Supporting Information

Catalytic Synthesis of Cyclic and Linear Germoxanes Mediated by Iron Complex

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All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. Methyl iron complex CpFe(CO)$_2$(Me) (1) and Et$_3$SnH$^2$ were prepared according to the literature methods. Benzene, hexane, ether and THF were distilled from sodium and benzophenone prior to use and stored under nitrogen. The other chemicals except ($^\text{c}$Hex)$_2$GeH$_2$ and (PhCH$_2$)$_2$GeH$_2$ were purchased. NMR spectra ($^1$H, $^{13}$C{$^1$H} and $^{29}$Si{$^1$H}) were recorded on a JEOL JNM-AL 400 spectrometer. $^1$H and $^{13}$C{$^1$H} NMR data were referred to residual peaks of solvent as an internal standard. Peak positions of the $^{29}$Si{$^1$H} NMR spectra were referenced to an external Me$_4$Si. IR spectra were recorded on a Perkin Elmer FTIR-Spectrum one. Elemental analysis data were obtained on a Perkin–Elmer 2400 CHN elemental analyzer. High-resolution mass spectra (HRMS) were recorded on a JMS-700T spectrometer. Characterizations of cyclotrigrermoxanes were carried out by SYNAPT G2 High Definition Mass Spectrometry (SYNAPT$^\text{TM}$ HDMS$^\text{TM}$), and the analysis of MS revealed that no other oligomers or polymers were formed in the cyclization of secondary germane.

With secondary germanes, Et$_2$GeH$_2$, $^n$Bu$_2$GeH$_2$, and Ph$_2$GeH$_2$ can be purchased, but ($^\text{c}$Hex)$_2$GeH$_2$, and (PhCH$_2$)$_2$GeH$_2$ have not been prepared to date. Therefore, we newly prepared and identified as follows.
Preparation of \((\text{cHex})_2\text{GeH}_2\): A solution of bromocyclohexane (41 mmol, 5.0 mL) in ether (10 mL) was added dropwise to a suspension of magnesium (41 mmol, 1.0 g) in ether (50 mL) at 0 °C under nitrogen atmosphere. After filtration to remove insoluble materials, the solution having the Grignard reagent was added to a solution of GeCl$_4$ (21 mmol, 4.4 g) in THF (50 mL) at -78 °C. The solution was allowed to warm to room temperature gradually and then stirred for more 4 h at room temperature. It should be noted here that ether (not THF) is used when the Grignard reagent is prepared and THF (not ether) is used when GeCl$_4$ is treated with the Grignard reagent. The temperature control was also important: -78 °C should be kept in the reaction of GeCl$_4$ with the Grignard reagent and the reaction mixture should be slowly (not rapidly) warmed to room temperature. Although the Grignard reagent vs GeCl$_4$ was 2:1 in the molar ratio, several germanes such as \((\text{cHex})\text{GeCl}_3\), \((\text{cHex})_2\text{GeCl}_2\) (the desired compound), \((\text{cHex})_3\text{GeCl}\), \((\text{cHex})_4\text{Ge}\) were formed. The mixture without purification was added into a suspension of LiAlH$_4$ (41 mmol, 1.5 g) in ether (50 mL) and quenched by H$_2$O at 0 °C. The organic layer was dried over MgSO$_4$. After filtration, the filtrate was dried under vacuum. The residue thus obtained was immediately passed through an alumina column (Merck 101097, aluminum oxide 90 standardized) with hexane/ethyl acetate eluent. The rate of the solvents was changed gradually from 99:1 to 80:20, and the $^1$H NMR measurements of each crop revealed that the third crop had the desired compound, which was collected and dried in vacuo to give \((\text{cHex})_2\text{GeH}_2\) as colorless oil (5.21 mmol, 609 mg, 25%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta =$ 1.12-1.24 (m, 12H, \text{cHex}), 1.51-1.65 (m, 10H, \text{cHex}), 3.95 (t, $J_{HH} = 3.2$ Hz, 2H, GeH$_2$). $^{13}$C{$^1$H} NMR (100.4 MHz, C$_6$D$_6$): $\delta =$ 23.12 (s, \text{cHex}), 26.76 (s, \text{cHex}), 28.03 (s, \text{cHex}), 32.06 (s, \text{cHex}). Elemental analysis; Calcd: C$_{12}$H$_{24}$Ge: C, 59.81; H, 10.04%; Found: C, 59.98; H, 10.22%.

