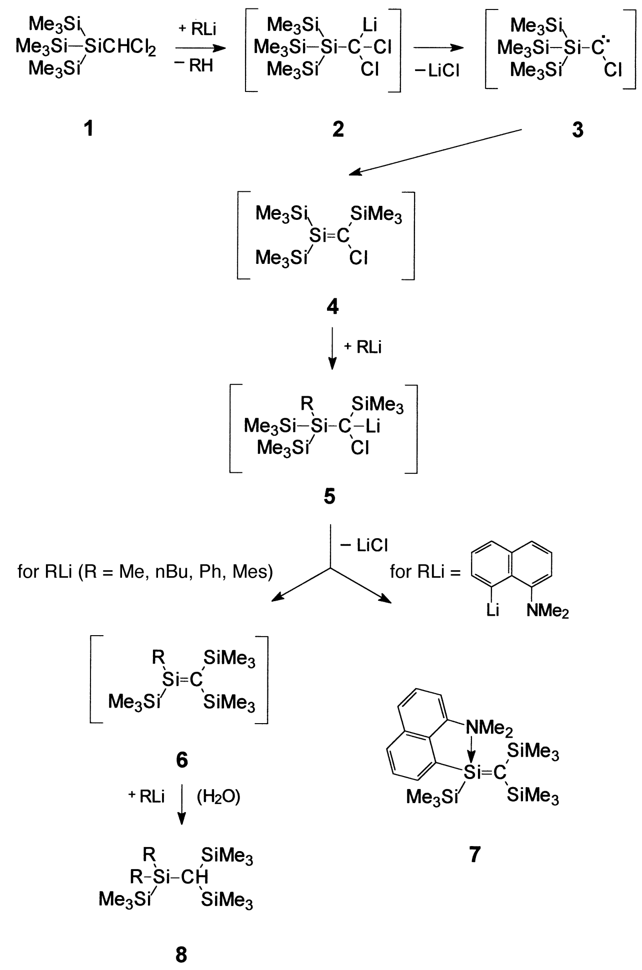
Reaction of Dichloromethyltris(trimethylsilyl)silane with Organolithium Reagents: Synthesis of an Intramolecularly Donor-Stabilized Silene**

Martin Mickoleit, Kathleen Schmohl, Rhett Kempe and Hartmut Oehme*

Derivatives of three-coordinate silicon, such as Si=X systems (X = CR_2, SiR_2, NR, PR, S) and silylium salts, are labile compounds that can only be isolated and handled under usual conditions when sufficient stabilization is provided by suitable structural effects.[1] Recently, besides kinetic stabilization by using space-filling substituents, above all the introduction of ligands with additional donor groups, which permit an intramolecular interaction with the electrophilic silicon center, have contributed decisively to the fact that compounds of this class have been isolated and in some cases structurally characterized.[2] Herein we report on an intramolecularly donor-stabilized silaethene, 1-(8-dimethylamino-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**7**), whose remarkable thermal stability and considerably limited reactivity are attributed to the intramolecular interaction of the 8-dimethylamino group of the naphthyl substituents with the silene-silicon atom. A stable dibenzosilafulvene with an 8-dimethylaminomethyl-1-naphthyl group at the Si atom, which could possibly also be regarded as an intramolecularly donor-stabilized silene, was isolated by Chernyshev and coworkers;[3] however, there is no X-ray crystal structure analysis of this compound.

In the course of investigations into the synthesis of geminal bis(hypersilyl) compounds,[4] we had observed that dichloromethyltris(trimethylsilyl)silane (**1**) reacts with an excess of organolithium reagents RLi (R = Me, *n*Bu, Ph, Mes) to give silanes of the type $R_2(Me_3Si)Si{-}CH(SiMe_3)_2$ **8** (Scheme 1). In this process the transient silenes **4** and **6** occur as intermediates, which are trapped by the organolithium reagent present in the reaction mixture, and the reaction affords **8** as the end product after aqueous workup.[5] However, if, for the reaction with **1**, an organolithium reagent is chosen with a group R which when introduced at the silene-Si atom of **6** provides suffficent stabilization of the silaethene because of its steric demand or through an intramolecular donor–acceptor interaction, it possible to halt the reaction at this stage and to isolate the silene. This was achieved, for example, in the reaction of **1** with 8-dimethylamino-1-naphthyllithium in the molar ratio 1:2, which led to the isolation of **7**.



Scheme 1. Reaction of dichloromethyltris(trimethylsilyl)silane (**1**) with organolithium reagents and synthesis of **7**.

