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Donor-Stabilized Silylenes with Guanidinato Ligands

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Dedicated to Professor Bernt Krebs on the occasion of his 75th birthday

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The first donor-stabilized silylenes with guanidinato ligands, compounds **4** and **6**, were synthesized and structurally characterized in the solid state and in solution. As demonstrated by single-crystal X-ray diffraction studies, compound **4** contains a bidentate and a monodentate guanidinato ligand of

the type $[iPrNC(NiPr_2)NiPr]^-$, and compound **6** contains the bidentate guanidinato ligand $[ArNC(NMe_2)NAr]^-$ (Ar = 2,6-diisopropylphenyl) and the monodentate amido ligand $[(Me_3Si)_2N]^-$. Both silicon(II) complexes exist also in solution.

Introduction

The chemistry of stable silvlenes is currently one of the most actively studied fields in silicon chemistry.^[1] In this context, donor-stabilized silicon(II) complexes with amidinato ligands, such as compounds 1 and 2, play an emerging role.^[2] We have now succeeded in synthesizing the first donor-stabilized silylenes that contain guanidinato ligands, compounds 4 and 6 (Scheme 1). Germylenes, stannylenes, and plumbylenes with guanidinato ligands have already been synthesized, starting from suitable germanium(II), tin(II), or lead(II) precursors.^[3,4] However, to the best of our knowledge, related guanidinatosilicon(II) complexes have not yet been described in the literature. This is probably due to the lack of suitable analogous silicon(II) precursors. To overcome this problem, we used a totally different strategy for the preparation of 4 and 6, a reductive HCl elimination of six- and five-coordinate silicon(IV) complexes 3 and 5, respectively (Scheme 1). This strategy has also been successfully used for the synthesis of the amidinatosilicon(II) complexes 1 and 2.^[2a,2g] As amidinato and



[a] Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany E-mail: r.tacke@uni-wuerzburg.de http://www-anorganik.chemie.uni-wuerzburg.de/ guanidinato ligands differ in their electronic properties, the title compounds 4 and 6 were very attractive targets to be synthesized and to be studied for their reactivity, especially in comparison with related silylenes that contain amidinato ligands.

Results and Discussion

Compounds 4 and 6 were synthesized according to Scheme 1. Treatment of the lithium guanidinate Li[*i*PrNC-(N*i*Pr₂)N*i*Pr] with trichlorosilane (molar ratio 2:1) in tetrahydrofuran afforded the six-coordinate silicon(IV) complex 3 (94% yield), which, upon reaction with potassium bis(trimethylsilyl)amide (molar ratio 1:1) in toluene, gave 4 (95% yield, after crystallization from *n*-hexane). Treatment of the lithium guanidinate Li[ArNC(NMe₂)NAr] (Ar = 2,6-diisopropylphenyl) with one molar equivalent of trichlorosilane in tetrahydrofuran afforded the five-coordinate silicon(IV) complex 5 (81% yield, after crystallization from acetonitrile), which, upon reaction with two molar equivalents of potassium bis(trimethylsilyl)amide, afforded 6 (75% yield, after crystallization from *n*-hexane).

The identities of 3-6 were established by elemental analysis, NMR spectroscopic studies in the solid state and in solution,^[5] and crystal structure analysis.^[6] The molecular structures of 3-6 are depicted in Figures 1–4.

The silicon coordination polyhedron of **3** (Figure 1) is a strongly distorted octahedron, with the chlorido and hydrido ligand in *cis* positions. The distortion mainly results from the two highly strained four-membered SiN_2C chelate rings formed by the silicon coordination center and the bidentate guanidinato ligands, with N–Si–N angles ranging from 68.40(6) to 68.70(6)°.





Scheme 1. Syntheses of compounds 3-6.