Preparation of \((\text{PhCH})_2\text{GeH}_2\): In a procedure analogous to that outlined above, BrCH$_2$Ph (41 mmol, 4.9 mL), Mg (41 mmol, 1.0 g), GeCl$_4$ (21 mmol, 4.4 g) and LiAlH$_4$ (41 mmol, 1.5 g) gave the title compound as colorless oil (3.71 mmol, 464 mg, 18%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta =$
2.11 (t, J<sub>HH</sub> = 2.4 Hz, 4H, CH<sub>2</sub>), 4.10 (quin, J<sub>HH</sub> = 2.4 Hz, 2H, GeH<sub>2</sub>), 6.91 (d, J<sub>HH</sub> = 7.8 Hz, 4H, Ph), 6.97 (t, J<sub>HH</sub> = 7.8 Hz, 2H, Ph), 7.10 (t, J<sub>HH</sub> = 7.8 Hz, 4H, Ph).<br>

13<sup>C</sup>{<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 19.41 (s, CH<sub>2</sub>), 124.96 (s, Ph), 128.55 (s, Ph), 128.81 (s, Ph), 140.90 (s, Ph).

Elemental analysis; Calcd: C<sub>14</sub>H<sub>16</sub>Ge: C, 65.45; H, 6.28%; Found: C, 65.55; H, 5.99%.

**Preparation of (Et<sub>2</sub>GeO)<sub>3</sub>:** Diethylgermane Et<sub>2</sub>GeH<sub>2</sub> (1.9 mmol, 240 µL) was treated with dimethylformamide (19 mmol, 1.5 mL, DMF) in the presence of CpFe(CO)<sub>2</sub>(Me) (0.019 mmol, 3.6 mg) at 100 °C for 24 hours in a well-sealed glass tube. After removal of the solvent, the title compound was purified from the residue by Kugelrohr (0.62 mmol, 274 mg, 99%).

1<sup>H</sup> NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 1.05 (q, J<sub>HH</sub> = 7.3 Hz, 12H, CH<sub>2</sub>), 1.18 (t, J<sub>HH</sub> = 7.3 Hz, 18H, CH<sub>3</sub>).

13<sup>C</sup>{<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.71 (s, CH<sub>2</sub>), 12.71 (s, CH<sub>3</sub>). HRMS (FAB) Calcd. for C<sub>12</sub>H<sub>31</sub>O<sub>3</sub>Ge<sub>3</sub>[M+H]<sup>+</sup>: 444.9909, Found: 444.9919.

**Preparation of (n-Bu<sub>2</sub>GeO)<sub>3</sub>:** In a procedure analogues to that outlined above, n-Bu<sub>2</sub>GeH<sub>2</sub> (1.8 mmol, 340 µL), DMF (18 mmol, 1.4 mL) and CpFe(CO)<sub>2</sub>(Me) (0.018 mmol, 3.4 mg) gave the title compound as colorless oil (0.59 mmol, 357 mg, 99%).

1<sup>H</sup> NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.94 (t, J<sub>HH</sub> = 6.8 Hz, 18H, CH<sub>3</sub>), 1.20 (t, J<sub>HH</sub> = 7.3 Hz, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.45 (quin, J<sub>HH</sub> = 7.3 Hz, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.70 (tq, J<sub>HH</sub> = 7.3, 6.8 Hz, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). 13<sup>C</sup>{<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 14.12 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.07 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 26.26 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 26.36 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). HRMS (FAB) Calcd. for C<sub>24</sub>H<sub>55</sub>O<sub>3</sub>Ge<sub>3</sub>[M+H]<sup>+</sup>: 613.1787, Found: 613.1783.

**Preparation of (c-Hex<sub>2</sub>GeO)<sub>3</sub>:** In a procedure analogues to that outlined above, c-Hex<sub>2</sub>GeH<sub>2</sub> (1.5 mmol, 361 mg), DMF (15 mmol, 1.2 mL) and CpFe(CO)<sub>2</sub>(Me) (0.015 mmol, 2.9 mg) gave the title compound as colorless oil (0.50 mmol, 383 mg, 99%).

