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Supporting Information

Cationic Si–H–Si Bridges in Polysilanes: Their Detection and Targeted Formation in Stable Ion Studies

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Supporting Information

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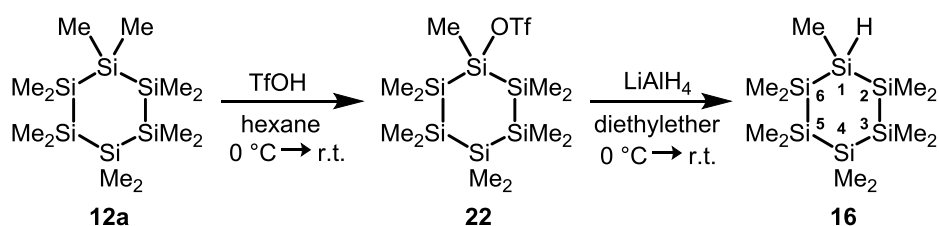
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Experimental Part

All manipulations of air- and moisture-sensitive compounds were carried out under an argon or nitrogen atmosphere using Schlenk techniques or a standard glove box (Braun Unilab). Glassware was dried in an oven at $T = 120\text{ }^{\circ}\text{C}$ and evacuated prior to use. The solvents tetrahydrofuran (THF), dimethoxyethane (DME), *n*-pentane, benzene and toluene were dried over sodium and distilled under a nitrogen atmosphere. Chlorobenzene, *o*-dichlorobenzene and dichloromethane were dried over CaCl_2 and stored over molecular sieves (4 \AA). Benzene- d_6 and toluene- d_8 were stored over molecular sieves (4 \AA) after drying over sodium. Chlorobenzene- d_5 and dichloromethane- d_2 were dried over molecular sieves (4 \AA). Triphenylmethyl tetrakis(pentafluorophenyl) borate ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$) was prepared according to a modified literature procedure.^{1, 2} Dodecamethylcyclohexasilane **3**³⁻⁵, dihydridocyclopentasilane **7**⁶ and 1,4-dihydridocyclohexasilane **17**⁷ were prepared according to literature procedures. NMR spectra were recorded on Bruker Avance 500, Bruker Avance III 500 and Varian Inova 300 spectrometers. ^1H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (benzene- d_6 : $\delta^1\text{H}(\text{C}_6\text{D}_5\text{H}) = 7.20$, toluene- d_8 : $\delta^1\text{H}(\text{CD}_2\text{H}) = 2.08$, dichloromethane- d_2 : $\delta^1\text{H}(\text{CDHCl}_2) = 5.32$, chlorobenzene- d_5 : $\delta^1\text{H}(\text{C}_6\text{D}_4\text{HCl}) = 7.14$, acetone- d_6 : $\delta^1\text{H}((\text{CD}_3)(\text{CD}_2\text{H})\text{CO}) = 2.05$ and ^{13}C NMR spectra by using the central line of the solvent signal (benzene- d_6 : $\delta^{13}\text{C}(\text{C}_6\text{D}_6) = 128.0$, toluene- d_8 : $\delta^{13}\text{C}(\text{CD}_3) = 20.4$, dichloromethane- d_2 : $\delta^{13}\text{C}(\text{CDHCl}_2) = 53.8$, chlorobenzene- d_5 : $\delta^{13}\text{C}(\text{C}_6\text{D}_5\text{Cl}) = 134.2$, acetone- d_6 : $\delta^{13}\text{C}(\text{CD}_3)_2\text{CO} = 29.8$). $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were calibrated against an external standard ($^{29}\text{Si}(\text{Me}_2\text{SiHCl}) = 11.1$ versus tetramethylsilane (TMS)). The $^{29}\text{Si}\{^1\text{H}\}$ NMR inverse gated spectra were recorded with a relaxation delay $D1 = 10\text{ s}$. Based on our experiences, at $-20\text{ }^{\circ}\text{C}$ or $-40\text{ }^{\circ}\text{C}$ this delay is long enough to allow a reliable integration of the peaks. The $^{29}\text{Si}\{^1\text{H}\}$ INEPT spectra were recorded with delays $D3 = 0.0084\text{ s}$ and $D4 = 0.0313\text{ s}$ for compound **22** and **16**, $D3 = D4 = 0.0056\text{ s}$ for cation **8** and $D3 = D4 = 0.0061\text{ s}$ for cation **19**. Combustion analysis values for carbon show often too low values, which we attribute to the formation and incomplete combustion of silicon carbide, although vanadium pentoxide as combustion aid was used.

Synthesis of starting materials

Hydridoundecamethylcyclohexasilane **16**



A solution of 3.00 g (1 equiv., 8.60 mmol) of dodecamethylcyclohexasilane **12a** in hexane (20 mL) was cooled to $T = 0\text{ }^{\circ}\text{C}$ in an ice bath and 0.91 mL (1.2 equiv., 1.55 g, 10.32 mmol) of trifluoromethanesulfuric acid was added dropwise. The mixture was stirred for several days at room temperature and the completeness of the reaction was confirmed by $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy. Complete consumption of the starting material was confirmed by the absence of a signal at $\delta^{29}\text{Si} = -42.0$.

To a suspension of 0.33 g (1 equiv., 8.60 mmol) of LiAlH₄ in Et₂O (10 mL) was added the solution of 8.60 mmol (1 equiv.) of silyl triflate **22** in hexane (10 mL) at $T = 0\text{ }^{\circ}\text{C}$ and the mixture was stirred at room temperature overnight. The progress of the reaction was followed by GC/MS. After aqueous workup (H₂SO₄, ice, Et₂O), the combined organic phases were dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure and the crude product **16** was purified by Kugelrohr distillation ($T = 150\text{ }^{\circ}\text{C}$, $p = 7 \cdot 10^{-3}$ mbar). The product **16** was obtained as a colourless wax (2.30 g, 6.90 mmol, 80 %).

Trifluoromethanesulfonylundecamethylcyclohexasilane **22**^{8,9}

$^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99.31 MHz, 305.0 K, hexane/D₂O-lock) δ : -42.6, -42.2, -39.2 (Si(CH₃)₂), 50.2 (SiOTf).