Our concept regarding the route to the formation of **7** is outlined in Scheme 1. Deprotonation of the dichlorosilane **1** by the organolithium reagent followed by elimination of lithium chloride from the carbenoid **2** resulted in the carbene **3**. In accordance with the known silylcarbene–silene rearrangement,[6] **3** isomerizes to give the transient silene **4**, which is trapped by excess organolithium reagent. Repeated elimination of LiCl from **5** and renewed 1,2-Si,C-trimethylsilyl migration afford **7**, which is isolated as a yellow crystalline compound in 79 % yield.

The structure formulated for **7** was confirmed by NMR and MS studies (see Experimental Section). The X-ray structure analysis (single crystals of **7** from pentane) gave the expected picture of an intramolecularly donor-stabilized silene with a four-coordinate silicon center (Figure 1).[7] The interaction of the dimethylamino group with the silene-Si atom is the reason for the high stability of **7**. This corresponds to our expectations, since Wiberg et al. have already shown in 1986 that silenes can be stabilized by adduct formation with donors such as amines, THF, or F^- ions.[8a]

The chelate-like coordination of the dimethylamino group with the silene-silicon atom (Si1−N1 distance 2.069(2) Å) leads to a pyramidalization at the Si1 atom (sum of angles 345.51°). In contrast, the configuration at the silene-carbon

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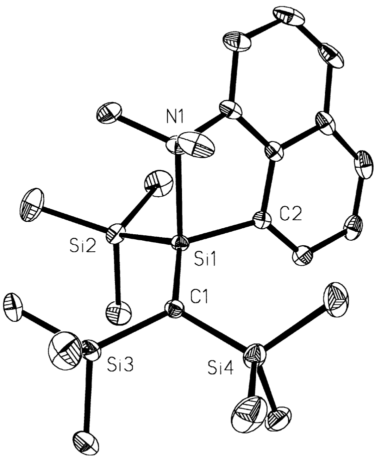
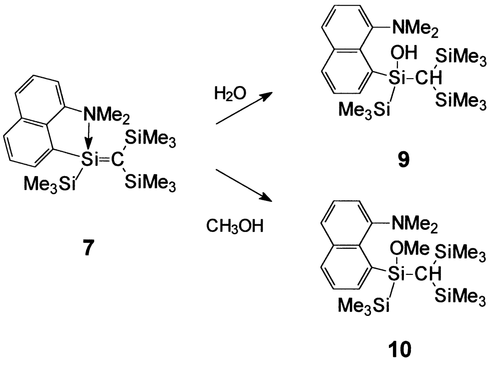


Figure 1. Structure of **7** in the crystal (hydrogen atoms omitted for clarity, thermal ellipsoids with 30 % probability). Selected bond lengths [Å] and angles [°]: C1-Si1 1.751(3), C1-Si3 1.830(3), C1-Si4 1.832(3), Si1-C2 1.889(3), Si1-Si2 2.3827(12), Si1-N1 2.069(2); Si1-C1-Si3 123.03(15), Si1-C1-Si4 120.17(15), Si3-C1-Si4 115.66(14), C1-Si1-C2 119.98(12), C1-Si1-Si2 125.63(10), C1-Si1-N1 113.93(11), C2-Si1-Si2 99.90(8), C2-Si1-N1 86.30(10), Si2-Si1-N1 103.28(7).

atom is almost trigonal-planar (sum of angles at C1 358.86°). The Si1−C1 bond length in **7** (1.751(3) Å) is in good agreement with the value reported by Wiberg et al. for the open-chain ethyldimethylamine adduct of the silene $Me_2Si{=}C(SiMe_2Ph)_2$ (1.761 Å).[8b] The Si=C distances in the stable silenes $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (1.764 Å; Ad = 1-adamantyl)[9] and $(Me_3Si)_2Si{=}Ad'$ (1.741 Å; Ad′ = 2-adamantylidene)[10] are similar to the value obtained for **7**. The Si=C distance in **7** is slightly longer than that reported for the uncomplexed stable silene $Me_2Si{=}C(SiMe_3)(SiMe\textit{t}Bu_2)$ (1.702 Å),[8c] which we regard as an indication of the ylide character of **7**.

The silene **7**, which is thermally stable up to about 140 °C, is converted with water to the silanol **9**, and methanol adds to the Si=C bond in **7** to give the methoxysilane **10** (Scheme 2). However, **7** behaves indifferently towards 2,3-dimethyl-1,3-butadiene, which reacts with reactive silenes by [2+4] cycloaddition.[1]



Scheme 2.

