

Electronic Supplementary Information

Three-membered cyclic digermynes stabilised by an N-heterocyclic carbene

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Table of Contents.

Experimental Part	S2
Crystallographic data	S15
Computational Details	S21
References	S26

Experimental part

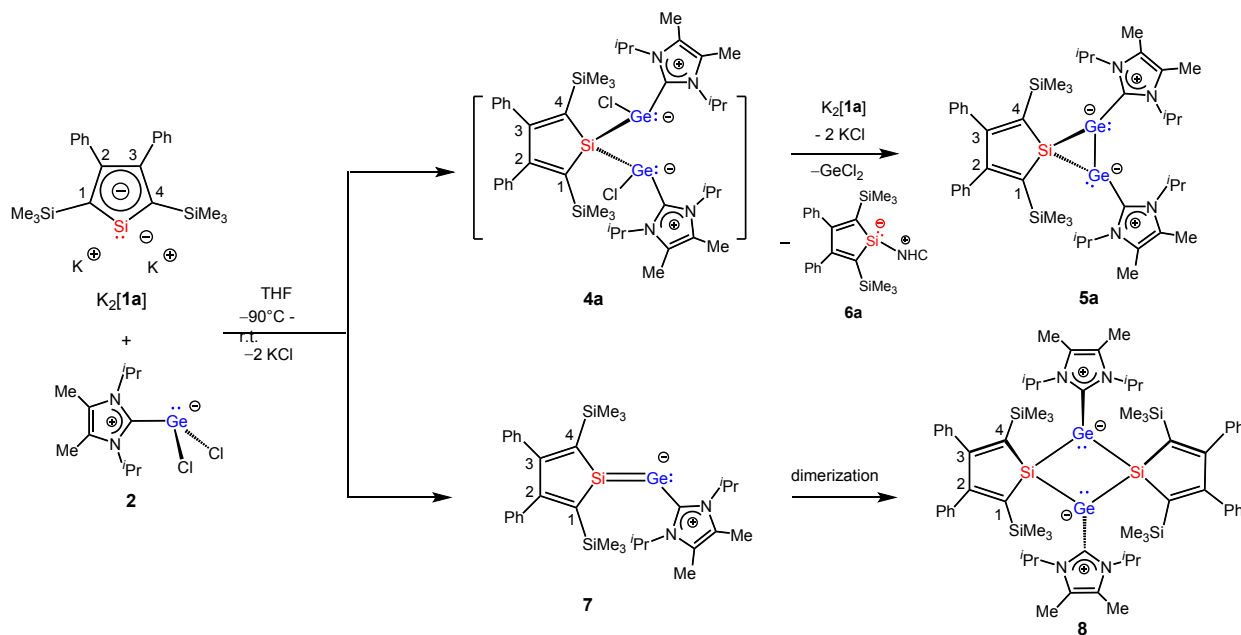
General. All reactions were performed under a controlled dry argon or nitrogen atmosphere using a high-vacuum line, standard Schlenk techniques, and an MBraun glovebox. The used glassware was dried in an oven at 140 °C and evacuated prior to use. The solvents diethyl ether, toluene and *n*-pentane were dried over sodium/potassium alloy, distilled and stored over molecular sieves (4 Å). Deuterated benzene- d_6 , were dried over sodium/potassium alloy, distilled and stored over molecular sieve (4 Å). All used standard chemicals were obtained from commercial suppliers and used as delivered if not mentioned otherwise. Dipotassium silole dianions $K_2[1]$,^{S1} $GeCl_2 \cdot NHC$ **2**^{S2} were synthesized according to the literature procedure. For new compounds, all available NMR spectra are provided.

NMR spectroscopy. NMR spectra were recorded on Bruker Avance 500 and Bruker Avance III 500 spectrometers. 1H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (benzene- d_6 : $\delta^1H(C_6D_5H) = 7.20$) and $^{13}C\{^1H\}$ NMR spectra by using the central line of the solvent signal (benzene- d_6 : $\delta^{13}C(C_6D_6) = 128.0$). The $^{29}Si\{^1H\}$ NMR inverse gated spectra were recorded with a relaxation delay $D1 = 10$ s. The $^{29}Si\{^1H\}$ INEPT spectra were recorded with the combination of $D3 = 0.0086$ s and $D4 = 0.0313$ s (6H atoms and $J(SiH) = 6$ Hz).

Mass spectrometry: High resolution mass spectra were recorded on a Waters Q-ToF Premier (ESI-MS).

UV-vis spectroscopy: UV-vis spectra were recorded in *n*-pentane at room temperature using a SPECORD 200 instrument (analytikjena).

NMR studies of the formation of NHC-stabilised siladigermirane **5a** and NHC-stabilised disiladigermetane **8**:



Scheme S1.

Formation of siladigermirane **5a** and disiladigermetane **8**.

1. General procedure

A THF (6 mL) solution of $^{iPr}NHC\cdot GeCl_2$ **2** (145 mg, 0.447 mmol) was slowly added to a freshly prepared THF solution (10 mL) of $K_2[1a]$ (0.447 mmol) at $-90^\circ C$. The reaction mixture was allowed to warm to room temperature after 0.5 h and then stirred for another 1 h to form a dark green solution. The solvent was removed under vacuum and the residue was dissolved in C_6D_6 for immediate NMR measurement. Based on the analysis of 1H NMR (Figure S1a) spectroscopy, siladigermirane **5a** and ^{iPr}NHC -stabilised silylene **6a** are the main products and disiladigermetane **8** is the minor product combined with free 1,3-di-*i*-propyl-4,5-dimethylimidazol-2-ylidene (^{iPr}NHC). The products siladigermirane **5a** and ^{iPr}NHC -stabilised silylene **6a** were formed in a ratio of 1:1 (for details, see Figure S1a). Furthermore, the ^{29}Si NMR spectrum indicated the formation of the siladigermirane **5a**, ^{iPr}NHC -stabilised silylene **6a**, NHC-stabilised silagermylidene **7** as well as disiladigermetane **8** (for details, see Figure S1b,c).

2. NMR investigation on the reaction course.

We tried to follow the course of the reaction by low temperature NMR in THF. At low temperature, we noticed a significant amount of precipitate (KCl) which did not allow locking and shimming and prevent meaningful NMR measurements directly from the reaction mixture. Therefore, the reaction was started as described in paragraph 1, but was stopped after app. 1h at $-30^\circ C$. The solvent was evaporated at this temperature, C_6D_6 was added and the sample was measured at room temperature (see Figure S1b). The relative intensity of the characteristic ^{29}Si NMR signal of silagermylidene **7** at $\delta^{29}Si = 157.9$ in this spectra

was significantly larger than in spectra recorded after the reaction mixture has reached room temperature (see Figure S1c).

3. Crystallization experiments.

Several crystallization attempts for isolating and obtaining suitable crystals of **7** for XRD analysis failed. THF was removed under vacuum while the reaction completed and the residue was re-dissolved in 10 mL Et₂O. The dark solution was filtered by using a PTFE syringe filter to remove potassium chloride and the filtrate was concentrated to 3 mL. The dark solution was then stored at -30 °C for one week to afford deep-green crystals of siladigermirane **5a**. After recrystallization and isolation of siladigermirane **5a**, Et₂O (3 mL) was again added to the mother liquor, the remaining Et₂O solution was stored at -30 °C. A few dark-red crystals are obtained after one week, and finally identified as the disiladigermetane **8** by X-ray diffraction analysis. The purification of dimer **8** was not successful; due to the low yield of dark-red crystals of **8** that were surrounded with sticky by-products.

NMR Spectra of reaction mixture.

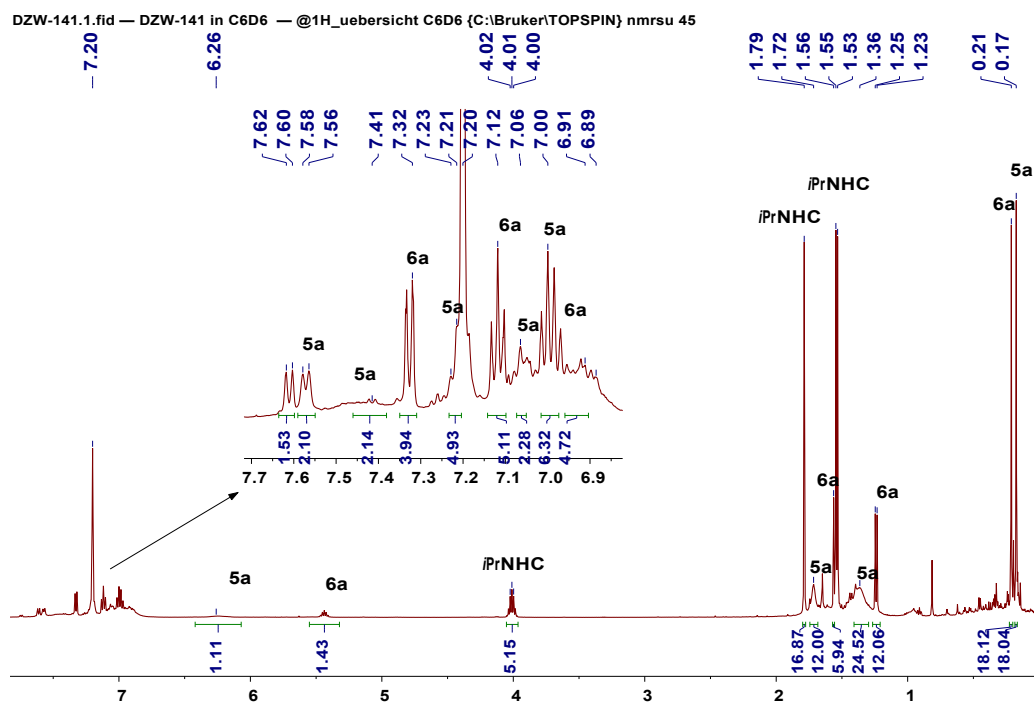


Figure S1a. ¹H NMR (499.9 MHz, 305.0 K, C₆D₆) spectrum of reaction mixture. (siladigermirane **5a**; *ipr*NHC-stabilised silylene **6a**; *ipr*NHC)