Hydridoundecamethylcyclohexasilane **16**⁹

^1H NMR (499.87 MHz, 305.1 K, C₆D₆) δ : 0.25 (s, 3 H, Si(CH₃)), 0.26 (s, 6 H, 2 x Si(CH₃)), 0.26 (s, 3 H, Si(CH₃)), 0.27 (s, 6 H, 2 x Si(CH₃)), 0.30 (s, 6 H, 2 x Si(CH₃)), 0.34 (s, 6 H, 2 x Si(CH₃)), 3.68 (q, 1 H, Si-H, $^3J_{\text{H,H}} = 5$ Hz, $^1J_{\text{Si,H}} = 166$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, 305.0 K, C₆D₆) δ : -6.2 (2 x Si(CH₃)), -6.0 (Si(CH₃)), -6.0 (2 x Si(CH₃)), -5.9 (Si(CH₃)), -5.1 (2 x Si(CH₃)), -4.4 (2 x Si(CH₃)), -12.3 (HSi(CH₃)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 305.0 K, C₆D₆) δ : -68.2 (Si-H), -42.2 (Si⁴), -42.0, -41.3 (Si^{2/6} or Si^{3/5}). HR/MS (m/z) found/calcd. for C₁₁H₃₄Si₆: 334.1266/334.1271. IR $\tilde{\nu}_{\text{Si-H}} = 2063\text{ cm}^{-1}$ (ATR, neat). Anal. found/calcd. for C₁₁H₃₄Si₆: C 37.27/39.45, H 11.04/10.23.

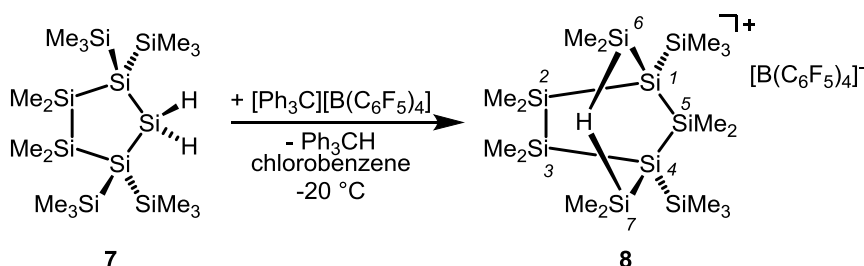
Cation preparation and rearrangements

Trityl tetrakis(pentafluorophenyl)borate was used as hydride abstraction reagent and the cations were obtained as salts of the tetrakis(pentafluorophenyl)borate. The NMR characterisation data for the anion are given below and not repeated for each cation preparation reaction. Negligible differences compared to these data were found for the NMR chemical shifts or coupling constants of the anion depending on the solvent or temperature.

[B(C₆F₅)₄]⁻:

¹³C{¹H} NMR (125.71 MHz, 243.1 K, C₆D₅Cl) δ: 148.9 (d, ¹J_{C,F} = 239 Hz, CF_{para}, [B(C₆F₅)₄]⁻), 138.8 (d, ¹J_{C,F} = 235 Hz, CF_{para}, [B(C₆F₅)₄]⁻), 136.9 (d, ¹J_{C,F} = 233 Hz, CF_{meta}, [B(C₆F₅)₄]⁻), 123.7-125.6 (m, C_{ipso}, [B(C₆F₅)₄]⁻). ¹⁹F{¹H} NMR (470.28 MHz, 243.1 K, C₆D₅Cl) δ: -131.9 (brs, 2 F, CF_{ortho}, [B(C₆F₅)₄]⁻), -161.9 (brs, 1 F, CF_{para}, [B(C₆F₅)₄]⁻), -165.8 (brs, 2 F, CF_{meta}, [B(C₆F₅)₄]⁻); ¹¹B{¹H} (160.38 MHz, 243.1 K, C₆D₅Cl) δ: -16.8 ([B(C₆F₅)₄]⁻).

Synthesis of hydrogen-bridged bissilyl borate **8**[B(C₆F₅)₄]⁻ from dihydridocyclopentasilane **7** in chlorobenzene

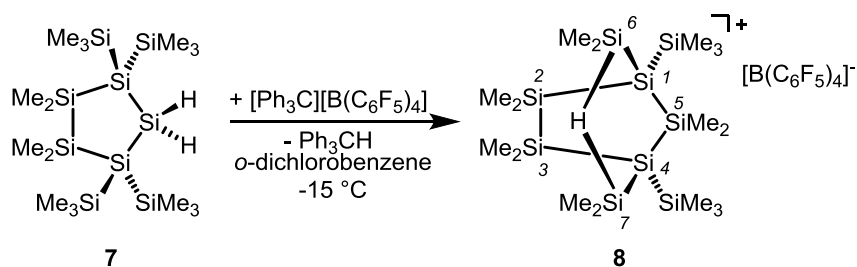


87 mg (1 equiv., 0.18 mmol) of dihydridocyclopentasilane **7** and 0.162 g (1 equiv., 0.18 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** were evacuated in different Schlenk tubes for 1 h and then each dissolved in chlorobenzene or chlorobenzene-d₅ (0.5 mL). The solution of trityl tetrakis(pentafluorophenyl)borate **9** was cooled to T = -20 °C with an EtOH/N₂ bath. The silane was added via a Teflon tube and the reaction mixture was stirred at T = -20 °C for 1.5 h. The solution was then transferred into an NMR tube and stored at T = -60 °C overnight. The NMR spectra were recorded at T = -20 °C.

8: ¹H NMR (499.87 MHz, 253.0 K, C₆H₅Cl, acetone-d₆ lock) δ: 1.10 (m, 1H, ¹J_{Si,H} = 46 Hz, ³J_{H,H} = 2.3 Hz, Si-H-Si), 0.56 (d, 6H, ³J_{H,H} = 2.3 Hz; (H₃C)MeSi^{6,7}), 0.48 (d, 6H, ³J_{H,H} = 2.3 Hz; Me(H₃C)Si^{6,7}), 0.32 (2s, 2×3H, Si⁵(CH₃)₂), 0.20 (s, 6H, Si^{2,3}Me(CH₃)), 0.19 (s, 6H, Si^{2,3}(CH₃)Me), 0.17 (s, 18H, Si(CH₃)₃). ¹³C{¹H} NMR (125.71 MHz, 253.0 K, C₆H₅Cl, acetone-d₆ lock) δ: 1.8 (Si(CH₃)₃), 1.8 ((H₃C)MeSi^{6,7}), 1.1 (Me(H₃C)Si^{6,7}), -0.9 (Me(H₃C)Si⁵), -1.0 ((H₃C)MeSi⁵), -2.6 (Si^{2,3}Me(CH₃)), -3.5 (Si^{2,3}(CH₃)Me). ²⁹Si{¹H} NMR (99.31 MHz, 253 K, C₆H₅Cl, acetone-d₆ lock) δ: 94.2 (Si^{6,7}), -5.7 (2 x SiMe₃), -16.3 (Si⁵), -32.8 (Si^{2,3}), -128.8

(Si^{1,4}). ²⁹Si INEPT NMR (99.31 MHz, 253 K, C₆H₅Cl, acetone-d₆ lock) δ: 94.2 (dsept, ¹J_{Si,H} = 46 Hz, ²J_{Si,H} = 6 Hz, Si^{6,7}), -5.7 (m, 2 x SiMe₃), -16.3 (sept, ²J_{Si,H} = 6 Hz, Si⁵), -32.8 (m, Si^{2,3}), -128.8 (s, Si^{1,4}).

