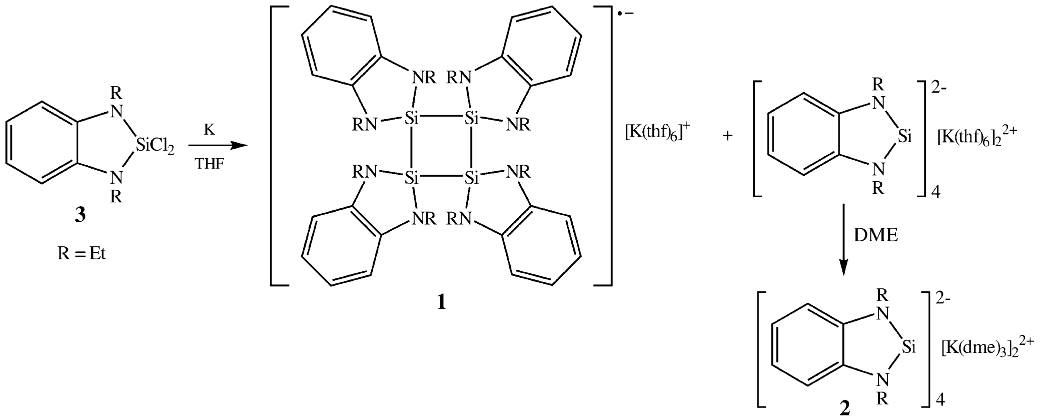


Figure 1. Molecular structure of **1** (thermal ellipsoids set at 20 % probability).



Scheme 1.

The structure of **1**[10] shows the potassium cation solvent-separated from the cyclotetrasilane radical anion (Figure 1) whilst for the structure of **2**[11] the solvated potassium cations have η^2-coordination to the 3,3′-C atoms (C14, C15) of the *o*-phenylene ring (Figure 2). In both, **1** and **2**, the cyclotetrasilane ring lies on an inversion centre and the $\{\mathrm{Si_4}\}$ core is planar. The Si1−Si2 bond length in **1** of 2.347(2) Å (see Table 1) is slightly shorter compared to Si−Si bond lengths which are found in cyclopolysilanes (av. 2.372 Å)[12] or for tetrasilacyclobutanes (2.363–2.445 Å).[13] Even further reduction of the Si1−Si2 bond length is found for complex **2** (2.284(2) Å), which is close to the range of Si−Si double bonds (2.138–2.261 Å)[12] and may also be compared to the Si=Si bonds in a *Z*-diaminodisilyldisilene (the tetramer of **C**; 2.289 Å)[8] or cyclotetrasilenes (2.174, 2.257 Å).[14,15] The substantial shortening of the Si−Si bond in **1** and **2** can be

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[*] Dr. B. Gehrhus, Dr. P. B. Hitchcock, L. Zhang
Department of Chemistry
School of Life Science
University of Sussex
Brighton, BN1 9QJ (UK)
Fax: (+44) 1273-677-196
E-mail: b.gehrhus@sussex.ac.uk

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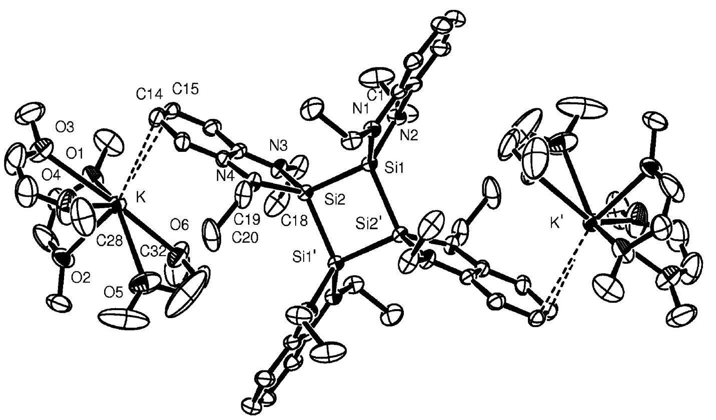


Figure 2. Molecular structure of **2** (thermal ellipsoids set at 20 % probability).

Table 1: Selected bond lengths [Å] and angles [°] of compounds **1** and **2**.