Figure 1. Molecular structure of **3** in the crystal (ellipsoids set at 50% probability; hydrogen atoms apart from H1 omitted for clarity).^[7] Selected bond lengths [Å] and angles [°]: Si–Cl 2.2742(8), Si–N1 1.9305(16), Si–N2 1.8920(15), Si–N4 1.9304(15), Si–N5 1.8797(14), N1–Cl 1.326(2), N2–Cl 1.347(2), N3–Cl 1.390(2), N4–Cl4 1.323(2), N5–Cl4 1.344(2), N6–Cl4 1.386(2); Cl–Si–N1 164.74(5), Cl–Si–N2 96.07(5), Cl–Si–N4 86.08(5), Cl–Si–N5 95.39(5), N1–Si–N2 68.70(6), N1–Si–N4 94.96(7), N1–Si–N5 99.14(6), N2–Si–N4 98.15(7), N2–Si–N5 161.65(7), N4–Si–N5 68.40(6), Si–N1–Cl 91.16(11), Si–N2–Cl 92.19(10), Si–N4–Cl4 91.29(11), Si–N5–Cl4 92.87(10), N1–Cl–N2 107.59(14), N1–Cl–N3 126.80(16), N2–Cl–N3 125.61(15), N4–Cl4–N5 106.87(14), N4–Cl4–N6 128.18(16), N5–Cl4–N6 124.94(15).

The silicon coordination polyhedron of **4** (Figure 2) is best described as a distorted pseudo-tetrahedron, with the lone pair as the fourth ligand. The three N–Si–N angles amount to 68.37(7), 102.98(8), and $104.71(8)^\circ$. The Si–N distance of the monodentate ligand [1.7633(18) Å] is significantly shorter than those of the bidentate ligand [1.9220(17) and 1.8901(18) Å], clearly reflecting the different coordination modes of the two guanidinato ligands. Furthermore, the significant difference between the two N–C distances in the monodentate ligand [1.433(3) vs. 1.284(3) Å] indicates the higher degree of localization of the N=C double bond compared to the bidentate ligand [1.334(3) vs. 1.344(2) Å]. Generally, the structural features of **4** are very similar to those of compound **2**.



Figure 2. Molecular structure of **4** in the crystal (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–N1 1.9220(17), Si–N2 1.8901(18), Si–N4 1.7633(18), N1–C1 1.334(3), N2–C1 1.344(2), N3–C1 1.402(3), N4–C14 1.433(3), N5–C14 1.284(3), N6–C14 1.400(3); N1–Si–N2 68.37(7), N1–Si–N4 104.71(8), N2–Si–N4 102.98(8), Si–N1–C1 91.05(12), Si–N2–C1 92.14(13), Si–N4–C14 117.77(12), N1–C1–N2 106.23(17), N1–C1–N3 125.28(17), N2–C1–N3 128.32(19), N4–C14–N5 125.40(19), N4–C14–N6 115.58(16), N5–C14–N6 118.99(18).

The silicon coordination polyhedron of **5** (Figure 3) is a strongly distorted trigonal bipyramid, with the chlorine atom Cl1 and the nitrogen atom N2 at the axial positions. The Berry distortion (transition from trigonal bipyramid to square pyramid) amounts to 33.4%.^[8]



Figure 3. Molecular structure of **5** in the crystal (ellipsoids set at 50% probability; hydrogen atoms apart from H1 omitted for clarity). Selected bond lengths [Å] and angles [°]: Si–Cl1 2.1590(8), Si– Cl2 2.0821(7), Si–N1 1.8006(15), Si–N2 1.9113(15), Si–H1 1.382(19), N1–Cl 1.369(2), N2–Cl 1.335(2), N3–Cl 1.330(2); Cl1– Si–Cl2 93.47(3), Cl1–Si–N1 93.31(5), Cl1–Si–N2 162.71(5), Cl1–Si– H1 95.7(8), Cl2–Si–N1 128.93(5), Cl2–Si–N2 93.26(5), Cl2–Si–H1 110.8(8), N1–Si–N2 70.16(6), N1–Si–H1 118.8(8), N2–Si–H1 96.8(8), Si–N1–Cl 94.44(11), Si–N2–Cl 90.71(10), N1–C1–N2 104.33(15), N1–C1–N3 127.69(16), N2–C1–N3 127.94(15).