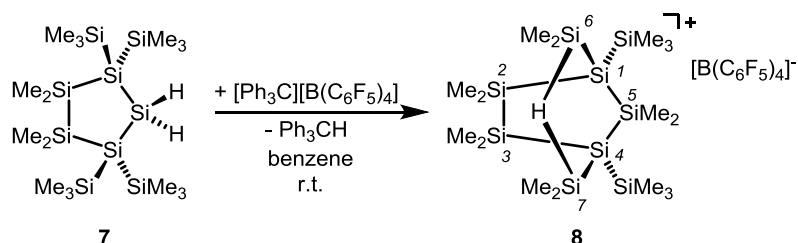
Synthesis of hydrogen-bridged bissilyl borate **8**[B(C₆F₅)₄] from dihydridocyclopentasilane **7** in *o*-dichlorobenzene



50 mg (1 equiv., 0.10 mmol) of dihydridocyclopentasilane **7** and 92 mg (1 equiv., 0.10 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** were evacuated in different Schlenk tubes for 1 h and then dissolved each in *o*-dichlorobenzene (1 mL). The solution of trityl tetrakis(pentafluoro)phenyl borate **9** was cooled to T = -15 °C with an EtOH/N₂ bath. The silane was added via a Teflon tube and the reaction mixture was stirred at T = -15 °C for 2 h. The solution was then transferred into an NMR tube and stored at T = -25 °C overnight. The NMR spectra were recorded at T = -15 °C with an external acetone-d₆ lock.

²⁹Si{¹H} NMR (99.31 MHz, 253 K, C₆H₄Cl₂, acetone-d₆ lock) δ: 94.1 (Si^{6,7}), -5.9 (2 x SiMe₃), -16.4 (Si⁵), -32.9 (Si^{2,3}), -128.8 (Si^{1,4}). ²⁹Si INEPT NMR (99.31 MHz, 253 K, C₆H₄Cl₂, acetone-d₆ lock) δ: 94.1 (dsept, ¹J_{Si,H} = 46 Hz, ²J_{Si,H} = 6 Hz, Si^{6,7}), -5.9 (m, 2 x SiMe₃), -16.4 (m, Si⁵), -32.9 (m, Si^{2,3}), -128.8 (s, Si^{1,4}).

Synthesis of hydrogen-bridged bissilyl borate **8**[B(C₆F₅)₄] from dihydridocyclopentasilane **7** in benzene



157 mg (1 equiv., 0.32 mmol) of dihydridocyclopentasilane **7** and 295 mg (1 equiv., 0.30 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** were evacuated in different Schlenk tubes for 1 h and then dissolved each in benzene-d₆ (0.5 mL). The solution of silane **7** was added to the solution of the trityl salt via a Teflon tube and the biphasic reaction mixture was stirred at r.t. for 0.5 h. The phases were

allowed to separate. The upper phase was decanted off and the lower phase was transferred into an NMR tube. The NMR spectra were recorded at T = 32 °C.

8: ^1H NMR (499.87 MHz, 305.0 K, C_6D_6) δ : 1.01 (m, 1H, $^1J_{\text{Si,H}} = 46$ Hz, Si-H-Si), 0.38 (s, 6H; $(\text{H}_3\text{C})\text{MeSi}^{6,7}$), 0.33 (s, 6H; $\text{Me}(\text{H}_3\text{C})\text{Si}^{6,7}$), 0.25 (s, 3H, $\text{Si}^5(\text{CH}_3)_2$), 0.23 (s, 3H, $\text{Si}^5(\text{CH}_3)_2$), 0.13 (s, 6H, $\text{Si}^{2,3}\text{Me}(\text{CH}_3)$), 0.12 (s, 6H, $\text{Si}^{2,3}(\text{CH}_3)\text{Me}$), 0.11 (s, 18H, $\text{Si}(\text{CH}_3)_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 305.0 K, C_6D_6) δ : 95.5 ($\text{Si}^{6,7}$), -4.6 (2 x SiMe_3), -14.9 (Si^5), -31.2 ($\text{Si}^{2,3}$), -126.3 ($\text{Si}^{1,4}$). ^{29}Si INEPT NMR (99.31 MHz, 305.0 K, C_6D_6) δ : 95.5 (dsept, $^1J_{\text{Si,H}} = 46$ Hz, $^2J_{\text{Si,H}} = 6$ Hz, $\text{Si}^{6,7}$), -4.6 (m, 2 x SiMe_3), -14.9 (sept, $^2J_{\text{Si,H}} = 6$ Hz, Si^5), -31.2 (m, $\text{Si}^{2,3}$), -126.3 (s, $\text{Si}^{1,4}$).

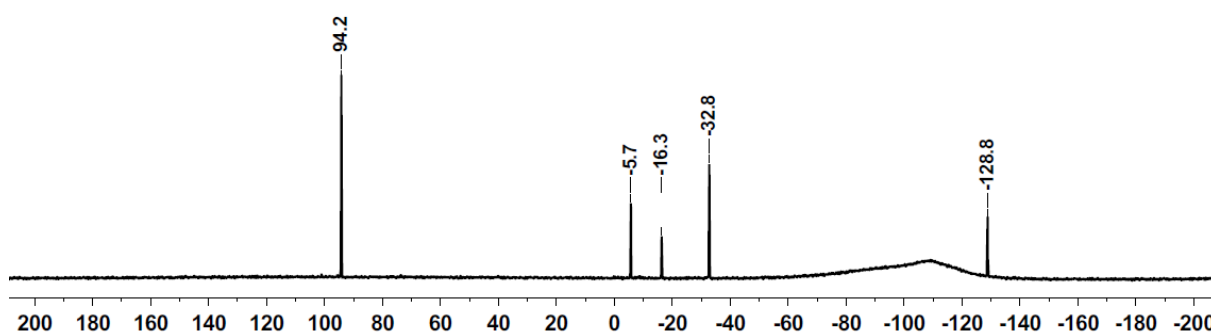


Figure S1: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of borate **8** $[\text{B}(\text{C}_6\text{F}_5)_4]$ (99.31 MHz, 253 K, $\text{C}_6\text{H}_5\text{Cl}$, acetone- d_6 lock, $\delta^{29}\text{Si} = 250.0 - -250.0$; line broadening factor, lb: 2.0)