Experimental Section

7: Compound **1** (0.60 g, 1.8 mmol) was added at − 78 °C to a suspension of 8-dimethylamino-1-naphthyllithium diethyl ether complex (1.00 g, 3.9 mmol) in diethyl ether (30 mL). After the mixture had been allowed to warm slowly to room temperature and then left to stand for about 14 h, the LiCl precipitate was removed by filtration. The remaining yellow solution was concentrated and the 1-dimethylaminonaphthaline formed was removed by distillation at 100 °C/10^{-2} mbar. The residue was recrystallized from *n*-pentane. Yellow prisms, yield 0.61 g (79 %), m.p. 139 – 140 °C. ^1H NMR (250 MHz, [D_6]benzene): $\delta = -0.17$, 0.28 and 0.60 (3 s, $SiCH_3$, 3 × 9 H), 2.39 and 2.44 (2 s, NCH_3, 2 × 3 H), 6.55 – 7.83 (m, Ar-H, 6 H); ^{13}C NMR (75.5 MHz, [D_6]benzene): $\delta = 0.6$ ($SiSiCH_3$), 7.9 and 8.2 ($CSi\textit{C}H_3$), 22.4 (Si=C), 46.1 and 52.0 (NCH_3), 115.1, 125.6, 127.1, 127.6, 128.3, and 132.7 (arom. CH), 132.9, 133.3, 139.2, and 148.2 (arom. quat. C); ^{29}Si NMR (79.5 MHz, [D_6]benzene): $\delta = -18.2$ ($Si\textit{Si}Me_3$), − 8.0 and − 7.0 ($CSiMe_3$), 39.4 (Si=C); MS (70 eV): *m*/*z* (%): 429 (6) [M^+], 414 (10) [$M^+ - CH_3$], 356 (100) [$M^+ - SiMe_3$]; UV/Vis (*n*-heptane): $\lambda_{max}(\varepsilon) = 301$ nm (4400); elemental analysis (%): calcd for $C_{22}H_{39}NSi_4$ (429.91): C 61.47, H 9.14, N 3.26; found: C 60.81, H 8.93, N 3.43.

9: Colorless crystals from acetonitrile, m.p. 81 – 83 °C. IR (cap.): $\tilde{\nu} = 3300$ – 3450 cm^{-1} (br., O-$H_{ass.}$); ^1H NMR (250 MHz, [D_6]benzene): $\delta = -0.18$, 0.28 and 0.47 (3 s, $SiCH_3$, 3 × 9 H), the CH signal is covered by a Me_3Si signal (in [D_6]acetone: $\delta = 0.10$ (s, CH, 1 H)), 2.30 and 2.45 (2 s, NCH_3, 2 × 3 H), 6.95 – 7.64 (m, Ar-H, 6 H), 9.15 (br. s, OH, 1 H); ^{13}C NMR (75.5 MHz, [D_6]benzene): $\delta = 0.6$, 3.5, and 4.0 ($SiCH_3$), 8.1 (CH), 44.1 and 48.6 (NCH_3), 118.8, 124.6, 125.3, 128.1, 130.5, and 136.2 (arom. CH), 134.3, 136.6, 140.2, and 151.4 (arom. quat. C); ^{29}Si NMR (79.5 MHz, [D_6]benzene): $\delta = -19.7$ ($Si\textit{Si}Me_3$), − 0.1 ($CSiMe_3$), 1.1 (SiOH); MS (70 eV): *m*/*z* (%): 447 (7) [M^+], 432 (95) [$M^+ - CH_3$], 374 (100) [$M^+ - SiMe_3$], 288 (20) [$M^+ - CH(SiMe_3)_2$]; elemental analysis (%): calcd for $C_{22}H_{41}NOSi_4$ (447.96): C 58.99, H 9.23, N 3.13; found: C 59.13, H 9.13, N 3.11.

10: Colorless needles from methanol, m.p. 121 °C, yield 68 %. IR (KBr): $\tilde{\nu} = 1107$ cm^{-1} ($SiOCH_3$); ^1H NMR (250 MHz, [D_6]benzene): $\delta = -0.21$, 0.35, and 0.38 (3 s, $SiCH_3$, 3 × 9 H), 0.43 (s, CH, 1 H), 2.30 and 2.48 (2 s, NCH_3, 2 × 3 H), 3.46 (OCH_3), 6.90 – 8.00 (m, Ar-H, 6 H); ^{13}C NMR (75.5 MHz, [D_6]benzene): $\delta = 2.5$, 3.7, and 4.2 ($SiCH_3$), 6.4 (CH), 43.4 (OCH_3), 51.2 and 52.7 (NCH_3), 114.7, 125.3, 125.6, 129.4, 136.0, and 136.1 (arom. CH), 125.6, 134.4, 138.3, and 153.6 (arom. quat. C); ^{29}Si NMR (79.5 MHz, [D_6]benzene): $\delta = -17.5$ ($Si\textit{Si}Me_3$), 0.1 and 1.8 ($CSiMe_3$), 4.2 (SiOMe); MS (70 eV): *m*/*z* (%): 461 (0.5) [M^+], 446 (14) [$M^+ - CH_3$], 388 (100) [$M^+ - SiMe_3$]; elemental analysis (%): calcd for $C_{23}H_{43}NOSi_4$ (461.95): C 59.80, H 9.38, N 3.03; found: C 59.53, H 9.21, N 3.13.