Bond	1	2	Angle	1	2
Si1-Si2′	2.346(2)	2.284(2)	Si2′-Si1-Si2	90.27(6)	89.87(5)
Si1-Si2	2.347(2)	2.284(2)	Si1′-Si2-Si1	89.73(6)	90.13(5)
Si1-N1	1.768(4)	1.814(3)	N1-Si1-N2	88.6(2)	85.2(2)
Si1-N2	1.775(4)	1.799(4)	N3-Si2-N4	88.6(2)	84.7(2)
Si2-N3	1.770(4)	1.807(3)			
Si2-N4	1.765(4)	1.812(3)			
K⋯C14		3.137(5)			
K⋯C15		3.266(5)			

attributed to the additional one or two electrons, respectively, which are delocalized in the Si_4 ring.

ESR-spectroscopic analysis[16] (Figure 3a) of **1** ($g_{iso} = 2.0025$, $a = 3.5$ G) shows 15 of the 17 expected lines ($2nI+1$, $I=1$, $n=8$) consistent with the electron being delocalized over the Si_4 ring and is in good agreement with the simulated spectrum (Figure 3b).

Alkali-metal reduction of a cyclosilane to obtain a radical anion is a long established method. A wide range of ESR spectroscopic analysis shows that the unpaired electron is delocalized over the resulting cyclopolysilane ring.[17–19] All of these radical anions of cyclosilanes are labile and are only detected at low temperature. Persistent radical anions of ladder oligosilanes were reported recently.[20] The radical anion $\mathbf{1}^{-\bullet}$ of complex **1** is the first thermally robust, crystalline and structurally characterized radical anion of a cyclopolysilane.

The proposed mechanism leading to **1** and **2** may involve pathways (a), (b) and/or (c) (Scheme 2). Precedence for pathway (a) is found in the reported formation of **6** and **7** (where (NN)Si = **C**)[21] by reduction of **C** with Na/K or the formation of **7** (where (NN)Si = **B**) by reduction of **B** with potassium.[22] Precedence for pathway (b) is the report that the transient silylene (tBu_3Si)SiCl inserts into the Si–Na bond of its precursor (tBuSi)$SiCl_2Na$; in the present context this corresponds to the insertion of **5** into the Si–K bond of **4** to form **8**. This insertion was found to proceed more readily than insertion into the Si–H bond of the common silylene trap Et_3SiH and was accompanied by one or two further insertions of (tBuSi)SiCl into the Si–Na bond of the successive intermediates, which led, after elimination of NaCl, to the corresponding cyclosilanes (tBuSiSiCl)$_3$ and (tBuSiSiCl)$_4$.[23] A third pathway (c) is possible, which is commonly suggested for the synthesis of cyclooligosilanes by reductive dehalogenation of halosilanes, which in this case would proceed by reaction of **4** with the dichlorosilane **3** to yield a 1,2-dichlorodisilane **10**. Successive metallation and reaction with **3** followed by elimination of NaCl would also lead to intermediate **9**.

Complex **2** can readily be converted into **1** by, for example, treatment with **3**. Attempts to isolate the neutral cyclotetrasilane [Si{1,2-$(NEt)_2C_6H_4$}]$_4$ (cf., **9** in Scheme 2) have so far been unsuccessful, presumably owing

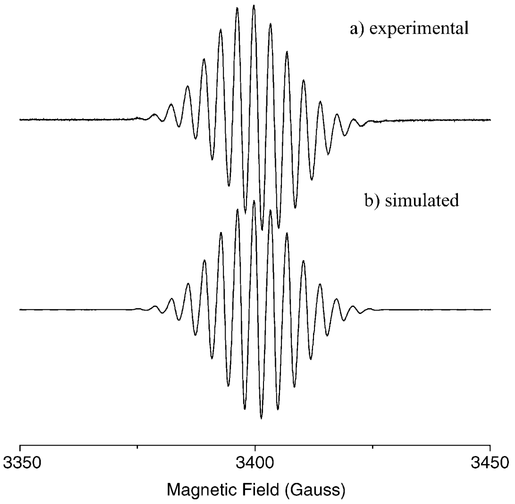
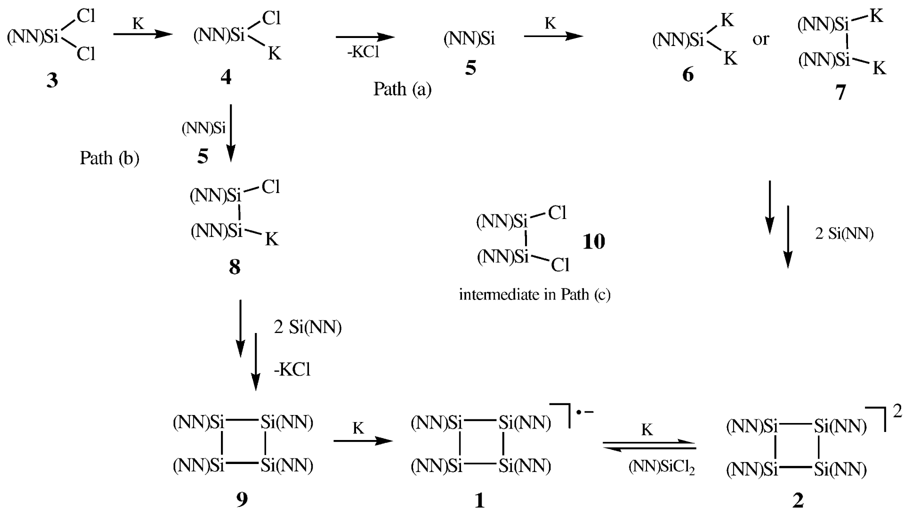