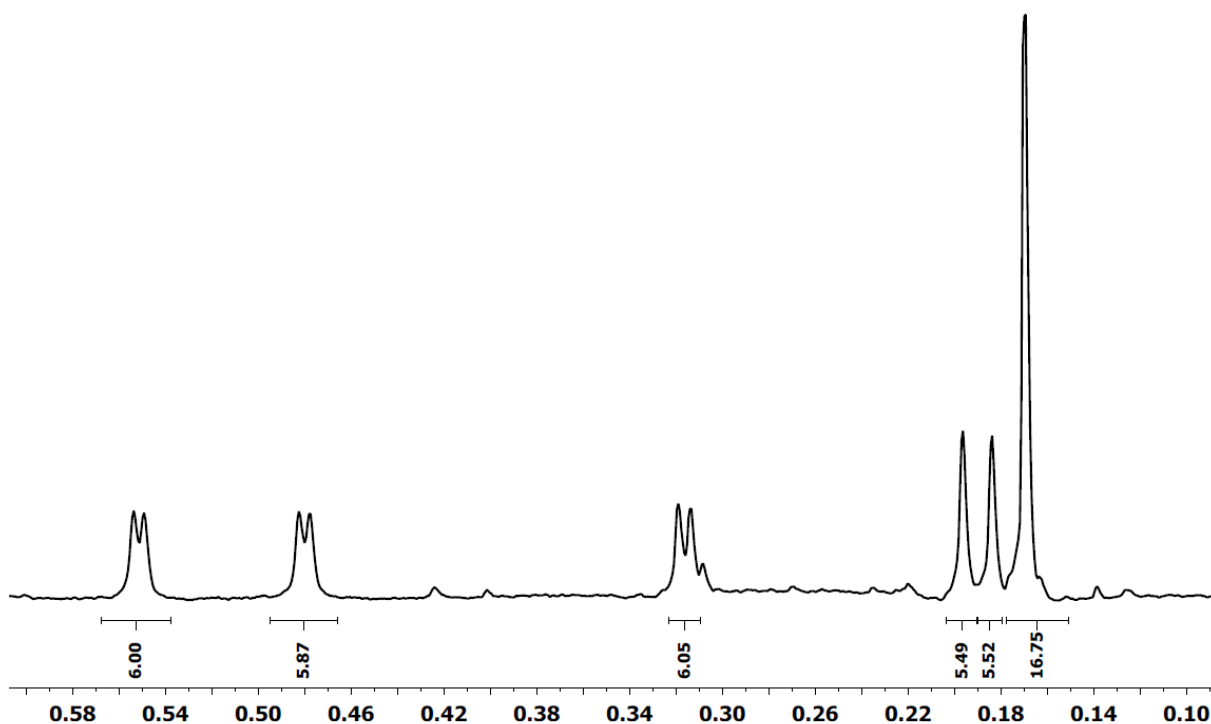


Figure S2: Part of the ^1H NMR spectrum of borate **8** $[\text{B}(\text{C}_6\text{F}_5)_4]$ (500 MHz 253 K, $\text{C}_6\text{H}_5\text{Cl}$, acetone- d_6 lock, $\delta^1\text{H} = 0.6 - 0.1$, lb -0.6; gb 0.7).

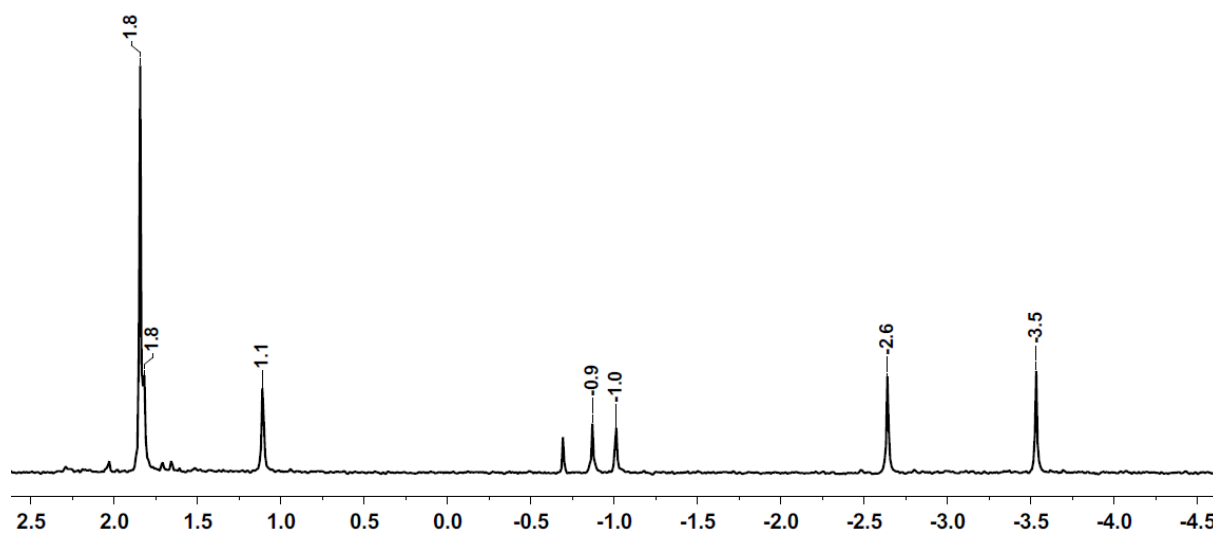


Figure S3: Part of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of borate $\mathbf{8}[\text{B}(\text{C}_6\text{F}_5)_4]$ (125.71 MHz, 253 K, $\text{C}_6\text{H}_5\text{Cl}$, acetone- d_6 lock, $\delta^{13}\text{C} = 2.5 - -4.5$, lb: 0.5; gaussian function, gf: 0.7)

