Supporting Information

for

Dispersion-Energy-Driven Wagner-Meerwein Rearrangements in Oligosilanes

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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 °C and evacuated prior to use. The solvents tetrahydrofuran (THF), benzene and toluene were dried over sodium and distilled under a nitrogen atmosphere. Chlorobenzene, o-dichlorobenzene and dichloromethane were dried over CaCl₂ and stored over molecular sieves (4 Å). Benzene-d₆ and toluene-d₈ were stored over molecular sieves (4 Å) after drying over sodium. Chlorobenzene-d₅ and dichloromethane-d₂ were dried over molecular sieves (4 Å). Triphenylmethyl tetrakis(pentafluorophenyl) borate ([Ph₃C][B(C₆F₅)₄]) was prepared according to a modified literature procedure.⁸ Tris(trimethylsilyl)silylpotassium,⁴ tris(trimethylsilyl)germylpotassium,⁷ 2,2,2,5,5-tetakis(trimethylsilyl)decamethylhexasilane ⁶,¹⁷ 2,5-dihydrido-2,5-bis(trimethylsilyl)-decamethylhexasilane ⁵ and 2,2,2,5,5-tetakis(trimethylsilyl)decamethyl-2,5-digermahexasilane ¹⁹ were prepared according to literature procedures. NMR spectra were recorded on Bruker Avance 500 and Bruker Avance III 500 spectrometers.¹¹ H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (benzene-d₆: δ¹H(C₆D₆H) = 7.20, toluene-d₈: δ¹H(CD₂H) = 2.08, dichloromethane-d₂: δ¹H(CDHCl₂) = 5.32, chlorobenzene-d₅: δ¹H(C₆D₅HCl) = 7.14, water-d₂: δ¹H(DHO) = 4.79).¹¹ H NMR spectra of polysilanyl borates in chlorobenzene were calibrated versus triphenylmethane as internal standard δ¹H(Ph₃CH) = 5.45).¹³ C NMR spectra were calibrated by using the central line of the solvent signal (benzene-d₆: δ¹³C(C₆D₆) = 128.0, toluene-d₈: δ¹³C(CD₂) = 20.4, dichloromethane-d₂: δ¹³C(CDHCl₂) = 53.8, chlorobenzene-d₅: δ¹³C(C₆D₅Cl) = 134.2).²⁹Si{¹H} NMR spectra were calibrated against an external standard (δ²⁹Si(Me₂SiHCl) = 11.1 versus tetramethylsilane (TMS)). The²⁹Si{¹H} NMR inverse gated spectra were recorded with a relaxation delay D₁ = 10 s. Based on our experiences, at temperatures T = -20 °C to -80 °C, this delay is long enough to allow a reliable integration of the peaks. The²⁹Si{¹H} INEPT spectra were recorded with delays D₃ = 0.0084 s and D₄ = 0.0313 s for compounds ⁹, ¹⁰ and ²⁰ and D₃ = D₄ = 0.0056 s for cations ⁸ and ¹¹. 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**

### 2,2,5,5'-Tetakis(trimethylsilyl)-decamethylhexasilane 17

![Chemical Structure of 2,2,5,5'-Tetakis(trimethylsilyl)-decamethylhexasilane](structure17.png)

A solution of 1.03 g (1 equiv., 5.50 mmol) of 1,2-dichlorotetramethylsilane in toluene (10 mL) at \( T = -78 \, ^\circ\text{C} \) was added to a solution of 11.00 mmol (2 equiv.) of tris(trimethylsilyl)silylpotassium in toluene (20 mL) within 30 min. After stirring overnight at room temperature, the mixture was subjected to aqueous workup (dilute sulfuric acid, extraction with ether, drying over sodium sulfate). After removal of the solvent the title compound, 17, was obtained as colorless wax (3.18 g, 5.20 mmol, 95%).

\(^1\)H NMR (499.87 MHz, 305.0 K, CDCl\(_3\), \( \delta \) ppm): 0.22 (s, 54 H, Si(CH\(_3\))\(_3\)), 0.36 (s, 12 H, Si(CH\(_3\))\(_2\)). \(^{13}\)C{\(^1\)H} NMR (125.71 MHz, 305.0 K, CDCl\(_3\), \( \delta \) ppm): 1.2 (Si(CH\(_3\))\(_2\)), 3.5 (Si(CH\(_3\))\(_3\)). \(^{29}\)Si{\(^1\)H} NMR (99.31 MHz, 305.0 K, CDCl\(_3\), \( \delta \) ppm): -127.7 (Si\(_4\)Si), -29.8 (Si(CH\(_3\))\(_3\)), -9.5 (Si(CH\(_3\))\(_3\)).

### 2,5-Dihydrido-2,5-bis(trimethylsilyl)-decamethylhexasilane 5

![Chemical Structure of 2,5-Dihydrido-2,5-bis(trimethylsilyl)-decamethylhexasilane](structure5.png)

A solution of 0.27 g (2.2 equiv., 2.20 mmol) of potassium tert-butoxide and 0.53 g (2 equiv., 2.00 mmol) of 18-crown-6 ether in benzene (10 mL) was added to a solution of 0.61 g (1 equiv., 1.00 mmol) of tetrasilane 17 in benzene (10 mL) at room temperature. The reaction mixture immediately turned yellow and was stirred overnight. The formation of the dianion 18 was confirmed by \(^{29}\)Si{\(^1\)H} NMR spectroscopy. Then the solution of dipotassiumhexasilane-2,5-diide · 2 18-crown-6 18 was hydrolyzed by adding it to a mixture of ice, 1M sulfuric acid (25 mL) and diethyl ether (15 mL). The two phases were separated and the aqueous phase washed two times with pentane (10 mL). The combined organic phases were dried over Na\(_2\)SO\(_4\). The Na\(_2\)SO\(_4\) was removed by
filtration and the solvent was evacuated under reduced pressure. After recrystallisation from acetone, the product 5 was obtained as colorless solid (0.39 g, 0.84 mmol, 84 %).

**Dipotassium-2,5-bis(trimethylsilyl)decamethylhexasilane-2,5-diide - 2 18-crown-6 18[4]**

$^1$H NMR (499.87 MHz, 305.1 K, C₆H₆, D₂O-lock δ ppm): 0.81 (s, 36 H, Si(CH₃)₃), 0.92 (s, 12 H Si(CH₃)₂), 3.43 (s, 48 H, CH₂O). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C₆H₆, D₂O-lock, δ ppm): 5.0 (Si(CH₃)₃), 8.4 (Si(CH₃)₂), 69.7 (CH₂O). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C₆H₆, D₂O-lock, δ ppm): -189.6 (SiK), -24.5 (Si(CH₃)₂), -3.8 (Si(CH₃)₃).