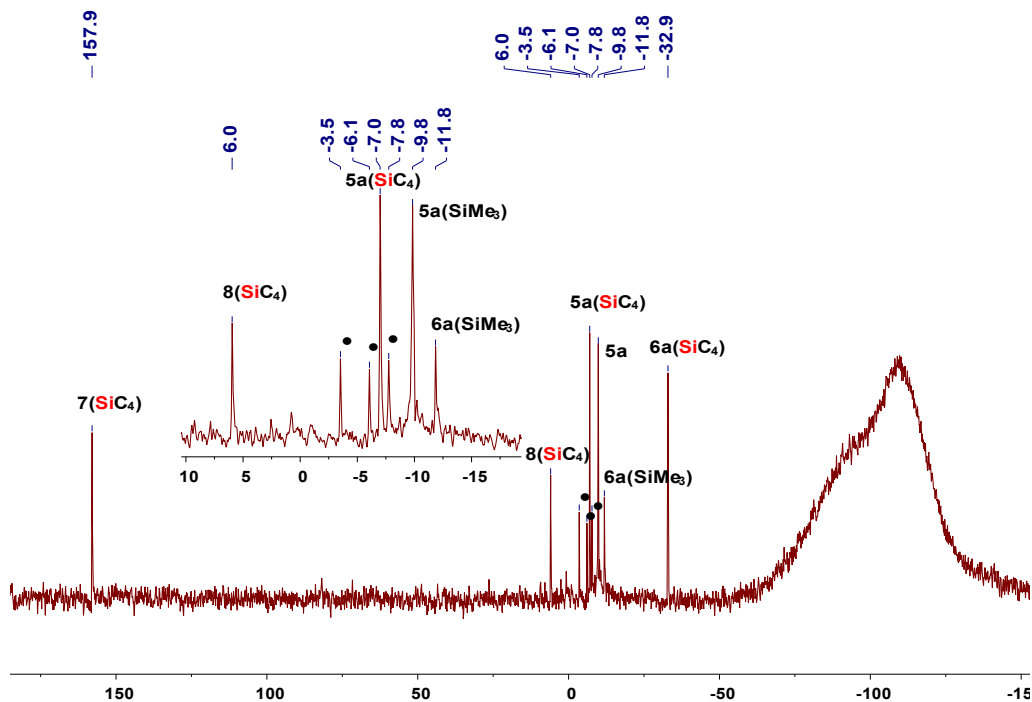


Figure S1b. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6) spectrum of reaction mixture after quenching the reaction at $T = -30^\circ\text{C}$. (siladigermirane **5a**; $^i\text{PrNHC}$ -stabilised silylene **6a**; silagermylidene **7**; disiladigermethane **8**; ●: signals from the Me_3Si group of **7** and **8**, preliminary assignments were done using the relative integrals.)

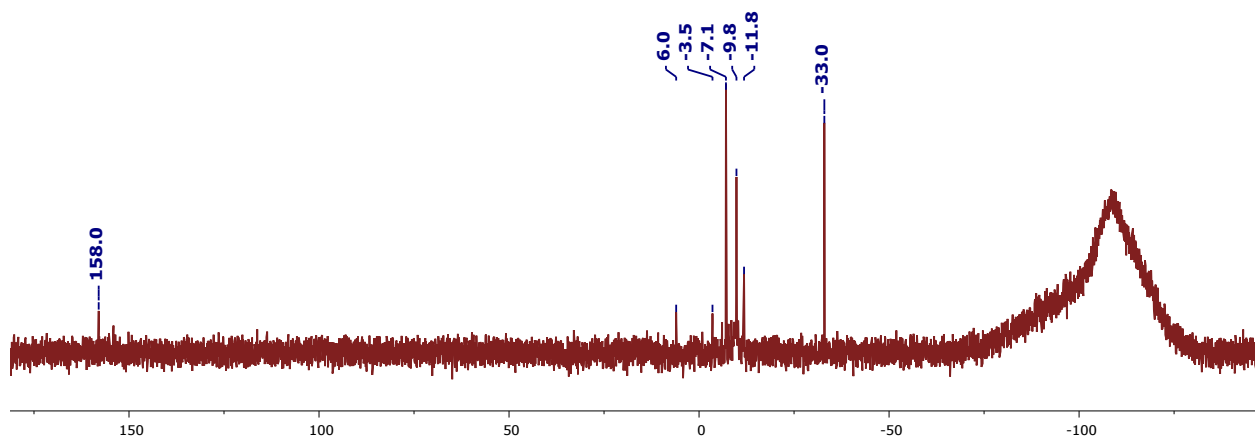
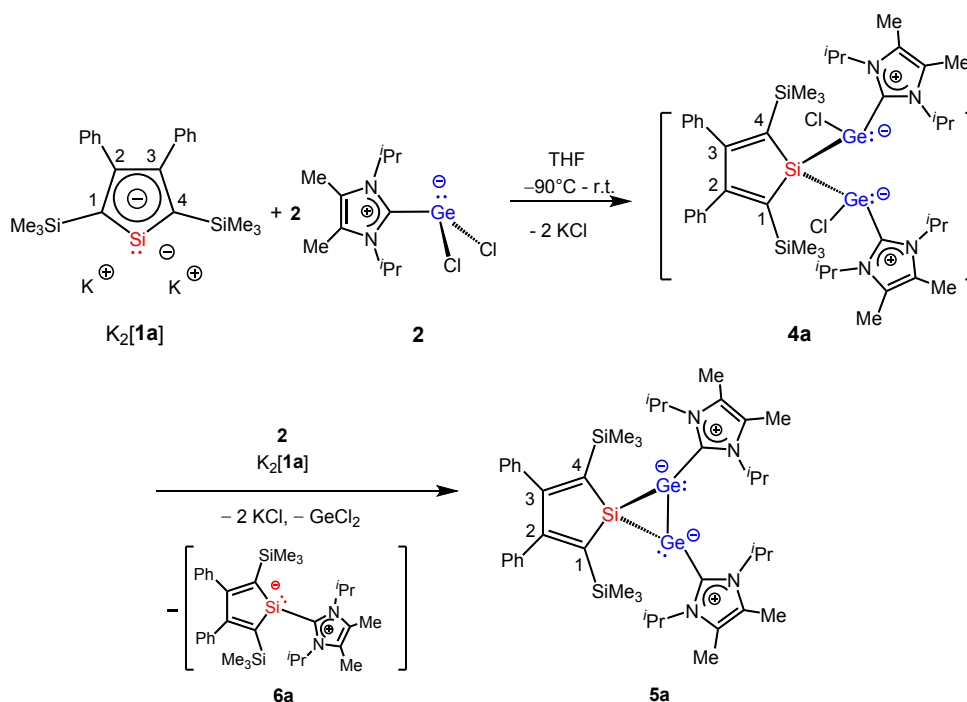


Figure S1c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6) spectrum of reaction mixture after stopping the reaction at r.t.. For signal assignments, see Figure S1b.

Synthesis and isolation of siladigermirane **5a**:



Scheme S2.

Isolation of siladigermirane **5a.** A THF (6 mL) solution of *i*PrNHC-GeCl₂ **2** (145 mg, 0.447 mmol) was slowly added to a freshly prepared THF solution (10 mL) of K₂[**1a**] (0.447 mmol) at -90 °C. The reaction mixture was allowed to warm to room temperature after 0.5 h and then stirred for another 1 h to form a dark green solution. After that, THF was removed under vacuum and the residue was re-dissolved in 10 mL Et₂O. The dark solution was filtered by using a PTFE syringe filter to remove KCl and the filtrate was concentrated to 3 mL. The dark solution was then stored at -30 °C for one week to afford deep-green crystals of siladigermirane **5a** (Yield: 30.6 mg (0.035 mmol, 23 %)).

¹H NMR (499.9 MHz, 305.0 K, C₆D₆): δ = 7.58–7.59 (m, 2H, Ph), 7.41 (br, 2H, CH(CH₃)₂), 7.20–7.24 (m, 4H, Ph), 7.06–7.07 (m, 2H, Ph), 6.99–7.02 (m, 2H, Ph), 6.26 (br, 2H, CH(CH₃)₂), 1.71 (s, 12H, NC=CCH₃), 1.37–1.58 (br, 24H, CH(CH₃)₂), 0.19 (m, 18H, SiMe₃).