1<sup>H</sup> NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.91 (quin, J<sub>HH</sub> = 7.3 Hz, 12H, c-Hex), 1.25-1.45 (m, 48H, c-Hex), 1.77 (quin, J<sub>HH</sub> = 7.3 Hz, 6H, c-Hex).
$^{13}$C\{\textsuperscript{1}H\} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 14.05$ (s), 20.96 (s), 26.17 (s), 26.30 (s). HRMS (FAB) Calcd. for C\textsubscript{36}H\textsubscript{67}O\textsubscript{3}Ge\textsubscript{3} [M+H]$^+$: 769.2726, Found 769.2722.

**Preparation of ((PhCH\textsubscript{2})\textsubscript{2}GeO)\textsubscript{3}:** In a procedure analogous to that outlined above, (PhCH\textsubscript{2})\textsubscript{2}GeH\textsubscript{2} (1.6 mmol, 401 µL), DMF (16 mmol, 1.2 mL) and CpFe(CO)\textsubscript{2}(Me) (0.016 mmol, 3.0 mg) gave the title compound as white powder (0.14 mmol, 114 mg, 27%). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 2.25$ (s, 12H, CH\textsubscript{2}), 6.98 (t, $J_{HH} = 7.3$ Hz, 6H, Ph), 7.04 (d, $J_{HH} = 7.3$ Hz, 12H, Ph), 7.11 (t, $J_{HH} = 7.3$ Hz, 12H, Ph). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 28.63$ (s, CH\textsubscript{2}), 125.38 (s, Ph), 128.68 (s, Ph), 129.24 (s, Ph), 137.12 (s, Ph). HRMS (FAB) Calcd. for C\textsubscript{42}H\textsubscript{43}O\textsubscript{3}Ge\textsubscript{3} [M+H]$^+$: 817.0848; Found: 817.0831.

**Preparation of Et\textsubscript{3}SiOGePh\textsubscript{2}OSiEt\textsubscript{3}:** A DMF solution (0.12 mL) containing CpFe(CO)\textsubscript{2}(Me) (0.031 mmol, 6.0 mg), Ph\textsubscript{2}GeH\textsubscript{2} (0.31 mmol, 59 µL) and Et\textsubscript{3}SiH (0.62 mmol, 100 µL) was heated at 100 °C for 24 hours in a well-sealed glass tube. After the solvent was removed under reduced pressure, the residue was put on celite and eluted with ether. The filtrate was dried in vacuo to give the title compound as colorless oil (0.277 mmol, 136 mg, 88%). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 0.67$ (q, $J_{HH} = 8.0$ Hz, 12H, CH\textsubscript{2}), 1.05 (t, $J_{HH} = 8.0$ Hz, 18H, CH\textsubscript{3}), 7.16 (m, 6H, Ph), 7.60 (d, $J_{HH} = 8.0$ Hz, 4H, Ph). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 7.43$ (s, CH\textsubscript{2}), 7.48 (s, CH\textsubscript{3}), 128.62 (s, Ph), 130.80 (s, Ph), 133.88 (s, Ph), 136.05 (s, Ph). \textsuperscript{29}Si \{\textsuperscript{1}H \} NMR (79.3 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 14.56$. Elemental analysis; Calcd: C\textsubscript{24}H\textsubscript{40}O\textsubscript{2}Si\textsubscript{2}Ge: C, 58.90; H, 8.24%; Found: C, 59.03; H, 8.28%.

**Preparation of Et\textsubscript{3}GeOGePh\textsubscript{2}OGeEt\textsubscript{3}:** In a procedure analogous to that outlined above, CpFe(CO)\textsubscript{2}(Me) (0.072 mmol, 14 mg), Ph\textsubscript{2}GeH\textsubscript{2} (0.72 mmol, 135 µL), Et\textsubscript{3}GeH (1.4 mmol, 230 µL) and DMF (0.28 mL) gave the title compound as colorless oil (0.30 mmol, 175 mg, 42%). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 0.92$ (q, $J_{HH} = 8.0$ Hz, 12H, CH\textsubscript{2}), 1.09 (t, $J_{HH} = 8.0$ Hz, 18H, CH\textsubscript{3}),
7.16 (m, 6H, Ph), 7.87 (m, 4H, Ph). $^{13}$C{\textsuperscript{1}H} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ = 8.33 (s, CH\textsubscript{2}), 9.40 (s, CH\textsubscript{3}), 128.39 (s, Ph), 130.18 (s, Ph), 134.32 (s, Ph), 139.26 (s, Ph). Elemental analysis; Calcd: C\textsubscript{24}H\textsubscript{40}O\textsubscript{2}Ge\textsubscript{3}: C, 49.83; H, 6.97%; Found: C, 50.02; H, 6.95%.