**2,5-Dihydrido-2,5-bis(trimethylsilyl)-decamethylhexasilane 5[6]**

$^1$H NMR (499.87 MHz, 305.1 K, C₆D₆, δ ppm): 0.34 (s, 36 H, Si(CH₃)₃), 0.49 (s, 12 H, Si(CH₃)₂), 2.74 (s, 2 H, $^1$J_Si,H = 155 Hz, SiH). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C₆D₆, δ ppm): -1.3 (Si(CH₃)₃), 2.4 (Si(CH₃)₂). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C₆D₆, δ ppm): -116.2 (SiH), -36.4 (Si(CH₃)₂), -11.2 (Si(CH₃)₃). IR: $\tilde{\nu}_{Si-H}$ 2085 cm⁻¹ (ATR, neat).

**2,2,5,5-Tetrais(trimethylsilyl)decamethyl-2,5-digermahexasilane 19[7]**

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{Me}_3\text{Si} \\
\text{Me}_3\text{Si} & \quad \text{Me}_3\text{Si}
\end{align*}
\]

\[
\begin{align*}
\text{Me}_3\text{Si} - \text{Ge} - \text{K} + \text{Cl} - \text{SiMe}_2 - \text{SiMe}_2 - \text{Cl} & \quad \text{toluene} \\
 & \quad -78 \degree \text{C} \\
 & \quad \text{r.t.}
\end{align*}
\]

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{Me}_3\text{Si} \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3
\end{align*}
\]

A solution of 0.69 g (1 equiv., 3.70 mmol) of 1,2-dichlorotetramethyldisilane in toluene (10 mL) at T = -78 °C was added to a solution of 7.40 mmol (2 equiv.) of tris(trimethylsilyl)germylpotassium in toluene (20 mL) within 30 min. After stirring overnight at room temperature, the mixture was subjected to aqueous workup (dilute sulfuric acid, extraction with ether, drying over sodium sulfate). After removal of the solvent, the product 19 was obtained as colorless wax (2.03 g, 2.90 mmol, 78 %).

$^1$H NMR (499.87 MHz, 305.0 K, C₆D₆, δ ppm): 0.41 (s, 54 H, Si(CH₃)₃), 0.62 (s, 12 H, Si(CH₃)₂). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, CDCl₃, δ ppm): 2.2 (Si(CH₃)₂), 4.3 (Si(CH₃)₃). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, CDCl₃, δ ppm): -24.3 (Si(CH₃)₂), -5.0 (Si(CH₃)₃).
2,5-Dihydrido-2,5-bis(trimethylsilyl)decamethyl-2,5-digermahexasilane 10

A solution of 0.35 g (2.2 equiv., 3.14 mmol) of potassium tert-butoxide in degassed THF (10 mL) was added to a solution of 1.00 g (1 equiv., 1.43 mmol) of 2,5-digermahexasilane 19 in degassed THF (10 mL) at room temperature. The reaction mixture immediately turned yellow and was stirred overnight. The completeness of the reaction was confirmed by $^{29}$Si($^1$H) NMR spectroscopy. Then the solution of 20 was hydrolyzed by adding it to a cooled ($T = 0 ^\circ C$) mixture of degassed aqueous NH$_4$Cl-solution (1 M, 30 mL) and degassed diethyl ether (30 mL). The organic phases was decanted and the aqueous phase was extracted three times with degassed diethyl ether (5 mL). The combined organic phases were dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure and the product 10 was obtained as colorless wax (0.48 g, 0.86 mmol, 61 %). The product is sensitive to temperature and oxygen and was stored under argon atmosphere at $T = -20 ^\circ C$.

Dipotassium-2,5-bis(trimethylsilyl)decamethyl-2,5-digermahexasilane-2,5-diide 20

$^1$H NMR (499.87 MHz, 305.1 K, THF, D$_2$O-lock, $\delta$ ppm): 0.47 (s, 36 H, Si(CH$_3$)$_3$), 0.59 (s, 12 H Si(CH$_3$)$_2$). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, THF, D$_2$O-lock, $\delta$ ppm): 3.2 (Si(CH$_3$)$_3$), 4.5 (Si(CH$_3$)$_2$). $^{29}$Si($^1$H) INEPT NMR (99.31 MHz, 305.0 K, THF, D$_2$O-lock, $\delta$ ppm): -24.3 (Si(CH$_3$)$_2$), -3.2 (Si(CH$_3$)$_3$).

Figure S1: $^{29}$Si($^1$H) INEPT NMR spectrum (99 MHz, THF, D$_2$O-lock, 305 K) of dipotassium-digermahexasilane 20 (*$^t$BuOSiMe$_3$).
2,5-Dihydrido-2,5-bis(trimethylsilyl)-decamethyl-2,5-digermahexasilane 10

$^1$H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$, δ ppm): 0.38 (s, 36 H, Si(CH$_3$)$_3$), 0.54 (s, 12 H Si(CH$_3$)$_2$), 2.36 (s, 2 H, GeH). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$, δ ppm): -0.5 (Si(CH$_3$)$_3$), 3.1 (Si(CH$_3$)$_2$). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_6$D$_6$, δ ppm): -29.3 (Si(CH$_3$)$_3$), -5.5 (Si(CH$_3$)$_2$). HR/MS (m/z) found/calcd. for C$_{16}$H$_{50}$Ge$_2$Si$_6$: 558.0965/558.0946. IR $\tilde{\nu}_{Si-H}$ 1945 cm$^{-1}$ (ATR, neat). No satisfactory combustion analysis was obtained due to small amounts of by-products, which are visible in the $^1$H NMR spectrum. Anal. found/calcd. for C$_{16}$H$_{50}$Ge$_2$Si$_6$: C 37.12/34.54, H 8.99/9.06.

Figure S2: $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 305 K) of dihydridodigermahexasilane 10 (* C$_6$D$_5$H).

Figure S3: $^{13}$C($^1$H) NMR spectrum (126 MHz, C$_6$D$_6$, 305 K) of dihydridodigermahexasilane 10 (* C$_6$D$_5$).

Figure S4: $^{29}$Si($^1$H) INEPT NMR spectrum (99 MHz, C$_6$D$_6$, 305 K) of dihydridodigermahexasilane 10.
Cation Preparation

For the preparation of polysilanyl cations trityl tetrakis(pentafluorophenyl)borate was used. The NMR characterization data for the anion are given below and not repeated for each 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.

\[
[B(C_6F_5)_4^{-}]:
\]

\[^{13}C\{^1H\} \text{NMR (125.71 MHz, 243.1 K, C}_6D_5Cl\} \delta: 148.9 \text{ (d, } J_{CF} = 238.9 \text{ Hz, CF}^{\text{ortho}}, [B(C_6F_5)_4]) \text{, 138.8 (d,} J_{CF} = 235.4 \text{ Hz, CF}^{\text{para}}, [B(C_6F_5)_4]) \text{, 136.9 (d, } J_{CF} = 232.7 \text{ Hz, CF}^{\text{meta}}, [B(C_6F_5)_4]) \text{, 123.7-125.6 (m, CF}^{\text{ipso}}, [B(C_6F_5)_4]) \text{).}
\]

\[^{19}F\{^1H\} \text{NMR (470.28 MHz, 243.1 K, C}_6D_5Cl\} \delta: -131.9 \text{ (brs, } 2 \text{ F, CF}^{\text{ortho}}, [B(C_6F_5)_4]), -161.9 \text{ (brs, } 1 \text{ F, CF}^{\text{para}}, [B(C_6F_5)_4]), -165.8 \text{ (brs, } 2 \text{ F, CF}^{\text{meta}}, [B(C_6F_5)_4]); ^{11}B\{^1H\} \text{ (160.38 MHz, 243.1 K, C}_6D_5Cl\} \delta: -16.8 ([B(C_6F_5)_4]).
\]