¹³C{¹H} NMR (125.7 MHz, 305.0 K, C₆D₆): δ = 178.0 (NCN), 162.4 (2x $\underline{\text{C}}^{2/3}$), 154.8 (2x $\underline{\text{C}}^{1/4}$), 147.8 (*i*-Ph), 125.0, 126.7, 126.8, 130.0, 130.4 (Ph), 52.5 (br, -CH(CH₃)₂), 21.3 (CH(CH₃)₂), 10.0 (NC=CCH₃), 3.3 (SiMe₃). (Note: One carbon atom's (N-C=C) chemical shift cannot be assigned due to overlap with solvent peak (C₆D₅H)).

²⁹Si{¹H} NMR (99.3 MHz, 305.0 K, C₆D₆): δ = -7.1 (SiGe₂), -9.8 (SiMe₃).

HRMS (ESI) *m/z* [M+MeOH+H]⁺ Calcd for C₄₅H₇₃N₄OSi₃Ge₂: 917.3516 Found: 917.3518.

UV-vis (*n*-pentane solution) [nm]: λ = 262, 376, 465-511(br), 610.

NHC-stabilised silylene 6a:

The analytical data is in agreement with data from Cui et al.⁵³

^1H NMR (499.9 MHz, 305.1 K, C_6D_6): δ = 0.16 (s, 18 H, $\text{Si}(\text{CH}_3)_3$), 1.20 (d, $^3J_{\text{H,H}} = 7.1$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.54 (s, 6 H, $\text{C}=\text{C}-\text{CH}_3$), 5.39 (sept., $^3J_{\text{H,H}} = 7.1$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 6.90–6.93 (m, 2 H, C_6H_5), 7.05–7.09 (m, 4 H, C_6H_5), 7.26–7.29 (m, 4 H, C_6H_5).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, 304.9 K, C_6D_6): δ = 3.1 ($\text{Si}(\text{CH}_3)_3$), 9.9 ($\text{C}=\text{C}-\text{CH}_3$), 21.8 ($\text{CH}(\text{CH}_3)_2$), 51.9 ($\text{CH}(\text{CH}_3)_2$), 125.2 (C_6H_5), 126.9 ($\text{C}=\text{C}-\text{CH}_3$), 127.0 (C_6H_5), 130.7 (C_6H_5), 147.0 (C_6H_5), 156.0 ($\text{C}-\text{SiMe}_3$), 157.2 ($\text{C}-\text{Ph}$), 162.0 ($\text{N}-\text{C}-\text{N}$).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6): δ = -33.0 (SiC_4), -11.8 (SiMe_3).

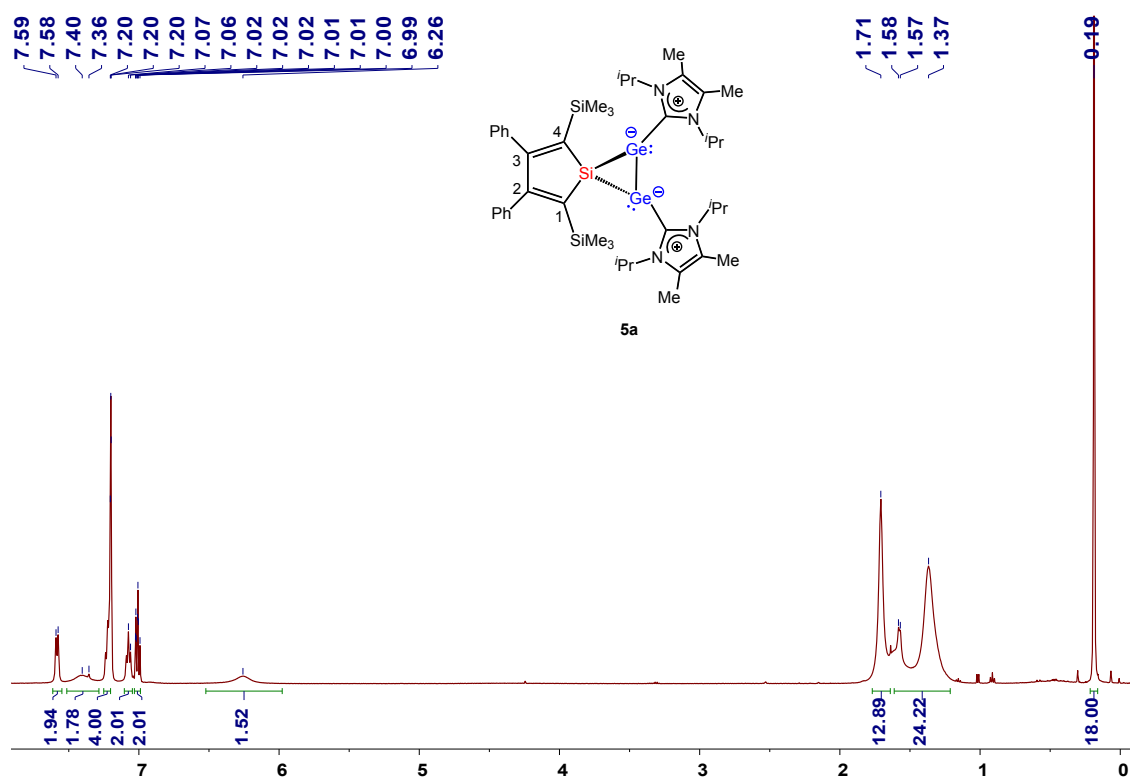


Figure S2a. ^1H NMR (499.9 MHz, 305.0 K, C_6D_6) spectrum of siladigermirane 5a.

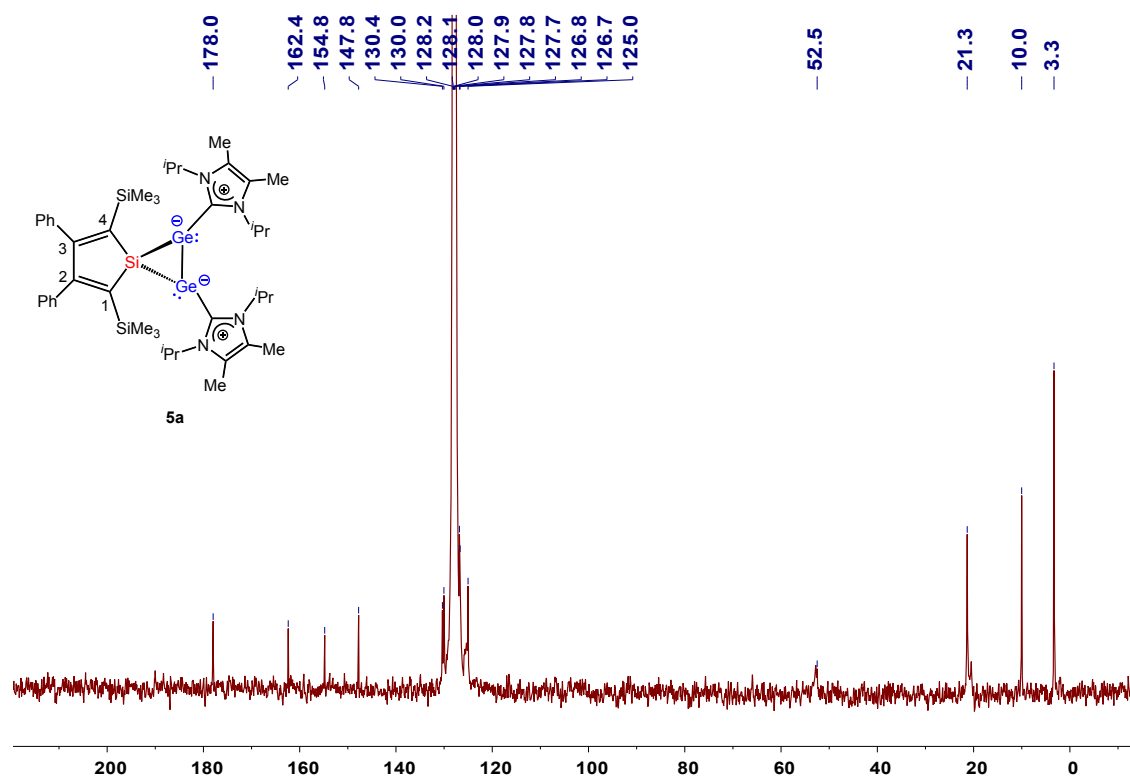


Figure S2b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, 305.0 K, C_6D_6) spectrum of siladigermirane **5a**.