The silicon coordination polyhedron of **6** (Figure 4) is best described as a distorted pseudo-tetrahedron, with the lone pair as the fourth ligand. The three N–Si–N bond angles [67.83(6), 108.72(6), and 113.09(6)°] are similar to those observed for **4**. Also, the Si–N distance of the monodentate ligand [1.7745(14) Å] is significantly shorter than



those of the bidentate ligand [1.9433(14) and 1.9384(15) Å]. The latter two distances are somewhat longer than the analogous Si–N distances of **4** [1.9220(17) and 1.8901(18) Å], probably because of the steric demand of the two bulky aryl groups.



Figure 4. Molecular structure of **6** in the crystal (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1–N1 1.9433(14), Si1–N2 1.9384(15), Si1–N4 1.7745(14), Si2–N4 1.7522(15), Si3–N4 1.7538(14), N1–C1 1.350(2), N2–C1 1.342(2), N3–C1 1.361(2); N1–Si1–N2 67.83(6), N1–Si1–N4 113.09(6), N2–Si–N4 108.72(6), Si1–N1–C1 89.99(10), Si1–N2–C1 90.44(10), Si1–N4–Si2 112.61(7), Si1–N4–Si3 127.44(9), Si2–N4–Si3 119.31(8), N1–C1–N2 107.18(14), N1–C1–N3 126.40(15), N2–C1–N3 126.18(15).

Compounds 3-6 were studied by NMR spectroscopy in the solid state (¹⁵N, ²⁹Si) and in solution (¹H, ¹³C, ²⁹Si). The isotropic 29 Si chemical shifts of **3–6** in the solid state and in solution (Table 1) are similar ($\Delta \delta^{29}$ Si = 0.3–8.1 ppm), indicating that these compounds also exist in solution. The isotropic chemical shifts of guanidinatosilicon(II) complex 4 [solid state: $\delta = -20.6$ ppm; solution (C₆D₆): $\delta =$ -25.6 ppm] and the related amidinatosilicon(II) complex 2 [solid state: $\delta = -15.4$ ppm; solution (C₆D₆): $\delta =$ -31.4 ppm]^[2g] differ significantly. The same holds true for the difference in chemical shift between the solid state and solution (2, $\Delta \delta^{29}$ Si = 16.0 ppm; 4, $\Delta \delta^{29}$ Si = 5.0 ppm), which is much more pronounced for 2. In the case of 2, this difference in shift has been interpreted in terms of a rapid exchange of the four nitrogen sites, possibly involving a fourcoordinate silicon(II) species with two bidentate amidinato ligands. An analogous process can also be assumed for 4; however, the four-coordinate species does not seem to play as important a role as in the case of 2. The dynamic behavior of **4** in solution is strongly supported by the ¹H and ¹³C NMR spectra at room temperature, which show very broad resonance signals but well-resolved peaks at -70 °C. The ¹H and ¹³C NMR spectra of 6 at room temperature do not indicate a dynamic behavior. The difference in chemical shift observed in the solid-state and solution ²⁹Si NMR spectra of 6 ($\Delta \delta^{29}$ Si = 8.1 ppm) is not fully understood. The same holds true for the significantly different isotropic ²⁹Si chemical shifts of the two guanidinatosilicon(II) species 4 and 6, both of which contain an SiN_3 skeleton. Nevertheless, the different ²⁹Si NMR spectroscopic data of the donor-stabilized silylenes 2, 4, and 6 reflect different electronic properties at the silicon atom, which are expected to affect the reactivity profiles of these silicon(II) species. We have started a program to investigate the reactivities of 2, 4, and 6 systematically.

Table 1. Isotropic ²⁹Si chemical shifts [ppm] of the silicon coordination centers of **3–6** in the solid state (T = 22 °C) and in solution (C₆D₆, T = 23 °C).