**Synthesis of hydrogen-bridged silyl borate \([B(C_6F_5)_4]^+\) from 2,5-dihydridohexasilane \(5\)**

92 mg (1 equiv., 0.10 mmol) of trityl tetrakis(pentafluorophenyl)borate was evacuated in the NMR tube and then cooled to \(T = -80 \text{ } ^\circ\text{C}\). A solution of 47 mg (1 equiv., 0.10 mmol) of 2,5-dihydridohexasilane \(5^{[6]}\) 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 slowly reached the trityl borate. At that point, the NMR tube, which was wrapped in a gauze bandage soaked by \(T = -70 \text{ } ^\circ\text{C}\) cold ethanol, was quickly shaken with a vortex mixer and then quickly transferred to the NMR spectrometer pre-cooled to \(T = -30 \text{ } ^\circ\text{C}\).

**Cation \(8\)**

\[^{1H} \text{NMR (499.87 MHz, 243.1 K, C}_6D_5Cl, \delta \text{ ppm): 0.21 (s, 36 H, Si}^3(\text{CH}_3), 0.67 (s, 12 H, Si}^1(\text{CH}_3), 2.15 (\text{brs, } 1 \text{H, } J_{\text{Si,H}} = 43 \text{ Hz, Si-H-Si}). \]

\[^{13}C\{^1H\} \text{NMR (125.71 MHz, 243.1 K, C}_6D_5Cl, \delta \text{ ppm): 3.3 (Si}^3(\text{CH}_3)), 2.9 (\text{Si}^2(\text{CH}_3)). \]

\[^{29}Si\{^1H\} \text{NMR (99.31 MHz, 243.1 K, C}_6D_5Cl, \delta \text{ ppm): -120.9 (Si}^3), -6.4 (Si}^3), 108.9 (Si}^3). \]

\[^{29}Si \text{ INEPT NMR (99.31 MHz, 243.1 K, C}_6D_5Cl, \delta \text{ ppm): -120.9 (\text{brs, Si}^3), -6.4 (\text{decet, } J_{\text{Si,H}} = 6 \text{ Hz, Si}^3), 108.9 (\text{dsept, } J_{\text{Si,H}} = 43 \text{ Hz, } J_{\text{Si,H}} = 5 \text{ Hz, Si}^3).} \]
**Figure S5**: $^1$H NMR spectrum (500 MHz, C$_6$D$_5$Cl, 243 K) of hydrogen-bridged silyl borate $8[B(C_6F_5)_4]$ (*C$_6$D$_4$HCl, #Ph$_3$CH).

**Figure S6**: $^{13}$C($^1$H) NMR spectrum (126 MHz, C$_6$D$_5$Cl, 243 K) of hydrogen-bridged silyl borate $8[B(C_6F_5)_4]$ (*C$_6$D$_4$HCl, #Ph$_3$CH, o [B(C$_6$F$_5$)$_4$]).

**Figure S7**: $^{29}$Si($^1$H) NMR spectrum (99 MHz, C$_6$D$_5$Cl, 243 K) of hydrogen-bridged silyl borate $8[B(C_6F_5)_4]$.
Trapping reaction of hydrogen-bridged silyl cation \(8\)\(^{[8]}\)

0.1 mL (0.10 mmol, 1 M in toluene) of sodium triethylborohydride was added to the NMR sample of bis-silyl borate \(8\)\([B(C_6F_5)_4]\) at \(T = -30 ^\circ C\). The mixture was allowed to warm to room temperature and the NMR spectra were recorded. The NMR data are identical with reported literature data.\(^{[8]}\)

\(29\)Si INEPT NMR (99.31 MHz, 305.1 K, \(C_6D_5Cl\), \(\delta\) ppm): -132.9 (Si\(_4\)Si), -30.2 (HSi(CH\(_3\))\(_2\)), -8.8 (Si(CH\(_3\))\(_3\)).

Synthesis of hydrogen-bridged silyl borate \(11\)\([B(C_6F_5)_4]\) from 2,5-dihydrido-2,5-digermahexasilane \(10\)

a) Preparation in chlorobenzene:

92 mg (1 equiv., 0.10 mmol) of trityl tetrakis(pentafluorophenyl)borate was evacuated in the NMR tube and then cooled to \(T = -80 ^\circ C\). A solution of 56 mg (1 equiv., 0.10 mmol) of 2,5-dihydrido-2,5-digermahexasilane \(10\) in chlorobenzene-\(d_5\) (0.7 mL) was added to the cold trityl borate via 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 slowly reached the trityl borate. At that point, the NMR tube, which was wrapped in a gauze bandage soaked by \(T = -70 ^\circ C\) cold ethanol, was quickly shaken with a vortex mixer and then quickly transferred to the NMR spectrometer pre-cooled at \(T = -20 ^\circ C\) or \(T = -40 ^\circ C\). (Decomposition of the cation \(11\) is indicated by the presence of additional signals in the \(29\)Si\([^1\text{H}]\) NMR spectrum.)

Cation \(11\)

\(^1\)H NMR (499.87 MHz, 232.9 K, \(C_6D_5Cl\), \(\delta\) ppm): 0.25 (s, 36 H, Si(CH\(_3\))\(_3\)), 0.71 (s, 12 H, Si(CH\(_3\))\(_2\)), 2.47 (brs, 1 H, \(^{1}J_{\text{Si,H}} = 45 Hz\), (CH\(_3\))\(_2\)Si-H-Si(CH\(_3\))\(_2\)). \(^{13}\)C\([^1\text{H}]\) NMR (125.71 MHz, 233.3 K, \(C_6D_5Cl\), \(\delta\) ppm): 4.1 ((CH\(_3\))\(_2\)Si-H-Si(CH\(_3\))\(_2\)), 3.4 (Si(CH\(_3\))\(_3\)). \(29\)Si\([^1\text{H}]\) NMR (99.31 MHz, 233.0 K, \(C_6D_5Cl\), \(\delta\) ppm): 0.5 (Si(CH\(_3\))\(_3\)), 2.0
\(117.5 \text{ (Si(CH}_3\text{)_2).} \) \(^{29}\text{Si INEPT NMR (99.31 MHz, 233.0 K, C}_6\text{D}_5\text{Cl, } \delta \text{ ppm): 0.4 (m, Si(CH}_3\text{)_3), 117.3 (dsept,} \)
\(J_{\text{Si,H}} = 45 \text{ Hz, } J_{\text{Si,H}} = 6 \text{ Hz, (CH}_3\text{)_2Si-H-Si(CH}_3\text{)_2).}\)

b) Preparation in dichloromethane:

92 mg (1 equiv., 0.10 mmol) of trityl tetrakis(pentafluorophenyl)borate was evacuated in the NMR tube, dissolved dichloromethane-d\(_2\) (0.20 mL) and then cooled to \(T = -95^\circ\text{C}.\) A solution of 56 mg (1 equiv., 0.10 mmol) of 2,5-dihydrido-2,5-digermahexasilane 10 in dichloromethane-d\(_2\) (0.3 mL) was added to the cold trityl borate via 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 slowly reached the trityl borate. At that point, the NMR tube, which was wrapped in a gauze bandage soaked by \(T = -95^\circ\text{C}\) cold ethanol, was quickly shaken with a vortex mixer. The sample as frozen in liquid nitrogen and then quickly transferred to the NMR spectrometer pre-cooled at \(T = -80^\circ\text{C}.\)

Cation 11

\(^1\text{H NMR (499.87 MHz, 182.8 K, CD}_2\text{Cl}_2, \delta \text{ ppm): 0.39 (s, 36 H, Si(CH}_3\text{)_3), 1.02 (s, 12 H, Si(CH}_3\text{)_2), 2.66 (brs, 1 H,} \)
\(J_{\text{Si,H}} = 45 \text{ Hz, (CH}_3\text{)_2Si-H-Si(CH}_3\text{)_3).} \) \(^{13}\text{C}^{1}\text{H} \text{ NMR (125.71 MHz, 193.0 K, CD}_2\text{Cl}_2, \delta \text{ ppm): 4.1 (CH}_3\text{)_2Si-H-Si(CH}_3\text{)_3), 2.8 (Si(CH}_3\text{)_3),} \)
\(^{29}\text{Si}^{1}\text{H} \text{ NMR (99.31 MHz, 233.0 K, CD}_2\text{Cl}_2, \delta \text{ ppm): 0.9 (Si(CH}_3\text{)_3), 117.7 (Si(CH}_3\text{)_2).} \) \(^{29}\text{Si INEPT NMR (99.31 MHz, 233.0 K, CD}_2\text{Cl}_2, \delta \text{ ppm): 0.9 (m, Si(CH}_3\text{)_3), 117.6 (dsept,} \)
\(J_{\text{Si,H}} = 45 \text{ Hz, } J_{\text{Si,H}} = 6 \text{ Hz, (CH}_3\text{)_2Si-H-Si(CH}_3\text{)_2).}\)

**Figure S8:** \(^1\text{H NMR spectrum (500 MHz, CD}_2\text{Cl}_2, 193 K) of hydrogen-bridged silyl borate 11[B(C}_6\text{F}_5\text{)_4] (\text{* CDHCl}_2, \# Ph}_3\text{CH).}**
Figure S9: $^{13}$C$\{^1\text{H}\}$ NMR spectrum (126 MHz, CD$_2$Cl$_2$, 193 K) of hydrogen-bridged silyl borate $^{11}$[B(C$_6$F$_5$)$_4$] (* CDHCl$_2$, # Ph$_3$CH, o [B(C$_6$F$_5$)$_4$], $\Delta$ hexane).

Figure S10: $^{29}$Si$\{^1\text{H}\}$ NMR spectrum (99 MHz, CD$_2$Cl$_2$, 193 K) of hydrogen-bridged silyl borate $^{11}$[B(C$_6$F$_5$)$_4$].
Figure S11: $^{29}\text{Si}[^1\text{H}]$ NMR spectra (99 MHz) of hydrogen-bridged silyl borate 11[B(C₆F₅)₄]. a) in C₆D₅Cl, at 253 K; b) in C₆D₅Cl, at 233 K; c) in CD₂Cl₂, at 193 K, d) simulated $^{29}\text{Si}$ NMR spectrum, calculated at M06-L/6-311G(d,p)/M06-2X/6-311+G(d,p) level of theory.
Computational Details

General

All quantum chemical calculations were carried out using the Gaussian09 package, Versions B01 and D01.\textsuperscript{[9]} The molecular structure optimizations were performed using the M06-2X functional\textsuperscript{[10]} 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). Table S1 summarizes the SCF energies, $E_{\text{SCF}}$, and the absolute Gibbs energies ($T = 298.15$ K, $p = 0.101$ MPa (1 atm)) in the gas phase, $G^{298}$, obtained with this method for all optimized molecular structures of compounds containing only Si, C and H atoms. Relative energies and Gibbs energies, $E^{\text{rel}}$ and $G^{298\text{rel}}$, are calculated using the respective quantities of cation 6 or of cation/chlorobenzene complex 6(PhCl) as fix points. Table S2 shows the SCF energies, $E_{\text{SCF}}$, relative energies, $E^{\text{rel}}$, absolute Gibbs energies, $G^{298}$, and relative Gibbs energies, $G^{298\text{rel}}$, for all optimized molecular structures of compounds containing also Ge atoms. In this case, the energies and Gibbs energies of cation 24 or cation/chlorobenzene complex 24(PhCl) are used to calculate the relative quantities. The corresponding computed molecular structures are given in the xyz-files and are ordered by the reaction scheme numbers or by the figure 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.\textsuperscript{[11]} The obtained absolute shieldings $\sigma(^{29}\text{Si})$ were transferred to the chemical shift $\delta$-scale by using the absolute shielding of tetramethylsilane calculated at the same level of theory ($\sigma(^{29}\text{Si}) = 362.2$). Simulated $^{29}\text{Si}$ NMR spectra were obtained by plotting the calculated $^{29}\text{Si}$ 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 \( E^{\text{rel}} \)) and Gibbs energies (\( G^{298} \) and \( G^{298,\text{rel}} \)) for polysilanyl cations and related compounds. The results for SCRF computations using chlorobenzene as solvent are given in italics.