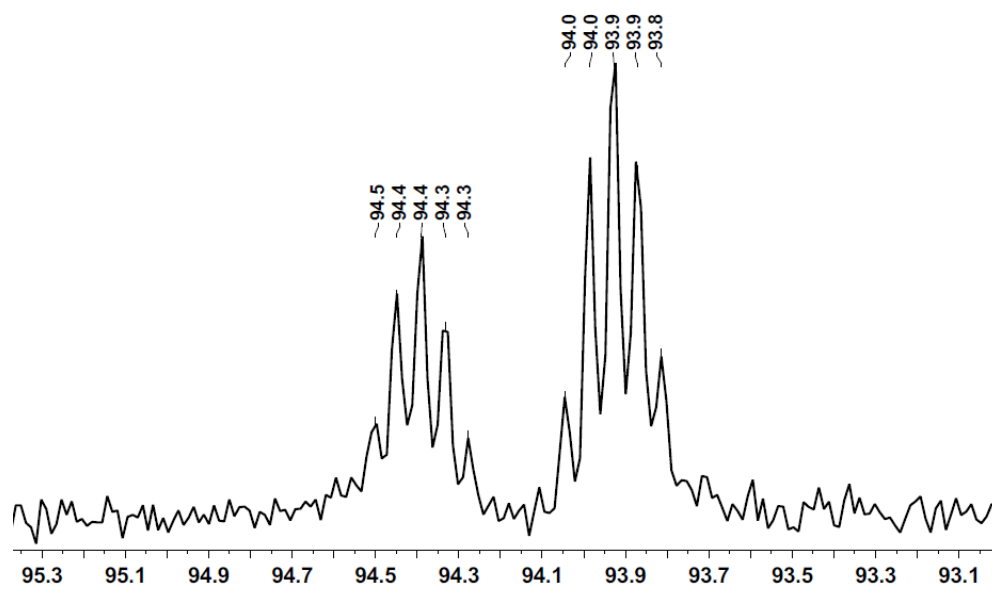


Figure S4: Part of the ^{29}Si INEPT NMR spectrum of borate $\mathbf{8}[\text{B}(\text{C}_6\text{F}_5)_4]$: (99.31 MHz, 253 K, $\text{C}_6\text{H}_5\text{Cl}$, acetone- d_6 lock, $\delta^{29}\text{Si} = 96.3 - 93.1$; lb: -0.2; gf: 0.1)

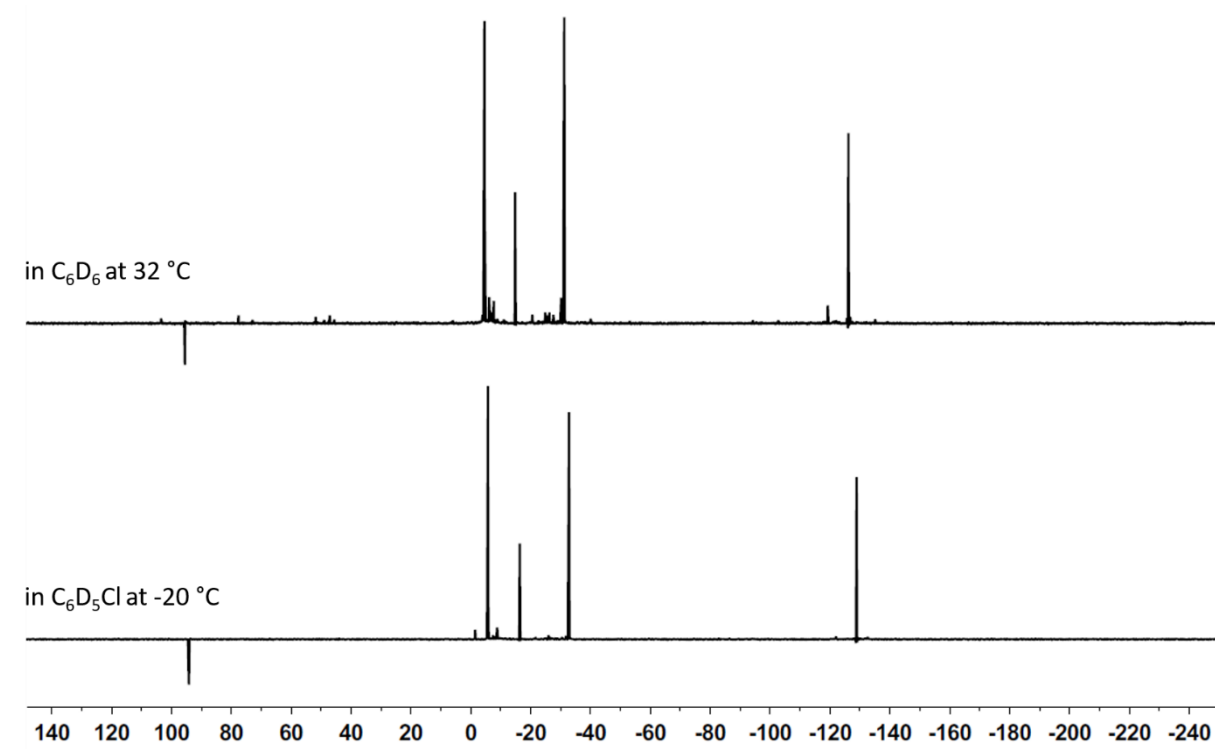
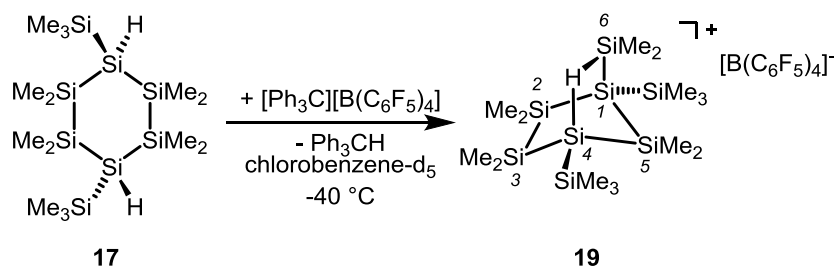


Figure S5: Comparison of the $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectra (99.31 MHz) of borate $\mathbf{8}[\text{B}(\text{C}_6\text{F}_5)_4]$: prepared in C_6D_6 at r.t. and measured at 32 °C. Lower trace: prepared and measured in $\text{C}_6\text{H}_5\text{Cl}$ at -20 °C (acetone- d_6 lock).

Synthesis of hydrogen-bridged bissilyl borate **19**[B(C₆F₅)₄]⁻ from 1,4-dihydridocyclohexasilane **17**



92 mg (1 equiv., 0.10 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** was evacuated in the NMR tube and cooled to $T = -80$ °C. A solution of 44 mg (1 equiv., 0.10 mmol) of 1,4-dihydridocyclohexasilane **17** in chlorobenzene- d_5 (0.7 mL) was added to the cold trityl borate via a syringe. The addition was performed so slowly that the solution froze before it reached the trityl borate. The NMR tube was slowly allowed to warm until the solvent melted and the silane **17** slowly reached the trityl borate **9**. At that point, the NMR tube, which was wrapped in a gauze bandage soaked by $T = -70$ °C cold ethanol, was quickly shaken with a vortex mixer and then quickly transferred to the NMR spectrometer pre-cooled to $T = -40$ °C.