Compound	δ^{29} Si (solid state)	δ^{29} Si (solution)	$ \Delta \delta $	Skeleton
3	-186.2	-186.5	0.3	SiN ₄ ClH
4	-20.6	-25.6	5.0	SiN_3
5	-99.6	-96.2	3.4	SiN_2Cl_2H
6	6.8	14.9	8.1	SiN_3

Experimental Section

The syntheses were carried out under a dry argon atmosphere in oven-dried glassware by using standard Schlenk techniques. The solvents were dried, purified, and deoxygenated according to standard procedures.

Compound 3: Trichlorosilane (26.9 g, 199 mmol) was added in a single portion at -20 °C to a stirred solution of Li[iPrNC(NiPr2)-NiPr]-THF^[9] (121.3 g, 397 mmol) in tetrahydrofuran (1.5 L), and the stirred reaction mixture was then warmed to 20 °C over 16 h. The solvent was removed in vacuo, dichloromethane (500 mL) was added to the residue, and the remaining solid was filtered off and discarded. The solvent of the filtrate was removed in vacuo, followed by the addition of tetrahydrofuran (100 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -30 °C and kept undisturbed at this temperature for 1 d. The resulting colorless crystalline solid was isolated by filtration, washed with cold (-30 °C) *n*-pentane (2× 200 mL), and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 96.5 g (187 mmol, 94%). ¹H NMR (C₆D₆, 23 °C): δ = 1.10 (d, ³J_{H,H} = 6.9 Hz, 12 H, CH₃), 1.14 (d, ${}^{3}J_{H,H}$ = 6.9 Hz, 12 H, CH₃), 1.24 (d, ${}^{3}J_{\rm H,H} = 6.7$ Hz, 6 H, CH₃), 1.50 (d, ${}^{3}J_{\rm H,H} = 6.7$ Hz, 6 H, CH₃), 1.63 (d, ${}^{3}J_{H,H}$ = 6.7 Hz, 6 H, CH₃), 1.89 (d, ${}^{3}J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 3.50 (sept., ${}^{3}J_{H,H} = 6.9$ Hz, 4 H, CH_3CHCH_3), 3.74 (sept., ${}^{3}J_{H,H} = 6.7 \text{ Hz}, 2 \text{ H}, \text{ CH}_{3}\text{CHCH}_{3}$), 3.82 (sept., ${}^{3}J_{H,H} = 6.7 \text{ Hz}, 2$ H, CH₃CHCH₃), 5.57 (s, 1 H, SiH; ²⁹Si satellites, ${}^{1}J_{H,Si} = 296$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 23 °C): δ = 22.8 (2 C), 22.9 (4 C), 23.70 (2 C), 23.72 (2 C), 24.8 (2 C), 25.0 (4 C) (CH₃), 45.4 (2 C), 47.2 (2 C), 50.1 (4 C) (CH₃CHCH₃), 166.8 (2 C, N₃C) ppm. ²⁹Si{¹H} NMR (C₆D₆, 23 °C): δ = -186.5 ppm. ¹⁵N VACP/MAS NMR: $\delta = -235.0, -233.3, -230.3, -229.2, -213.2, -206.1$ ppm. ²⁹Si VACP/MAS NMR: $\delta = -186.2$ ppm. C₂₆H₅₇ClN₆Si (517.32): calcd. C 60.37, H 11.11, N 16.25; found C 60.1, H 11.0, N 16.1.