| Cpd. | Density Functional [a] | E(SCF) [a.u.] | \( E^{\text{ref}} \) [kJ mol\(^{-1}\)] | NIMAG, \( \tilde{v} \) [cm\(^{-1}\)] | ZPVE [kJ mol\(^{-1}\)] | \( G^{298} \) [a.u.] | \( G^{298,\text{rel}} \) [kJ mol\(^{-1}\)] |
|------|------------------------|---------------|-------------------|-----------------|-----------------|----------------|------------------|
| 2    | M06-2X                 | -3034.34149   | 0; 1780           | -3033.74793     |                 |                 |                  |
| 3    | M06-2X                 | -3034.34949   | 0; 1785           | -3033.75012     |                 |                 |                  |
| 4    | M06-2X                 | -3034.36017   | 0; 1789           | -3033.75720     |                 |                 |                  |
| 5    | M06-2X                 | -2955.70454   | 0; 1625           | -2955.16748     |                 |                 |                  |
| 6    | M06-2X                 | -2954.86568   | 0 \( ^{b} \)       | 0; 1605         | -2954.33555     | 0 \( ^{b} \)   |                  |
| 6(PhCl) | M06-2X               | -3646.68975   | 0 \( ^{c} \)       | 0; 1852         | -3646.07429     | 0 \( ^{c} \)   |                  |
| 7    | M06-2X                 | -2954.88640   | -54 \( ^{b} \)     | 0; 1606         | -2954.35350     | -47 \( ^{b} \) |                  |
| 7(PhCl) | M06-2X(SECF)          | -3646.70274   | -34 \( ^{c} \)     | 0; 1854         | -3646.08683     | -33 \( ^{c} \) |                  |
| 8    | M06-2X                 | -2954.89085   | -85 \( ^{b} \)     | 0; 1611         | -2954.36109     | -67 \( ^{b} \) |                  |
| 8(PhCl) | M06-2X(SECF)          | -3646.71256   | -60 \( ^{c} \)     | 0; 1858         | -3646.09354     | -50 \( ^{c} \) |                  |
| 9    | M06-2X                 | -2955.72121   | 0; 1635           | -2955.17523     |                 |                 |                  |
| 13   | M06-2X                 | -2954.86831   | -7 \( ^{b} \)      | 0; 1607         | -2954.33457     | +3 \( ^{b} \)  |                  |
| 13(PhCl) | M06-2X(SECF)          | -3646.69711   | -19 \( ^{c} \)     | 0; 1856         | -3646.07785     | -9 \( ^{c} \)  |                  |
| 14   | M06-2X                 | -2954.89189   | -69 \( ^{b} \)     | 0; 1607         | -2954.35943     | -63 \( ^{b} \) |                  |
| 14a(PhCl) | M06-2X(SECF)          | -3646.70777   | -47 \( ^{c} \)     | 0; 1853         | -3646.09357     | -51 \( ^{c} \) |                  |
| 14b(PhCl) | M06-2X(SECF)          | -3646.70946   | -52 \( ^{c} \)     | 0; 1854         | -3646.09339     | -50 \( ^{c} \) |                  |
| 15   | M06-2X                 | -2954.86560   | 0 \( ^{b} \)       | 0; 1607         | -2954.33282     | +7 \( ^{b} \)  |                  |
| 15(PhCl) | M06-2X(SECF)          | -3646.69407   | -11 \( ^{c} \)     | 0; 1860         | -3646.07147     | +7 \( ^{c} \)  |                  |
|    |     |             |     |     |             |     |
|----|-----|-------------|-----|-----|-------------|-----|
| 16 | M06-2X | -2954.87588 | -26 | 0, 1611 | -2954.33762 | -5  |
|    | M06-2X | -3646.70202 | -32 | 0; 1860 | -3646.08187 | -20 |
|    | M06-2X | -3646.74726 | -31 | 0; 1860 | -3646.12452 | -25 |
| 16(PhCl) | M06-2X | -1477.59634 | 0; 811 | -1477.33970 |     |
| 21 | M06-2X | -1478.42847 | 0; 830 | -1477.33970 |     |
| 22 | B3LYP | -2956.39235 | 0; 1615 | -2955.86123 |     |
| 5  | B3LYP | -2955.56376 | 0; 1597 | -2955.03694 |     |
| 7  | B3LYP | -2955.56707 | 0; 1602 | -2955.03456 |     |
| 8  | B3LYP | -2956.39138 | 0; 1620 | -2955.85301 |     |
| 9  | B3LYP | -2955.57149 | 0; 1600 | -2955.04234 |     |
| 14 | B3LYP | -1477.95043 | 0; 807 | -1477.69556 |     |
| 21 | B3LYP | -1478.78713 | 0; 826 | -1478.52868 |     |
| 22 | B3LYP | -2956.47319 | 0; 1615 | -2955.93919 |     |
| 5  | B3LYP/D3 | -2955.64993 | 0; 1597 | -2955.12132 |     |
| 7  | B3LYP/D3 | -2955.65766 | 0; 1604 | -2955.12302 |     |
| 8  | B3LYP/D3 | -2956.48700 | 0; 1624 | -2955.94437 |     |
| 9  | B3LYP/D3 | -2955.65545 | 0; 1599 | -2955.12649 |     |
| 14 | B3LYP/D3 | -1477.98031 | 0; 806 | -1477.72604 |     |
| 21 | B3LYP/D3 | -1478.81895 | 0; 826 | -1478.55873 |     |
| 22 | B3LYP/D3 | -691.79955 | 0; 240 | -691.73766 | -691.74062 |
| PhCl | M06-2X | -691.80240 |     |     |             |     |

[a] A 6-311+G(d,p) basis set was applied throughout. [b] $E_{\text{rel}}$ and $G_{298\text{rel}}$ are calculated relative to the energy of cation 6. [c] $E_{\text{rel}}$ and $G_{298\text{rel}}$ are calculated relative to the energy of cation/chlorobenzene complex 6(PhCl). [d] For these compounds, see eqs. S1 and S2.
### Table S2. Absolute and relative energies ($E$ and $E_{\text{rel}}$) and Gibbs energies ($G_{298}^\circ$ and $G_{298 \text{ rel}}^\circ$) for germanium containing cations and related compounds.

| Cpd. | Density Functional [a] | E(SCF) [a.u.] | $E_{\text{rel}}$ [kJ mol$^{-1}$] | NIMAG, $\tilde{\nu}$ [cm$^{-1}$] | ZPVE [kJ mol$^{-1}$] | $G_{298}^\circ$ [a.u.] | $G_{298 \text{ rel}}^\circ$ [kJ mol$^{-1}$] |
|------|------------------------|---------------|-------------------------------|----------------------------------|--------------------------|-------------------|-------------------------|
| 10   | M06-2X                 | -6530.72016   | 0; 1617                       | -6530.18691                     |                          |                   |                         |
| 11   | M06-2X                 | -6529.92457   | 97 $^b$ 0; 1602               | -6529.39477                     | -80 $^b$                 |                   |                         |
| 11(PhCl) | M06-2X             | -7221.74007   | -58 $^c$ 0; 1849              | -7221.12496                     | -45 $^c$                 |                   |                         |
| 12   | M06-2X                 | -6529.89141   | 0; 1602                       | -6529.36179                     |                          |                   |                         |
| 23   | M06-2X                 | -6529.91457   | -71 $^b$ 0; 1600              | -6529.38606                     | -57 $^b$                 |                   |                         |
| 23(PhCl) | M06-2X                | -7221.73099   | -34 $^c$ 0; 1843              | -7221.11885                     | -29 $^c$                 |                   |                         |
| 24   | M06-2X                 | -6529.88768   | 0 $^b$ 0; 1596               | -6529.36434                     | 0 $^b$                   |                   |                         |
| 24(PhCl) | M06-2X                 | -7221.71793   | 0 $^c$ 0; 1845               | -7221.10799                     | 0 $^c$                   |                   |                         |
| 25   | M06-2X                 | -6529.89084   | -8 $^b$ 0; 1598              | -6529.36494                     | -2 $^b$                  |                   |                         |
| 25(PhCl) | M06-2X                | -7221.72185   | -10 $^c$ 0; 1847             | -7221.10933                     | -4 $^c$                  |                   |                         |
| 26   | M06-2X                 | -6529.91810   | -80 $^b$ 0; 1601             | -6529.39063                     | -69 $^b$                 |                   |                         |
| 26a(PhCl) | M06-2X                | -7221.73253   | -38 $^c$ 0; 1846             | -7221.12558                     | -46 $^c$                 |                   |                         |
| 26b(PhCl) | M06-2X                | -7221.73715   | -50 $^c$ 0; 1846             | -7221.12800                     | -53 $^c$                 |                   |                         |
| 27   | M06-2X                 | -6529.90079   | -34 $^b$ 0; 1601             | -6529.37341                     | -24 $^b$                 |                   |                         |
| 27(PhCl) | M06-2X                | -7221.72913   | -29 $^c$ 0; 1852             | -7221.11314                     | -14 $^c$                 |                   |                         |
| 28   | M06-2X                 | -6529.90294   | -40 $^b$ 0; 1604             | -6529.37102                     | -18 $^b$                 |                   |                         |
| 28(PhCl) | M06-2X                | -7221.72909   | -29 $^c$ 0; 1853             | -7221.11255                     | -12 $^c$                 |                   |                         |

