Supporting Information

for

Wagner Meerwein-Type Rearrangements of Germapolysilanes - A Stable Ion Study

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Experimental part

All manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen atmosphere using Schlenk techniques or a standard glove box (Braun Unilab). Glassware was dried in an oven at 120 °C and evacuated prior to use. The solvents tetrahydrofuran (THF), dimethoxyethane (DME), n-pentane, benzene and toluene were dried over sodium and distilled under nitrogen atmosphere. Chlorobenzene was dried over CaCl₂ and stored over molecular sieves. Deuterated benzene and toluene were stored over molecular sieves after drying over sodium. Dichlorodimethylgermane, chlorodimethylsilane, triethylsilane, tri-iso-propylsilane and trimethylchlorosilane were obtained from commercial suppliers and the silanes were dried over molecular sieves. Sodium methanolate was prepared by addition of sodium to an excess of abs. methanol. After all sodium was consumed the solvent was removed in vacuo. Triphenylmethyl tetrakis(pentafluorophenyl) borate 9 ([Ph₃C][B(C₆F₅)₄]) was prepared according to a modified literature procedure.¹ Tetraakis(trimethylsilyl)silane², tetrakis(trimethylsilyl)germane³, tris(trimethylsilyl)silylpotassium⁴, tris(trimethylsilyl)germylpotassium⁵, tris(trimethylsilyl)silyltrimethylgermane⁶,¹ chloropentamethyldisilane⁷ and trimethylsilane⁸ were synthesized according to reported procedures. GC-MS spectra were performed on a Thermo Focus DSQ. 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-d₆: δ¹H(C₆D₆) = 7.20, toluene-d₈: δ¹H(CD₂H) = 2.08, chloroform-d₄: δ¹H(CHCl₃) = 7.24, chlorobenzene-d₅: δ¹H(C₆D₄HCl) = 7.14) and ¹³C NMR spectra by using the central line of the solvent signal (benzene-d₆: δ¹³C(C₆D₆) = 128.0, toluene-d₈: δ¹³C(CD₂) = 20.4, chloroform-d₄: δ¹³C(CDCl₃) = 77.0, chlorobenzene-d₅: δ¹³C(C₆D₅Cl) = 134.2). ²⁹Si{¹H} NMR spectra were calibrated against an external standard (²⁹Si(Me₂SiHCl) = 11.1 versus tetramethylsilane (TMS)). The ²⁹Si{¹H} NMR inverse gated spectra were recorded with a relaxation delay D1 = 10 s. Based on our experiences, at -20 °C this delay is long enough to allow a reliable integration of the peaks. The ²⁹Si{¹H} INEPT spectra were recorded with delays D3 = 0.0084 s and D4 = 0.0313 s. IR spectra were recorded on a Bruker Tensor 27 instrument. 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.

**Dimethoxydimethylgermane**⁹ (17)

\[
\begin{align*}
\text{Cl} & \quad \text{Ge} & \quad \text{Cl} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

2.84 g (3.5 eq., 52.57 mmol) NaOMe was suspended in 40 mL pentane and 1.74 mL (15.00 mmol) dichlorodimethylgermane was slowly added with a syringe. The mixture was stirred overnight at room temperature. The excess of NaOMe and formed NaCl were separated from the solution by using a centrifuge
(20 min, 2000 rpm) and then the product-containing pentane solution was decanted using a Teflon tube. The salts were washed with 10 mL pentane and again centrifuged and decanted. The pentane solutions were combined and the product was separated from the solvent by fractionated distillation (bp.:118 °C at ambient pressure (1.45 g, 58 %). $^1$H NMR (500.13 MHz, 297.9 K, $^{13}$CD$_6$, $\delta$): 0.30 (s, 6H, (CH$_3$)$_2$Ge), 3.54 (s, 6H, Ge(OCH$_3$)$_2$). $^{13}$C($^1$H) NMR (125.77 MHz, 298.1K, $^{13}$CD$_6$, $\delta$): -2.9 ((CH$_3$)$_2$Ge), 51.6 (Ge(OCH$_3$)$_2$). Mass required for C$_4$H$_{12}$GeO$_2$: 166.0. Mass found GC/MS: 164.9 (0.5) [M$^+$-H], 150.8 (100) [M$^+$-Me], 135.9 (72) [M$^+$-OMe], 120.9 (88) [M$^+$-OMe-Me], 104.9 (84) [M$^+$-OMe-2Me].

Figure S1. GC spectrum of dimethoxydimethylgermane (17)

**Tris(trimethylsilyl)silyldimethoxymethoxygermane (18)**

A solution of 4.50 mmol tris(trimethylsilyl)silylpotassium$^4$ in 40 mL pentane and a solution of 0.75 g (4.50 mmol) dimethoxydimethylgermane 17 in 10 mL pentane were cooled to 0 °C. The silyl potassium compound was added drop wise to the germane solution. The ice bath was allowed to warm to room temperature overnight. The reaction mixture was then hydrolyzed with 1 M hydrochloric acid. The organic layer was separated and dried over sodium sulfate. The solvent was removed under reduced pressure and the product was purified by Kugelrohr distillation (0.62 g, 36 %). Due to the use of hydrochloric acid about 14% of the corresponding germyl chloride was formed as a by-product, which was detected in the GC chromatograms and NMR spectra. $^1$H NMR (499.87 MHz, 305.0 K, $^{13}$CD$_6$, $\delta$ ppm): 0.34 (s, 27H, (CH$_3$)$_3$Si), 0.60 (s, 6H, (CH$_3$)$_2$Ge), 3.54 (s, 3H, CH$_3$OGe). $^{29}$Si($^1$H) INEPT NMR (99.31 MHz, 305.0 K, $^{13}$CD$_6$, $\delta$ ppm): -124.6 (((CH$_3$)$_3$Si)$_3$Si), -9.9 (((CH$_3$)$_3$Si)$_3$Si). Mass required for C$_{12}$H$_{36}$GeOSi$_4$: 382.1. Mass found GC/MS: 367.2 (1) [M$^+$-Me], 351.2 (0.5) [M$^+$-OMe], 278.0 (8) [M$^+$-SiMe$_3$-OMe], 205.1 (13) [M$^+$-SiMe$_3$-OMe], 73.0 (100) [Me$_3$Si$^+$]. No satisfactory combustion analysis available due to contamination with the chloride side-product.

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Figure S2a. $^1$H NMR spectrum of a mixture of tris(trimethylsilyl)silyldimethylmethoxygermane (18) and tris(trimethylsilyl)silylchlorodimethylgermane in C₆D₆.

Figure S2b. $^{13}$C($^1$H) NMR spectrum of a mixture of tris(trimethylsilyl)silyldimethylmethoxygermane (18) and tris(trimethylsilyl)silylchlorodimethylgermane in C₆D₆.

Figure S2c. $^{29}$Si($^1$H) NMR spectrum of a mixture of tris(trimethylsilyl)silyldimethylmethoxygermane (18) and tris(trimethylsilyl)silylchlorodimethylgermane in C₆D₆.
Tris(trimethylsilyl)silyldimethylgermane (14)

A solution of 0.62 g (1.62 mmol) tris(trimethylsilyl)silyldimethylmethoxygermane 18 in 30 mL THF and a suspension of 0.062 g (1.62 mmol) LiAlH₄ in 50 mL THF were cooled to 0 °C with an ice bath. The solution of silagermane 18 was added to the LiAlH₄ suspension and the reaction mixture was stirred for 20 min at 0 °C before it was allowed to warm to room temperature and stirred for another 20 min. The mixture was slowly added to ice cold 2 M sulfuric acid. The phases were separated and the aqueous phase was extracted two times with 50 mL diethyl ether. The combined organic phases were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was crystallized from ethanol as a waxy, colorless solid (0.38 g, 1.09 mmol, 67%).

$^1$H NMR (499.87 MHz, 305.0 K, C₆D₆, δ ppm): 0.30 (s, 27H, (CH₃)₃Si), 0.50 (d, $^3J_{H,H}$ = 4.2 Hz, 6H, (CH₃)₂Ge), 4.04 (sept, $^3J_{H,H}$ = 4.2 Hz, 1H, GeH).

$^{13}$C($^1$H) NMR (125.69 MHz, 305.0 K, C₆D₆, δ ppm): -2.3 ((CH₃)₂Ge), 2.5 ((CH₃)₃Si).

$^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C₆D₆, δ ppm): -128.3 (((CH₃)₃Si)₃Si), -9.4 (((CH₃)₃Si)₂Si). Mass required for C₁₁H₃₄GeSi₄: 352.1. Mass found GC/MS: 351.1 (0.1) [M⁺-H], 337.1 (0.6) [M⁺-Me-H], 278.0 (30) [M⁺-SiMe₃-H], 189.1 (13) [M⁺-2SiMe₃-Me-H], 174.0 (4) [M⁺-SiMe₃-GeMe₃H], 73.1 (100) [Me₃Si⁺]. IR (ATR, neat): νGe-H 1982 cm⁻¹, Anal. found/calcd. for C₁₁H₃₄GeSi₄: C 37.63/37.60, H 10.67/9.75.

Figure S3a. $^1$H NMR spectrum of tris(trimethylsilyl)silyldimethylgermane (14) in C₆D₆.

Figure S3b. $^{13}$C($^1$H) NMR spectrum of tris(trimethylsilyl)silyldimethylgermane (14) in C₆D₆.
Solutions of 2.99 mmol tris(trimethylsilyl)germylpotassium\(^5\) in 30 mL DME and of 0.6 mL (excess, 5.52 mmol) chlorodimethylsilane in 30 mL DME were cooled to 0 °C with an ice bath. The germylpotassium compound was slowly added to the chlorosilane solution during 1 h. The ice bath was allowed to warm to room temperature overnight. The reaction mixture was then hydrolyzed with 1 M sulfuric acid. The organic layer was separated and the aqueous phase was extracted with 10 mL diethyl ether. The combined organic phases were dried over sodium sulfate and the filtrate was concentrated to 5 mL under reduced pressure. The product crystallized by adding 2 mL acetonitrile as a colorless, waxy solid (0.847 g, 80.6 %). \(^1\)H NMR (499.87 MHz, 305.0 K, CDCl\(_3\), \(\delta\) ppm): 0.22 (s, 27H, (CH\(_3\))\(_3\)Si), 0.27 (d, \(^{3}J_{\text{H,H}} = 4.2\) Hz, 6H, (CH\(_3\))\(_2\)Si), 4.12 (sept, \(^{3}J_{\text{H,H}} = 4.2\) Hz, 1H, SiH). \(^{13}\)C\(^{1}\)H NMR (125.71 MHz, 305.0 K, CDCl\(_3\), \(\delta\) ppm): -1.4 ((CH\(_3\))\(_2\)Si), 3.1 ((CH\(_3\))\(_3\)Si). \(^{29}\)Si INEPT NMR (99.31 MHz, 305.0 K, CDCl\(_3\), \(\delta\) ppm): -29.8 (dsept, \(^{1J_{\text{Si,H}}} = 180.5\) Hz, \(^{2J_{\text{Si,H}}} = 7.0\) Hz, SiH), -4.7 ((CH\(_3\))\(_3\)Si). Mass required for C\(_{11}\)H\(_{34}\)GeSi\(_4\): 352.1. Mass found GC/MS: m/z (%): 351.1 (0.3) [M\(^+\)-H], 337.1 (2.5) [M\(^+\)-Me-H], 278.1 (64) [M\(^+\)-SiMe\(_3\)-H], 189.9 (22) [M\(^+\)-2SiMe\(_3\)-Me-H], 174.0 (2) [M\(^+\)-SiMe\(_2\)-GeMe\(_2\)], 73.0 (100) [Me\(_3\)Si\(^+\)]. IR (ATR, neat): \(\nu_{\text{Si-H}}\) 2085 cm\(^{-1}\), Anal. found/calcd. for C\(_{11}\)H\(_{34}\)GeSi\(_4\): C 36.31/37.60, H 9.98/9.75.

