Supporting information (experimental details and computational studies) belonging to the publication

A Monolithiated and Its Related 1,3-Dilithiated Allylsilane: Syntheses, Crystal Structures and Reactivity

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1. General considerations

All manipulations were conducted under an atmosphere of dry argon using standard Schlenk techniques. Solvents were purified by distillation from sodium/benzophenone (pentane, toluene, THF) and stored under an atmosphere of argon. NMR spectra were recorded with a Bruker AMX 400 or Bruker AMX 500 spectrometer, chemical shifts are referenced to TMS with the deuterium signal of the solvent serving as internal lock and the residual solvent signals as additional reference. A Trio-1000 (Fisons Instrument) with a Zebron column (Phenomenex) was used for GC-MS analysis. Temperature program for GC-MS: 80°C (2 min) – 280°C (10 min) with 20°C/min. Microanalyses were performed by the analytical laboratory of the Institut für Anorganische Chemie using a Leco CHNS-932 instrument for trapping products with a reaction selectivity >95%. The carbon values determined for the trapping product *E*-$Me_2Si(CH_2NC_5H_{10})(CH{=}CHCH_2SiMe_3)$ were usually too low (~1.5%) due to silicon carbide formation.

2. Syntheses

$[Me_2Si(CH_2NC_5H_{10})(C_3H_5Li)]$ (2):

A solution of $[Me_2Si(CH_2NC_5H_{10})(CH_2CH{=}CH_2)]$ (**1**) (200 mg, 1.01 mmol) in *n*-pentane (3 mL) was cooled to –90 °C. The reaction mixture was treated with *t*-BuLi [solution in pentane, c = 1.5 $mol{\cdot}L^{-1}$] (700 µL, 1.05 mmol), the temperature was kept at –90 °C for 1 h and was stored afterwards at 20 °C. After 6 – 24 h, colorless block-shape crystals of **2** were obtained, which were seperated, washed with *n*-pentane (2 x 2 mL) and dried under vacuum. Yield 170 mg (0.82 mmol, 82%).

$[Me_2Si(CH_2NC_5H_{10})(C_3H_4Li_2)]$ (3):

A solution of $[Me_2Si(CH_2NC_5H_{10})(CH_2CH{=}CH_2)]$ (**1**) (300 mg, 1.52 mmol) in *n*-pentane (4 mL) was cooled to –90 °C. The reaction mixture was treated with *t*-BuLi [solution in *n*-pentane, c = 1.5 $mol{\cdot}L^{-1}$] (2.3 mL, 3.45 mmol), the temperature was kept at –90 °C for 1 h and was stored afterwards at 20 °C. After 48 – 72 h, colorless needles of **3** were obtained, which were seperated, washed with *n*-pentane (2 x 2 mL) and dried under vacuum. Yield 300 mg (1.45 mmol, 95%).

Trapping reactions of $[Me_2Si(CH_2NC_5H_{10})(C_3H_5Li)]$ (2), general procedure:

The lithiated allylsilane **2** was dissolved in THF or toluene (2 mL) and cooled to –90 °C. A solution of 1 eq of the electrophile (MeI, Me_3SiCl or Me_3SnCl) in THF or toluene (2 ml) was cooled to –90 °C and added dropwise. The reaction mixture was stirred at –90 °C for 1 h, followed by 2 h stirring at 20 °C. All volatile compounds were removed under vacuum, the residue was taken up in *n*-pentane (3 mL), filtered and washed with *n*-pentane (2 mL). The solvent was removed under vacuum, leaving behind colorless or slighly yellow oils, yields of the isomeric mixtures typically between 75% – 90%.

MeI trapping products:

[$Me_2Si(CH_2NC_5H_{10})(CHMeCH{=}CH_2)$] (5a):
^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.01 (s, 3H; Si(CH_3)$_2$), 0.01 (s, 3H; Si(CH_3)$_2$), 1.05 (d, ^3J = 7.1 Hz, 3H; SiCH(CH_3)), 1.29 – 1.40 (m, 2H; NCCCH_2), 1.48 – 1.57 (m, 4H; NCCH_2), 1.61 – 1.72 (m, 1H; SiCH(CH$_3$)), 1.88 (s, 2H; SiCH_2N), 2.21 – 2.39 (m, 4H; NCH_2), 4.75 – 4.86 (m, 2H; CH=CH_2), 5.82 – 5.94 (m, 1H; CH=CH$_2$). – ^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = –4.6 (s; Si(*C*H$_3$)$_2$), –4.5 (s; Si(*C*H$_3$)$_2$), 13.0 (s; SiCH(*C*H$_3$)), 23.8 (s; NCC*C*H$_2$), 26.3 (s; NC*C*H$_2$), 26.9 (s; Si*C*H(CH$_3$)), 48.8 (s; Si*C*H$_2$N), 58.7 (s; N*C*H$_2$), 110.2 (s; CH=*C*H$_2$), 141.6 (s; *C*H=CH$_2$). – ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ = 0.3 (s; *Si*(CH$_3$)$_2$). – GC-MS retention time: 4.87. – El-MS, *m/z* (%): 211 (2) [M^+], 98 (100) [$CH_2NC_5H_{10}^+$].