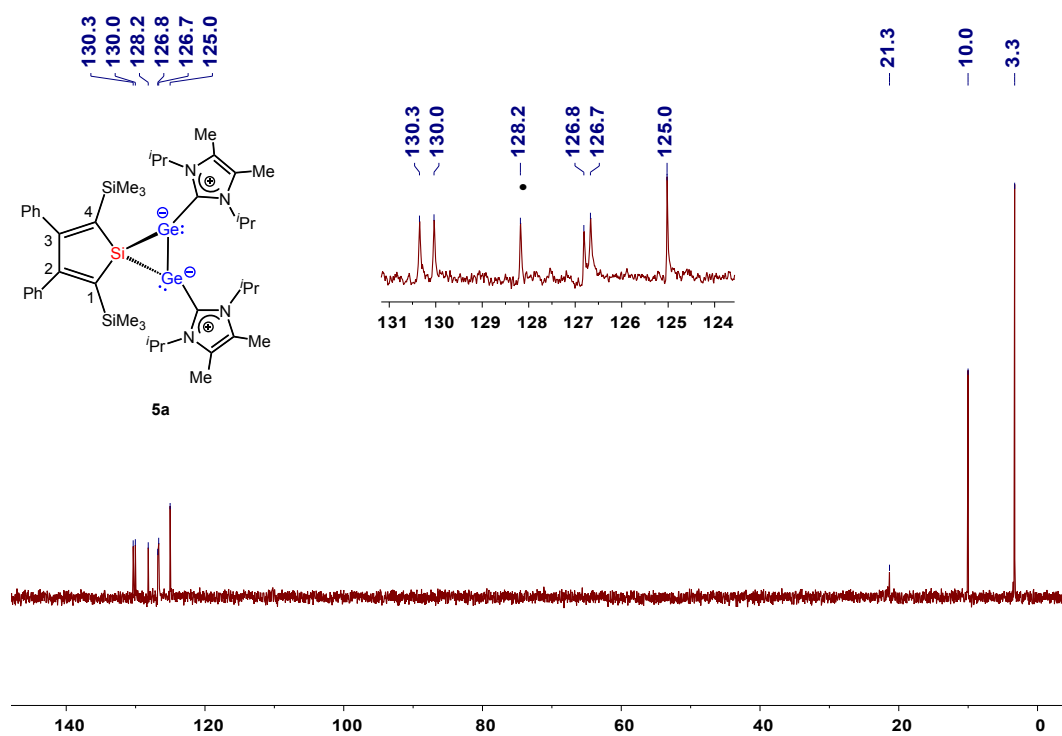


Figure S2c. ^{13}C DEPT NMR (125.7 MHz, 305.0 K, C_6D_6) spectrum of siladigermirane **5a**. (●: $\text{C}_6\text{D}_5\text{H}$).

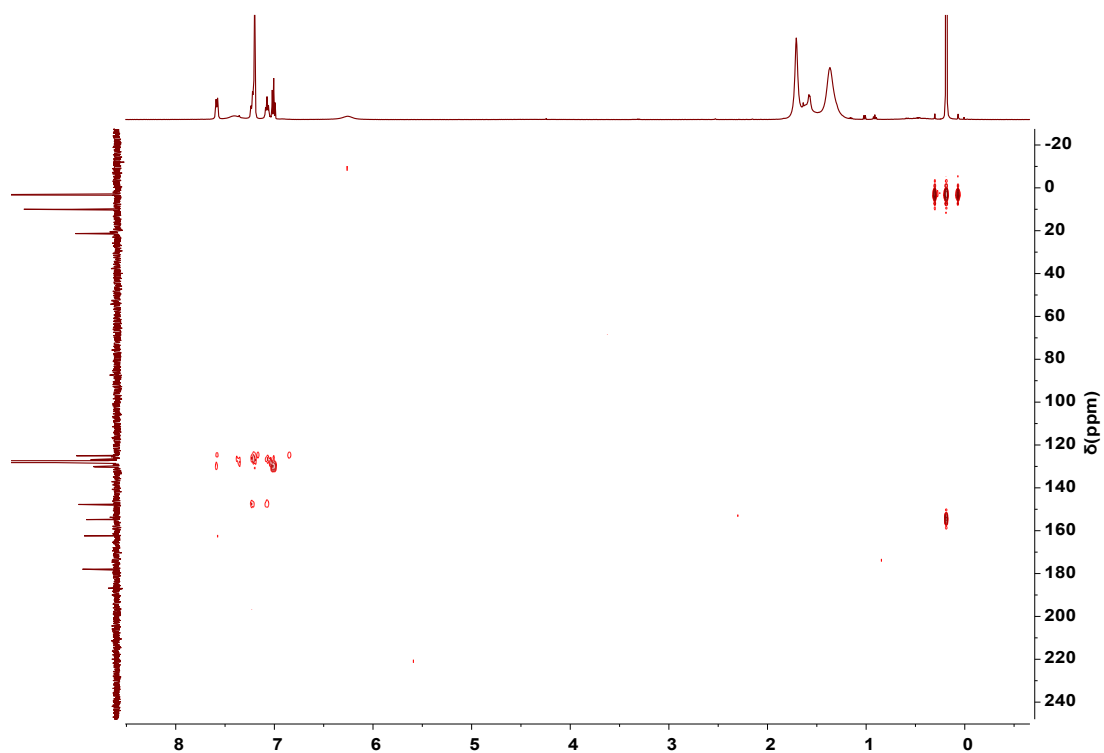


Figure S2d. $^1\text{H}^{13}\text{C}$ HMBC NMR (305.0 K, C_6D_6) spectrum of siladigermirane **5a**.

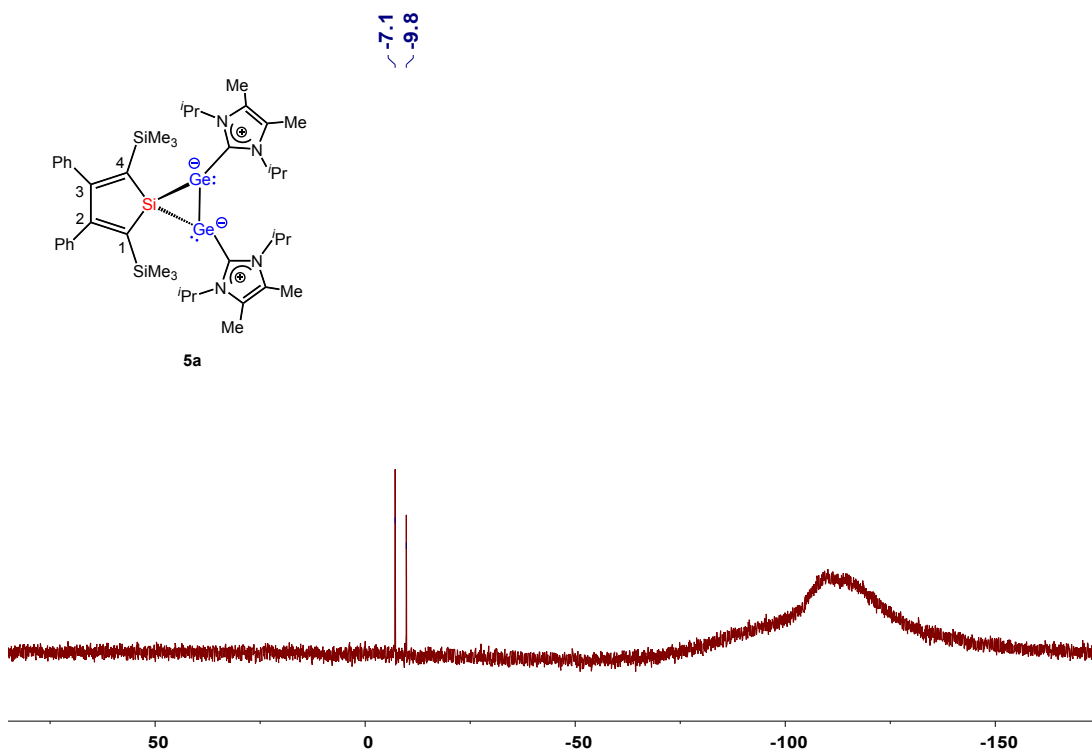


Figure S2e. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6) spectrum of siladigermirane **5a**.