[a] A 6-311+G(d,p) basis set was applied throughout.  
[b] $E_{\text{rel}}$ and $G_{298 \text{ rel}}^\circ$ are calculated relative to the energy of cation 24.  
[c] $E_{\text{rel}}$ and $G_{298 \text{ rel}}^\circ$ are calculated relative to the energy of cation/chlorobenzene complex 24(PhCl).  
[d] For these compounds, see Figures S17 and S18.
Calculations of the PES and Reaction Coordinates

The structure optimization of the non-hydrogen-bridged cations 6, 13, 15 and 16 revealed a strong tendency for these cations to form intramolecularly stabilized structures. As an example, structure optimizations for the polysilanyl cation 6 are documented here in more detail. Figure S12 shows the progress of the structure optimization at the M062X/6-311+G(d,p) level for a molecular arrangement which corresponds to anti-6. The data shown in Figure S12 indicates that there is no stationary point that resembles anti-6. Instead, cation 13 in its syn-conformation is formed during the structure optimization. In contrast, a stationary point was located for a molecular arrangement corresponding to syn-6 (Figure S13). Its optimized structure reveals clear indications of an intramolecular stabilization by a methyl group from a remote trimethylsilyl substituent. Structural indications for such intramolecular interactions between the positively charged silicon atom and remote methyl groups are also visible in the optimized structures of cations 15 and 16. Although such molecular structures are important for gas-phase investigations, in the condensed phase or in solution intermolecular interactions for example between solvent molecules and the cations are stronger and therefore dominant. Even in the case of a relatively weakly coordinating solvent such as chlorobenzene, solvent/cation interaction are decisive as shown for the chlorobenzene complex of cation anti-6, anti-6(PhCl). In contrast to the isolated cation, the complex anti-6(PhCl) is a stationary point on the PES with no obvious structural indications for an intramolecular interaction (see Figure S13). Complexation with chlorobenzene does not influence the structure of the hydrogen-bridged cations 7, 8 and 14 significantly, which is represented very well by cation 8 (Figure S14). Structure optimizations of the isolated cation 8 and the cation/chlorobenzene complex 8(PhCl) result in virtually identical structures for the cation and the electronic interaction energy $\Delta E^{\text{diss}}$ is small ($\Delta E^{\text{diss}} = 39 \text{ kJ mol}^{-1}$). Taking into account thermal and entropy effects by quoting the calculated Gibbs energy at 298 K the results of the computations reveal that the complex is not existent at ambient temperatures ($\Delta G^{\text{diss}}(298) = -14 \text{ kJ mol}^{-1}$). In addition, the relative stabilities of the hydrogen-bridged cations 7, 8 and 14 are not influenced by complex formation with the solvent chlorobenzene (see Table S1).

Parts of the potential energy surface (PES) connecting cations 7, 8 and 14 were calculated for the isolated cations in the gas phase (Figure S15). Figure S16 shows the PES determined for the cation/chlorobenzene complexes in the gas-phase. The results of calculations using the polarized continuum model (PCM) to mimic the influences of the solvent chlorobenzene on the structure optimizations of the cation/chlorobenzene complexes are summarized in Figure 5 in the main text. All three PESSs show the same signature for the relative energies of the supposed intermediates. The main difference occurs between the calculations for the free cations and the solvent complexes. As outlined above, the complex formation between the open cations 6, 13, 15 and 16 and
chlorobenzene stabilizes these complexes relative to the related complexes between the hydrogen-bridged cations 7, 8 and 14 and chlorobenzene. Therefore, their energy differences are decreased by approximately 20 kJ mol\(^{-1}\) (compare Figures S15 and S16). Modeling the indirect influence of the solvent by means of PCM calculations has only little impact on the relative energies of the cations of interest, as shown by comparison of Figure S16 and Figure 5). We started an intensive computational search for transition states on all three PES shown in Figures S15, S16 and 5, which was however not successful as we were not able to locate transitions states, which are relevant for the investigated rearrangement reactions. Only transition states belonging to methyl- or silyl group rotations were found as indicated by the inspection of the respective imaginary frequency. Therefore, we have to discuss the main features of the PES based on the energy differences between the intermediate cations. We think that in this particular case, this is a valid approximation, since the PESs around the high-lying open cations 6, 13, 15 and 16 are dominated by the mentioned rotational modes and the surfaces in this regions are extremely flat. A typical barrier for a methyl rotation is app. 5 kJ mol\(^{-1}\) (calculated for the complex 6(PhCl)).