19: ^1H NMR (499.87 MHz, 233.0 K, $\text{C}_6\text{D}_5\text{Cl}$) δ : 0.62 ($\text{Si}^6(\text{CH}_3)_2$), 0.50 ($\text{Si}^3(\text{CH}_3)_2$), 0.32 ($\text{Si}^5(\text{CH}_3)_2$), 0.23 ($\text{Si}^2(\text{CH}_3)_2$), 0.20 ($\text{Si}^4\text{-Si}(\text{CH}_3)_3$), 0.17 ($\text{Si}^1\text{-Si}(\text{CH}_3)_3$), -1.07 (br, Si-H-Si, $^1J_{\text{Si,H}} = 40$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, 233.0 K, $\text{C}_6\text{D}_5\text{Cl}$) δ : 1.8 (SiMe_3), 0.2 (SiMe_3), -0.9 (SiMe_2), -1.6 (SiMe_2), -2.4 (SiMe_2), -2.5 (SiMe_2), -2.7 (SiMe_2), -3.4 (SiMe_2), -5.0 (SiMe_2). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 233 K, $\text{C}_6\text{D}_5\text{Cl}$) δ : 78.1 (Si^6), 64.1 (Si^4), -0.7 ($\text{Si}^4\text{-SiMe}_3$), -4.2 ($\text{Si}^1\text{-SiMe}_3$), -33.0 (Si^3), -33.4 (Si^5), -35.3 (Si^2), -107.5 (Si^1). ^{29}Si INEPT NMR (99.31 MHz, 233 K, $\text{C}_6\text{D}_5\text{Cl}$) δ : 78.1 (dsept, $^1J_{\text{Si,H}} = 39$ Hz, $^3J_{\text{Si,H}} = 5$ Hz, Si^6), 64.1 (d, $^1J_{\text{Si,H}} = 43$ Hz, Si^4), -0.7 (oct, $^3J_{\text{Si,H}} = 7$ Hz, ($\text{Si}^4\text{-SiMe}_3$)), -4.2 (m, $\text{Si}^1\text{-SiMe}_3$), -33.0 (m, Si^3), -33.4 (m, Si^5), -35.3 (m, Si^2), -107.5 (m, Si^1).

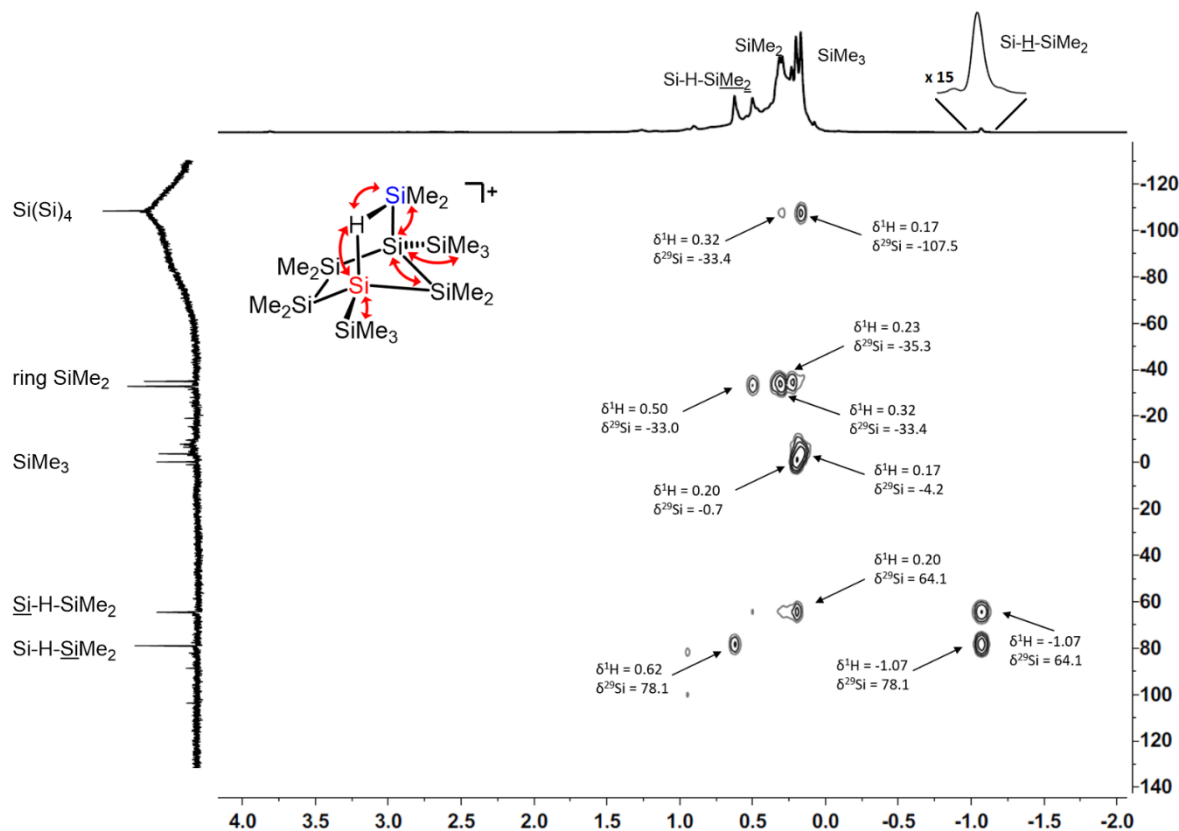
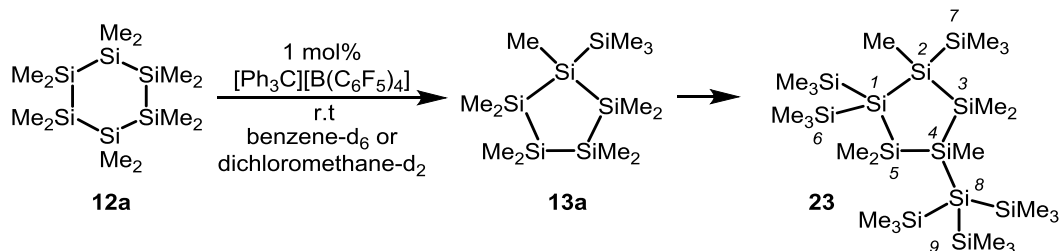


Figure S6: $^1\text{H}/^{29}\text{Si}$ HMQC NMR spectrum (499.87/99.31 MHz, 233 K, $\text{C}_6\text{D}_5\text{Cl}$, $^1J(\text{SiH}) = 41$ Hz) of borate **19** $[\text{B}(\text{C}_6\text{F}_5)_4]$.

Catalytic rearrangement of cyclohexasilane **12a** to cyclopentasilanes **13a** and **23**



Two preparations were performed simultaneously which contained 5 mg (0.01 equiv., 5 μmol) of trityl tetrakis(pentafluorophenyl)borate **9** and 0.175 g (1 equiv., 0.50 mmol) of cyclohexasilane **12a**. Both starting materials were evacuated together in a Schlenk tube for 1 h and dichloromethane- d_2 (2 mL) was added into one tube and benzene- d_6 (2 mL) into the second tube. The mixtures were stirred overnight at room temperature and the progress of the reactions was monitored by ^{29}Si NMR spectroscopy. The reaction products were identified by comparison the ^{29}Si NMR chemical shifts with literature data.