Preparation of $^{\textit{n}}$Bu\textsubscript{3}GeOGePh\textsubscript{2}OGe$^{\textit{n}}$Bu\textsubscript{3}: In a procedure analogous to that outlined above, CpFe(CO)\textsubscript{2}(Me) (0.064 mmol, 12 mg), Ph\textsubscript{2}GeH\textsubscript{2} (0.64 mmol, 120 µL), $^{\textit{n}}$BuGeH (1.28 mmol, 331 µL) and DMF (0.25 mL) gave the title compound as colorless oil (0.35 mmol, 259 mg, 54%). $^{1}$H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ = 0.94 (m, 18H, C\textsubscript{H}\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.38 (m, 12H, C\textsubscript{H}\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 7.22 (m, 6H, Ph), 7.89 (m, 4H, Ph). $^{13}$C{\textsuperscript{1}H} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ = 14.07, 18.18, 26.85, 26.89 (s, C\textsubscript{H}\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 128.38 (s, Ph), 130.16 (s, Ph), 134.42 (s, Ph), 139.37 (s, Ph). Elemental analysis; Calcd: C\textsubscript{36}H\textsubscript{64}O\textsubscript{2}Ge\textsubscript{3}: C, 57.90; H, 8.64%; Found: C, 57.82; H, 8.61%.

Preparation of $^{\textit{n}}$Bu\textsubscript{3}SnOGePh\textsubscript{2}OSn$^{\textit{n}}$Bu\textsubscript{3}: In a procedure analogous to that outlined above, CpFe(CO)\textsubscript{2}(Me) (0.075 mmol, 15 mg), Ph\textsubscript{2}GeH\textsubscript{2} (0.750 mmol, 141 µL), $^{\textit{n}}$BuSnH (1.50 mmol, 440 µL) and DMF (0.30 mL) gave the title compound as colorless oil (0.26 mmol, 220 mg, 35%). $^{1}$H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ = 0.91 (m, 30H, C\textsubscript{H}\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.35 (m, 12H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.59 (m, 12H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 7.22 (d, $J_{HH}$ = 8.0 Hz, 6H, Ph), 7.90 (d, $J_{HH}$ = 8.0 Hz, 4H, Ph). $^{13}$C{\textsuperscript{1}H} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ = 14.00, 16.75, 27.71, 28.53 (s, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 128.62 (s, Ph), 129.77 (s, Ph), 134.34 (s, Ph), 136.03 (s, Ph). Elemental analysis; Calcd: C\textsubscript{36}H\textsubscript{64}O\textsubscript{2}GeSn\textsubscript{2}: C, 51.54; H, 8.64%; Found: C, 51.42; H, 8.61%.

Preparation of Me\textsubscript{2}$^{\textit{t}}$BuSiOGePh\textsubscript{2}OSi$^{\textit{t}}$BuMe\textsubscript{2}: A solution of CpFe(CO)\textsubscript{2}(Me) (0.063 mmol, 12 mg), Ph\textsubscript{2}GeH\textsubscript{2} (0.625 mmol, 117 µL) and $^{\textit{t}}$Bu(Me)\textsubscript{2}SiH (1.25 mmol, 206 µL) in DMF (0.24 mL) was heated at 100 °C for 48 hours in a well-sealed glass tube. After the solvent was removed under reduced pressure, the residue was put on celite and eluted with ether. The filtrate was
dried in vacuo to give the title compound as colorless oil (0.418 mmol, 204 mg, 67%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.12$ (s, 12H, SiCH$_3$), 1.04 (s, 18H, CCH$_3$), 7.16 (m, 6H, Ph), 7.73 (d, $J_{HH} = 8.0$ Hz, 4H, Ph). $^{13}$C{$^1$H} NMR (100.4 MHz, C$_6$D$_6$): $\delta = -1.77$ (s, SiCH$_3$), 19.16 (s, CCH$_3$), 26.43 (s, CCH$_3$), 128.72 (s, Ph), 130.88 (s, Ph), 134.04 (s, Ph), 135.87 (s, Ph). $^{29}$Si {$^1$H} NMR (79.3 MHz, C$_6$D$_6$): $\delta = 15.71$. Elemental analysis; Calcd: C$_{24}$H$_{40}$O$_2$Si$_2$Ge: C, 58.90; H, 8.24%; Found: C, 58.70; H, 8.17%.