The PESs calculated for the Germanium containing cations and their chlorobenzene complexes are very similar in their signature and in their relative energies to the persila case (compare Figures S15/S17 and S16/S18). For the free cations in the gas phase (Figure S17) the energetic preference of the hydrogen-bridged cations 23, 26 and 11 compared to their open analogues is even slightly more pronounced as in the persila case. The calculations for the complexes of cations with chlorobenzene (Figure S18) revealed an virtually identical reaction coordinate than for the persila case.
Figure S12. Course of a structure optimization at M06-2X/6-311+G(d,p) starting from a molecular configuration resembling the linear open cation \textit{anti-6} and finalizing with a stationary point for the rearranged cation \textit{syn-13} (wire and stick presentation of intermediate structures, all hydrogen atoms but the Si-H hydrogen atom are omitted (color code: Si violet, C grey, H white).
**Figure S13.** Left side: Optimized molecular structure of cation \textit{syn}-6 which indicates interaction between the remote methyl group Me$^{\text{brl}}$ and the positively charged silicon atom Si$^1$ (gas phase, M06-2X/6-311+G(d,p); pertinent bond lengths [pm]: Si1 – Si2 236.0, Si2 – Si3 235.9, Si3 – Si4 235.6, Si4 – Si5 234.7, Si5 – Me 187.2, Si5 – Me$^{\text{brl}}$ 197.1, Si1 – Me$^{\text{brl}}$ 230.6). Right side: Optimized molecular structure of cation / solvent complex \textit{anti}-6 (PhCl) (M06-2X/6-311+G(d,p), pertinent bond lengths [pm] for the gas phase and in chlorobenzene (in parenthesis): Si1 – Si2 236.0 (236.2), Si2 – Si3 234.8 (234.9), Si3 – Si4 234.2 (234.0), Si1 – Cl 245.1 (243.0), Cl – C^ipso 177.9 (177.9); ball and stick presentation, methyl and trimethylsilyl groups are shown as wireframe, all hydrogen atoms but the Si-H hydrogen atom are omitted (color code: Si violet, C grey, H white, Cl green).

**Figure S14.** Left side: Optimized molecular structure of cation 8 (gas phase, M06-2X/6-311+G(d,p); pertinent bond lengths [pm]: Si1 – Si2 234.6, Si2 – Si3 237.8, Si3 – Si4 235.1, Si4 – H 165.4, Si1 – H 165.3). Right side: Optimized molecular structure of cation/solvent complex 8(PhCl) (M06-2X/6-311+G(d,p), pertinent bond lengths [pm] for the gas phase and in chlorobenzene (in parenthesis): Si1 – H 165.5 (164.3), Si4 – H 163.1 (163.5), Si1 – Si2 234.6 (234.5), Si2 – Si3 237.8 (237.6), Si3 – Si4 234.7 (235.0), Si1 – Cl 388.1 (406.0), Cl – C^ipso 175.0 (175.4); ball and stick presentation, methyl and trimethylsilyl groups are shown as wireframe, all hydrogen atoms but the Si-H hydrogen atom are omitted (color code: Si violet, C grey, H white, Cl green).
Figure S15. Approximate reaction coordinate for the formation of the hydrogen-bridged cation 8 starting from cation 6. Relative energies $E^{\text{rel}}$ (black) and Gibbs energies $G^{\text{rel}}(298)$ (blue) are computed using the M06-2X/6-311+G(d,p) functional and are given relative to the values of the cation 6. The barriers shown are drawn arbitrarily.

Figure S16. Approximate reaction coordinate for the formation of the hydrogen-bridged cation 8(PhCl) starting from the complex 6(PhCl) in the gas phase. Relative energies $E^{\text{rel}}$ (black) and Gibbs energies $G^{\text{rel}}(298)$ (blue) are computed using the M06-2X/6-311+G(d,p) functional and are given relative to the values of the complex 6(PhCl). The barriers shown are drawn arbitrarily.
Figure S17. Approximate reaction coordinate for the formation of the hydrogen-bridged cation 11 starting from cation 24. Relative energies $E^{\text{rel}}$ (black) and Gibbs energies $G^{\text{rel}}(298)$ (blue) are computed using the M06-2X/6-311+G(d,p) functional and are given relative to the values of the cation 24. The barriers shown are drawn arbitrarily.

Figure S18. Approximate reaction coordinate for the formation of the hydrogen-bridged cation 11 starting from the complex between cation 24 and PhCl. The relative energies $E^{\text{rel}}$ (black) and Gibbs energies $G^{\text{rel}}(298)$ (blue) of the aggregates between cations and solvent are computed using the M06-2X/6-311+G(d,p) functional and are given relative to the energy of the complex 24(PhCl). The barriers shown are drawn arbitrarily.
Evaluation of the Effect of Dispersion Interaction

In general, the effect of dispersion interactions is already taken into account by using the M06-2X functional. To our experience this functional provides optimized molecular structures that are close to those obtained from experimental methods. These theoretical structures are also a good basis for reliable NMR calculations. For a quantitative evaluation of the size of the dispersion energy contribution to the relative stability of the investigated cations molecular structure optimizations with the standard B3LYP functional were performed.[12] The obtained structures and energies were then compared to results from B3LYP/D3 calculations, which uses Grimme’s D3 dispersion correction.[13, 14] The evaluation of the energetic effects is given in the main text. For a comparison of structural data, see Table S3 in which we compiled data of hydrogen-bridged cation 8 obtained with the different methods. In general, the interatomic distances computed with the different methods are very similar. The exception here is the molecular structure computed with the standard B3LYP functional that predicts the longest Si – Si bonds from all methods tested here. Of particular interest is the fact that the central Si2 – Si3 bond is calculated with the standard B3LYP to be 244 pm which is 3 pm longer than predicted by the dispersion corrected B3LYP/D3 and 6 pm longer than calculated using the M06-2X method (Table S3). Clearly, this is also a structural indication for the attractive dispersion interactions operating in the hydrogen-bridged cation 8.

**Table S3.** Comparison of structural parameter of cation 8 calculated using different DFT methods and model chemistries. For all methods the 6-311+G(d,p) basis set was applied. For the assignment of the atoms, see Figure S14.

|         | M06-2X | SCRF M06-2X[a] | B3LYP | B3LYP/D3 |
|---------|--------|----------------|-------|----------|
| Si1 – Si2 [pm] | 234.6  | 234.0          | 237.4 | 235.7    |
| Si2 – Si3 [pm] | 237.8  | 237.4          | 243.6 | 240.7    |
| Si3 – Si4 [pm] | 235.1  | 235.1          | 238.6 | 237.2    |
| Si1 – H [pm]  | 165.4  | 164.8          | 165.2 | 165.1    |
| Si1 – H [pm]  | 165.2  | 164.9          | 165.3 | 165.3    |

[a] The SCRF calculation applied the polarized continuum model (PCM) using chlorobenzene as solvent.
Substituent Effects on the Stability of Molecules with Cationic Si – H – Si - Bridges

The effect of silyl groups on the thermodynamic stability of carbocations is well documented and in particular, the so-called β-silyl effect is significant for the stability of carbocations.\cite{15,16} Therefore, we probed the effect of trimethylsilyl substitution on the stability of hydrogen-bridged silyl cations by calculating the reaction energy of isodesmic reactions S1 and S2. Equation S1 evaluates the α-effect of four trimethylsilyl groups (as in cation 7) and equation S2 probes the β-effect of four trimethylsilyl groups as in cation 8, in both cases compared to substituent effect of methyl groups. Finally, the isodesmic reaction S3 compares the effect of the substituents on the relative stability of the isomeric cations 7 and 8. The results obtained using different density functionals are summarized in Table S4

\[
\begin{align*}
\text{S1:} & \quad \alpha\text{-effect} \quad [\text{kJ mol}^{-1}] \\
\text{S2:} & \quad \beta\text{-effect} \quad [\text{kJ mol}^{-1}] \\
\text{S3:} & \quad \text{net-effect 7 vs 8} \quad [\text{kJ mol}^{-1}] \\
\end{align*}
\]