**Figure S3c.** \(^{29}\)Si\(^{1}\)H NMR spectrum of tris(trimethylsilyl)silyldimethylgermane (14) in C\(_6\)D\(_6\).
Tris(trimethylsilyl)pentamethyldisilanylgermane (19)

A solution of 1.37 mmol tris(trimethylsilyl)germylpotassium·18-crown-65 in 3 mL benzene was added drop wise to a solution of 0.25 g (1.51 mmol) chloropentamethyldisilane7 in 3 mL benzene. After 5 h the solution mixture was quenched with 1M sulfuric acid and the phases were separated. The aqueous phase was extracted with pentane and the combined organic phases were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was obtained as colorless crystals by crystallization from methanol/diethylether 1:2 (0.42 g, 73%). 1H NMR (299.94 MHz, 298.0 K, C6D6, δ ppm): 0.22 (s, 9H, Si(CH3)2Si(CH3)3), 0.36 (s, 27H, ((CH3)3Si)3Ge), 0.40 (s, 6H, Si(CH3)2Si(CH3)3). 13C{1H} NMR (75.43 MHz, 298.0 K, C6D6, δ ppm): -0.8 (Si(CH3)2Si(CH3)3), -0.4 (Si(CH3)2Si(CH3)3), 4.0 ((((CH3)3Si)2Ge). 29Si{1H} INEPT NMR (59.59 MHz, 295.0 K, C6D6, δ ppm): -34.0 (Si(CH3)2Si(CH3)3), -15.5 (Si(CH3)2Si(CH3)3), -5.2 (((CH3)3Si)2Ge). Mass required for C14H42GeSi5: 424.1. Mass found GC/MS: m/z (%) = 424 (1) [M+]; 408 (1) [M+-Me-H]; 351 (3) [M+-SiMe3]; 278 (10) [M+-2SiMe3]; 259 (1) [GeSi3C6H17+]; 243 (1) [GeSi3C6H13+]; 219 (3) [GeSi2C6H17+]; 203 (11) [M+-3SiMe3-2H]; 187(8)[M+-3SiMe3-Me-4H]; 147 (7) [GeSiMe3+]; 131 (35) [SiMe3SiMe3+]; 73 (100) [SiMe3+]. Anal. found/calcd. for C14H42GeSi5 C 39.33/39.70, H 9.50/9.99.
Bis(trimethylsilyl)pentamethyldisilanylgermane (16)

A mixture of 0.21 g (0.49 mmol) germapolysilane 19, 0.062 g (0.51 mmol) KO'Bu and 0.134 g (0.51 mmol) 18-crown-6 ether was dissolved in 2 mL benzene. After the complete formation of the germylpotassium compound 20 was confirmed by NMR spectroscopy, the solution was added to a stirred mixture of 10 mL degassed diethyl ether and 20 mL degassed 2M sulfuric acid cooled with an ice bath. The phases were separated,
the aqueous phase was extracted with degassed diethyl ether and the combined organic phases dried over sodium sulfate. The solvents were removed under reduced pressure and the product was obtained as a colorless oil (0.15 g, 91%) The germane is sensible to oxygen and should be stored under argon at -20 °C.

Bis(trimethylsilyl)pentamethyldisilanygermylpotassium (20)

$^1$H NMR (299.94 MHz, 298.0 K, C$_6$D$_6$, δ ppm): 0.39 (s, 9H (Si(CH$_3$)$_2$)Si(CH$_3$)$_3$), 0.59 (s, 18H ((CH$_3$)$_2$Si)$_2$GeK), 0.64 (s, 6H, Si(CH$_3$)$_2$Si(CH$_3$)$_3$), 3.25 (s, 24H, CH$_2$O).

$^{13}$C($^1$H) NMR (75.43 MHz, 295.0 K, C$_6$D$_6$, δ ppm): 0.0 (Si(CH$_3$)$_2$)Si(CH$_3$)$_3$), 3.5 ((CH$_3$)$_2$Si)$_2$GeK), 70.0 (CH$_2$O).

$^{29}$Si($^1$H) INEPT NMR (59.59 MHz, 295.0 K, C$_6$D$_6$, δ ppm): -33.0 (Si(CH$_3$)$_2$Si(CH$_3$)$_3$), -16.6 (Si(CH$_3$)$_2$Si(CH$_3$)$_3$), -3.4 ((CH$_3$)$_2$Si)$_2$GeK). Mass required for C$_{13}$H$_{38}$GeSi$_4$ after ethylbromide derivatization: 380.1. Mass found after ethylbromide derivatization GC/MS: m/z (%) = 380 (1) [M$^+$]; 365 (1) [M$^+$-Me]; 350 (3) [M$^+$-Et-H]; 307 (1) [M$^+$-SiMe$_3$]; 292 (1) [M$^+$-SiMe$_2$-Me]; 277 (3) [M$^+$-SiMe$_2$-2Me]; 262 (1) [M$^+$-SiMe$_3$-3Me]; 234 (3) [M$^+$-2SiMe$_3$]; 219 (8) [M$^+$-2SiMe$_3$-Me]; 203 (17) [M$^+$-2SiMe$_3$-2Me-H]; 187 (6) [M$^+$-2SiMe$_3$-3Me-2H]; 159 (4) [M$^+$-3SiMe$_3$-H]; 145 (10) [M$^+$-3SiMe$_3$-Me]; 131 (33) [GeSiC$_5$H$_5$]; 115 (9) [GeSiCH$_3$]; 73 (100) [SiMe$_3$].

Figure S6a. $^1$H NMR spectrum of the reaction mixture of the synthesis of germylpotassium compound 18-crown-6 (20) in C$_6$D$_6$.

Figure S6b. $^{13}$C($^1$H) NMR spectrum of the reaction mixture of the synthesis of germylpotassium compound 18-crown-6 (20) in C$_6$D$_6$. 
**Figure S6c.** $^{29}$Si NMR spectrum of the reaction mixture of the synthesis of germylpotassium compound 18-crown-6 (20) in C$_6$D$_6$.

**Bis(trimethylsilyl)pentamethyldisilanylgermane (16)**

$^1$H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$, δ ppm): 0.22 (s, 9H, Si(CH$_3$)$_3$Si(CH$_3$)$_3$), 0.35 (s, 18H, ((CH$_3$)$_3$Si)$_2$Ge), 0.40 (s, 6H, Si(CH$_3$)$_3$Si(CH$_3$)$_3$), 2.25 (s, 1H, GeH). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, CDCl$_3$, δ ppm): -1.7 (Si(CH$_3$)$_3$Si(CH$_3$)$_3$), -1.6 (Si(CH$_3$)$_3$Si(CH$_3$)$_3$), 3.1 (((CH$_3$)$_3$Si)$_2$Ge). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_6$D$_6$, δ ppm): -34.3 (Si(CH$_3$)$_3$Si(CH$_3$)$_3$), -16.2 (Si(CH$_3$)$_3$Si(CH$_3$)$_3$), -5.7 (((CH$_3$)$_3$Si)$_2$Ge). Mass required for C$_{11}$H$_{34}$GeSi$_4$: 352.1. Mass found GC/MS: 335 (2) [M$^+$-Me-2H]; 278 (27) [M$^+$-SiMe$_3$-H]; 263 (2) [M$^+$-SiMe$_3$-Me-H]; 203 (13) [M$^+$-2SiMe$_3$-2H]; 189 (10) [M$^+$-2SiMe$_3$-Me-2H]; 173 (2) [M$^+$-2SiMe$_3$-2Me-2H]; 131 (24) [SiMe$_3$SiMe$_2$]; 115 (14) [Si$_2$C$_4$H$_{11}$$^+$]; 73 (100) [SiMe$_3$$^+$. IR (ATR, neat) $\nu$$_{Ge-H}$ 1951 cm$^{-1}$. Anal. found/calcd. for C$_{11}$H$_{34}$GeSi$_4$ C 38.85/37.60, H 9.41/9.75.

**Figure S7a.** $^1$H NMR spectrum of bis(trimethylsilyl)pentamethyldisilanylgermane (16) in C$_6$D$_6$. 
Figure S7b. $^{13}$C($^1$H) NMR spectrum of bis(trimethylsilyl)pentamethyldisilanylgermane (16) in C$_6$D$_6$.

Figure S7c. $^{29}$Si($^1$H) NMR spectrum of bis(trimethylsilyl)pentamethyldisilanylgermane (16) in C$_6$D$_6$.

General preparation of trialkylsilyl arenium borates (10a-d)

$$R_3\text{SiH} \quad + \quad [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] \quad \xrightarrow{\text{arene}} \quad [R_3\text{Si(arene)}][\text{B}(\text{C}_6\text{F}_5)_4]$$

Triphenylmethyl tetrakis(pentafluorophenyl)borate was dissolved in 3 mL of the indicated solvent and the silane was added. The formation of two phases could be observed and the biphasic reaction mixture was vigorously stirred for 30 min. The upper, non-polar phase was removed and the lower, polar phase was washed with 2 mL of the used solvent and again the non-polar phase was removed. The polar phase was dried under reduced pressure for 30 min and then dissolved in the respective deuterated solvent.

**Triethyldiethylbenzenium borate (10a)** 0.50 g (0.54 mmol) Triphenylmethyl tetrakis(pentafluorophenyl)borate was dissolved in 3 mL benzene and 0.14 mL (1.6 eq., 0.87 mmol) triethylsilane was added.