**Preparation of Et$_3$SiOGeEt$_2$OSiEt$_3$:** A DMF solution (0.34 mL) containing CpFe(CO)$_2$(Me) (0.087 mmol, 17 mg), Et$_2$GeH$_2$ (0.870 mmol, 111 µL) and Et$_3$SiH (1.74 mmol, 278 µL) was heated at 100 °C for 24 hours in a well-sealed glass tube. After removal of volatile materials under reduced pressure at room temperature, the title compound was separated from the residue containing cyclogermoxane by Kugelrohr (0.333 mmol, 131 mg, 38%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.67$ (q, $J_{HH} = 8.0$ Hz, 12H, SiC$_2$H$_3$CH$_3$), 0.89 (q, $J_{HH} = 8.0$ Hz, 4H, GeC$_2$H$_3$CH$_3$), 1.06 (t, $J_{HH} = 8.0$ Hz, 6H, GeC$_2$H$_3$CH$_3$), 1.09 (t, $J_{HH} = 8.0$ Hz, 18H, SiC$_2$H$_3$CH$_3$). $^{13}$C{$^1$H} NMR (100.4 MHz, C$_6$D$_6$): $\delta = 7.40$ (s, SiC$_2$H$_3$CH$_3$), 7.43 (s, SiC$_2$H$_3$CH$_3$), 7.51 (s, GeC$_2$H$_3$CH$_3$), 12.06 (s, GeC$_2$H$_3$CH$_3$). $^{29}$Si {$^1$H} NMR (79.3 MHz, C$_6$D$_6$): $\delta = 10.66$. Elemental analysis; Calcd: C$_{16}$H$_{40}$O$_2$Si$_2$Ge: C, 48.86; H, 10.25%; Found: C, 48.86; H, 10.28%.

**Preparation of Et$_3$SiOGe"Bu$_2$OSiEt$_3$:** A DMF solution (0.30 mL) containing CpFe(CO)$_2$(Me) (0.078 mmol, 15 mg), $^t$Bu$_2$GeH$_2$ (0.781 mmol, 151 µL) and Et$_3$SiH (1.56 mmol, 250 µL) was heated at 100 °C for 24 hours in a well-sealed glass tube. After removal of volatile materials under reduced pressure at room temperature, the title compound was separated from the residue containing cyclogermoxane by Kugelrohr (0.219 mmol, 98.2 mg, 28%). $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.71$ (q, $J_{HH} = 8.0$ Hz, 12H, SiC$_2$H$_3$CH$_3$), 0.91 (q, $J_{HH} = 7.2$ Hz, 6H, GeC$_2$H$_3$CH$_2$CH$_2$CH$_3$), 1.04 (t, $J_{HH} = 8.0$ Hz, 4H, GeC$_2$H$_2$CH$_2$CH$_3$CH$_3$), 1.12 (t, $J_{HH} = 8.0$ Hz, 18H, SiC$_2$H$_3$CH$_3$), 1.34 (m, 4H, GeC$_2$H$_2$CH$_2$CH$_3$CH$_3$), 1.55 (m, 4H, GeC$_2$H$_2$CH$_2$CH$_3$CH$_3$). $^{13}$C{$^1$H}
NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 7.46$ (s, SiCH\textsubscript{2}CH\textsubscript{3}), 7.50 (s, SiCH\textsubscript{2}CH\textsubscript{3}), 13.90, 20.23, 25.95, 26.11 (s, GeCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{29}Si {\textsuperscript{1}H } NMR (79.3 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 11.25$. Elemental analysis; Calcd: C\textsubscript{20}H\textsubscript{48}O\textsubscript{2}Si\textsubscript{2}Ge: C, 53.45; H, 10.77%; Found: C, 53.80; H, 10.88%.