***E*-[$Me_2Si(CH_2NC_5H_{10})(CH{=}CHCH_2Me)$] (6a):**
^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.08 (s, 6H; Si(CH_3)$_2$), 0.97 (t, ^3J = 7.4 Hz, 3H; CH$_2$CH_3), 1.29 – 1.40 (m, 2H; NCCCH_2), 1.48 – 1.57 (m, 4H; NCCH_2), 1.88 (s, 2H; SiCH_2N), 2.06 – 2.16 (m, 2H; CH_2CH$_3$), 2.21 – 2.39 (m, 4H; NCH_2), 5.62 (dt, ^3J = 18.6 Hz, ^4J = 1.7 Hz, 1H; SiCH=CH), 6.12 (dt, ^3J = 18.6 Hz, ^3J = 5.9 Hz, 1H; SiCH=CH). – ^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = –2.4 (s; Si(*C*H$_3$)$_2$), 12.8 (s; CH$_2$*C*H$_3$), 23.6 (s; NCC*C*H$_2$), 26.1 (s; NC*C*H$_2$), 29.5 (s; *C*H$_2$CH$_3$), 48.8 (s; Si*C*H$_2$N), 58.7 (s; N*C*H$_2$), 126.9 (s; Si*C*H=CH), 149.7 (s; SiCH=*C*H). – ^{29}Si NMR ($CDCl_3$, 99.4 MHz): δ = –10.2 (s; *Si*(CH$_3$)$_2$). – GC-MS retention time: 4.94. – El-MS, *m/z* (%): 211 (2) [M^+], 98 (100) [$CH_2NC_5H_{10}^+$].

***Z*-[$Me_2Si(CH_2NC_5H_{10})(CH{=}CHCH_2Me)$] (7a):**
^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.14 (s, 6H; Si(CH_3)$_2$), 0.84 (t, ^3J = 7.4 Hz, 3H; CH$_2$CH_3), 1.29 – 1.40 (m, 2H; NCCCH_2), 1.48 – 1.57 (m, 4H; NCCH_2), 1.88 (s, 2H; SiCH_2N), 2.06 – 2.16 (m, 2H; CH_2CH$_3$), 2.21 – 2.39 (m, 4H; NCH_2), 5.45 (dt, ^3J = 14.0 Hz, ^4J = 1.3 Hz, 1H; SiCH=CH), 6.29 (dt, ^3J = 14.0 Hz, ^3J = 7.4 Hz, 1H; SiCH=CH). – ^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = –3.1 (s; Si(*C*H$_3$)$_2$), 14.2 (s; CH$_2$*C*H$_3$), 23.6 (s; NCC*C*H$_2$), 26.1 (s; NC*C*H$_2$), 29.3 (s; *C*H$_2$CH$_3$), 48.8 (s; Si*C*H$_2$N), 58.3 (s; N*C*H$_2$), 127.1 (s; Si*C*H=CH), 151.2 (s; SiCH=*C*H). – ^{29}Si NMR ($CDCl_3$, 99.4 MHz): δ = –12.5 (s; *Si*(CH$_3$)$_2$).

Me_3SiCl trapping products:

[$Me_2Si(CH_2NC_5H_{10})(CH(SiMe_3)CH{=}CH_2)$] (5b):
not detected by GC/MS or NMR spectroscopy

***E*-[$Me_2Si(CH_2NC_5H_{10})(CH{=}CHCH_2SiMe_3)$] (6b):**
^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = –0.03 (s, 9H; Si(CH_3)$_3$), 0.06 (s, 6H; Si(CH_3)$_2$), 1.27 – 1.39 (m, 2H; NCCCH_2), 1.45 – 1.57 (m, 4H; NCCH_2), 1.61 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 2H; CH_2Si(CH$_3$)$_3$), 1.91 (s, 2H; SiCH_2N), 2.30 (s, b, 4H; NCH_2), 5.42 (dt, ^3J = 18.4 Hz, ^4J = 1.3 Hz, 1H; SiCH), 6.04 (dt, ^3J = 18.4 Hz, ^3J = 7.8 Hz, 1H; SiCH=CH). – ^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = –2.3 (s; Si(*C*H$_3$)$_2$), –1.9 (s; Si(*C*H$_3$)$_3$), 23.9 (s; NCC*C*H$_2$), 26.3 (s; NC*C*H$_2$), 28.6 (s; *C*H$_2$Si(CH$_3$)$_3$), 51.2 (s; Si*C*H$_2$N), 58.5 (s; N*C*H$_2$), 126.7 (s; Si*C*H), 144.7 (s; SiCH=*C*H). – ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ = 0.4 (s; *Si*(CH$_3$)$_3$), –10.8 (s; *Si*(CH$_3$)$_2$). – GC-MS retention time: 6.42. – El-MS, *m/z* (%): 269 (2) [M^+], 98 (100) [$CH_2NC_5H_{10}^+$] – $C_{14}H_{31}NSi_2$ (269.57); calc. C 62.38, H 11.59, N 5.20; found C 60.19, H 11.05, N 5.14.