**Tri-iso-propylsilyl toluenium borate (10b)** 0.46 g (0.50 mmol) Triphenylmethyl tetrakis(pentafluorophenyl)borate was dissolved in 3 mL toluene and 0.11 mL (1.1 eq., 0.55 mmol) tri-iso-propylsilane was added.

**Trimethylsilyl toluenium borate (10c)** 0.46 g (0.50 mmol) Triphenylmethyl tetrakis(pentafluorophenyl)borate was dissolved in 3 mL toluene and 0.06 mL (1.1 eq., 0.55 mmol) trimethylsilane was added.
General procedure for the rearrangement of tris(trimethylsilyl)silyltrimethylgermane (1) with trialkylsilyl arenium borates (10a-c)

A solution of 0.18 g (0.50 mmol) silagermane 1 in 1 mL of the named deuterated solvent was added to a precooled solution of the named trialkylsilyl arenium borate 10a-c. The reaction mixture was stirred for 2 h at the specified temperature and then allowed to warm to room temperature. The polar phase and the non-polar phase were each transferred to separate NMR tubes to be analyzed independently. In the following reactions the NMR spectra of the polar phase showed too many signals to be analyzable but the compounds in the non-polar phase were identified by NMR and GC/MS spectroscopy.

Tris(trimethylsilyl)silyltrimethylgermane (1) with triethylsilyl benzenium borate (10a)

The reaction was performed at 6 °C in benzene-d₆.

Non-polar phase:

¹H NMR (499.87 MHz, 305.0 K, C₆D₆, δ ppm): 0.32-0.38 (m, 1H, CH₃), 0.78-0.92 (m, 0.19H, CH₂CH₃), 1.04-1.11 (m, 0.27H, CH₂CH₃). ¹³C[¹H] NMR (125.69 MHz, 298.0 K, C₆D₆, δ ppm): 0.57 (CH₃), 0.64 (CH₃), 0.72 (CH₃), 0.80 (CH₃), 0.89 (CH₃), 3.47 (CH₃), 3.60 (CH₃), 3.73 (CH₃), 3.76 (CH₃), 3.86 (CH₃), 3.89 (CH₃), 4.02 (CH₃), 7.97 (CH₂CH₃), 8.66 (CH₂CH₃), 8.68 (CH₂CH₃), 8.71 (CH₂CH₃), 9.72 (CH₂CH₃), 9.82 (CH₂CH₃), 11.45 (CH₂CH₃), 11.52 (CH₂CH₃), 11.58 (CH₂CH₃), 11.65 (CH₂CH₃), 11.72 (CH₂CH₃). ²⁹Si[¹H] INEPT NMR (99.31 MHz, 305.0 K, C₆D₆, δ ppm): -5.13, -5.10, -1.39, -1.37, -1.30, -1.27, -1.23.

GC/MS:

rt = 3.58 min, tetramethylsilane

m/z (%) = 88.0 (2) [M⁺], 73.0 (100) [M⁺-Me].

rt = 4.1 min, ethyltrimethylsilane

m/z (%) = 101.0 (4) [M⁺], 87.0 (47) [M⁺-Me], 73.0 (97) [M⁺-2Me], 58.0 (100) [M⁺-3Me].

rt = 5.18 min, diethyldimethylsilane

m/z (%) = 116.4 (4) [M⁺], 101.0 (11) [M⁺-Me], 87.0 (92) [M⁺-2Me], 73.0 (13) [M⁺-3Me], 58.0 (100) [M⁺-4Me].

rt = 18.1 min, (2)

m/z (%): 366.1 (32) [M⁺], 351.1 (18) [M⁺-Me], 278.0 (27) [M⁺-SiMe₃-Me], 219.0 (30) [C₆H₁₃GeSi₂⁺], 203.0 (16) [C₆H₁₂GeSi₃⁺], 145.0 (28) [C₆H₁₂GeSi⁺], 131.0 (49) [C₆H₁₂GeSi⁺], 73.0 (100) [SiMe₃⁺].

rt = 19.5 min, (11, n = 3)

m/z (%): 380.0 (48) [M⁺], 365.0 (10) [M⁺-Me], 292.0 (72) [M⁺-SiMe₃-Me], 278.0 (93) [C₆H₁₂GeSi₃⁺], 264.0 (24) [C₆H₁₂GeSi₃⁺], 145.0 (25) [C₆H₁₂GeSi⁺], 131.0 (44) [C₆H₁₂GeSi⁺], 87.0 (43) [C₆H₁₂Si⁺], 73.0 (100) [SiMe₃⁺].

rt = 20.8 min, (11, n = 2)

m/z (%): 394.0 (44) [M⁺], 379.0 (10) [M⁺-Me], 306.0 (31) [M⁺-SiMe₃-Me], 292.0 (100) [C₆H₁₂GeSi₃⁺], 278.0 (45) [C₆H₁₂GeSi₃⁺], 264.0 (26) [C₆H₁₂GeSi₃⁺], 131.0 (32) [C₆H₁₂GeSi⁺], 87 (70) [C₆H₁₂Si⁺], 73 (80) [SiMe₃⁺], 57 (73) [C₆H₁₂Si⁺].
rt = 21.9 min, (11, n = 1)
m/z (%): 408.2 (43) [M⁺], 306.0 (90) [C₁₀H₂₈GeSi₃⁺], 292.0 (80) [C₉H₂₆GeSi₃⁺], 278.0 (40) [C₈H₂₄GeSi₃⁺], 131.0 (28) [C₇H₂₄GeSi⁺], 87.0 (100) [C₆H₁₂Si⁺], 73.0 (68) [SiMe₃⁺], 57.0 (94) [C₂H₅Si⁺].

rt = 23.0 min, (11, n = 0)
m/z (%): 422.2 (39) [M⁺], 320.0 (51) [C₁₁H₃₀GeSi₃⁺], 306.0 (93) [C₁₀H₂₈GeSi₃⁺], 292.0 (49) [C₉H₂₆GeSi₃⁺], 278.0 (33) [C₈H₂₄GeSi₃⁺], 131.0 (25) [C₇H₂₄GeSi⁺], 101.0 (39) [C₅H₁₃Si⁺], 87.0 (100) [C₄H₁₁Si⁺], 73.0 (59) [SiMe₃⁺], 57.0 (97) [C₂H₅Si⁺].

rt = 24.0 min, (12)
m/z (%): 436.2 (39) [M⁺], 407.0 (10) [C₁₅H₄₁GeSi⁺⁺], 334.0 (32) [C₁₂H₃₂GeSi⁺⁺], 320.0 (100) [C₁₁H₃₀GeSi₃⁺], 306.0 (60) [C₁₀H₂₈GeSi₃⁺], 292.0 (47) [C₉H₂₆GeSi₃⁺], 278.0 (20) [C₈H₂₄GeSi⁺⁺], 131.0 (21) [C₇H₂₄GeSi⁺], 101.0 (74) [C₅H₁₃Si⁺], 87 (96) [C₄H₁₁Si⁺], 73 (78) [SiMe₃⁺], 57 (100) [C₂H₅Si⁺].

Figure S8. Part of the GC trace of the non-polar phase of the reaction of tris(trimethylsilyl)silyltrimethylgermane (1) with triethylsilyl benzenium borate (10a).

Tris(trimethylsilyl)silyltrimethylgermane (1) with tri-iso-propylsilyl toluenium borate (10b)
The reaction was performed at -15 °C in toluene-d₈.

Non-polar phase
$^{29}$Si{¹H} NMR (99.31 MHz, 305.0 K, C₆D₆, δ ppm)²²: -5.1 (((CH₃)₂Si)₄Ge), -4.5 (((CH₃)₂((CH₃)₂CH)SiGe(Si(CH₃)₃)), 5.1 (((CH₃)₂((CH₃)₂CH)SiGe(Si(CH₃)₃)), 9.0 (((CH₃)₂CH)₃SiCH₃).
Figure S9. $^{29}$Si$^{1}$H NMR spectrum of the non-polar phase of the reaction of tris(trimethylsilyl)silyltrimethylgermane (1) with tri-iso-propylsilyl toluenium borate (10b).

GC-MS:

rt = 8.2 min, $^3$Pr$_3$SiMe

m/z (%): 172.2 (5) [M$^+$], 157.2 (1) [M$^+$-Me], 129.1 (100) [M$^+$-$^3$Pr], 115.1 (1) [M$^+$-$^3$Pr-Me], 101.0 (17) [M$^+$-$^3$Pr-2Me], 87.0 (45) [M$^+$-2$^3$Pr].

rt = 15.4 min, (2)

m/z (%): 366.2 (12) [M$^+$], 351.1 (10) [M$^+$-Me], 278.0 (55) [M$^+$-SiMe$_3$-Me], 219.0 (17) [C$_6$H$_{12}$GeSi$_2$$^+$], 204.0 (15) [C$_6$H$_{13}$GeSi$_2$$^+$], 145.0 (20) [C$_3$H$_7$GeSi$_3$$^+$], 131.0 (40) [C$_2$H$_6$GeSi$^+$], 73.0 (100) [SiMe$_3^+$].

rt = 17.9 min, (Me$_3$Si)$_3$GeSiMe$_2$Pr

m/z (%): 394.0 (14) [M$^+$], 351.1 (14) [C$_{11}$H$_{33}$GeSi$_4$], 278.0 (48) [C$_8$H$_{24}$GeSi$_5$$^+$], 203.0 (28) [C$_5$H$_{13}$GeSi$_2$$^+$], 131.0 (27) [C$_2$H$_6$GeSi$^+$], 73.0 (100) [SiMe$_3^+$].

Figure S10. Part of the GC trace of the non-polar phase of the reaction tris(trimethylsilyl)silyltrimethylgermane (1) with tri-iso-propylsilyl toluenium borate (10b).
Tris(trimethylsilyl)silyltrimethylgermane (1) with trimethylsilyl toluenium borate (10c)

The reaction was performed at 0 °C in toluene-d₈.

Non-polar phase

$^1$H NMR (499.87 MHz, 297.0 K, C₇D₈, δ ppm): 0.0 ($\text{[(CH}_3\text{)}_4\text{Si]}$, 0.26 ($\text{[(CH}_3\text{)}_3\text{Si]}_4\text{Ge]}$). $^{13}$C($^1$H) NMR (125.70 MHz, 299.0 K, C₇D₈, δ ppm): 0.0 ($\text{[(CH}_3\text{)}_4\text{Si]}$, 3.6 ($\text{[(CH}_3\text{)}_3\text{Si]}_4\text{Ge]}$). $^{29}$Si($^1$H) NMR (99.31 MHz, 295.5 K, C₇D₈, δ ppm): -5.1 ($\text{[(CH}_3\text{)}_3\text{Si]}_4\text{Ge]}$, 0.0 ($\text{[(CH}_3\text{)}_4\text{Si]}$).