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Crystallogr. Sect. A **1990**, *46*, 467), refinement with full-matrix least-squares methods against F^2 (SHELXL-93: G. M. Sheldrick, unpublished results), graphical representation of the structure: XP (Siemens), yellow prisms $0.4 \times 0.1 \times 0.1$ mm, space group $P2_1/c$, monoclinic, $a = 8.938(2)$, $b = 14.528(3)$, $c = 20.225(4)$ Å, $\beta = 99.28(3)°$, $V = 2591.9(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.102$ g cm^{-3}, 6363 measured, 3899 symmetry-independent reflections, of which 2531 observed ($I \leq 2\sigma(I)$), $R = 0.039$, wR^2 (all data) = 0.088, 244 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137407. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Linking Icosahedral, Strong Molecular Magnets $\{Mo^{VI}_{72}Fe^{III}_{30}\}$ to Layers—A Solid-State Reaction at Room Temperature**

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Dedicated to Professor Heinrich Vahrenkamp
on the occasion of his 60th birthday

The controlled generation of nanostructured materials and building units defines one of the contemporary challenges in chemistry. In this context, designed properties such as mesoporosity (in the form of well defined cavities or channels), electron and ion transport capabilities, and (high spin) nanomagnetism (including switching) are of particular interest[1]. Following the successful synthesis of nanostructured icosahedrally or spherically shaped clusters of the Keplerate type with, for example, the metal frame $\{(Mo)Mo_5\}_{12}Fe^{III}_{30}$ **1a**[2] of 30 high-spin, and in principle, switchable Fe^{III} centers, it is now possible to interconnect the strong molecular magnets of that type. The linking of the icosahedral entities, which is in itself an interesting crystallographic problem (see below), takes place in a solid-state reaction at room temperature.

The aforementioned clusters **1a** in the compound **1a** $\cdot \approx 150\,H_2O$ comprise Fe centers, with H_2O ligands which become linked according to the inorganic-condensation reactions known for the formation of polycations with a low activation energies[3] (Scheme 1). The corresponding reaction product **2** results from several subsequent reaction steps. Product **2**,

$$\cdots Fe(OH_2) + (H_2O)Fe\cdots \xrightarrow{-H^+}$$

$$\cdots Fe(OH_2) + (HO)Fe\cdots \xrightarrow{-H_2O/-H^+} \cdots Fe\text{-}O\text{-}Fe\cdots$$

Scheme 1.

with a layer structure, was characterized by elemental analysis, thermogravimetry (to determine the number of crystallized water molecules), bond valence sum (BVS) calculations,[4] spectroscopy (IR, Raman, UV/Vis, and ^{57}Fe Mössbauer), magnetochemical measurements, and single-crystal X-ray structure analysis.[5]

$$[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}] \cdot \approx 150\,H_2O \qquad \mathbf{1}^{[2]}$$

$$[H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{87}] \cdot \approx 80\,H_2O \qquad \mathbf{2}^{[5]}$$

Compound **2** crystallizes in the space group *Cm*ca. In this structure, every cluster unit of the **1a** type is covalently linked to four other units through Fe-O-Fe bridges (Fe-Fe = 3.79(4) Å) and thereby forms a two-dimensional layer structure (Figure 1). The geometrical parameters of each single cluster building unit in **2** are, as expected, equal to the corresponding values found in the discrete cluster **1a**.[2,5]. A

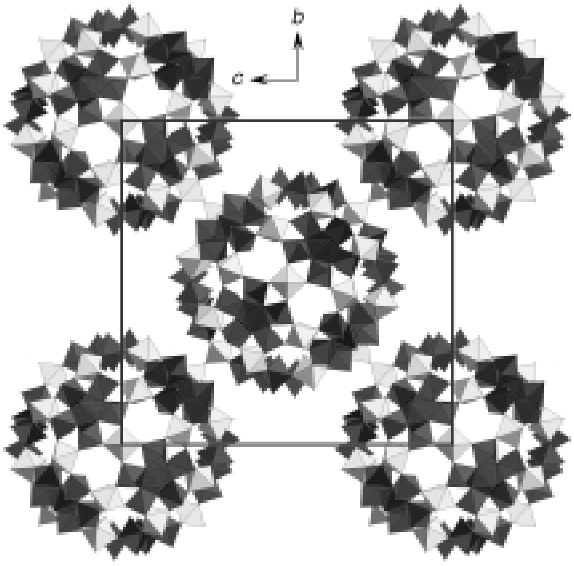

Figure 1. Structure of one layer of **2** as a polyhedral representation.

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