***Z*-[$Me_2Si(CH_2NC_5H_{10})(CH{=}CHCH_2SiMe_3)$] (7b):**
GC/MS retention time: 6.61. – El-MS, *m/z* (%): 269 (2) [M^+], 98 (100) [$CH_2NC_5H_{10}^+$].

A complete analysis by NMR spectroscopy was not possible due to the formation of <2% of the product.

Me_3SnCl trapping products:

[$Me_2Si(CH_2NC_5H_{10})(CH(SnMe_3)CH=CH_2)$] (5c):
^{1}H NMR ($CDCl_3$, 500.1 MHz): δ = 0.09 (s, 9H; Sn(CH_3)$_3$), 1.30 – 1.37 (m, 2H; NCCCH_2), 1.47 – 1.56 (m, 5H; NCCH_2 and SiCH(Sn(CH_3)$_3$)CH=CH_2), 1.89 (s, 2H; SiCH_2N), 2.29 (s, b, 4H; NCH_2), 4.59 – 4.71 (m, 2H; CH=CH_2), 5.71 – 5.82 (m, 1H; CH=CH_2). – ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = –8.6 (s, ^1J(Sn^{119}C) = 326 Hz, ^1J(Sn^{117}C) = 311 Hz; Sn(CH$_3$)$_3$), –1.7 (s; Si(CH$_3$)$_2$), –1.5 (s; Si(CH$_3$)$_2$), 22.2 (s, ^1J(Sn^{119}C) = 288 Hz, ^1J(Sn^{117}C) = 275 Hz; SiCH(Sn(CH$_3$)$_3$)CH=CH$_2$), 23.9 (s; NCCCH$_2$), 26.4 (s; NCCH$_2$), 50.8 (s; SiCH$_2$N), 58.6 (s; NCH$_2$), 109.7 (s; CH=CH$_2$), 138.5 (s; CH=CH$_2$). – ^{29}Si NMR ($CDCl_3$, 99.4 MHz): δ = –1.0. (s; Si(CH$_3$)$_2$) – ^{119}Sn NMR ($CDCl_3$, 186.5 MHz): δ = 1.4 (s; Sn(CH$_3$)$_3$). – Si(CH_3)$_2$ not detected. – GC-MS retention time: 7.07. – El-MS, *m/z* (%): 346 (2) [M^+ – CH_3], 98 (100) [$CH_2NC_5H_{10}^+$].

***E*-[$Me_2Si(CH_2NC_5H_{10})(CH=CHCH_2SnMe_3)$] (6c):**
^{1}H NMR ($CDCl_3$, 500.1 MHz): δ = –0.06 (s, ^2J(Sn^{119}H) = 53.5 Hz, ^2J(Sn^{117}H) = 51.1 Hz, 9H; Sn(CH_3)$_3$), 0.05 (s, 6H; Si(CH_3)$_2$), 1.30 – 1.37 (m, 2H; NCCCH_2), 1.47 – 1.56 (m, 4H; NCCH_2), 1.88 (dd, ^2J(Sn^{119}H) = 68.7 Hz, ^2J(Sn^{117}H) = 66.0 Hz, ^3J = 8.3 Hz, ^4J = 1.2 Hz, 2H; CH_2Sn(CH$_3$)$_3$), 1.89 (s, 2H; SiCH_2N), 2.29 (s, b, 4H; NCH_2), 5.42 (dt, ^3J = 18.3 Hz, ^4J = 1.2 Hz, 1H; SiCH), 6.16 (dt, ^3J = 18.3 Hz, ^3J = 8.3 Hz, 1H; SiCH=CH). – ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = –10.1 (s, ^1J(Sn^{119}C) = 328 Hz, ^1J(Sn^{117}C) = 313 Hz; Sn(CH$_3$)$_3$), –2.2 (s, ^1J(SiC) = 52 Hz; Si(CH$_3$)$_2$), 22.1 (s, ^1J(Sn^{119}C) = 280 Hz, ^1J(Sn^{117}C) = 267 Hz; CH$_2$Sn(CH$_3$)$_3$), 23.9 (s; NCCCH$_2$), 26.4 (s; NCCH$_2$), 51.4 (s, ^1J(SiC) = 58 Hz; SiCH$_2$N), 58.6 (s; NCH$_2$), 122.8 (s; SiCH), 146.9 (s; SiCH=CH). – ^{29}Si NMR ($CDCl_3$, 99.4 MHz): δ = –10.8 (s; Si(CH$_3$)$_2$) – ^{119}Sn NMR ($CDCl_3$, 186.5 MHz): δ = –3.1 (s; Sn(CH$_3$)$_3$). – GC-MS retention time: 7.35. – El-MS, *m/z* (%): 346 (2) [M^+ – CH_3], 98 (100) [$CH_2NC_5H_{10}^+$]. – $C_{14}H_{31}NSiSn$ (360.20); calc. C 46.68, H 8.67, N 3.89; found C 46.87, H 8.60, N 4.11.