Compound 4: Toluene (20 mL) was added at 20 °C in a single portion to a mixture of **3** (5.00 g, 9.67 mmol) and potassium bis(trimethylsilyl)amide (2.21 g, 11.1 mmol), and the reaction mixture was stirred at this temperature for 3 h. The resulting precipitate was filtered off and discarded, and the solvent of the filtrate was removed in vacuo, followed by the addition of *n*-hexane (5 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -30 °C and kept undisturbed at this temperature for 2 d. The resulting colorless crystalline solid was isolated by filtration and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 4.40 g (9.15 mmol, 95%). ¹H NMR ([D₈]toluene, -70 °C): $\delta = 0.72$ (d, ${}^{3}J_{H,H} = 6.1$ Hz, 3 H, CH₃), 0.75 (d, ${}^{3}J_{H,H} =$



6.1 Hz, 3 H, CH₃), 0.80 (d, ${}^{3}J_{H,H}$ = 6.3 Hz, 3 H, CH₃), 0.88 (d, ${}^{3}J_{H,H} = 6.3 \text{ Hz}, 3 \text{ H}, \text{ }CH_{3}), 1.15 \text{ (d, }{}^{3}J_{H,H} = 6.4 \text{ Hz}, 3 \text{ H}, \text{ }CH_{3}),$ 1.16 (d, ${}^{3}J_{H,H}$ = 6.6 Hz, 6 H, CH₃), 1.22 (d, ${}^{3}J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.30 (d, ${}^{3}J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 1.34 (d, ${}^{3}J_{H,H}$ = 6.4 Hz, 6 H, CH₃), 1.38 (d, ${}^{3}J_{H,H}$ = 6.7 Hz, 3 H, CH₃), 1.52 (d, ${}^{3}J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 1.71 (d, ${}^{3}J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.75 (d, ${}^{3}J_{\text{H,H}} = 6.0 \text{ Hz}, 3 \text{ H}, \text{ C}H_{3}$), 1.96 (d, ${}^{3}J_{\text{H,H}} = 6.6 \text{ Hz}, 3 \text{ H}, \text{ C}H_{3}$), 2.88 (sept., ${}^{3}J_{H,H} = 6.1$ Hz, 1 H, CH₃CHCH₃), 2.93 (sept., ${}^{3}J_{H,H} =$ 6.3 Hz, 1 H, CH₃CHCH₃), 3.40 (sept., ${}^{3}J_{H,H} = 6.6$ Hz, 1 H, CH₃CHCH₃), 3.47 (sept., ${}^{3}J_{H,H} = 6.7$ Hz, 1 H, CH₃CHCH₃), 3.64 (sept., ${}^{3}J_{H,H} = 6.4 \text{ Hz}, 2 \text{ H}, \text{ CH}_{3}\text{CHCH}_{3}$), 4.20 (sept., ${}^{3}J_{H,H} =$ 6.0 Hz, 1 H, CH₃CHCH₃), 4.57 (sept., ${}^{3}J_{H,H} = 6.6$ Hz, 1 H, CH₃CHCH₃) ppm. ¹³C{¹H} NMR ([D₈]toluene, -70 °C): $\delta = 21.5$, 21.6, 22.2, 22.3, 22.4, 23.0, 23.1, 23.6, 23.9, 24.7, 25.5, 25.6, 25.8, 26.3, 27.8, 28.0 (CH₃), 45.6, 45.7, 46.0, 47.5, 48.1, 48.2, 49.3, 49.4 (CH₃CHCH₃), 150.9, 155.5 (N₃C) ppm. ²⁹Si{¹H} NMR ([D₈]toluene, -70 °C): δ = -26.0 ppm. ²⁹Si{¹H} NMR (C₆D₆, 23 °C): δ = -25.6 ppm. ¹⁵N VACP/MAS NMR: $\delta = -308.3, -279.6, -269.6,$ -208.7, -204.6, -117.1 ppm. ²⁹Si VACP/MAS NMR: δ = -20.6 ppm. C₂₆H₅₆N₆Si (480.86): calcd. C 64.94, H 11.74, N 17.48; found C 64.9, H 11.6, N 17.3.