Using our standard M06-2X functional the calculations reveal that the replacement of four methyl groups in the α-position by four trimethylsilyl substituents is favored by -37 kJ mol\(^{-1}\) (Table S4, eq S1). More interesting is the small size of the β-effect. According to eq. S2 cation 8 is stabilized by only -24 kJ mol\(^{-1}\) compared to the permethylated cation 21. The relative small size of the effect compared to those calculated for carbocations can be attributed (i) to the long Si\(^{+}\) - Si\(^{2-}\) bonds, which severely hampers the orbital overlap required for hyperconjugation, and, (ii) to the conformation of...
the cyclic cation 8, which prevents an optimal alignment of the Si\(\beta\)-SiMe\(3\) bonds for hyperconjugation in respect of the LUMO of the cation (see Figure S19 for the molecular structure and the depiction of the LUMO). The LUMO of the molecule is in essence an antisymmetric combination of unoccupied 3p(Si) atomic orbitals directed to the bridging H-Atom. The \(\alpha\)-effect of the four trimethylsilyl groups in cation 7 is larger than the \(\beta\)-effect of these substituents in cation 8. Consequently, the net result of both stabilizing electronic substituent effects is a destabilization of cation 8 compared to cation 7 by 13 kJ mol\(^{-1}\). This result contradicts the direct comparison of the calculated absolute energies of the two isomeric cations, which predicts cation 8 to be more stable than cation 7 by -31 kJ mol\(^{-1}\). Furthermore, the higher thermodynamic stability of cation 8 versus cation 7 is in agreement with the experiment.Obviously, the more favorable attractive dispersion forces between the vicinal trimethylsilyl groups in cation 8 overrule the unfavorable balance of the electronic substituent effects. This fact points to the decisive role that attractive dispersion forces play in these systems.

Calculations using the dispersion corrected B3LYP/D3 functional result in nearly identical results (see Table S4). In contrast, the standard B3LYP functional predicts a smaller \(\alpha\)-effect but larger \(\beta\)-effect. In consequence, calculations based on the standard B3LYP functional predict a net stabilization of cation 8 compared to cation 7 by the electronic substituent effects. A clear analysis of the influence of dispersion on the reaction energies of the isodesmic reaction S1-3 is however not straightforward. Dispersion energy contributions are also important for silanes and the effects are even greater than calculated for the cations. For example, the energy difference calculated for the silanes 5 and 9 at B3LYP is -3 kJ mol\(^{-1}\) in favor of silane 5, while the dispersion corrected B3LYP/D3 method favors silane 9 by -36 kJ mol\(^{-1}\). Therefore, the effect of the dispersion energy for the silanes 5 and 9 is -39 kJ mol\(^{-1}\) in favor of silane 9. The same calculations reveals an additional stabilization of cation 8 compared to cation 7 by only -11 kJ mol\(^{-1}\). This imbalance makes an easy breakdown of the isodesmic reactions S1-S3 in terms for the electronic substituent effects and dispersion energy effects not straightforward and only the net effects of the trimethylsilyl substituents (dispersion + electronic) are evaluated.
Figure S19. Calculated molecular structure of cation 8 (gas phase, M06-2X/6-311+G(d,p)). The surface diagram of the LUMO is shown (E = -1.63 eV, isodensity surface value: 0.055).
Comparison of calculated $^{29}\text{Si}$ NMR spectra for cations 8 and 14 with the experimental data

Figure S20. a) Experimental $^{29}\text{Si}^1(\text{H})$ NMR spectrum (99 MHz) of hydrogen-bridged silyl borate $8[\text{B(C}_6\text{F}_5)_4]$ in C$_6$D$_5$Cl, at 243 K; b) simulated $^{29}\text{Si}$ NMR spectrum of hydrogen-bridged silyl cation $8$; c) simulated $^{29}\text{Si}$ NMR spectrum of hydrogen-bridged silyl cation $14$. The simulations of the NMR spectra are based on $^{29}\text{Si}$ NMR chemical shifts which were calculated at the M06-L/6-311G(d,p)//M06-2X/6-311+G(d,p) level of theory.
References

[1] A. G. Massey, A. J. Park, J. Organomet. Chem. 1964, 2, 245.
[2] J. C. W. Chien, W. M. Tsai, M. D. Rausch, J. Am. Chem. Soc. 1991, 113, 8570.
[3] M. Ishikawa, J. Iyoda, H. Ikeda, K. Kotake, T. Hashimoto, M. Kumada, J. Am. Chem. Soc. 1981, 103, 4845.
[4] R. Fischer, D. Frank, W. Gaderbauer, C. Kayser, C. Mechtler, J. Baumgartner, C. Marschner, Organometallics 2003, 22, 3723.
[5] S. M. Whittaker, M.-C. Brun, F. Cervantes-Lee, K. H. Pannell, J. Organomet. Chem. 1995, 499, 247.
[6] C. Kayser, G. Kickelbick, C. Marschner, Angew. Chem. Int. Ed. 2002, 41, 989.
[7] J. Fischer, J. Baumgartner, C. Marschner, Organometallics 2005, 24, 1263.
[8] F. Stella, Dissertation Thesis, Technical University Graz (Graz), 2016.
[9] M. J. T. Frisch, G. W.; Cheeseman, J. R.; Scalmani, G.; Caricato, M.; Frisch, H. P.; Li, X.; Barone, V.; Bloino, J.; Zheng, G.; Vreven, T.; Montgomery, J. A.; Petersson, G., G. E. S. A.; Scuseria, H. B.; Nakatsuji, H.; Izmaylov, A. F.; Martin, R. L.;; J. L. P. Sonnenberg, J. E.; Heyd, J. J.; Brothers, E.; Ogliaro, F.; Bearpark, M.; Robb, B. K. M. A.; Mennucci, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.;; A. G. Rendell, R.; Zakrzewski, V. G.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda,, J. I. R.; Hasegawa, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H., Gaussian 09.
[10] Y. Zhao, N. E. Schultz, D. G. Truhlar, J. Chem. Theory Comput. 2006, 2, 364.
[11] Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 2008, 120, 215.
[12] a) A. D. Becke, Phys. Rev. 1988, A 38, 3098. b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785. c) A. D. Becke, J. Chem. Phys. 1993, 98, 5648. d) B. G. Johnson, P. M. W. Gill, J. A. Pople, J. Chem. Phys. 1993, 98, 5612.
[13] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[14] S. Grimme, Wiley Interdisciplinary Reviews: Computational Molecular Science 2011, 1, 211.
[15] H.-U. Siehl, T. Müller, in The chemistry of organic silicon compounds Vol. 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, 1998, pp. 595 - 701.
[16] A. R. Bassindale, S. J. Glynn, P. G. Taylor, in The chemistry of organic silicon compounds Vol. 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, 1998, pp. 355 - 429.