***Z*-[$Me_2Si(CH_2NC_5H_{10})(CH=CHCH_2SnMe_3)$] (7c):**
not detected by GC/MS or NMR spectroscopy

Side products:
The following two side products were always observed (~ 15%) in the trapping reactions with THF as solvent, probably due to THF cleavage.

***E*-[$Me_2Si(CH_2NC_5H_{10})(CH=CHCH_3)$] (8):**
^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.07 (s, 6H; Si(CH_3)$_2$), 1.27 – 1.39 (m, 2H; NCCCH_2), 1.45 – 1.57 (m, 4H; NCCH_2), 1.78 (dd, ^3J = 6.1 Hz, ^4J = 1.6 Hz, 3H; CH=CHCH_3) 1.90 (s, 2H; SiCH_2N), 2.30 (s, b, 4H; NCH_2), 5.65 (dq, ^3J = 18.3 Hz, ^4J = 1.6 Hz, 1H; SiCH), 6.07 (dq, ^3J = 18.3 Hz, ^3J = 6.1 Hz, 1H; SiCH=CH). – ^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = –2.5 (s; Si(CH$_3$)$_2$), 22.7 (s; CH=CHCH$_3$), 23.9 (s; NCCCH$_2$), 26.3 (s; NCCH$_2$), 51.0 (s; SiCH$_2$N), 58.5 (s; NCH$_2$), 130.2 (s; SiCH), 142.9 (s; SiCH=CH). – ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ = –10.6 (s; Si(CH$_3$)$_2$). – $C_{11}H_{22}NSi$ (196.39); El-MS, *m/z* (%): 197 (6) [M^+], 98 (100) [$CH_2NC_5H_{10}^+$]. – GC-MS retention time: 4.15.

***Z*-[$Me_2Si(CH_2NC_5H_{10})(CH=CHCH_3)$] (9):**

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = = 0.04 (s, 6H; Si(CH_3)$_2$), 1.27 – 1.39 (m, 2H; NCCCH_2), 1.45 – 1.57 (m, 4H; NCCH_2), 1.76 (dd, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 3H; CH=CHCH_3) 1.95 (s, 2H; SiCH_2N), 2.30 (s, b, 4H; NCH_2), 5.51 (dq, ^3J = 14.0 Hz, ^4J = 1.5 Hz, 1H; SiCH), 6.38 (dq, ^3J = 14.0 Hz, ^3J = 6.8 Hz, 1H; SiCH=CH). – ^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = –1.2 (s; Si(CH_3)$_2$), 19.3 (s; CH=CHCH_3), 23.9 (s; NCCCH_2), 26.3 (s; NCCH_2), 51.4 (s; SiCH_2N), 58.5 (s; NCH_2), 128.9 (s; SiCH), 143.7 (s; SiCH=CH). – ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ = –12.5 (s; *Si*(CH_3)$_2$). – $C_{11}H_{22}NSi$ (196.39); El-MS, *m/z* (%): 197 (6) [M^+], 98 (100) [$CH_2NC_5H_{10}^+$]. – GC-MS retention time: 4.33.

3. Crystal Structure Determination of Compounds $(2)_4$ and $(3)_6$

Stoe IPDS diffractometer; data collection: Expose in IPDS (Stoe & Cie, 1999), cell determination and –refinement: Cell in IPDS (Stoe & Cie, 1999), integration: Integrate in IPDS (Stoe & Cie, 1999); numerical absorption correction: Faceit in IPDS (Stoe & Cie, 1999). The crystals of both compounds were mounted in an inert oil (perfluoropolyalkylether) at –60 °C (N_2 stream), using the X-TEMP 2 device (Kottke, T.; Stalke, D. *J. Appl. Cryst.* **1993**, *26*, 615. Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Cryst.* **1996**, *29*, 615. Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.), the crystal structure determinations were effected at –100 °C (type of radiation: Mo-Kα, λ = 0.71073 Å). Both structures were solved applying direct and fourier methods, using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 298764 [compound $(\mathbf{2})_4$] and CCDC 298765 [compound $(\mathbf{3})_6$]. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Crystallographic data for compound $(\mathbf{2})_4$ (colorless blocks from *n*-pentane, 0.50 × 0.50 × 0.30 mm^3): $C_{44}H_{88}Li_4N_4Si_4 \cdot n\text{-}C_7H_{16}$, M = 913.50, tetragonal, space group I-4 (no. 82), a = 15.607(2), c = 12.157(2), V = 2961.2(7) Å^3, Z = 2, D_c = 1.025 Mg·m^{-3}, μ = 0.134 mm^{-1}. 11891 reflections measured with 2θ in the range 5.22-52.00°, 2898 unique reflections; 2340 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms (except H1, H2, H3a and H3b) were refined on a riding model in their ideal geometric positions; $R1$ = 0.0476 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1388 (all data), absolute structure (Flack-) parameter -0.12(17).