Compound 5: A solution of lithium dimethylamide (1.89 g, 37.0 mmol) in tetrahydrofuran (60 mL) was added within 10 min at -78 °C to a stirred solution of bis(2,6-diisopropylphenyl)carbodiimide (13.4 g, 37.0 mmol) in tetrahydrofuran (250 mL), and the stirred reaction mixture was warmed to 20 °C over 2 h. The solution was cooled to -78 °C, and trichlorosilane (5.01 g, 37.0 mmol) was added in a single portion. The stirred reaction mixture was then warmed to 20 °C over 16 h. The solvent was removed in vacuo, dichloromethane (150 mL) was added to the residue, and the remaining solid was filtered off and discarded. The solvent of the filtrate was removed in vacuo, followed by the addition of acetonitrile (500 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -30 °C and kept undisturbed at this temperature for 1 d. The resulting colorless crystalline solid was isolated by filtration, washed with cold (-30 °C) *n*-pentane (2×100 mL), and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 15.1 g (29.8 mmol, 81%). ¹H NMR $(CD_2Cl_2, 23 \text{ °C}): \delta = 1.24 \text{ (d, } {}^3J_{H,H} = 6.9 \text{ Hz}, 12 \text{ H}, CH_3), 1.31 \text{ (d,}$ ${}^{3}J_{H,H} = 6.9 \text{ Hz}, 12 \text{ H}, CH_{3}), 2.41 \text{ [s, 6 H, N(CH_{3})_{2}]}, 3.35 \text{ (sept.,}$ ${}^{3}J_{H,H} = 6.9 \text{ Hz}, 4 \text{ H}, \text{CH}_{3}\text{CHCH}_{3}$), 6.16 (s, 1 H, Si*H*; ²⁹Si satellites, ${}^{1}J_{H,Si} = 352 \text{ Hz}$, 7.18–7.21 (m, 4 H, *m*-C₆*H*₃), 7.27–7.32 (m, 2 H, *p*-C₆*H*₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 23 °C): δ = 23.5 (4 C) (CH₃CHCH₃), 25.1 (4 C), 29.0 (4 C) (CH₃), 39.7 [2 C, N(CH₃)₂], 124.4 (4 C, $o\text{-}C_6\mathrm{H}_3),$ 127.9 (2 C, $i\text{-}C_6\mathrm{H}_3),$ 134.8 (2 C, $p\text{-}C_6\mathrm{H}_3),$ 146.6 (4 C, *m*-C₆H₃), 160.7 (N₃C) ppm. ²⁹Si{¹H} NMR (CD₂Cl₂, 23 °C): $\delta = -97.7$ ppm. ²⁹Si{¹H} NMR (C₆D₆, 23 °C): $\delta = -96.2$ ppm. ¹⁵N VACP/MAS NMR: δ = -304.3, -250.1, -238.0 ppm. ²⁹Si VACP/ MAS NMR: $\delta = -99.6$ ppm. $C_{27}H_{41}Cl_2N_3Si$ (506.63): calcd. C 64.01, H 8.16, N 8.29; found C 64.0, H 8.2, N 8.3.

Compound 6: Toluene (200 mL) was added at 20 °C in a single portion to a mixture of **5** (11.8 g, 23.3 mmol) and potassium bis(trime-thylsilyl)amide (8.82 g, 44.2 mmol), and the reaction mixture was stirred at this temperature for 18 h. The resulting precipitate was filtered off and discarded, and the solvent of the filtrate was removed in vacuo, followed by the addition of toluene (15 mL). The resulting suspension was heated until a clear solution was obtained, which was then cooled slowly to -30 °C and kept undisturbed at this temperature for 2 d. The resulting colorless crystalline solid was isolated by filtration and dried in vacuo (20 °C, 6 h, 0.01 mbar). Yield: 10.4 g (17.5 mmol, 75%). ¹H NMR (C₆D₆, 23 °C): $\delta = 0.31$ [s, 18 H, Si(CH₃)₃], 1.19 (d, ³J_{H,H} = 6.7 Hz, 6 H, CH₃), 1.21 (d, ³J_{H,H} = 6.7 Hz, 6 H, CH₃), 1.33 (d, ³J_{H,H} = 6.7 Hz,