Figure S11. $^{29}$Si($^1$H) NMR spectrum of the non-polar phase of the reaction of tris(trimethylsilyl)silyltrimethylgermane (1) with trimethylsilyl toluenium borate (10c).

Rearrangement of tris(trimethylsilyl)silyldimethylgermyl toluenium borate (3(C₇D₈)[B(C₆F₅)₄]) to tris(trimethylsilyl)germyldimethylsilyl toluenium borate (8(C₇D₈)[B(C₆F₅)₄]) starting from silagermane (1)

To a solution of 0.18 g (0.50 mmol) tris(trimethylsilyl)silyltrimethylgermane 1 in 1 mL toluene-d₈ cooled to -20°C 1 eq. tri-iso-propylsilyl toluenium borate 10b was slowly added via a Teflon tube. The mixture was stirred for 1 h at -20 °C. The brown polar phase and the light yellow non-polar phase were each transferred to separate NMR tubes at -20 °C and stored at -60 °C overnight until the NMR spectra were recorded the next morning. The polar phase contained borates [3(C₇D₈)][B(C₆F₅)₄] and [8(C₇D₈)][B(C₆F₅)₄]. The non-polar phase contained methyl-tri-iso-propylsilane and the rearrangement product 2.

Polar phase:

$^1$H NMR (499.87 MHz, 253.0 K, C₇D₈, δ ppm): -0.15 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{GeSi(CH}_3\text{)}_2\text{]}$), 0.07 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{GeSi(CH}_3\text{)}_2\text{]}$), 0.12 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{SiGe(CH}_3\text{)}_2\text{]}$), 0.28 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{SiGe(CH}_3\text{)}_2\text{]}$). $^{13}$C($^1$H) NMR (125.71 MHz, 253.0 K, C₇D₈, δ ppm): 1.6 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{SiGe(CH}_3\text{)}_2\text{]}$), 2.5 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{GeSi(CH}_3\text{)}_2\text{]}$), 5.5 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{GeSi(CH}_3\text{)}_2\text{]}$), 12.1 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{SiGe(CH}_3\text{)}_2\text{]}$).

$^{29}$Si($^1$H) NMR (99.31 MHz, 253.0 K, C₇D₈, δ ppm): -87.9 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{SiGe(CH}_3\text{)}_2\text{]}$), -7.9 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{SiGe(CH}_3\text{)}_2\text{]}$), -2.4 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{GeSi(CH}_3\text{)}_2\text{]}$), 98.1 ($\text{[(CH}_3\text{)}_3\text{Si]}_3\text{GeSi(CH}_3\text{)}_2\text{]}$).
Figure S12a. $^1$H NMR spectrum obtained from the polar phase of the reaction of silagermane 1 with tri-iso-propylsilyl toluenium borate (10b) after 1h at -20°C.

Figure S12b. $^{13}$C($^1$H) NMR spectrum obtained from the polar phase of the reaction of silagermane 1 with tri-iso-propylsilyl toluenium borate (10b) after 1h at -20°C.

Figure S12c. $^{29}$Si($^1$H) NMR spectrum obtained from the polar phase of the reaction of silagermane 1 with tri-iso-propylsilyl toluenium borate (10b) after 1h at -20°C.
Non-polar phase:

$^1$H NMR (499.87 MHz, 305.0 K, C$_7$D$_8$, δ ppm): -0.17 (s, ((CH$_3$)$_2$CH)$_3$SiCH$_3$), 0.26 (s, ((CH$_3$)$_3$Si)$_4$Ge), 0.86 (sept, $^3$$J_{H,H}$ = 7.3 Hz, ((CH$_3$)$_2$CH)$_3$SiCH$_3$), 0.97 (d, $^3$$J_{H,H}$ = 7.3 Hz, ((CH$_3$)$_2$CH)$_3$SiCH$_3$). $^{13}$C($^1$H) NMR (127.71 MHz, 305.0 K, C$_7$D$_8$, δ ppm): -10.1 ( ((CH$_3$)$_2$CH)$_3$SiCH$_3$), 3.5 ( ((CH$_3$)$_3$Si)$_4$Ge), 11.8 ( ((CH$_3$)$_2$CH)$_3$SiCH$_3$), 18.8 ( ((CH$_3$)$_2$CH)$_3$SiCH$_3$). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_7$D$_8$, δ ppm): -5.1 ( ((CH$_3$)$_3$Si)$_4$Ge), 9.0 ( ((CH$_3$)$_2$CH)$_3$SiCH$_3$).

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Figure S13a. Part of the GC trace obtained from the non-polar phase of the reaction of silagermane 1 with tri-isopropylsilyl toluenium borate (10b) after 1h at -20°C.

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Figure S13b. $^1$H NMR spectrum obtained from the non-polar phase of the reaction of silagermane 1 with tri-isopropylsilyl toluenium borate (10b) after 1h at -20°C.

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Figure S13c. $^{13}$C($^1$H) NMR spectrum obtained from the non-polar phase of the reaction of silagermane 1 with tri-isopropylsilyl toluenium borate (10b) after 1h at -20°C.
Figure S13d. $^{29}$Si$^{1}$H NMR spectrum obtained from the non-polar phase of the reaction of silagermane 1 with tri-isopropylsilyl toluenium borate (10b) after 1h at -20°C.

Rearrangement of tris(trimethylsilyl)silyldimethylgermyl toluenium borate (3(C$_7$D$_8$)[B(C$_6$F$_5$)$_4$]) to tris(trimethylsilyl)germyldimethylsilyl toluenium borate (8(C$_7$D$_8$)[B(C$_6$F$_5$)$_4$]) starting from hydrogen substituted silagermane (14)

0.14 g (0.40 mmol) tris(trimethylsilyl)silyldimethylgermane 14 and 0.37 g (0.40 mmol) triphenylmethyl tetrakis(pentafluorophenyl)borate were each dissolved in 1 mL toluene-d$_8$ and cooled to -20 °C. Silagermane 14 was slowly added to the borate salt via a Teflon tube and the mixture was stirred at -20 °C for 1.5 h. The brown polar phase and the light yellow non-polar phase were each transferred to NMR tubes at -20 °C. The NMR spectra were recorded at -20 °C. The polar phase contained borates [3(C$_7$D$_8$)[B(C$_6$F$_5$)$_4$]] and [8(C$_7$D$_8$)][B(C$_6$F$_5$)$_4$]). The non-polar phase contained triphenylmethane and the rearrangement product 2.

Polar phase:

$^1$H NMR (499.87 MHz, 253.0 K, C$_7$D$_8$, δ ppm): -0.15 (((CH$_3$)$_3$Si)$_3$SiGeSi(CH$_3$)$_2$’), 0.07 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’), 0.12 (((CH$_3$)$_3$Si)$_3$SiGeSi(CH$_3$)$_2$’), 0.28 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’). $^{13}$C$^{1}$H NMR (125.71 MHz, 253.0 K, C$_7$D$_8$, δ ppm): 1.6 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’), 2.4 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’), 5.5 (((CH$_3$)$_3$Si)$_3$SiGeSi(CH$_3$)$_2$’), 12.1 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’).

$^{29}$Si$^{1}$H NMR (99.31 MHz, 253.0 K, C$_7$D$_8$, δ ppm): -87.9 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’), -7.9 (((CH$_3$)$_3$Si)$_3$SiGe(CH$_3$)$_2$’), -2.4 (((CH$_3$)$_3$Si)$_3$SiGeSi(CH$_3$)$_2$’)), 98.1 (((CH$_3$)$_3$Si)$_3$SiGeSi(CH$_3$)$_2$’).
Figure S14a. $^1$H NMR spectrum obtained from the polar phase of the reaction of germane 14 with [Ph$_3$C][B(C$_6$F$_5$)$_4$] after 2h at -20°C.

Figure S14b. $^{13}$C$^1$H NMR spectrum obtained from the polar phase of the reaction of germane 14 with [Ph$_3$C][B(C$_6$F$_5$)$_4$] after 2h at -20°C.
Figure S14c. $^{29}$Si($^1$H) NMR spectrum obtained from the polar phase of the reaction of germane 14 with [Ph₃C][B(C₆F₅)₄] after 2h at -20°C.

Figure S15a. $^{29}$Si($^1$H) NMR spectrum obtained from the polar phase of the reaction of germane 14 with [Ph₃C][B(C₆F₅)₄] after 20h at -20°C.

Figure S15b. $^1$H NMR spectrum obtained from the polar phase of the reaction of germane 14 with [Ph₃C][B(C₆F₅)₄] after 20h at -20°C.
Non-polar phase:

\(^1\)H NMR (499.87 MHz, 305.0 K, C\(_7\)D\(_8\), \(\delta\) ppm): 0.30 (s, ((CH\(_3\))\(_3\)Si)\(_4\)Ge), 5.38 (s, Ph\(_3\)CH), 6.98-7.09 (m, Ph\(_3\)CH). \(^{13}\)C\(^{1}\)H\) NMR (127.71 MHz, 305.0 K, C\(_7\)D\(_8\), \(\delta\) ppm): 3.5 ((CH\(_3\))\(_3\)Si)\(_4\)Ge), 57.1 (Ph\(_3\)CH), 125.4 (Ph\(_3\)CH), 128.3 (Ph\(_3\)CH), 129.2 (Ph\(_3\)CH), 144.3 (Ph\(_3\)CH). \(^{29}\)Si\(^{1}\)H\) NMR (99.31 MHz, 305.0 K, C\(_7\)D\(_8\), \(\delta\) ppm): -5.1 ((CH\(_3\))\(_3\)Si)\(_4\)Ge).

Figure S16a. \(^1\)H NMR spectrum obtained from the non-polar phase of the reaction of germane 14 with [Ph\(_3\)C][B(C\(_6\)F\(_5\))\(_4\)] after 20h at -20°C.

Figure S16b. \(^{13}\)C\(^{1}\)H\) NMR spectrum obtained from the non-polar phase of the reaction of germane 14 with [Ph\(_3\)C][B(C\(_6\)F\(_5\))\(_4\)] after 20h at -20°C.