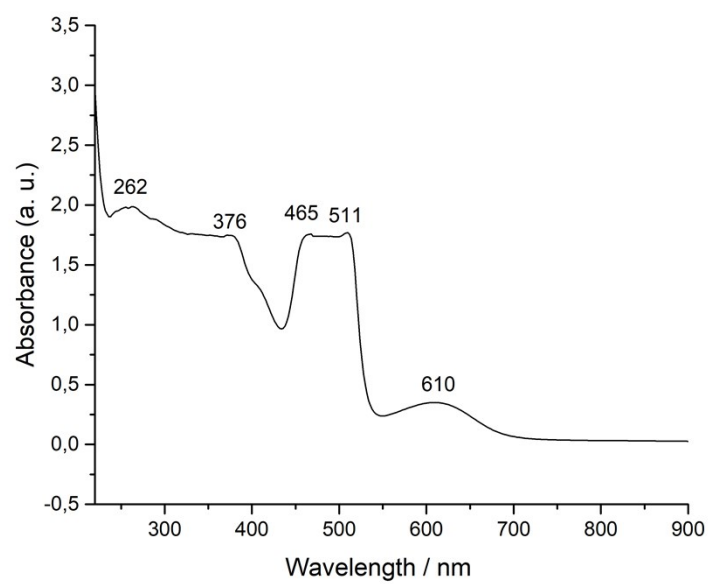
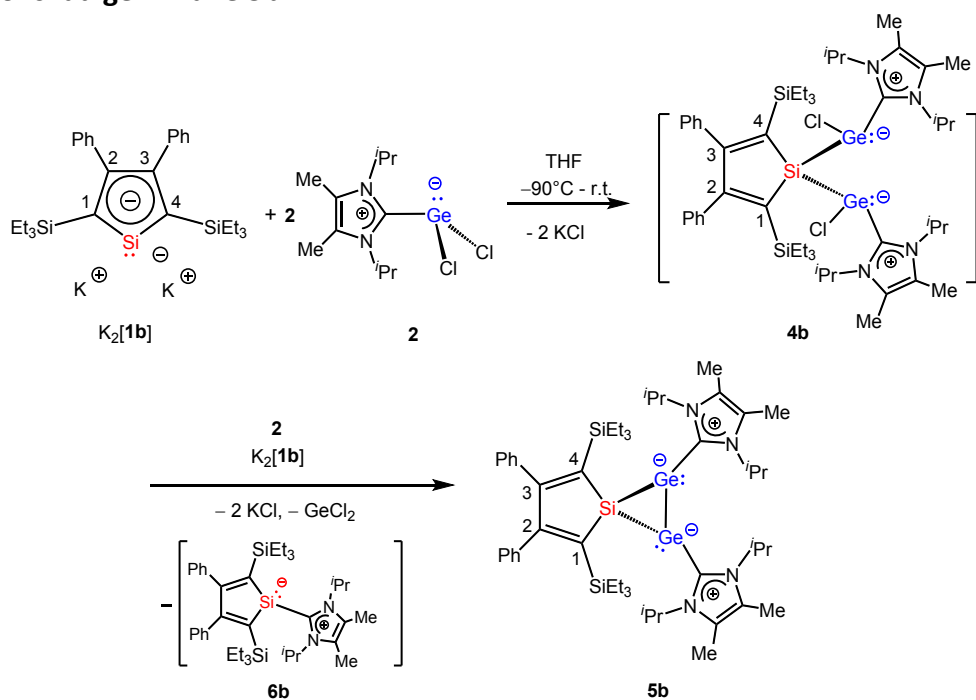


Figure S2f. UV-vis spectra of siladigermirane **5a** (in *n*-pentane).

Synthesis of siladigermirane **5b**:



Scheme S3.

Isolation of siladigermirane **5b.** A THF (6 mL) solution of $i\text{PrNHC-GeCl}_2$ **2** (122 mg, 0.376 mmol) was slowly added to a freshly prepared THF solution (10 mL) of $K_2[1b]$ (0.376 mmol) at -90°C . The reaction mixture was allowed to warm to room temperature after 0.5 h and then stirred for another 1 h to form a dark green solution. The solvent was removed under vacuum and the residue was re-dissolved in 10 mL Et_2O and the filtrate was concentrated to 3 mL. The dark green solution was stored at -30°C for 3 days to afford deep green crystals of siladigermirane **5b**. (Yield: 77.2 mg (0.08 mmol, 64 %)).

^1H NMR (499.9 MHz, 305.0 K, C_6D_6): δ = 7.49–7.50 (m, 2H, Ph), 7.42 (br, 2H, $\text{CH}(\text{CH}_3)_2$), 7.20–7.21 (m, 2H, Ph), 7.15–7.18 (m, 2H, Ph), 7.05–7.07 (m, 2H, Ph), 7.00–7.02 (m, 2H, Ph), 6.31 (br, 2H, $\text{CH}(\text{CH}_3)_2$), 1.75, 1.80 (s, 12H, $\text{NC}=\text{CCH}_3$), 1.31, 1.39, 1.68 (br, 24H, $\text{CH}(\text{CH}_3)_2$), 1.11–1.15 (t, 18H, $^3J_{\text{H,H}} = 7.8 \text{ Hz}$, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.79–0.86 (m, 6H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.40–0.47 (m, 6H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, 305.0 K, C_6D_6): δ = 178.4 (NCN), 162.6 ($2x\text{C}^{2/3}$), 152.4 ($2x\text{C}^{1/4}$), 147.8 (*i*-Ph), 130.5, 130.1, 126.4, 126.4, 125.0 (Ph), 129.2 (N-C=C), 52.4, 53.7 ($\text{CH}(\text{CH}_3)_2$), 21.4 ($\text{CH}(\text{CH}_3)_2$), 10.0 ($\text{NC}=\text{CCH}_3$), 9.3 ($\text{Si}(\text{CH}_2\text{CH}_3)_3$), 7.0 ($\text{Si}(\text{CH}_2\text{CH}_3)_3$).

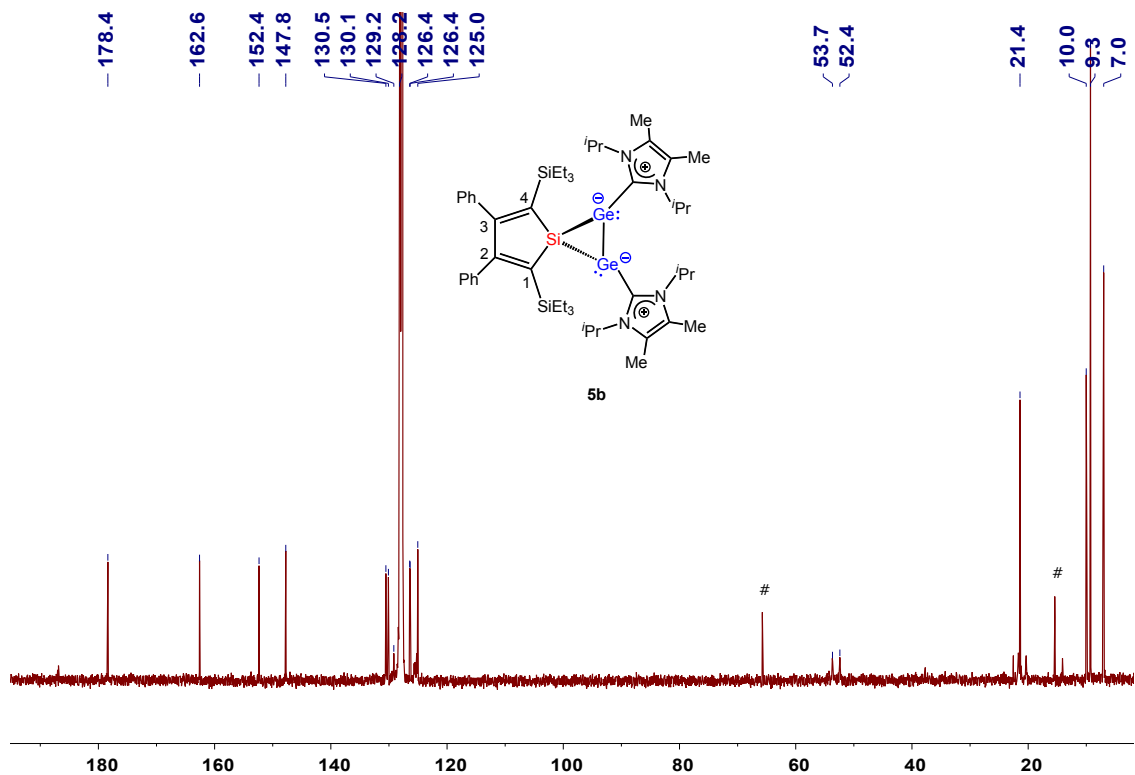
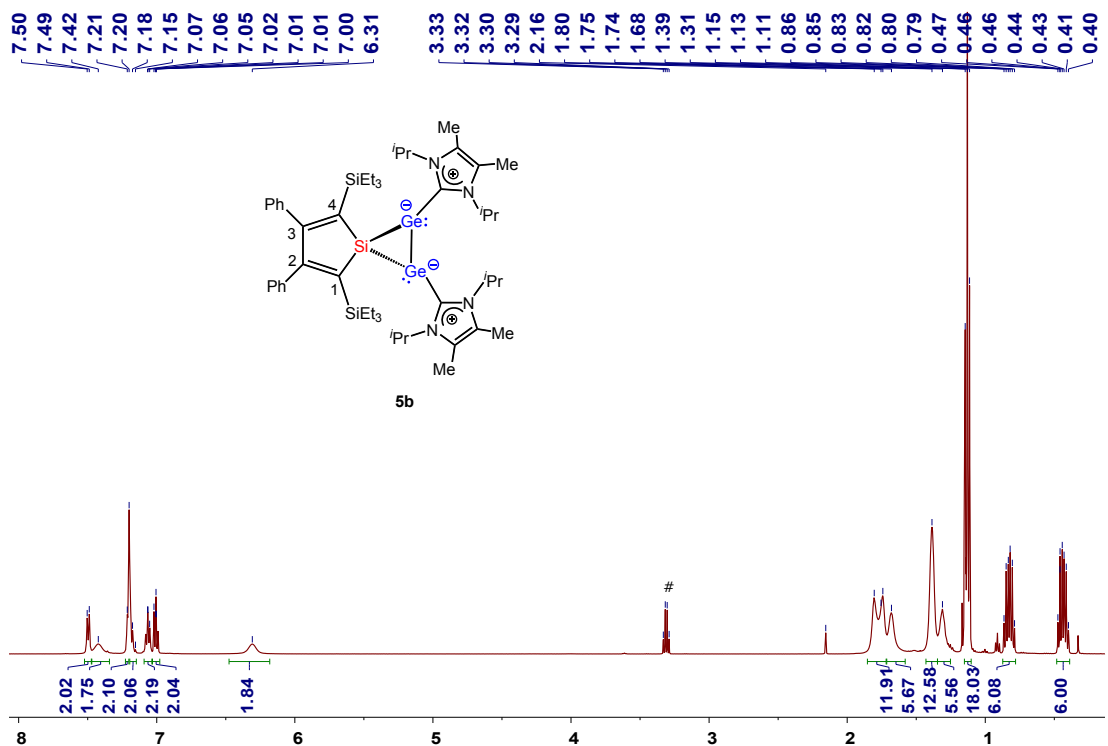
$^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6): δ = -2.1 ($\text{Si}(\text{CH}_2\text{CH}_3)_3$), -4.9 (SiGe_2).