**Synthesis of Cp*Fe(CO)(CHNMe\textsubscript{2})(SGeEt\textsubscript{3}) (7):** Complex 5 (0.20 mmol, 100 mg) was treated with N, N-dimethylthioformamide (0.23 mmol, 20 $\mu$L) in toluene (5 ml) at 50 °C for 24 hours. Removal of volatile materials under reduced pressure led to the formation of the corresponding carbene complex 7 as dark-red powder which was purified by washing with ether (0.16 mmol, 86 mg, 81%). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 1.13$ (q, $J_{HH} = 8.0$ Hz, 6H, GeCH\textsubscript{2}CH\textsubscript{3}), 1.36 (t, $J_{HH} = 8.0$ Hz, 9H, GeCH\textsubscript{2}CH\textsubscript{3}), 1.58 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 2.49 (s, 3H, NCH\textsubscript{3}), 3.17 (s, 3H, NCH\textsubscript{3}), 11.52 (s, 1H, Fe=CH). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 9.62$ (s, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 9.76 (s, GeCH\textsubscript{2}CH\textsubscript{3}), 10.95 (s, GeCH\textsubscript{2}CH\textsubscript{3}), 44.66 (s, NCH\textsubscript{3}), 53.53 (s, NCH\textsubscript{3}), 93.42 (s, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 224.79 (s, CO), 269.72 (s, Fe=C). IR (cm$^{-1}$, KBr): $\nu$(CO) 1902 (s). Elemental analysis; Calcd: C\textsubscript{20}H\textsubscript{48}O\textsubscript{2}Si\textsubscript{2}GeFe: C, 51.32; H, 7.97; N, 2.99%; Found: C, 51.58; H, 8.02; N, 2.87%.

**Synthesis of Cp*(CO)Fe(CHNMe\textsubscript{2})(SGePh\textsubscript{3}) (8):** In a procedure analogous to that outlined above, Complex 6 (0.16 mmol, 92 mg) and N, N-dimethylthioformamide (0.16 mmol, 13 $\mu$L) in toluene (5 mL) gave dark red powder of 8 (0.14 mmol, 85 mg, 87%). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 1.48$ (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 2.27 (s, 3H, NCH\textsubscript{3}), 2.73 (s, 3H, NCH\textsubscript{3}), 7.18 (m, 9H, Ph), 7.96 (d, $J_{HH} = 6.6$ Hz, 6H, Ph). 11.54 (s, 1H, Fe=CH). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.4 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta = 9.41$ (s, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 44.62 (s, NCH\textsubscript{3}), 53.89 (s, NCH\textsubscript{3}), 92.84 (s, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), 127.82 (s, Ph), 128.24 (s, Ph), 135.63 (s, Ph), 143.13 (s, Ph), 223.43 (s, CO), 268.33 (s, Fe=C). IR (cm$^{-1}$, KBr): $\nu$(CO) 1907 (s). Elemental analysis; Calcd: C\textsubscript{30}H\textsubscript{57}ONSGeFe: C, 62.78; H, 6.09; N, 2.29%; Found: C, 62.64; H, 6.03; N, 2.22%.

**Thermal Reaction of complex 7 (or 8) with Ph\textsubscript{2}GeH\textsubscript{2} in C\textsubscript{6}D\textsubscript{6}:** To a solution of 7 (or 8) (21.4
µmol (16.3), 10 (10) mg) in C₆D₆ (0.5 mL) in a NMR tube were added diphenylgermane (128.2 (98.0) µmol, 25 (18) µl) and triphenylmethane (34.2 (29.4) µmol, 8.4 (7.2) mg) as an internal standard. After heating for 12 hours at 50 °C, in ¹H NMR spectra the proton signal (11.5 ppm) on the carbene completely disappeared and a new signal characterized as NMe₃ appeared at 2.05 ppm in both cases. The thio coupling compounds could not be isolated from the mixture due to its thermal instability, however they could be detected by GC-MS spectra. GCMS data for Et₃Ge–S–GePh₂H: [M] = 422, [M-Et] = 393, [M–GeEt₃] = 260, [M–SGeEt₃] = 229. The isotope patterns in each peak were fitted with simulation.

**X-ray Crystal structure determination of 8:** Deep-red crystals of 8 suitable for an X-ray diffraction study were obtained through crystallization from toluene/pentane. The single crystal was mounted in a glass capillary. Data for 8 were collected at -70 °C on Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. Calculations for 8 were performed with the teXane crystallographic software package of Molecular Structure Corporation. Crystal Data: C₃₂H₃₇ONSGeFe, M = 612.13, red prism, 0.25 × 0.25 × 0.13 mm³, monoclinic, space group P2₁/c (No. 14), a = 14.2808(19) Å, b = 10.8004(14) Å, c = 19.383(3) Å, β = 98.592(3)°, V = 2956.0(7) Å³, Z = 4, Dcalc = 1.375 g/cm³, 6731 reflections collected, 5921 (I > 3σI) unique reflections were used in all calculations, number of variables = 344, R = 0.0469, Rw = 0.0816, and goodness of fit = 1.162. CCDC 818209.

**References**