Figure S16c. \(^{29}\)Si\(^{1}\)H\) NMR spectrum obtained from the non-polar phase of the reaction of germane 14 with [Ph\(_3\)C][B(C\(_6\)F\(_5\))\(_4\)] after 20h at -20°C. The signal is due to the product germane 2.
Tris(trimethylsilyl)germyldimethylsilyl toluenium borate \((8(C_7H_8)[B(C_6F_5)_4])\) from silane 15

0.18 g (0.50 mmol) tris(trimethylsilyl)germyldimethylsilane 15 and 0.46 g (0.50 mmol) triphenylmethyl tetrakis(pentafluorophenyl)borate were both dissolved in 1 mL toluene-d_8 and cooled to -20 °C. Germysilane 15 was slowly added to the borate salt via a Teflon tube and the mixture was stirred at -20 °C for 1.5 h. The brown polar phase and the light yellow non-polar phase were each transferred to separate NMR tubes at -20 °C and stored at -60 °C overnight until the NMR spectra were recorded the next morning. The polar phase contained borate \([8(C_7D_8)][B(C_6F_5)_4]\). The non-polar phase contained triphenylmethane and the rearrangement product 2.

**Polar phase:**

\(^1H\) NMR (499.87 MHz, 253.0 K, \(C_7D_8\), δ ppm): -0.15 \(((CH_3)₃Si)₂GeSi(CH₃)₂^+\), 0.12 \(((CH_3)₃Si)₂GeSi(CH₃)₂^+\). \(^{13}C\)\(^{1}H\) NMR (125.71 MHz, 253.0 K, \(C_7D_8\), δ ppm): 2.5 \(((CH_3)₃Si)₂GeSi(CH₃)₂^+\), 5.5 \(((CH_3)₃Si)₂GeSi(CH₃)₂^+\). \(^{29}Si\)\(^{1}H\) NMR (99.31 MHz, 253.0 K, \(C_7D_8\), δ ppm): -2.4 \(((CH_3)₃Si)₂GeSi(CH₃)₂^+\), 98.1 \(((CH_3)₃Si)₂GeSi(CH₃)₂^+\).

**Figure S17a.** \(^1H\) NMR spectrum obtained from the polar phase of the reaction of silane 15 with \([Ph₃C][B(C_6F_5)_4]\) after 1.5h at -20°C.

**Figure S17b.** \(^{13}C\)\(^{1}H\) NMR spectrum obtained from the polar phase of the reaction of silane 15 with \([Ph₃C][B(C_6F_5)_4]\) after 1.5h at -20°C.
Figure S17c. $^{29}$Si-$^1$H NMR spectrum obtained from the polar phase of the reaction of silane 15 with [Ph$_3$C][B(C$_6$F$_5$)$_4$] after 1.5h at -20°C.

Non-polar phase:
$^1$H NMR (499.87 MHz, 305.0 K, C$_7$D$_8$, δ ppm): 0.29 (s, ((CH$_3$)$_3$Si)$_4$Ge), 5.38 (s, Ph$_3$CH), 6.98-7.10 (m, Ph$_3$CH). $^{13}$C-$^1$H) NMR (125.69 MHz, 305.0 K, C$_7$D$_8$, δ ppm): 3.5 (((CH$_3$)$_3$Si)$_4$Ge), 57.2 (Ph$_3$CH), 125.4 (Ph$_3$CH), 128.3 (Ph$_3$CH), 129.2 (Ph$_3$CH), 144.3 (Ph$_3$CH). $^{29}$Si-$^1$H NMR (99.31 MHz, 305.0 K, C$_7$D$_8$, δ ppm): -5.1 (((CH$_3$)$_3$Si)$_4$Ge).

Figure S18a. $^1$H NMR spectrum obtained from the non-polar phase of the reaction of silane 15 with [Ph$_3$C][B(C$_6$F$_5$)$_4$].
**Figure S18b.** $^{13}$C{\textsuperscript{1}H} NMR spectrum obtained from the non-polar phase of the reaction of silane 15 with [Ph3C][B(C6F5)4].

**Figure S18c.** $^{29}$Si{\textsuperscript{1}H} NMR spectrum obtained from the non-polar phase of the reaction of silane 15 with [Ph3C][B(C6F5)4].

Tris(trimethylsilyl)germyldimethylsilyl-phenylchloronium borate ([8(C6D5Cl)3][B(C6F5)4]) from silane 15

0.09 g (0.25 mmol) tris(trimethylsilyl)germyldimethylsilane 15 and 0.23 g (0.25 mmol) triphenylmethyl tetrakis(pentafluorophenyl)borate were both dissolved in 0.5 mL chlorobenzene-d\textsubscript{5} and cooled to -20 °C. Germysilane 15 was slowly added to the borate salt via a Teflon tube and the mixture was stirred at -20 °C for 1.5 h. The brown solution was transferred into a NMR tube at -20 °C and stored at -60 °C overnight until the NMR spectra were recorded the next morning. The mixture contained borate [8(C6D5Cl)3][B(C6F5)4], the rearrangement product 2 and triphenylmethane.

$^{29}$Si{\textsuperscript{1}H} NMR (99.31 MHz, 253.0 K, C\textsubscript{6}D\textsubscript{6}Cl, δ ppm): -5.1 (((CH\textsubscript{3})\textsubscript{3}Si)\textsubscript{4}Ge), -1.4 (((CH\textsubscript{3})\textsubscript{3}Si)\textsubscript{3}GeSi(CH\textsubscript{3})\textsubscript{2}+), 154.3 (((CH\textsubscript{3})\textsubscript{3}Si)\textsubscript{3}GeSi(CH\textsubscript{3})\textsubscript{2}+).

Tris(trimethylsilyl)germyldimethylsilyl toluenium borate (8(C7D8)[B(C6F5)4]) from germane 16

0.11 g (0.32 mmol) Bis(trimethylsilyl)pentamethyldisilanylgermane 16 and 0.29 g (0.32 mmol) triphenylmethyl tetrakis(pentafluorophenyl)borate were both dissolved in 1 mL toluene-d\textsubscript{8} and cooled to -20 °C.
Silylgermane 18 was slowly added to the borate salt via a Teflon tube and the mixture was stirred at -20 °C for 5 min. The brown polar phase and the light yellow non-polar phase were each transferred to separate NMR tubes at -20 °C and stored at -60 °C for 5 h until the NMR spectra were recorded. At -60°C the polar phase solidifies and no further reaction is expected. The NMR spectra of the polar phase recorded at -20°C contained nearly exclusively borate $\left[\text{B}(\text{C}_7\text{D}_8)\right]\left[\text{B}(\text{C}_6\text{F}_5)_4\right]$ (see Figure S12). The non-polar phase contained triphenylmethane and the rearrangement product 2.

**Polar phase:**

$^1\text{H}$ NMR (499.87 MHz, 253.0 K, C$_7$D$_8$, δ ppm): -0.16 (features of $\text{GeSi(CH}_3\text{)}_2^+$), 0.12 (features of $\text{GeSi(CH}_3\text{)}_2^+$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, 253.0 K, C$_7$D$_8$, δ ppm): 2.5 (features of $\text{GeSi(CH}_3\text{)}_2^+$), 5.5 (features of $\text{GeSi(CH}_3\text{)}_2^+$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 253.0 K, C$_7$D$_8$, δ ppm): -2.4 (features of $\text{GeSi(CH}_3\text{)}_2^+$), 98.2 (features of $\text{GeSi(CH}_3\text{)}_2^+$).

![Figure S19a](image)

Figure S19a. $^1\text{H}$ NMR spectrum obtained from the polar phase of the reaction of germane 16 with $\left[\text{Ph}_3\text{C}\right]\left[\text{B}(\text{C}_6\text{F}_5)_4\right]$ after 5 min at -20°C.

![Figure S19b](image)

Figure S19b. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum obtained from the polar phase of the reaction of germane 16 with $\left[\text{Ph}_3\text{C}\right]\left[\text{B}(\text{C}_6\text{F}_5)_4\right]$ after 5 min at -20°C.
**Figure S19c.** $^{29}$Si($^1$H) NMR spectrum obtained from the polar phase of the reaction of germane 16 with [Ph$_3$C][B(C$_6$F$_5$)$_4$] after 5 min at -20°C.

**Non-polar phase:**

$^1$H NMR (499.87 MHz, 305.0 K, C$_7$D$_8$, $\delta$ ppm): 0.30 (s, ((CH$_3$)$_3$Si)$_4$Ge), 5.38 (s, Ph$_3$CH), 6.98-7.10 (m, Ph$_3$CH).

$^{13}$C($^1$H) NMR (125.69 MHz, 305.0 K, C$_7$D$_8$, $\delta$ ppm): 3.5 ([(CH$_3$)$_3$Si]$_4$Ge), 57.1 (Ph$_3$CH), 125.4 (Ph$_3$CH), 128.2 (Ph$_3$CH), 129.1 (Ph$_3$CH), 144.3 (Ph$_2$CH).

$^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_7$D$_8$, $\delta$ ppm): -5.1 ([(CH$_3$)$_3$Si]$_4$Ge).

**Figure S20a.** $^1$H NMR spectrum obtained from the non-polar phase of the reaction of germane 16 with [Ph$_3$C][B(C$_6$F$_5$)$_4$].

**Figure S20b.** $^1$H NMR spectrum obtained from the non-polar phase of the reaction of germane 16 with [Ph$_3$C][B(C$_6$F$_5$)$_4$].
**Figure S20c.** $^{29}$Si($^1$H) NMR spectrum obtained from the non-polar phase of the reaction of germane 16 with [Ph$_3$C][B(C$_6$F$_5$)$_4$].
Decomposition of silyl toluenium ion $8(C_7D_8)$ at higher temperatures

The thermolability of silyl toluenium ion $8(C_7D_8)$ is shown by $^{29}$Si$^{1}$H NMR spectroscopy at different temperatures. The amount of decomposition products increases with higher temperatures (Figure S14, b-f)) and the intensity of $8(C_7D_8)$ decreases. In the independent synthesis of $8(C_7D_8)$ the same decomposition products already appear at -20 °C (Figure S14, a)).