HRMS (ESI) m/z [$\text{M}+\text{MeOH}+\text{H}$] $^+$ Calcd for $\text{C}_{51}\text{H}_{85}\text{N}_4\text{OSi}_3\text{Ge}_2$: 1001.4455 Found: 1001.4474.

UV-vis (*n*-pentane solution) [nm]: λ = 258(sh), 392, 455–530(br), 625.

Compound **6b** was detected in the reaction mixture by its characteristic ^{29}Si NMR resonances:

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6): δ = -28.8 (SiC_4), -10.0 (SiEt_3).



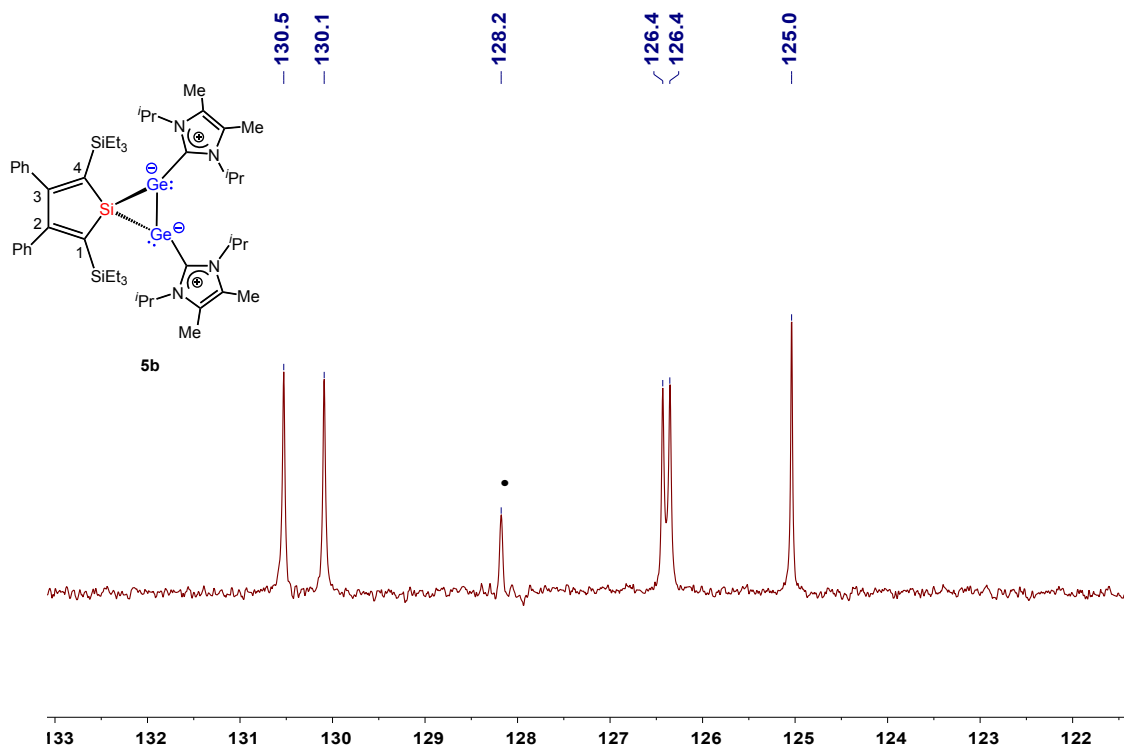


Figure S3c. ^{13}C DEPT NMR (125.7 MHz, 305.0 K, C_6D_6) spectrum of siladigermirane **5b** (\bullet : $\text{C}_6\text{D}_5\text{H}$).

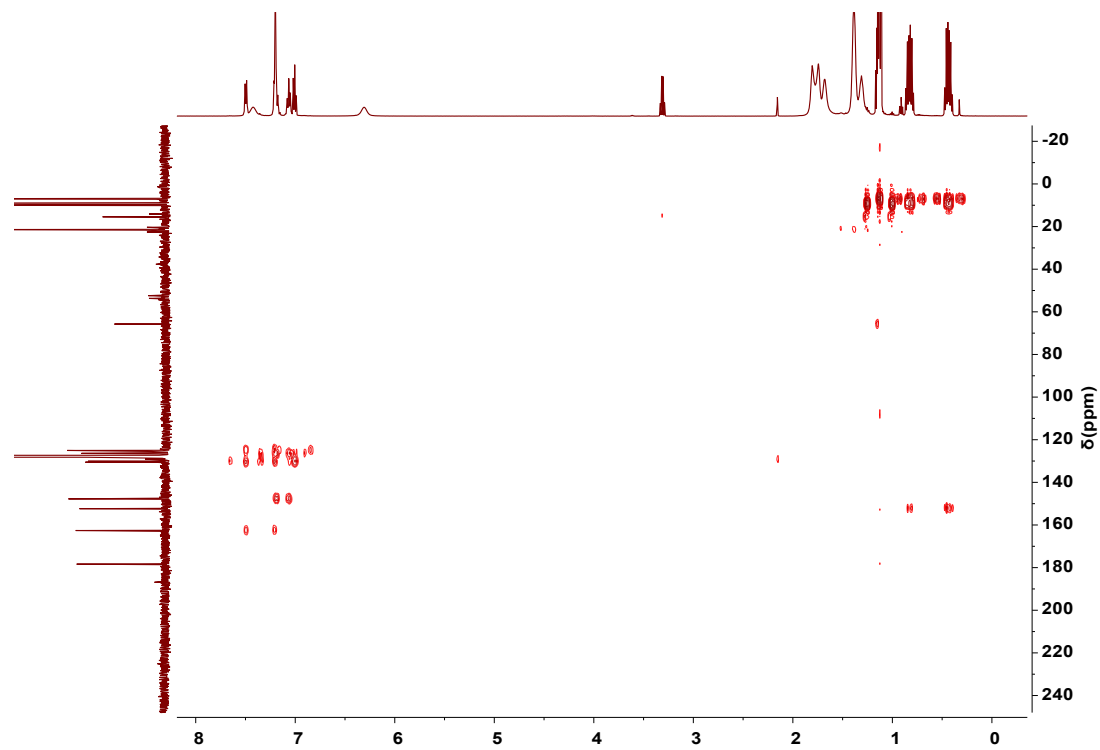


Figure S3d. $^1\text{H}^{13}\text{C}$ HMBC NMR (305.0 K, C_6D_6) spectrum of siladigermirane **5b**.

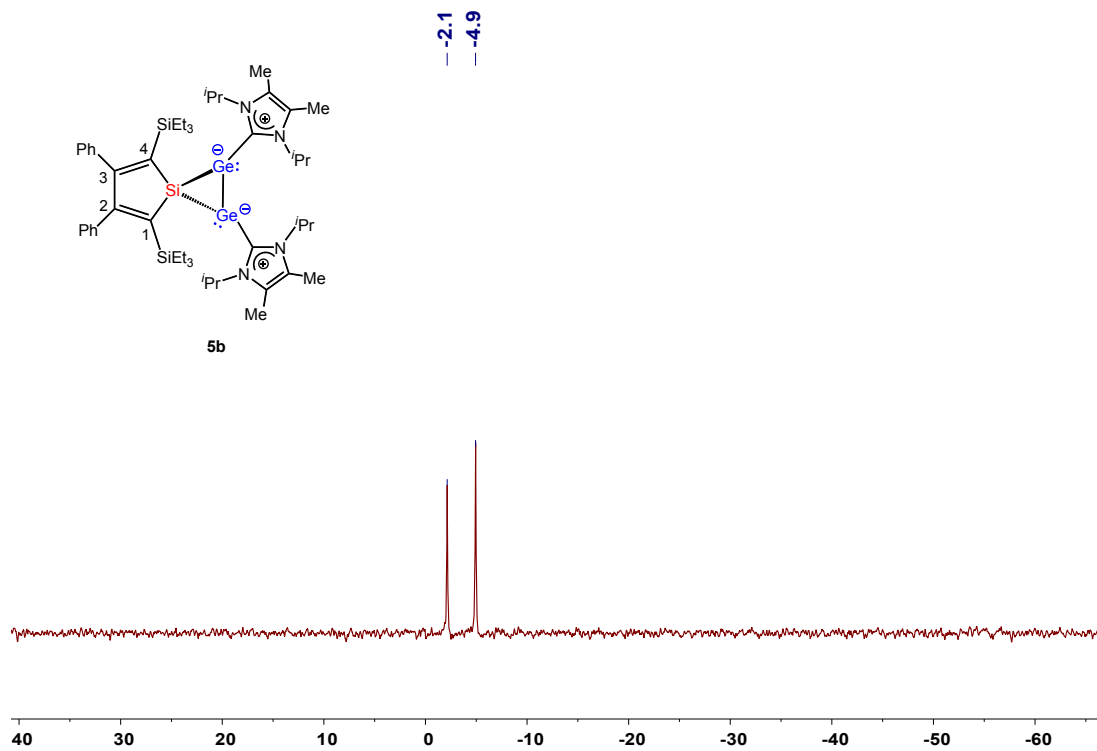


Figure S3e. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.3 MHz, 305.0 K, C_6D_6) spectrum of siladigermirane **5b**.