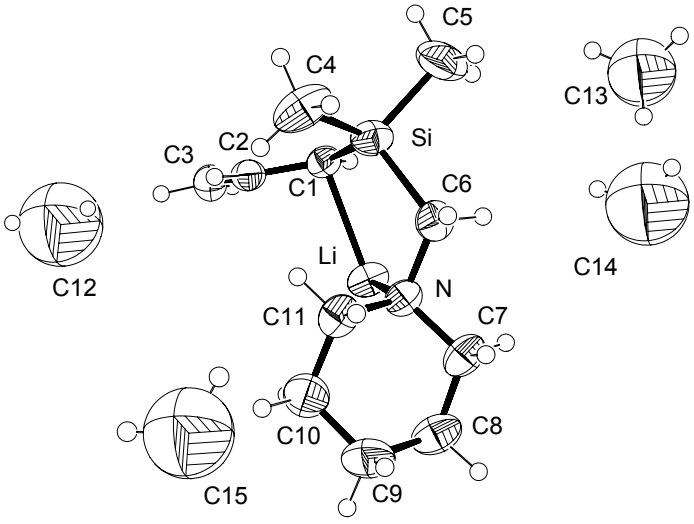

Fig. 1 ORTEP plot of **2** at 50 % probability level; C12 to C15 belong to a disordered solvent molecule.

Crystallographic data for compound $(\mathbf{3})_6$ (colorless needles from *n*-pentane, 0.40 × 0.10 × 0.10 mm^3): $C_{66}H_{126}Li_{12}N_6Si_6$, M = 913.50, hexagonal, space group $R\bar{3}$ (no. 148), a = 27.706(4) Å, c = 9.123(2) Å, V = 6064.8(18) $Å^3$, Z = 3, D_c = 1.031 $Mg \cdot m^{-3}$, μ = 0.141 mm^{-1}. 9454 reflections measured with 2θ in the range 4.78-52.00°, 2642 unique reflections; 1512 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined free with individual thermal parameters; $R1$ = 0.0566 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1422 (all data).

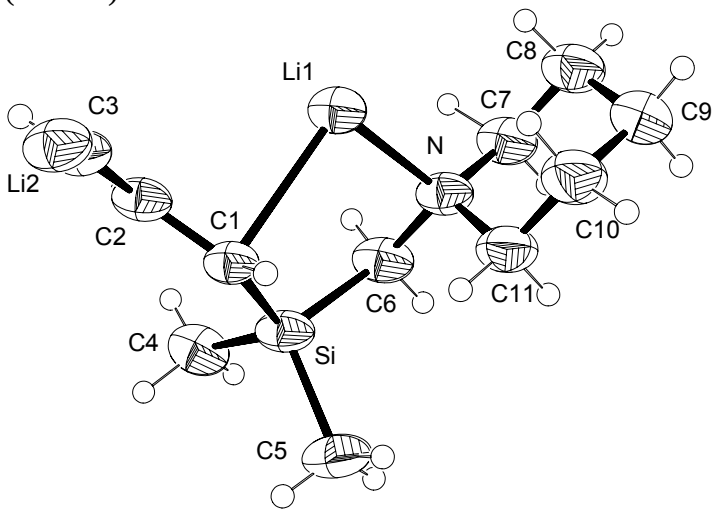

Fig. 2 ORTEP plot of **3** at 50 % probability level.

4. Computational Studies

The calculations of $(\mathbf{4})_4$ were done with S4 symmetry restrictions. Starting coordinates for **4** correspond to the crystal structure analysis of $(\mathbf{2})_4$. Table 1 lists the total and zero-point energies of all isomers. The global minima were subsequently energy-optimized at B3LYP/6-31+G(d) level and showed no negative frequencies. The Transition state showed one negative frequency directed to the expected reaction coordinate.

Table 1 Results from Quantum Chemical Studies (B3LYP/6-31+G(d)).

model	.	total energy (Hartree)	zero point energy (Hartree)
monoanion allyltrimethylsilane		−525.984477	−525.818524
dianion allyltrimethylsilane		−525.174717	−525.023469
4·OMe_2		−898.976875	−898.623831
4 + H_3SiCl	educt	−1340.423115	−1340.205555
4 + H_3SiCl	TS	−1340.417780	−1340.199405
4 + H_3SiCl	product	−1340.477844	−1340.257760
H_3SiCl		−751.533856	−751.507490
$(\mathbf{4})_4$		−2355.629796	−2354.863610