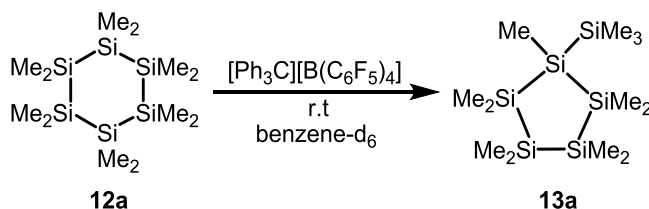
Cyclopentasilane **13a**¹⁰

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 305.0 K, C_6D_6) δ : -83.5 (Si_4Si), -41.2 ($\text{Si}(\text{CH}_3)_2$), -36.4 ($\text{Si}(\text{CH}_3)_2$), -10.5 ($\text{Si}(\text{CH}_3)_3$).

Cyclopentasilane **23**¹¹

²⁹Si{¹H} NMR (99.31 MHz, 305.0 K, C₆D₆) δ: -128.5 (Si⁸), -127.3 (Si¹), -74.7 (Si⁴), -72.0 (Si¹) (Si²), -24.0 (Si³), -22.0 (Si⁵), -9.6 (Si^{6/7/9}), -8.7 (Si^{6/7/9}), -8.0 (Si^{6/7/9}).

Rearrangement of cyclohexasilane **12a** to cyclopentasilane **13a**



37 mg (1 equiv., 0.4 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** and 0.139 g (1 equiv., 0.40 mmol) of cyclohexasilane **12a** were evacuated together in a Schlenk tube for 1 h and benzene-d₆ (2 mL) was added. The mixture was stirred for 1 h at room temperature and the progress of the reaction was monitored by ²⁹Si NMR spectroscopy. The non-polar phase contained the rearrangement product **13a** and starting material **12a** as identified by comparison the ²⁹Si NMR chemical shifts with literature data.

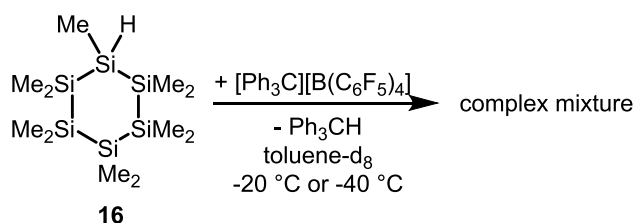
Cyclopentasilane **13a**¹⁰

²⁹Si{¹H} NMR (99.31 MHz, 305.0 K, C₆D₆) δ: -83.3 (Si₄Si), -41.1 (Si(CH₃)₂), -36.3 (Si(CH₃)₂), -10.4 (Si(CH₃)₃).

Dodecamethylcyclohexasilane **12a**¹⁰

²⁹Si{¹H} NMR (99.31 MHz, 305.0 K, C₆D₆) δ: -42.2 (Si(CH₃)₂).

Hydride abstraction from hydridocyclohexasilane **16**

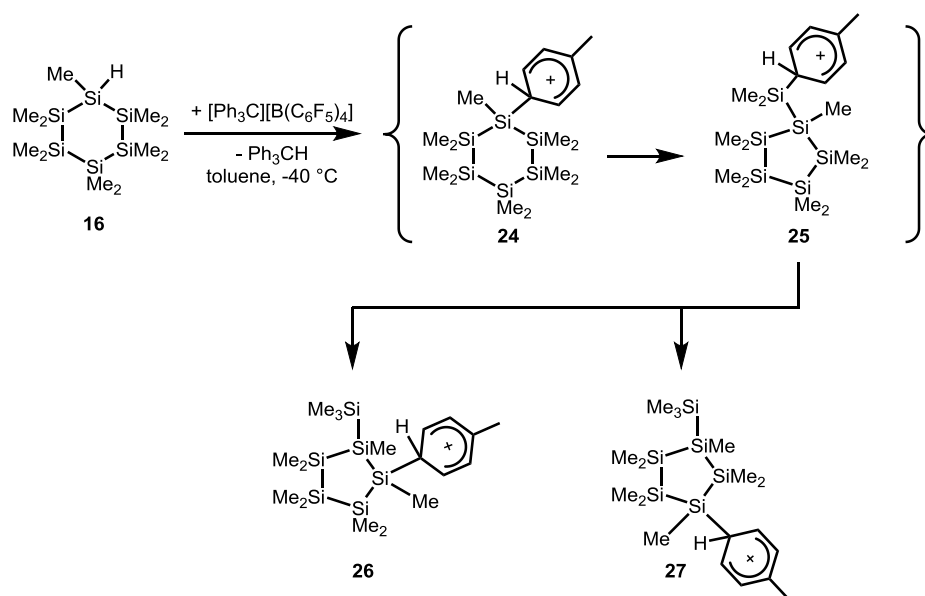


For the reaction at $T = -20\text{ }^{\circ}\text{C}$, 0.369 g (1 equiv., 0.40 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** and 0.134 g (1 equiv., 0.40 mmol) of hydridocyclohexasilane **16** were both dissolved in toluene- d_8 (0.5 mL) in separate Schlenk flasks and cooled to $T = -20\text{ }^{\circ}\text{C}$. Hydridocyclohexasilane **16** was slowly added to the borate salt via a Teflon tube and the mixture was stirred at $T = -20\text{ }^{\circ}\text{C}$ for 2 h. The polar and non-polar phase were each transferred to separate NMR tubes at $T = -20\text{ }^{\circ}\text{C}$ and the NMR spectra were recorded.

For the reaction at $T = -40\text{ }^{\circ}\text{C}$, 0.369 g (1 equiv., 0.40 mmol) of trityl tetrakis(pentafluorophenyl)borate **9** was evacuated in the NMR tube and dissolved in toluene- d_8 (0.5 mL). The hydridocyclohexasilane **16** was evacuated in a Schlenk tube and also dissolved in toluene- d_8 (0.5 mL). The trityl borate **9** containing NMR tube was cooled to $T = -40\text{ }^{\circ}\text{C}$ and the silane **16** was added slowly. The sample was quickly shaken with a vortex mixer and the NMR spectra were acquired immediately at $T = -40\text{ }^{\circ}\text{C}$.

Main signals and possible assignments

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 233.0 K, C_7D_8) δ : -88.6 (Si $_4$ Si), -42.9 (Si(CH $_3$) $_2$), -35.2, -24.7 (Si(CH $_3$) $_2$), -7.3 (Si(CH $_3$) $_3$), 68.3 (Si(C $_7\text{D}_8$) $^+$).



Scheme S1. Ionization of hydridocyclohexasilane **16** with trityl cation and possible rearrangement reactions of their toluene complexes.