Figure 3. ESR spectrum of **1**.



Scheme 2.

to the readiness of $[Si\{1,2\text{-}(NEt)_2C_6H_4\}]_4$ to take up a single electron. Surprisingly, the reduction of $Cl_2Si[1,2\text{-}(NR)_2C_6H_4]$ upon changing the substituent at N from R = Et to the bulkier *i*Bu led to a similar formation of a cyclotetrasilane radical anion and dianion, which will be reported in the full paper. The neopentyl substituent ($R = CH_2t\text{Bu}$) therefore seems ideally suited to provide steric protection for the silylene **B**.

Experimental Section

1: Potassium (1.45 g, 0.037 mol) was added to a solution of **3** (4.85 g, 0.019 mol) in THF (150 mL) at ambient temperature. The mixture initially turned green and after stirring for 2 days to green brown. The mixture was filtered and the green residue was extracted with hot THF. The extract was concentrated and green crystals of compound **1** were obtained at −25 °C.

2: Potassium (3.5 g, 0.89 mol) was added to a solution of **3** (5.85 g, 0.022 mol) in THF (150 mL) at ambient temperature. The mixture initially turned green. The mixture was stirred for 5 days then filtered and the solvent was removed from the red-brown filtrate. The residue was crystallized from DME yielding orange crystals of compound **2** (4.9 g, 64 %). ^{1}H NMR (300 MHz, $[D]_8$THF): $\delta = 1.05$ (br,s, 6 H, CH_3), 3.26 (dme), 3.42 (dme), 3.78 (br,d, 4 H, CH_2), 5.95 (m, 2 H, phenyl), 6.09 ppm (m, 2 H, phenyl). ^{29}Si{^{1}H} NMR (99.3 MHz, $[D]_8$THF): $\delta = -45.2$ ppm.

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[9] Synthesis of **3** is similar to the synthesis of $Cl_2Si[1,2\text{-}(NCH_2t\text{Bu})_2C_6H_4]$ in ref. [4].

[10] Crystal data for **1**: C_{64} $H_{104}KN_8O_6Si_4$, $M_r = 1233.01$, specimen $0.20 \times 0.05 \times 0.05$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 18.2955(7)$, $b = 9.4645(4)$, $c = 20.0260(8)$ Å, $\beta = 91.757(2)°$, $U = 3466.0(2)$ Å^3, $Z = 2$, $\mu = 0.20$ mm^{-1}, $T = 173(2)$ K, 4775 unique reflections collected, $R_1 = 0.069$ for 3212 reflections with $I > 2\sigma(I)$, $wR_2 = 0.174$ for all reflections, Data collection KappaCCD, full-matrix least-squares refinement on F^2, SHELX-97. CCDC-218118 (**1**) and CCDC-218119 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] Crystal data for **2**: $C_{64}H_{116}K_2N_8O_{12}Si_4$, $M_r = 1380.21$, specimen $0.20 \times 0.20 \times 0.05$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.7165(2)$, $b = 19.0891(4)$, $c = 17.2205(4)$ Å, $\beta = 109.724(1)°$, $U = 3934.96(14)$ Å^3, $Z = 2$, $\mu = 0.24$ mm^{-1}, $T = 173(2)$ K, 5295 unique reflections collected, $R_1 = 0.0631$ for 3774 reflections with $I > 2\sigma(I)$, $wR_2 = 0.178$ for all reflections, Data collection KappaCCD, full-matrix least-squares refinement on F^2, SHELX-97. (CCDC reference number 218119.)

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