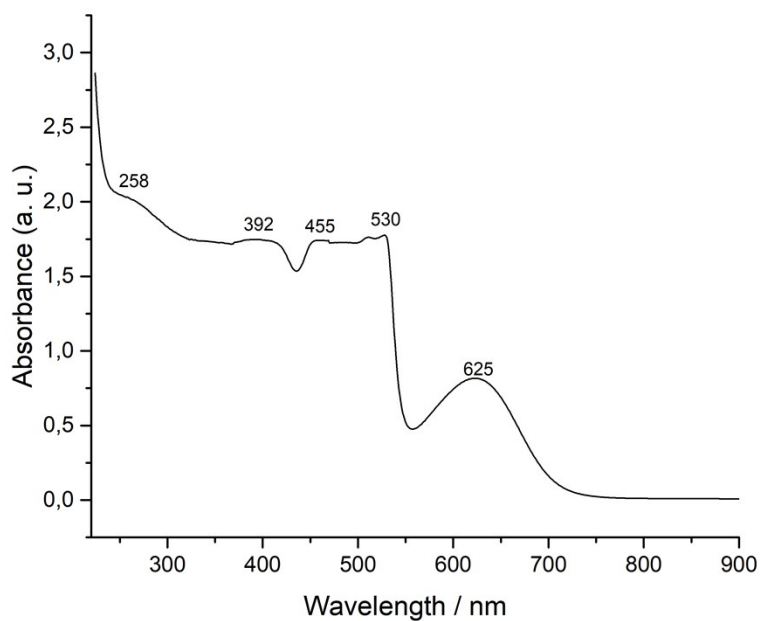


Figure S3f. UV-vis spectra of siladigermirane **5b** (in *n*-pentane).

Details of X-ray diffraction analysis of siladigermiranes 5 and disiladigermetanes 8.

Single crystal X-ray data were obtained on a Bruker AXS Apex II diffractometer (Mo-K α radiation, $\lambda = 0.71073\text{\AA}$, Kappa 4 circle goniometer, Bruker Apex II detector). The crystal was kept at 100.0 K during data collection. Absorption corrections based on symmetry-related measurements (multi-scan) were performed with the program SADABS.^[S4] The structures were solved with the program SHELXS and refined with SHELXL.^[S5] Pertinent data are summarized in Tables S1–S3. CCDC-1893833 (**5a**), CCDC-1893832 (**5b**), CCDC-1893834 (**8**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table S1. Crystal data and structure refinement for siladigermirane **5a**.

Identification code	dzw165a	
Empirical formula	C52 H88 Ge2 N4 O2 Si3	
Formula weight	1030.71	
Temperature	100(2) K	
Wavelength	0.71073 \AA	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.5456(15) \AA b = 14.7302(18) \AA c = 15.0458(18) \AA	$\alpha = 70.717(3)^\circ$. $\beta = 84.150(3)^\circ$. $\gamma = 76.059(3)^\circ$.
Volume	2952.3(6) \AA^3	
Z	2	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	1.117 mm^{-1}	
F(000)	1100	
Crystal size	0.200 x 0.070 x 0.060 mm^3	
Theta range for data collection	1.434 to 23.256 $^\circ$	
Index ranges	-12 \leq h \leq 16, -16 \leq k \leq 16, -16 \leq l \leq 16	
Reflections collected	56657	
Independent reflections	8484 (R(int) = 0.1238)	
Observed reflections (I > 2(I))	5580	
Completeness to theta = 23.256 $^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8847	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8484 / 0 / 590	
Goodness-of-fit on F ²	1.076	
Final R indices (I > 2sigma(I))	R1 = 0.0665, wR2 = 0.1564	
R indices (all data)	R1 = 0.1152, wR2 = 0.1782	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.430 and -0.670 e.\AA^{-3}	

Table S2. Crystal data and structure refinement for siladigermirane **5b**.

Identification code	dzw130	
Empirical formula	C53.50 H84 Ge2 N4 Si3	
Formula weight	1012.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.7931(5) Å	$\alpha = 92.7304(15)^\circ$.
	b = 14.4290(6) Å	$\beta = 91.3450(16)^\circ$.
	c = 17.6548(6) Å	$\gamma = 111.8890(15)^\circ$.
Volume	2781.69(19) Å ³	
Z	2	
Density (calculated)	1.209 Mg/m ³	
Absorption coefficient	1.182 mm ⁻¹	
F(000)	1078	
Crystal size	0.240 x 0.220 x 0.080 mm ³	
Theta range for data collection	1.524 to 32.031°	
Index ranges	-17<=h<=17, -21<=k<=21, -26<=l<=26	
Reflections collected	119718	
Independent reflections	19379 (R(int) = 0.0467)	
Observed reflections (I > 2(I))	14851	
Completeness to theta = 32.031°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9272 and 0.7849	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19379 / 45 / 602	
Goodness-of-fit on F ²	1.019	
Final R indices (I > 2sigma(I))	R1 = 0.0350, wR2 = 0.0793	
R indices (all data)	R1 = 0.0564, wR2 = 0.0870	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.543 and -0.769 e.Å ⁻³	

Table S3. Crystal data and structure refinement for disiladigermetane **8**.

Identification code	dzw165	
Empirical formula	C73 H113.50 Ge2 N4 O1.75 Si6	
Formula weight	1388.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.9129(9) Å	$\alpha = 76.4735(19)^\circ$.
	b = 15.0880(11) Å	$\beta = 84.561(2)^\circ$.
	c = 22.7675(18) Å	$\gamma = 80.734(2)^\circ$.
Volume	3919.9(5) Å ³	
Z	2	
Density (calculated)	1.177 Mg/m ³	
Absorption coefficient	0.901 mm ⁻¹	
F(000)	1483	
Crystal size	0.160 x 0.080 x 0.060 mm ³	
Theta range for data collection	1.403 to 23.256°	
Index ranges	-13<=h<=13, -16<=k<=13, -25<=l<=25	
Reflections collected	76697	
Independent reflections	11249 (R(int) = 0.1318)	
Observed reflections (I > 2(I))	7164	
Completeness to theta = 23.256°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9829 and 0.8942	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11249 / 21 / 814	
Goodness-of-fit on F ²	1.059	
Final R indices (I>2sigma(I))	R1 = 0.0544, wR2 = 0.1136	
R indices (all data)	R1 = 0.1076, wR2 = 0.1329	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.737 and -0.657 e.Å ⁻³	

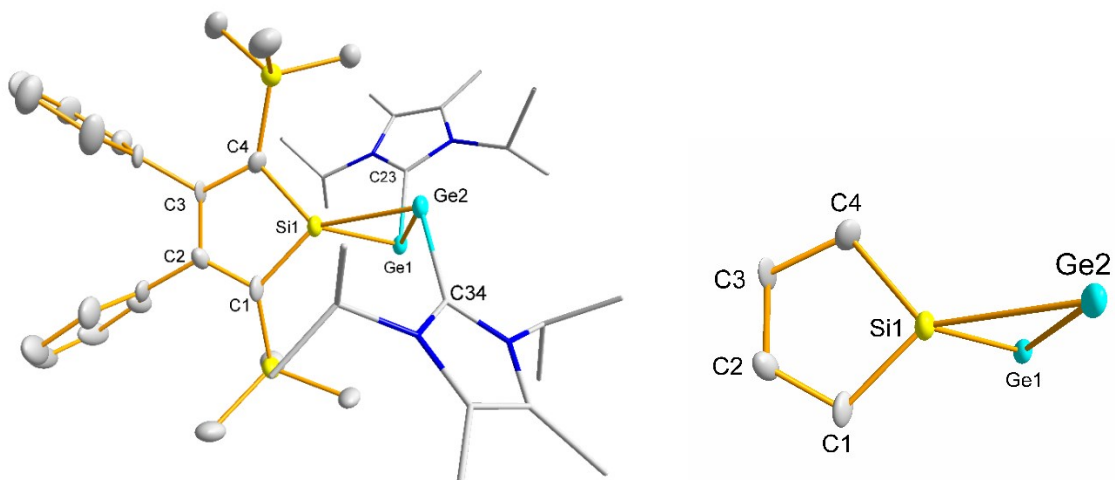


Figure S4. Molecular structure of siladigermirane **5a** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms are omitted for clarity. *iPr*₂Me₂NHC unit is simplified as wireframe). Selected atom distances [pm] and angles [°]: Ge1–Ge2 259.3(11), Si1–Ge1 244.6(2), Si1–Ge2 242.5(2), Ge1–C23 203.7(7), Ge2–C34 203.5(7), Si1–C1 185.4(7), Si1–C4 185.8(7), C1–C2 138.4(10), C2–C3 144.2(10), C3–C4 137.7(10), Ge1–Si1–Ge2 64.3(5), Ge1–Ge2–Si1 58.2(5), Si1–Ge1–Ge2 57.4(5), C1–Si1–C4 94.9(3), α (SiC₄/SiGe₂) 68.3 (The angle α is defined as the dihedral angle between the plane of the silole ring (SiC₄) and the plane of the three-membered ring (Si¹Ge¹Ge²)).