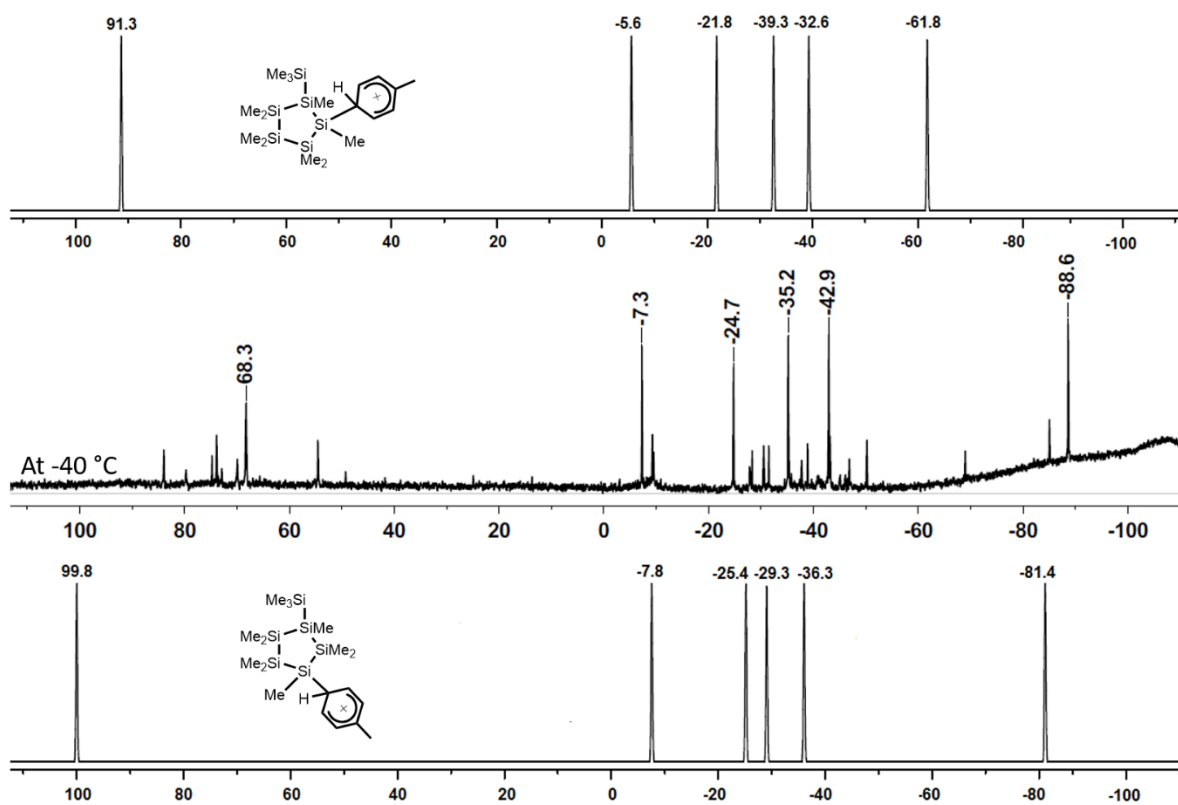


Figure S7. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (middle trace) at -40°C of the reaction mixture of cyclohexasilane **16** with trityl tetrakis(pentafluorophenyl)borate **9** in toluene. The upper and lower trace show the computed ^{29}Si NMR spectra of possible rearrangement products (at M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p)).

Computational Details

All quantum chemical calculations were carried out using the Gaussian09 package.¹² The molecular structure optimizations were performed using the M06-2X functional¹³ along with the 6-311+G(d,p) basis set. Every stationary point was identified by a subsequent frequency calculation either as minimum (Number of imaginary frequencies (NIMAG): 0) or transition state (NIMAG: 1). The SCF energies, $E(\text{SCF})$, for all optimized molecular structures obtained with this method are given in Table S1. The absolute, G^{298} , and relative, $G^{298 \text{ rel}}$, computed Gibbs free energies at $T = 298.15 \text{ K}$ and $p = 0.101 \text{ MPa}$ (1 atm) in the gas phase, are also given in Table S1. Intrinsic reaction coordinate (IRC) calculations^{14, 15} were used to connect transition state structures with the appropriate molecular structures of intermediates. The corresponding computed molecular structures are given in the xyz-files and are ordered by the reaction scheme numbers. NMR chemical shift computations were performed using the GIAO method as implemented in Gaussian 09 and the M06-L functional along with the 6-311G(2d,p) basis set for molecular structures obtained at the M06-2X/6-311+G(d,p) level of theory.¹⁶ Simulated ^{29}Si NMR spectra were obtained by plotting the calculated ^{29}Si NMR calculated shifts with the NMR simulation program gNMR, at revision level 5.1, marketed by Adept Scientific until May 2005.

Table S1. Absolute and relative energies (E and E^{rel}) and free Gibbs enthalpies (G²⁹⁸ and G^{298 rel}) for compounds of interest (at M06-2X/6-311+G(d,p)).

Compound	E [a.u.]	E ^{rel} [kJ mol ⁻¹]	NIMAG, v [cm ⁻¹] ZPVE [kJ mol ⁻¹]	G ²⁹⁸ [a.u.]	G ^{298 rel} [kJ mol ⁻¹]
8	-3244.40221	-67	0, 1610	-3243.87000	-61
6	-3244.37664	0	0, 1608	-3243.84686	0
TS6/10a	-3244.36699	+25	1, -95, 1678	-3243.83649	+27
10a	-3244.38017	-9	0, 1611	-3243.84799	-3
TS10a/10b	-3244.36515	+30	1, -115, 1609	-3243.83294	+37
10b	-3244.39159	-39	0, 1613	-3243.85767	-28
TS10b/10c	-3244.38072	-11	1, 23, 1608	-3243.85064	-10
10c	-3244.38153	-13	0, 1610	-3243.85121	-11
TS10c/10d	-3244.36644	+27	1, -106, 1613	-3243.83228	+38
10d	-3244.37937	-7	0, 1612	-3243.84516	+5
TS10d/10e	-3244.36401	+33	1, -100, 1613	-3243.82871	+48
10e	-3244.37278	+10	0, 1606	-3243.84462	+6
20	-2875.04286	0	0, 1413	-2874.57873	0
21	-2875.04872	-15.4	0, 1412	-2874.58720	-22.2
18	-2875.06263	-51.9	0, 1414	-2874.60029	-56.6
19	-2875.06937	-69.6	0, 1413	-2874.60699	-74.2
7	-3245.22208		0, 1630	-3244.68367	
Me₂SiH₂	-370.48787		0, 239	-370.42438	
Me₂Si⁺-H	-369.58870		0, 212	-369.53614	

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