Figure S21. a) 99 MHz $^{29}$Si$^{1}$H NMR spectrum (toluene-$d_8$, -20 °C) of silyl toluenium ion $8(C_7D_8)$ at -20 °C in toluene synthesized by hydride transfer from germane 16 at -20 °. b-f) 99 MHz $^{29}$Si$^{1}$H NMR spectra (toluene-$d_8$, -20 °C) of silyl toluenium ion $8(C_7D_8)$ in toluene synthesized by hydride transfer from silane 15. b) at -20°C c) at -10 °C; d) at 0 °C; e) at 10 °C, f) at 20 °C.
Computational Details

All quantum chemical calculations were carried out using the Gaussian09 package.\textsuperscript{13} In order to be consistent with previously reported data\textsuperscript{14}, the molecular structures of toluene complexes $[3(C_7H_8)]^+ - [8(C_7H_8)]^+$ were optimized at the density functional B3LYP level of theory\textsuperscript{15} using the 6-311+G(d,p) basis. Every stationary point was identified by a subsequent frequency calculation as minimum (Number of imaginary frequencies (NIMAG): 0). The SCF energies, $E(\text{SCF})$, for all optimized molecular structures obtained with this method are given in along with the corresponding Gibbs free energies at $T=298.15 \text{K}$ and $p=0.101 \text{ MPa (1 atm)}$ in the gas phase, $G^{298}$, are given in Table S1 and the Diagram of relative ground state energies $E$ and Gibbs free energies at 298.15 K, $G^{298}$, of toluene complexes of isomeric cations 3 – 8 is given in Figure S22. The corresponding computed molecular structures are given in the form of their Cartesian coordinates in Table S2. 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{16} The influence of the highly polar medium on the structure optimizations was modeled using the PCM model\textsuperscript{17} with a dielectric constant of 78.4.

Table S1. Absolute SCF energies ($E(\text{SCF})$) and free Gibbs enthalpies, $G^{298}$, for compounds of interest (at B3LYP/6-311+G(d,p)).

| Compound | PG | $E(\text{SCF})$ [H/particle] | $G^{298}$ [H/particle] | NIMAG |
|----------|----|-----------------------------|------------------------|-------|
| $[3(C_7H_8)]^+$ | C1 | -3945.83349 | -3945.36640 | 0 |
| $[4(C_7H_8)]^+$ | C1 | -3945.82084 | -3945.35656 | 0 |
| $[5(C_7H_8)]^+$ | C1 | -3945.83612 | -3945.37290 | 0 |
| $[6(C_7H_8)]^+$ | C1 | -3945.82962 | -3945.36412 | 0 |
| $[7(C_7H_8)]^+$ | C1 | -3945.84438 | -3945.37829 | 0 |
| $[8(C_7H_8)]^+$ | C1 | -3945.85031 | -3945.38359 | 0 |
Figure S22. Diagram of relative ground state energies $E$ and Gibbs free energies at 298.15 K, $G^{298}$ (in parentheses), of toluene complexes of isomeric cations $3 \rightarrow 8$ (relative to cation $[3(C_7H_8)]^+$, calculated at B3LYP/6-311+G(d,p), in black). The complete reaction diagram for the isomerization of cations $3 \rightarrow 8$ as previously computed at B3LYP/6-311+G(d,p) is displayed in grey (from ref. 14, $Si \equiv SiMe_3; C \equiv CH_3$).
Table S2. Calculated molecular structures at B3LYP/6-311+G(d,p) in the form of their Cartesian coordinates.

| Compound | Standard orientation: |
|----------|------------------------|
| Center   | Atomic Number          | Atomic Number | Type | Coordinates (Angstroms) | X     | Y     | Z     |
|----------|------------------------|----------------|------|-------------------------|-------|-------|-------|
| 1        | 14                     | 0              |      |                         | 1.221865 | 0.123391 | 0.070805 |
| 2        | 14                     | 0              |      |                         | 1.081128 | 2.500044 | 0.385119 |
| 3        | 14                     | 0              |      |                         | 2.113682 | -1.060703 | 1.960967 |
| 4        | 14                     | 0              |      |                         | 2.459659 | -0.373862 | -1.954384 |
| 5        | 6                      | 0              |      |                         | 0.561165 | 2.910511  | 2.159080 |
| 6        | 1                      | 0              |      |                         | 0.475922 | 3.996924  | 2.269067 |
| 7        | 1                      | 0              |      |                         | -0.400318 | 2.478490 | 2.447894 |
| 8        | 1                      | 0              |      |                         | 1.304899 | 2.570195  | 2.884272 |
| 9        | 6                      | 0              |      |                         | -0.136722 | 3.281153 | -0.835253 |
| 10       | 1                      | 0              |      |                         | -1.162543 | 2.932333 | -0.691650 |
| 11       | 1                      | 0              |      |                         | -0.139232 | 4.367791 | -0.698224 |
| 12       | 1                      | 0              |      |                         | 0.143867 | 3.083862  | -1.872918 |
| 13       | 6                      | 0              |      |                         | 2.801788 | 3.223889  | 0.08910 |
| 14       | 1                      | 0              |      |                         | 3.134306 | 3.096227  | -0.944110 |
| 15       | 1                      | 0              |      |                         | 2.779816 | 4.299454  | 0.294410 |
| 16       | 1                      | 0              |      |                         | 3.556080 | 2.781571  | 0.744461 |
| 17       | 6                      | 0              |      |                         | 3.615384 | -0.098154 | 2.585329 |
| 18       | 1                      | 0              |      |                         | 3.347277 | 0.897718  | 2.947320 |
| 19       | 1                      | 0              |      |                         | 4.069458 | -0.638763 | 3.422562 |
| 20       | 1                      | 0              |      |                         | 4.382351 | 0.016911  | 1.815309 |
| 21       | 6                      | 0              |      |                         | 4.293003 | -0.179540 | 1.537407 |
| 22       | 1                      | 0              |      |                         | 4.629685 | -0.910745 | -0.798470 |
| 23       | 1                      | 0              |      |                         | 4.883214 | -0.336836 | -2.446793 |
| 24       | 1                      | 0              |      |                         | 4.529090 | 0.818141  | -1.160370 |
| 25       | 6                      | 0              |      |                         | 0.825111 | -1.173948 | 3.345284 |
| 26       | 1                      | 0              |      |                         | 1.287784 | -1.612012 | 4.236005 |
| 27       | 1                      | 0              |      |                         | 0.432112 | -0.195050 | 3.632604 |
| 28       | 1                      | 0              |      |                         | -0.016089 | -1.819671 | 3.075649 |
| 29       | 6                      | 0              |      |                         | 2.644895 | -2.809994 | 1.477754 |
| 30       | 1                      | 0              |      |                         | 3.042790 | -3.322721 | 2.360076 |
| 31       | 1                      | 0              |      |                         | 1.816197 | -3.413292 | 1.097763 |
| 32       | 1                      | 0              |      |                         | 3.434296 | -2.807282 | 0.721883 |
| 33       | 6                      | 0              |      |                         | 2.144009 | -2.140184 | -2.556886 |
| 34       | 1                      | 0              |      |                         | 2.818200 | -2.355842 | -3.392703 |
| 35       | 1                      | 0              |      |                         | 2.336004 | -2.887842 | -1.783292 |
| 36       | 1                      | 0              |      |                         | 1.124906 | -2.283486 | -2.927746 |
| 37       | 6                      | 0              |      |                         | 1.990802 | 0.831197  | -3.333784 |
| 38       | 1                      | 0              |      |                         | 2.561545 | 0.584293  | -4.235520 |
| 39       | 1                      | 0              |      |                         | 0.930615 | 0.779204  | -3.595715 |
| 40       | 1                      | 0              |      |                         | 2.223980 | 1.867198  | -3.076096 |
| 41       | 32                     | 0              |      |                         | -0.893106 | -0.878612 | -0.542977 |
| Number | Compound | Atomic Number | Type | X       | Y       | Z       |
|--------|----------|---------------|------|---------|---------|---------|
| 1      | 4(C₇H₈)⁺ | 14            | 0    | -0.362778 | 0.379834 | 0.041261 |
| 2      | 4(C₇H₈)⁺ | 14            | 0    | -0.496110 | 2.787683 | 0.150304 |
| 3      | 4(C₇H₈)⁺ | 14            | 0    | -0.986991 | -0.770080 | 2.059852 |
| 4      | 4(C₇H₈)⁺ | 32            | 0    | 1.681838  | -0.424522 | -1.084065 |
| 5      | 4(C₇H₈)⁺ | 14            | 0    | 3.667820  | -0.651172 | 0.332827 |
| 6      | 4(C₇H₈)⁺ | 6             | 0    | 2.059985  | 0.806717  | -2.603184 |
| 7      | 4(C₇H₈)⁺ | 1             | 0    | 2.905986  | 0.406210  | -3.166815 |
| 8      | 4(C₇H₈)⁺ | 1             | 0    | 1.210627  | 0.880866  | -3.286343 |
| 9      | 4(C₇H₈)⁺ | 1             | 0    | 2.323546  | 1.808699  | -2.261624 |
| 10     | 4(C₇H₈)⁺ | 6             | 0    | 1.362272  | -2.213013 | -1.906630 |
| 11     | 4(C₇H₈)⁺ | 1             | 0    | 2.321402  | -2.606336 | -2.251330 |
| 12     | 4(C₇H₈)⁺ | 1             | 0    | 0.940319  | -2.925439 | -1.196350 |
| 13     | 4(C₇H₈)⁺ | 1             | 0    | 0.709007  | -2.136822 | -2.778441 |
| 14     | 4(C₇H₈)⁺ | 6             | 0    | 4.061145  | 0.897533  | 1.336350 |
| 15     | 4(C₇H₈)⁺ | 1             | 0    | 3.285354  | 1.140685  | 2.065946 |
| 16     | 4(C₇H₈)⁺ | 1             | 0    | 4.992166  | 0.737586  | 1.890722 |
| 17     | 4(C₇H₈)⁺ | 1             | 0    | 4.210953  | 1.771700  | 0.697507 |
| 18     | 4(C₇H₈)⁺ | 6             | 0    | 5.068531  | -0.978863 | -0.893360 |
19  1  0  5.227255 -0.134845 -1.569690
20  1  0  6.002605 -1.139061 -0.344072
21  1  0  4.890642 -1.870571 -1.500260
22  6  0  3.458602 -2.142701  1.473481
23  1  0  4.392353 -2.320939  2.017222
24  1  0  2.672112 -1.995666  2.217716
25  1  0  3.229516 -3.053158  0.912985
26  6  0  0.184168 -0.058262  3.366885
27  1  0  0.000811  1.003993  3.548481
28  1  0  0.011178 -0.583410  4.312727
29  1  0  1.239746 -0.183868  3.116172
30  6  0  -0.716471 -2.630148  1.891988
31  1  0  -0.924916 -3.112280  2.853133
32  6  0  -2.766079 -0.418396  2.582463
33  1  0  -2.948448 -0.899526  3.549540
34  1  0  -2.961412  0.649297  2.704660
35  6  0  -3.493427 -0.816576  1.873290
36  1  0  -0.588884  3.547385 -1.578446
37  1  0  -1.511941  3.312695 -2.114185
38  6  0  -0.545211  4.637640 -1.482308
39  1  0  0.250861  3.241936 -2.063020
40  6  0  1.096575  3.359058  0.990556
41  1  0  1.219052  2.939760  1.991898
42  1  0  1.986855  3.113517  0.407757
43  1  0  1.063314  4.448965  1.096064
44  6  0  -1.975714  3.332730  1.190177
45  1  0  -2.015544  4.427114  1.211111
46  1  0  -2.932076  2.978206  0.798983
47  1  0  -1.888614  2.991225  2.224852
48  6  0  -3.087413  0.740219 -1.346017
49  6  0  -4.272247  0.177552 -0.905244
50  6  0  -4.413344 -1.216089 -0.797436
51  6  0  -3.314704 -2.032153 -1.122273
52  6  0  -2.124172 -1.482895 -1.561293
53  6  0  -1.970407 -0.075098 -1.656567
54  1  0  -3.023036  1.811471 -1.484046
55  1  0  -5.115810  0.816752 -0.671318
56  1  0  -3.415868 -3.110038 -1.058563
57  1  0  -1.308483 -2.130095 -1.853974
58  1  0  -1.198978  0.326568 -2.309263
59  6  0  -5.713453 -1.832623 -0.367413
60  1  0  -6.116808 -2.464689 -1.164759
61  6  0  -5.713453 -1.832623 -0.367413
62  1  0  -6.116808 -2.464689 -1.164759
Compound \([5\text{C}_{14}^2\text{H}_{22}]^{+}\)