6 H, CH₃), 1.47 (d, ${}^{3}J_{H,H} = 6.7$ Hz, 6 H, CH₃), 2.01 [s, 6 H, N(CH₃)₂], 3.78 (sept., ${}^{3}J_{H,H} = 6.7$ Hz, 2 H, CH₃CHCH₃), 3.98 (sept., ${}^{3}J_{H,H} = 6.7$ Hz, 2 H, CH₃CHCH₃), 7.05–7.14 (m, 6 H, C₆H₃) ppm. ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): $\delta = 5.9$ [Si(CH₃)₃], 23.7 (2 C), 23.8 (2 C) (CH₃CHCH₃), 25.9 (2 C), 27.1 (2 C), 28.3 (2 C), 29.2 (2 C) (CH₃), 38.6 [2 C, N(CH₃)₂], 124.0 (2 C), 124.4 (2 C, *o*-C₆H₃), 126.3 (2 C, *i*-C₆H₃), 138.5 (2 C, *p*-C₆H₃), 145.0 (2 C), 145.0 (2 C) (*m*-C₆H₃), 152.3 (N₃C) ppm. ${}^{29}Si{}^{1}H{}$ NMR (C₆D₆): $\delta = -0.3$ [Si(CH₃)₃], 14.9 (SiN₃) ppm. ${}^{15}N$ VACP/MAS NMR: $\delta = -321.1$, -289.8, -232.5, -229.6 ppm. ${}^{29}Si{}_{3}N_{4}Si_{3}$ (595.11): calcd. C 66.60, H 9.82, N 9.41; found C 66.4, H 9.8, N 9.4.

Acknowledgments

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S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* 2012, 3, 659–682; f)
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7.28 ppm, C_6D_6), CHDCl₂ (¹H, $\delta = 5.32$ ppm, CD₂Cl₂), [D₇]toluene (¹H, δ = 2.09 ppm, [D₈]toluene), C₆D₆ (¹³C, δ = 128.0 ppm, C₆D₆), CD₂Cl₂ (¹³C, δ = 53.8 ppm, CD₂Cl₂), [D₈]toluene (¹³C, $\delta = 20.4$ ppm, [D₈]toluene), or external TMS (²⁹Si, $\delta = 0$ ppm; C₆D₆, CD₂Cl₂, [D₈]toluene). Assignment of the ¹H and ¹³C NMR spectroscopic data was supported by ¹H,¹H and ¹H,¹³C correlation experiments and DEPT 135 experiments. Compound 4 was additionally studied by VT NMR spectroscopic experiments. The thermocouple used with the probe for these studies was calibrated for lower temperatures according to ref.^[10] by using a 4% solution of MeOH in [D₄]MeOH containing a trace of HCl. Solid-state ¹⁵N and ²⁹Si VACP/MAS NMR spectra were recorded at 22 °C with a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO₂ (diameter: 7 mm) containing ca. 200 mg of sample [¹⁵N, 40.6 MHz; ²⁹Si, 79.5 MHz; external standard: TMS (¹³C, ²⁹Si, $\delta = 0$ ppm) or glycine (¹⁵N, $\delta = -342.0$ ppm); spinning rate: 7 kHz; contact time: 3 ms (¹⁵N) or 5 ms (²⁹Si); 90° ¹H transmitter pulse length: 3.6 µs; repetition time: 7 s].