Table 2 Standard Orientation of monoanion allyltrimethylsilane (B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.720949	-0.051591	-0.003844
2	6	0	-0.990718	-0.632904	0.021404
3	6	0	-2.154166	0.178569	-0.010112
4	6	0	-3.493478	-0.157584	0.072254
5	6	0	1.883470	-1.311159	-0.874200
6	6	0	1.588014	0.236697	1.703191
7	6	0	0.932989	1.633503	-0.900665
8	1	0	-1.157655	-1.711340	0.138777
9	1	0	-1.970134	1.255685	-0.128677
10	1	0	-4.271189	0.601321	0.005503
11	1	0	-3.820284	-1.191463	0.193925
12	1	0	1.634499	-1.399707	-1.940114
13	1	0	1.768348	-2.310255	-0.428804
14	1	0	2.944456	-1.030605	-0.789828
15	1	0	1.590924	-0.690586	2.294206
16	1	0	1.039528	0.988297	2.288439
17	1	0	2.631883	0.577988	1.602713
18	1	0	0.315610	2.412548	-0.432070
19	1	0	0.626066	1.561147	-1.952405
20	1	0	1.977984	1.976508	-0.869084

Table 3 Standard Orientation of dianion allyltrimethylsilane (B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.658495	0.049504	0.025850
2	6	0	-1.066945	0.613604	0.135890
3	6	0	-2.271465	-0.172253	0.071804
4	6	0	-3.588693	0.278719	0.109901
5	6	0	1.791553	1.517495	-0.500014
6	6	0	0.920207	-1.322664	-1.309187
7	6	0	1.573380	-0.694221	1.568436
8	1	0	-1.232852	1.693891	0.234836
9	1	0	-2.066083	-1.265378	-0.030880
10	1	0	-4.269016	-0.580227	-0.114983
11	1	0	1.561689	2.404062	0.109787
12	1	0	1.628996	1.784905	-1.556346
13	1	0	2.856869	1.288993	-0.365303
14	1	0	0.681661	-0.934264	-2.310926
15	1	0	0.242713	-2.167189	-1.117427
16	1	0	1.947524	-1.711228	-1.320846
17	1	0	1.046509	-1.577671	1.960851
18	1	0	1.625726	0.045274	2.380460
19	1	0	2.609120	-0.998305	1.307894

Table 4 Standard Orientation of **4**·OMe_2 (B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.629320	-1.626613	-2.380813
2	6	0	-1.991367	1.145504	-0.339145
3	6	0	-2.324992	2.349046	0.218431
4	14	0	-1.481004	-1.692814	-0.478879
5	7	0	1.348775	-1.678600	-0.468518
6	6	0	0.204999	-2.562579	-0.078263

7	6	0	-1.415149	-0.028954	0.267216
8	6	0	-2.796911	-2.929479	0.143090
9	3	0	0.745900	0.253666	0.170159
10	8	0	1.682524	1.617947	-0.972936
11	8	0	1.547143	0.748566	1.975161
12	6	0	1.266336	2.080149	2.409298
13	6	0	1.467513	-0.195606	3.038136
14	6	0	1.017316	2.652244	-1.704467
15	6	0	3.061495	1.501638	-1.295842
16	1	0	-0.870152	-0.983566	-2.845941
17	1	0	-1.535636	-2.629789	-2.818197
18	1	0	-2.608185	-1.231358	-2.681541
19	1	0	-2.153180	1.079811	-1.422364
20	1	0	-2.757883	3.148048	-0.378546
21	1	0	-2.242767	2.528156	1.290941
22	1	0	1.361549	-1.588588	-1.485651
23	1	0	2.240289	-2.115137	-0.227253
24	1	0	0.288373	-3.566271	-0.526550
25	1	0	0.261483	-2.702422	1.010646
26	1	0	-1.430582	-0.010770	1.369128
27	1	0	-3.804786	-2.567713	-0.098474
28	1	0	-2.682090	-3.927631	-0.303712
29	1	0	-2.749986	-3.044493	1.234432
30	1	0	1.352855	2.725769	1.534388
31	1	0	1.990423	2.390834	3.175657
32	1	0	0.247716	2.150085	2.812291
33	1	0	2.197348	0.047478	3.823408
34	1	0	1.699917	-1.176287	2.617757
35	1	0	0.457987	-0.213791	3.471432
36	1	0	-0.008963	2.696814	-1.332790
37	1	0	1.024575	2.424569	-2.779754
38	1	0	1.518570	3.615957	-1.535587
39	1	0	3.194695	1.247027	-2.357593
40	1	0	3.475550	0.705984	-0.672366
41	1	0	3.590955	2.441687	-1.083947

Table 5 Standard Orientation of **4** + H_3SiCl (educt, B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	4.197751	0.298232	-0.049724
2	17	0	2.768718	-1.183018	0.431656
3	6	0	1.015006	2.227204	-0.066555
4	6	0	-0.326650	1.849911	-0.147905
5	6	0	-1.054376	1.017930	0.727838
6	6	0	-3.519785	0.802389	-1.167935
7	3	0	0.601710	-0.046404	-0.281879
8	14	0	-2.494819	0.007866	0.224831
9	7	0	-0.578507	-1.398353	-1.336546
10	6	0	-1.790751	-1.661255	-0.488399
11	6	0	-3.633596	-0.483040	1.658842
12	1	0	5.506282	-0.385769	0.067011
13	1	0	3.946891	0.736894	-1.435906
14	1	0	4.081858	1.390165	0.934589
15	1	0	1.425620	2.941490	-0.776288
16	1	0	1.540152	2.147293	0.888444
17	1	0	-0.817355	2.108283	-1.093919
18	1	0	-0.617888	0.853666	1.721663
19	1	0	-2.916203	1.057932	-2.049082