| Center Number | Atomic Number | Atomic Number | Type | X (Å) | Y (Å) | Z (Å) |
|---------------|---------------|---------------|------|-------|-------|-------|
| 1             | 32            | 0             |      | -0.437747 | 0.256388 | -0.565651 |
| 2             | 14            | 0             |      | -1.848288 | 2.242630 | -0.180697 |
| 3             | 14            | 0             |      | 1.635615  | -0.288111 | 0.619093  |
| 4             | 14            | 0             |      | 2.638387  | -2.310976 | -0.191730 |
| 5             | 14            | 0             |      | 3.059020  | 1.622235 | 0.286335  |
| 6             | 6             | 0             |      | -0.879410 | 3.638479 | -1.008291 |
| 7             | 1             | 0             |      | -1.269576 | 0.008859 | -3.009142 |
| 8             | 1             | 0             |      | 0.015837  | -1.181907 | -2.677224 |
| 9             | 6             | 0             |      | -3.505176 | 2.039596 | -0.922752 |
| 10            | 1             | 0             |      | -4.051714 | 2.987536 | -0.996367 |
| 11            | 1             | 0             |      | -3.383437 | 1.792401 | -2.108042 |
| 12            | 1             | 0             |      | -4.124984 | 1.270218 | -0.588627 |
| 13            | 6             | 0             |      | -2.046318 | 2.556331 | 1.663991  |
| 14            | 1             | 0             |      | -2.606175 | 1.758995 | 2.157722  |
| 15            | 1             | 0             |      | -1.081966 | 2.658591 | 2.168204  |
| 16            | 1             | 0             |      | -2.596845 | 3.490517 | 1.817644  |
| 17            | 6             | 0             |      | 3.415206  | -2.028022 | -1.891994 |
| 18            | 1             | 0             |      | 3.858316  | -2.962450 | -2.252066 |
| 19            | 1             | 0             |      | 2.683715  | -1.706610 | -2.638407 |
| 20            | 6             | 0             |      | 4.213613  | -1.281953 | -1.862826 |
| 21            | 1             | 0             |      | 1.386410  | -3.729144 | -0.319622 |
| 22            | 1             | 0             |      | 1.923639  | -4.653577 | -0.557201 |
| 23            | 1             | 0             |      | 0.850038  | -3.904540 | 0.617261  |
| 24            | 1             | 0             |      | 0.653424  | -3.577191 | -1.117260 |
| 25            | 6             | 0             |      | 3.966914  | -2.797588 | 1.062621  |
| 26            | 1             | 0             |      | 3.543892  | -2.987850 | 2.052877  |
| 27            | 1             | 0             |      | 4.459140  | -3.719181 | 0.734264  |
| 28            | 1             | 0             |      | 4.739091  | -2.031769 | 1.167373  |
| 29            | 6             | 0             |      | 4.817318  | 1.098626 | 0.745053  |
| 30            | 1             | 0             |      | 5.217240  | 0.344474 | 0.062807  |
| 31            | 1             | 0             |      | 5.477212  | 1.971323 | 0.692810  |
| 32            | 1             | 0             |      | 4.878794  | 0.703644 | 1.762538  |
| 33            | 6             | 0             |      | 3.032407  | 2.213809 | -1.510666 |
| 34            | 1             | 0             |      | 2.066319  | 2.633036 | -1.805392 |
| 35            | 1             | 0             |      | 3.778802  | 3.003706 | -1.645044 |
| Number | Atomic Number | Type | X    | Y    | Z    |
|--------|---------------|------|------|------|------|
| 1      | 32            | 0    | -0.966844 | -0.346516 | -0.387148 |
| 2      | 14            | 0    | -1.887664 | -2.306926 | 0.761038  |
| 3      | 14            | 0    | -2.744755 | 1.343867  | -0.644339 |
| 4      | 14            | 0    | 0.841495  | 0.794968  | 0.785910  |
| 5      | 14            | 0    | 1.664333  | 2.980807  | 0.175295  |
| 6      | 6             | 0    | 3.354066  | 3.250872  | 0.982275  |
| 7      | 1             | 0    | 3.656761  | 4.290693  | 0.818022  |
| 8      | 1             | 0    | 3.332007  | 3.094217  | 2.064580  |
| 9      | 1             | 0    | 4.142831  | 2.622095  | 0.560944  |
| 10     | 6             | 0    | 0.438100  | 4.219541  | 0.905164  |
| 11     | 1             | 0    | -0.557778 | 4.142482  | 0.465046  |
| 12     | 1             | 0    | 0.342411  | 4.114224  | 1.989079  |
| 13     | 1             | 0    | 0.804030  | 5.232914  | 0.707796  |
| 14     | 6             | 0    | 1.793333  | 3.188835  | -1.695293 |
| 15     | 1             | 0    | 2.560164  | 2.549736  | -2.139866 |
| 16     | 1             | 0    | 0.849446  | 2.979119  | -2.202902 |
| 17     | 1             | 0    | 2.065125  | 4.224602  | -1.924422 |
| 18     | 6             | 0    | 0.610356  | 0.742968  | 2.665259  |

Compound \(\text{[6} \text{(C}_7\text{H}_8)]^+\)

Standard orientation:

| Center Number | Atomic Number | Type | X    | Y    | Z    |
|---------------|---------------|------|------|------|------|
| 1             | 32            | 0    | -0.966844 | -0.346516 | -0.387148 |
| 2             | 14            | 0    | -1.887664 | -2.306926 | 0.761038  |
| 3             | 14            | 0    | -2.744755 | 1.343867  | -0.644339 |
| 4             | 14            | 0    | 0.841495  | 0.794968  | 0.785910  |
| 5             | 14            | 0    | 1.664333  | 2.980807  | 0.175295  |
| 6             | 6             | 0    | 3.354066  | 3.250872  | 0.982275  |
| 7             | 1             | 0    | 3.656761  | 4.290693  | 0.818022  |
| 8             | 1             | 0    | 3.332007  | 3.094217  | 2.064580  |
| 9             | 1             | 0    | 4.142831  | 2.622095  | 0.560944  |
| 10            | 6             | 0    | 0.438100  | 4.219541  | 0.905164  |
| 11            | 1             | 0    | -0.557778 | 4.142482  | 0.465046  |
| 12            | 1             | 0    | 0.342411  | 4.114224  | 1.989079  |
| 13            | 1             | 0    | 0.804030  | 5.232914  | 0.707796  |
| 14            | 6             | 0    | 1.793333  | 3.188835  | -1.695293 |
| 15            | 1             | 0    | 2.560164  | 2.549736  | -2.139866 |
| 16            | 1             | 0    | 0.849446  | 2.979119  | -2.202902 |
| 17            | 1             | 0    | 2.065125  | 4.224602  | -1.924422 |
| 18            | 6             | 0    | 0.610356  | 0.742968  | 2.665259  |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 19| 1| 0 | 0.418090 | -0.262049 | 3.045496 |
| 20| 1| 0 | 1.450422 | 1.174702 | 3.214793 |
| 21| 1| 0 | -0.274192 | 1.348288 | 2.896815 |
| 22| 6| 0 | -3.144539 | 2.180728 | 1.003225 |
| 23| 1| 0 | -3.466062 | 1.457739 | 1.757303 |
| 24| 1| 0 | -2.298372 | 2.738562 | 1.412376 |
| 25| 1| 0 | -3.964812 | 2.892810 | 0.863458 |
|   |   |   |   |   |   |
| 26| 6| 0 | -2.246274 | 2.629503 | -1.937209 |
| 27| 1| 0 | -1.991960 | 2.164780 | -2.893777 |
| 28| 1| 0 | -3.087268 | 3.307702 | -2.117366 |
| 29| 1| 0 | -1.397745 | 3.239426 | -1.621179 |
| 30| 6| 0 | -4.281299 | 0.437010 | -1.270889 |
| 31| 1| 0 | -5.072558 | 1.170561 | -1.461228 |
| 32| 1| 0 | -4.096956 | -0.093274 | -2.208852 |
| 33| 1| 0 | -4.670263 | -0.280136 | -0.544317 |
| 34| 6| 0 | -0.573313 | -3.506433 | 1.401459 |
| 35| 1| 0 | 0.058729 | -3.89027 | 0.596721 |
| 36| 1| 0 | 0.070684 | -3.055886 | 2.160598 |
| 37| 1| 0 | -1.073461 | -4.364466 | 1.863562 |
| 38| 6| 0 | -2.946993 | -3.209336 | -0.517084 |
| 39| 1| 0 | -3.416460 | -4.083742 | -0.052569 |
| 40| 1| 0 | -3.745164 | -2.580613 | -0.916649 |
| 41| 1| 0 | -2.348541 | -3.568000 | -1.359345 |
| 42| 6| 0 | -2.951141 | -1.744613 | 2.219649 |
| 43| 1| 0 | -3.795054 | -1.125071 | 1.906163 |
| 44| 1| 0 | -3.364552 | -2.622418 | 2.727577 |
| 45| 1| 0 | -2.377169 | -1.180542 | 2.960205 |
| 46| 6| 0 | 2.958029 | -0.315351 | 0.717066 |
| 47| 6| 0 | 2.737720 | -1.584702 | 1.300528 |
| 48| 6| 0 | 3.313542 | -0.254922 | -0.653916 |
| 49| 6| 0 | 2.809076 | -2.731660 | 0.528888 |
| 50| 1| 0 | 2.538973 | -1.658356 | 2.363041 |
| 51| 6| 0 | 3.370118 | -1.406580 | -1.415838 |
| 52| 1| 0 | 3.563490 | 0.698576 | -1.102198 |
| 53| 6| 0 | 3.126428 | -2.665512 | -0.937902 |
| 54| 1| 0 | 2.646951 | -3.698565 | 0.989926 |
| 55| 1| 0 | 3.640128 | -1.345345 | -2.464092 |
| 56| 6| 0 | 3.203698 | -3.912977 | -1.670766 |
| 57| 1| 0 | 3.371534 | -4.798102 | -1.055888 |
| 58| 1| 0 | 2.265310 | -4.062357 | -2.217358 |
| 59| 1| 0 | 4.000516 | -3.845465 | -2.414200 |
| 60| 6| 0 | -0.338554 | -0.817331 | -2.225191 |
| 61| 1| 0 | 0.077080 | 0.053647 | -2.733488 |
| 62| 1| 0 | 0.418516 | -1.600569 | -2.192655 |
| 63| 1| 0 | -1.188176 | -1.182175 | -2.805434 |
| 64| 1| 0 | 3.229692 | 0.513159 | 1.365804 |
Compound \([\text{7(C}_6\text{H}_5])^+\)

| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 32            | 0           | -0.176376     | 0.460499      | 0.226521      |
| 2             | 14            | 0           | -1.997492     | 0.830170      | 1.852293      |
| 3             | 14            | 0           | 0.211872      | 2.341948      | -1.327374     |
| 4             | 14            | 0           | 1.853411      | -0.629627     | 1.139415      |
| 5             | 14            | 0           | 3.643090      | -1.074685     | -0.378646     |
| 6             | 6             | 0           | 4.840062      | -2.197351     | 0.562735      |
| 7             | 1             | 0           | 5.701755      | -2.431939     | -0.071000     |
| 8             | 1             | 0           | 5.223202      | -1.720832     | 1.469432      |
| 9             | 1             | 0           | 4.376707      | -3.144763     | 0.850873      |
| 10            | 6             | 0           | 4.531571      | 0.525539      | -0.854412     |
| 11            | 1             | 0           | 3.909366      | 1.198993      | -1.449377     |
| 12            | 1             | 0           | 4.869427      | 1.073382      | 0.029706      |
| 13            | 1             | 0           | 5.419129      | 0.291717      | -1.451365     |
| 14            | 6             | 0           | 3.035717      | -1.972947     | -1.931338     |
| 15            | 1             | 0           | 2.488506      | -2.888755     | -1.689496     |
| 16            | 1             | 0           | 2.393841      | -1.344576     | -2.555401     |
| 17            | 1             | 0           | 3.892702      | -2.264044     | -2.547477     |
| 18            | 6             | 0           | 1.386060      | -2.235458     | 2.045044      |
| 19            | 1             | 0           | 2.203958      | -2.496675     | 2.724612      |
| 20            | 1             | 0           | 0.479486      | -2.139179     | 2.646247      |
| 21            | 1             | 0           | 1.258162      | -3.081672     | 1.365516      |
| 22            | 6             | 0           | 2.403462      | 0.641154      | 2.449352      |
| 23            | 1             | 0           | 1.665954      | 0.759927      | 3.247521      |
| 24            | 1             | 0           | 3.326564      | 0.281373      | 2.916013      |
| 25            | 1             | 0           | 2.615337      | 1.626380      | 2.028139      |
| 26            | 6             | 0           | 1.403764      | 3.473975      | -0.396672     |
| 27            | 1             | 0           | 0.988888      | 3.825494      | 0.551532      |
| 28            | 1             | 0           | 2.360053      | 2.987442      | -0.191944     |
| 29            | 1             | 0           | 1.608792      | 4.358221      | -1.009977     |
| 30            | 6             | 0           | 0.992172      | 1.752065      | -2.941444     |
| 31            | 1             | 0           | 0.324297      | 1.122723      | -3.535011     |
| 32            | 1             | 0           | 1.236488      | 2.626036      | -3.555023     |
| 33            | 1             | 0           | 1.920468      | 1.200784      | -2.778019     |
| 34            | 6             | 0           | -1.403322     | 3.252543      | -1.675592     |
| 35            | 1             | 0           | -1.210759     | 4.072549      | -2.375806     |
| 36            | 1             | 0           | -2.164017     | 2.609655      | -2.124677     |
| 37            | 1             | 0           | -1.825853     | 3.691783      | -0.768385     |
| 38            | 6             | 0           | -2.178200     | -0.030101     | 3.029525      |
| 39            | 1             | 0           | -2.447242     | -1.552274     | 2.509908      |
| 40            | 1             | 0           | -1.263755     | -0.812168     | 3.598873      |
| 41            | 1             | 0           | -2.072114     | -0.043127     | 3.750231      |
| 42            | 6             | 0           | -3.638019     | 1.210658      | 1.006196      |
| 43            | 1             | 0           | -4.381831     | 1.453714      | 1.772953      |
| Number | Atomic Type | Coordinates (Angstroms) X | Y     | Z     |
|--------|-------------|----------------------------|-------|-------|
| 1      | 14          | -1.101836                  | -0.842263 | 0.743822 |
| 2      | 32          | 1.007149                   | 0.045591  | -0.029523 |
| 3      | 14          | 0.876315                   | 2.356584  | -0.829667 |
| 4      | 14          | 1.923106                   | -1.492105 | -1.704257 |
| 5      | 14          | 2.334516                   | -0.031004 | 2.053026  |
| 6      | 6           | 1.116456                   | -2.708034 | 1.005521  |
| 7      | 1           | -0.298169                  | -2.952420 | 1.691007  |
| 8      | 1           | -2.046837                  | -3.056040 | 1.459434  |
| 9      | 1           | -0.940144                  | -3.267088 | 0.084160  |
| 10     | 6           | -1.980805                  | 0.016857  | 2.161495  |
| 11     | 1           | -1.932044                  | 1.103824  | 2.091672  |
| 12     | 1           | -3.027040                  | -0.288556 | 2.241820  |
| 13     | 1           | -1.483820                  | -0.285759 | 3.090424  |
| 14     | 6           | 0.621738                   | -1.893890 | -3.021543 |
| 15     | 1           | 0.212431                   | -0.994618 | -3.489957 |
| 16     | 1           | 1.078959                   | -2.493074 | -3.816313 |
| 17     | 1           | -0.207930                  | -2.483406 | -2.619672 |
| 18     | 6           | 2.613001                   | 3.095214  | -0.740935 |
| 19     | 1           | 2.595552                   | 4.113380  | -1.144561 |
| 20     | 1           | 2.986337                   | 3.157936  | 0.284275  |
| 21     | 1           | 3.333704                   | 2.522088  | -1.329964 |

**Compound [8 (C₈H₈)]⁺**

**Standard orientation:**
| 22 | 6  | 0   | 3.399291 | -0.648298 | -2.527058 |
| 23 | 1  | 0   | 3.856192 | -1.333544 | -3.249108 |
| 24 | 1  | 0   | 3.110730 | 0.254560  | -3.071582 |
| 25 | 1  | 0   | 4.170672 | -0.373405 | -1.803226 |
| 26 | 6  | 0   | 2.492822 | -3.100122 | -0.889535 |
| 27 | 1  | 0   | 1.676884 | -3.630520 | -0.392024 |
| 28 | 1  | 0   | 2.903219 | -3.771658 | -1.651365 |
| 29 | 1  | 0   | 3.279857 | -2.927344 | -0.150903 |
| 30 | 6  | 0   | -0.290601| 3.390776  | 0.243815  |
| 31 | 1  | 0   | -0.291669| 4.426697  | -0.111967 |
| 32 | 1  | 0   | -1.324118| 3.035801  | 0.216243  |
| 33 | 1  | 0   | 0.029568 | 3.404721  | 1.288735  |
| 34 | 6  | 0   | 0.306712 | 2.402326  | -2.635656 |
| 35 | 1  | 0   | 0.236998 | 3.443014  | -2.970092 |
| 36 | 1  | 0   | 1.023112 | 1.899171  | -3.290524 |
| 37 | 1  | 0   | -0.669606| 1.940255  | -2.803343 |
| 38 | 6  | 0   | 2.066472 | -1.646996 | 3.001492  |
| 39 | 1  | 0   | 2.258927 | -2.529118 | 2.385517  |
| 40 | 1  | 0   | 2.762033 | -1.682683 | 3.847062  |
| 41 | 1  | 0   | 1.058118 | -1.731544 | 3.416750  |
| 42 | 6  | 0   | 1.873380 | 1.420114  | 3.172449  |
| 43 | 1  | 0   | 2.461187 | 1.368504  | 4.095368  |
| 44 | 1  | 0   | 2.085068 | 2.384998  | 2.705363  |
| 45 | 1  | 0   | 0.817754 | 1.407840  | 3.456631  |
| 46 | 6  | 0   | 4.152550 | 0.093733  | 1.554623  |
| 47 | 1  | 0   | 4.772716 | 0.116222  | 2.457371  |
| 48 | 1  | 0   | 4.474236 | -0.763992 | 0.958649  |
| 49 | 1  | 0   | 4.366136 | 1.001238  | 0.985374  |
| 50 | 6  | 0   | -2.986618| 0.691628  | -0.975931 |
| 51 | 6  | 0   | -2.658586| -0.687247 | -1.026311 |
| 52 | 6  | 0   | -3.634637| -1.620724 | -0.596336 |
| 53 | 6  | 0   | -4.827774| -1.188383 | -0.044175 |
| 54 | 6  | 0   | -5.123928| 0.182810  | 0.054273  |
| 55 | 6  | 0   | -4.183817| 1.111767  | -0.426721 |
| 56 | 1  | 0   | -2.293237| 1.419932  | -1.376170 |
| 57 | 1  | 0   | -1.874025| -1.018351 | -1.701235 |
| 58 | 1  | 0   | -3.447078| -2.681628 | -0.707957 |
| 59 | 1  | 0   | -5.560056| -1.915384 | 0.288463  |
| 60 | 1  | 0   | -4.415785| 2.170203  | 0.389084  |
| 61 | 6  | 0   | -6.417747| 0.647976  | 0.657862  |
| 62 | 1  | 0   | -6.284376| 0.848712  | 1.727133  |
| 63 | 1  | 0   | -6.762713| 1.574568  | 0.195537  |
| 64 | 1  | 0   | -7.199905| -0.106473 | 0.561901  |
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