Crystal structure analyses of 3-6: Suitable single crystals were [6] mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (3, Bruker X8-APEX II, graphite-monochromated Mo- K_{α} radiation, $\lambda = 0.71073$ Å; 4–6, Stoe IPDS, graphite-monochromated Mo- K_{α} radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97).^[11] SHELXLE was used as refinement GUI.^[12] For the CH hydrogen atoms, a riding model was employed. CCDC-955561, -955562, -955563, and -955564 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. Selected data for 3: single crystal of dimensions $0.97 \times 0.76 \times 0.25$ mm obtained by crystallization from THF at -30 °C, C₂₆H₅₇ClN₆Si, $M_r = 517.32$, analysis at 100(2) K, monoclinic, space group $P2_1/n$ (no. 14), a =14.128(3) Å, b = 13.784(5) Å, c = 16.312(3) Å, $\beta = 102.15(2)^{\circ}$, $V = 3105.4(14) \text{ Å}^3$, Z = 4, $\rho_{\text{calcd.}} = 1.106 \text{ g cm}^{-3}$, $\mu = 0.186 \text{ mm}^{-1}$, F(000) = 1144, $2\theta_{\text{max}} = 52.04^{\circ}$, 19052 collected reflections, 6018 unique reflections ($R_{int} = 0.0296$), 326 parameters, S = 1.062, $R_1 = 0.0428$ [I>2 σ (I)], w R_2 (all data) = 0.0951, max./min. residual electron density = +0.511/ $-0.402 \text{ e}^{\text{A}-3}$. Selected data for 4: single crystal of dimensions

 $0.6 \times 0.45 \times 0.25$ mm obtained by crystallization from Et₂O at -20 °C, C₂₆H₅₆N₆Si, $M_r = 480.86$, analysis at 173(2) K, monoclinic, space group $P2_1/n$ (no. 14), a = 12.261(2) Å, b =14.798(3) Å, c = 17.362(3) Å, $\beta = 99.56(2)^\circ$, V = 3106.4(9) Å³, Z = 4, $\rho_{\text{calcd.}} = 1.028 \text{ g cm}^{-3}$, $\mu = 0.098 \text{ mm}^{-1}$, F(000) = 1072, $2\theta_{\text{max}} = 52.04^{\circ}$, 28743 collected reflections, 5813 unique reflections ($R_{int} = 0.0786$), 314 parameters, S = 1.121, $R_1 = 0.0588$ $[I > 2\sigma(I)]$, wR_2 (all data) = 0.1547, max./min. residual electron density = +0.821/-0.323 eÅ⁻³. Selected data for 5: single crystal of dimensions $0.5 \times 0.4 \times 0.1$ mm obtained by crystallization from acetonitrile at -20 °C, $C_{27}H_{41}Cl_2N_3Si$, $M_r = 506.62$, analysis at 173(2) K, monoclinic, space group $P2_1/n$ (no. 14), a = 10.0989(18) Å, b = 15.9344(19) Å, c = 18.029(4) Å, β = 90.70(2)°, $V = 2901.0(9) \text{ Å}^3$, Z = 4, $\rho_{\text{calcd.}} = 1.160 \text{ g cm}^{-3}$, $\mu =$ 0.284 mm^{-1} , F(000) = 1088, $2\theta_{\text{max}} = 52.74^{\circ}$, 22447 collected reflections, 5816 unique reflections ($R_{int} = 0.0551$), 312 parameters, S = 0.952, $R_1 = 0.0374$ [I>2 σ (I)], w R_2 (all data) = 0.0974, max./min. residual electron density = +0.292/-0.291 eÅ⁻³. Selected data for 6: single crystal of dimensions $0.55 \times 0.35 \times 0.35$ mm obtained by crystallization from toluene at -20 °C, C₃₃H₅₈N₄Si₃, $M_r = 595.10$, analysis at 173(2) K, orthorhombic, space group *Pbca* (no. 61), a = 17.5441(19) Å, b = 18.4142(18) Å, c = 22.757(3) Å, V = 7351.9(15) Å³, Z = 8, $\rho_{\text{calcd.}} = 1.075 \text{ g cm}^{-3}, \mu = 0.155 \text{ mm}^{-1}, F(000) = 2608, 2\theta_{\text{max}} =$ 52.04°, 38082 collected reflections, 7204 unique reflections (R_{int} = 0.0508), 377 parameters, S = 0.982, $R_1 = 0.0401$ [I>2 σ (I)], wR_2 (all data) = 0.1084, max./min. residual electron density = +0.271/-0.248 eÅ⁻³.

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