20	1	0	-3.987433	1.731982	-0.820255
21	1	0	-4.320285	0.128877	-1.501747
22	1	0	-0.870119	-0.921037	-2.191345
23	1	0	-0.170772	-2.279996	-1.652231
24	1	0	-2.539029	-2.262395	-1.030844
25	1	0	-1.455165	-2.269436	0.362696
26	1	0	-4.165105	0.393805	2.049164
27	1	0	-3.059585	-0.913756	2.489699
28	1	0	-4.385782	-1.223222	1.354859

Table 6 Standard Orientation of **4** + H_3SiCl (Transition state, B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	3.639918	-0.492517	0.425168
2	17	0	2.764283	1.214441	-0.635791
3	6	0	1.475400	-1.871018	-0.270067
4	6	0	0.143609	-1.534359	0.061051
5	6	0	-0.819935	-0.895034	-0.724490
6	6	0	-2.928941	-0.890393	1.563157
7	3	0	0.574724	0.671235	-0.066465
8	14	0	-2.399178	-0.166137	-0.111337
9	7	0	-0.758635	1.920494	0.871664
10	6	0	-2.067524	1.724141	0.163008
11	6	0	-3.818169	-0.290567	-1.358411
12	1	0	4.910508	0.250049	0.706352
13	1	0	3.077794	-0.728494	1.776752
14	1	0	4.087318	-1.636313	-0.400733
15	1	0	1.950231	-2.633968	0.345925
16	1	0	1.733462	-1.924548	-1.330509
17	1	0	-0.123938	-1.712966	1.110398
18	1	0	-0.593865	-0.816265	-1.795638
19	1	0	-2.159143	-0.782207	2.338593
20	1	0	-3.143808	-1.962265	1.472340
21	1	0	-3.838235	-0.397912	1.931666
22	1	0	-0.856203	1.619696	1.842966
23	1	0	-0.526879	2.913699	0.925000
24	1	0	-2.890345	2.243392	0.679352
25	1	0	-1.969129	2.195423	-0.824065
26	1	0	-4.122367	-1.335524	-1.495818
27	1	0	-3.517721	0.094573	-2.341350
28	1	0	-4.701229	0.275510	-1.034164

Table 7 Standard Orientation of **4** + H_3SiCl (product, B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	3.150925	-1.329286	0.612592
2	17	0	2.176492	2.301440	-0.624525
3	6	0	1.954974	-1.531760	-0.865606
4	6	0	0.524142	-1.434843	-0.429018
5	6	0	-0.361497	-0.492916	-0.822134
6	6	0	-2.540216	-1.627797	1.083582
7	3	0	0.730253	1.330721	0.580790
8	14	0	-2.110912	-0.282550	-0.178306
9	7	0	-0.993534	1.588930	1.640294

10	6	0	-2.134805	1.433634	0.685947
11	6	0	-3.378006	-0.243508	-1.578255
12	1	0	2.657877	-0.263532	1.526986
13	1	0	3.169316	-2.600594	1.393342
14	1	0	4.527871	-1.022938	0.156981
15	1	0	2.156639	-2.519547	-1.306155
16	1	0	2.186621	-0.764712	-1.612246
17	1	0	0.204148	-2.190237	0.295177
18	1	0	-0.003148	0.227453	-1.566478
19	1	0	-1.837367	-1.658624	1.925849
20	1	0	-2.536201	-2.622493	0.620817
21	1	0	-3.543994	-1.464616	1.496245
22	1	0	-1.111944	0.949505	2.426836
23	1	0	-1.004384	2.525492	2.048106
24	1	0	-3.105189	1.623418	1.170503
25	1	0	-2.015890	2.204350	-0.086380
26	1	0	-3.416472	-1.208546	-2.098051
27	1	0	-3.125495	0.521768	-2.322426
28	1	0	-4.386503	-0.026450	-1.203697

Table 8 Standard Orientation of H_3SiCl (B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-1.000117	0.000005	-0.000003
2	17	0	1.082541	0.000008	-0.000006
3	1	0	-1.466992	-0.570849	1.283910
4	1	0	-1.467185	-0.826677	-1.136132
5	1	0	-1.467381	1.397315	-0.147637

Table 9 Standard Orientation of $(\mathbf{4})_4$ (B3LYP/6-31+G(d)).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	4.510868	-1.676859	3.723933
2	1	0	-4.510868	1.676859	3.723933
3	1	0	-3.421499	-1.259672	3.186733
4	1	0	3.421499	1.259672	3.186733
5	1	0	-5.181228	-1.248336	3.036067
6	1	0	5.181228	1.248336	3.036067
7	1	0	2.790401	-1.738841	3.286749
8	1	0	-2.790401	1.738841	3.286749
9	1	0	4.130273	3.218434	2.015045
10	1	0	-4.130273	-3.218434	2.015045
11	1	0	0.459979	2.391500	3.209493
12	1	0	-0.459979	-2.391500	3.209493
13	6	0	3.810182	-1.801816	2.886904
14	6	0	-3.810182	1.801816	2.886904
15	6	0	-4.242158	-1.184143	2.461638
16	6	0	4.242158	1.184143	2.461638
17	1	0	3.940729	-2.817634	2.491947
18	1	0	-3.940729	2.817634	2.491947
19	6	0	0.480669	2.058238	2.176103
20	6	0	-0.480669	-2.058238	2.176103
21	1	0	-0.432193	-0.982659	2.015964
22	1	0	0.432193	0.982659	2.015964

23	7	0	-4.085394	-2.330339	1.513987
24	7	0	4.085394	2.330339	1.513987
25	1	0	6.571390	-0.833427	1.454689
26	1	0	-6.571390	0.833427	1.454689
27	14	0	-4.085394	0.505039	1.529257
28	14	0	4.085394	-0.505039	1.529257
29	1	0	0.363721	4.010923	1.452076
30	1	0	-0.363721	-4.010923	1.452076
31	1	0	4.863032	2.343989	0.853611
32	1	0	-4.863032	-2.343989	0.853611
33	6	0	-0.385550	-2.961788	1.141873
34	6	0	0.385550	2.961788	1.141873
35	6	0	5.773978	-0.807058	0.700268
36	6	0	-5.773978	0.807058	0.700268
37	3	0	2.276890	1.862986	0.672673
38	3	0	-2.276890	-1.862986	0.672673
39	1	0	5.793430	-1.765201	0.165522
40	1	0	-5.793430	1.765201	0.165522
41	1	0	1.699835	-0.483726	0.613911
42	1	0	-1.699835	0.483726	0.613911
43	1	0	6.036555	-0.027017	-0.026791
44	1	0	-6.036555	0.027017	-0.026791
45	6	0	2.742173	-0.422996	0.273716
46	6	0	-2.742173	0.422996	0.273716
47	1	0	0.027017	6.036555	0.026791
48	1	0	-0.027017	-6.036555	0.026791
49	1	0	1.765201	5.793430	-0.165522
50	1	0	-1.765201	-5.793430	-0.165522
51	6	0	0.422996	2.742173	-0.273716
52	6	0	-0.422996	-2.742173	-0.273716
53	6	0	0.807058	5.773978	-0.700268
54	6	0	-0.807058	-5.773978	-0.700268
55	1	0	-0.483726	-1.699835	-0.613911
56	1	0	0.483726	1.699835	-0.613911
57	1	0	-2.343989	4.863032	-0.853611
58	1	0	2.343989	-4.863032	-0.853611
59	3	0	1.862986	-2.276890	-0.672673
60	3	0	-1.862986	2.276890	-0.672673
61	1	0	-0.833427	-6.571390	-1.454689
62	1	0	0.833427	6.571390	-1.454689
63	6	0	2.961788	-0.385550	-1.141873
64	6	0	-2.961788	0.385550	-1.141873
65	1	0	4.010923	-0.363721	-1.452076
66	1	0	-4.010923	0.363721	-1.452076
67	14	0	0.505039	4.085394	-1.529257
68	14	0	-0.505039	-4.085394	-1.529257
69	7	0	-2.330339	4.085394	-1.513987
70	7	0	2.330339	-4.085394	-1.513987
71	1	0	-0.982659	0.432193	-2.015964
72	1	0	0.982659	-0.432193	-2.015964
73	6	0	2.058238	-0.480669	-2.176103
74	6	0	-2.058238	0.480669	-2.176103
75	1	0	2.817634	3.940729	-2.491947
76	1	0	-2.817634	-3.940729	-2.491947
77	6	0	1.184143	-4.242158	-2.461638
78	6	0	-1.184143	4.242158	-2.461638
79	1	0	3.218434	-4.130273	-2.015045
80	1	0	-3.218434	4.130273	-2.015045
81	6	0	-1.801816	-3.810182	-2.886904
82	6	0	1.801816	3.810182	-2.886904
83	1	0	1.248336	-5.181228	-3.036067
84	1	0	-1.248336	5.181228	-3.036067
85	1	0	2.391500	-0.459979	-3.209493

86	1	0	-2.391500	0.459979	-3.209493
87	1	0	1.738841	2.790401	-3.286749
88	1	0	-1.738841	-2.790401	-3.286749
89	1	0	-1.259672	3.421499	-3.186733
90	1	0	1.259672	-3.421499	-3.186733
91	1	0	1.676859	4.510868	-3.723933
92	1	0	-1.676859	-4.510868	-3.723933

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