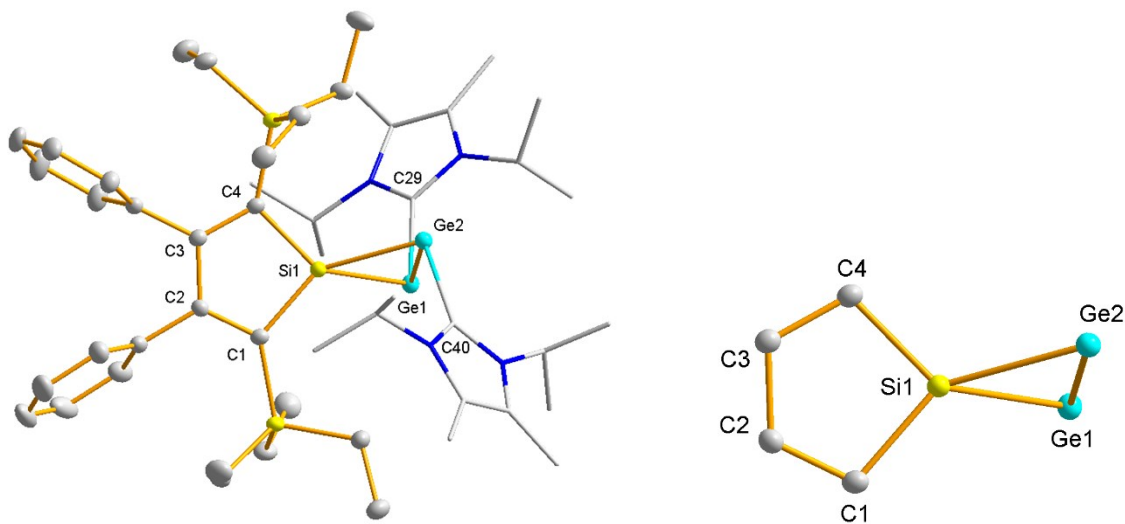


Figure S5. Molecular structure of siladigermirane **5b** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms are omitted for clarity. *iPr*₂Me₂NHC unit is simplified as wireframe). Selected atom distances [pm] and angles [°]: Ge1–Ge2 257.5(2), Si1–Ge1 245.9(4), Si1–Ge2 245.3(4), Ge1–C29 204.4(15), Ge2–C40 204.5(14), Si1–C1 187.0(15), Si1–C4 186.8(15), C1–C2 138.1(2), C2–C3 147.5(2), C3–C4 138.1(2), Ge1–Si1–Ge2 63.2(11), Ge1–Ge2–Si1 58.3(11), Si1–Ge1–Ge2 58.5(11), C1–Si1–C4 94.5(6), α (SiC₄/SiGe₂) 65.4 (The angle α is defined as the dihedral angle between the plane of the silole ring (SiC₄) and the plane of the three-membered ring (Si¹Ge¹Ge²)).

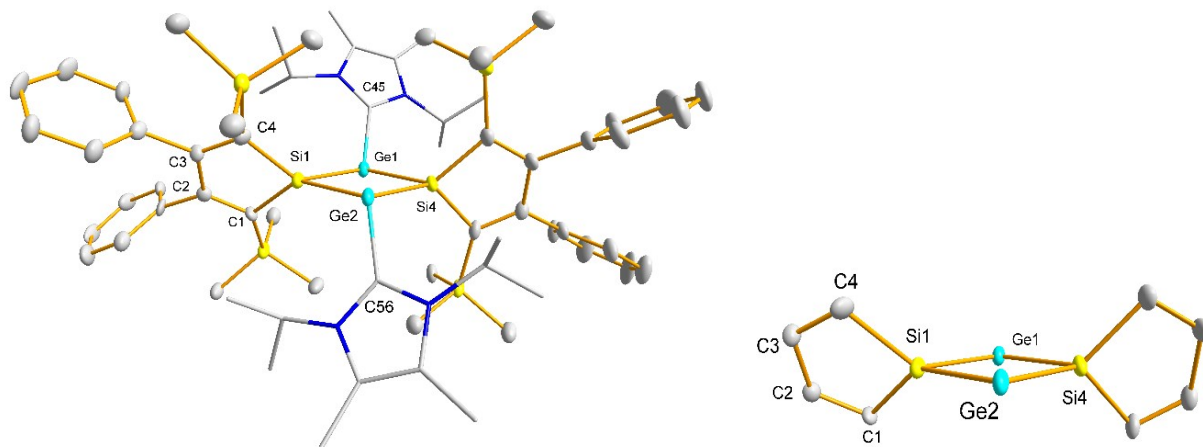
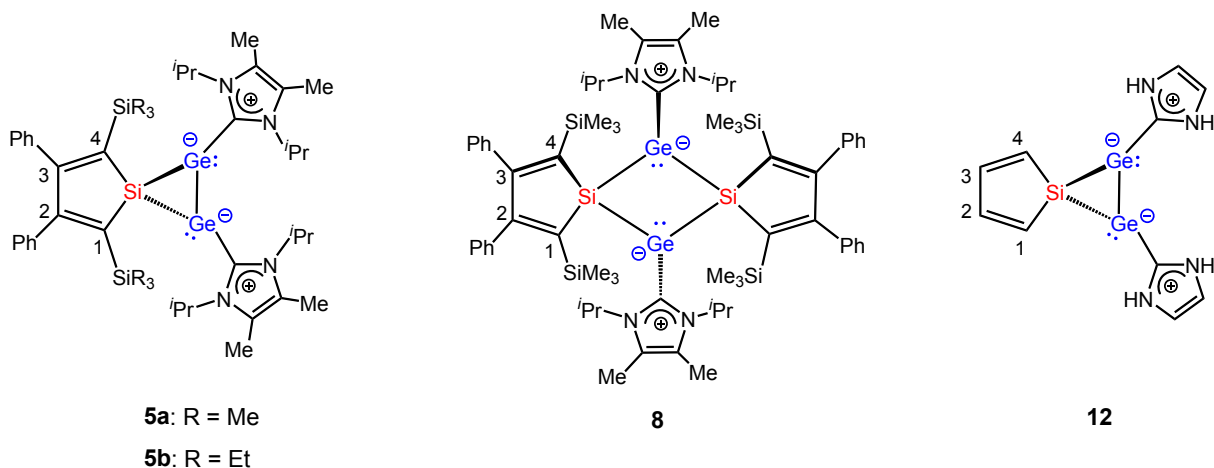


Figure S6. Molecular structure of disiladigermetane **8** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms are omitted for clarity. *i*Pr₂Me₂NHC unit is simplified as wireframe). Selected atom distances [pm] and angles [°]: Si1–Ge1 246.2(12), Si1–Ge2 245.0(16), Si4–Ge1 244.3(16), Si4–Ge2 243.1(16), Ge1···Ge2 339.8(11), Si1···Si4 352.1(20), Ge1–C45 200.2(6), Ge2–C56 201.6(5), Si1–C1 190.5(5), Si1–C4 190.9(5), C1–C2 138.2(7), C2–C3 148.7(7), C3–C4 136.1(7), Ge1–Si1–Ge2 87.5(5), Si1–Ge1–Si4 91.8(5), Si1–Ge2–Si4 92.3(5), Ge1–Si4–Ge2 88.4(5), C1–Si1–C41 92.5(2), α (SiC₄/Si₂Ge₂) 58.3 (The angle α is defined as the dihedral angle between the plane of the silole ring (SiC₄) and the plane of the four-membered ring (Si¹Ge¹Si⁴Ge²)).

Table S4. Comparison of structural parameter of compounds **5**, **8** and calculated structures **5a^{opt}**, **8^{opt}** and **12^{opt}**.



	5a ^[a]	5a ^{opt[b]}	5b ^[a]	12 ^{opt[b]}	8 ^[a]	8 ^{opt[b]}
Ge ¹ –Ge ²	259.3	261.0	257.5	261.8	–	
Si ¹ –Ge ¹	244.6	245.2	245.9	244.7	246.2	243.8
Si ¹ –Ge ²	242.5	244.9	245.3	244.7	245.0	243.8
Ge ¹ –C ^{NHC}	203.7	207.3	204.4	205.7	200.2	203.8
Ge ² –C ^{NHC}	203.5	207.3	204.5	205.7	201.6	203.8
Si ¹ –C ¹	185.4	185.8	187.0	184.9	190.5	188.7
Si ¹ –C ⁴	185.8	185.9	186.8	184.9	190.9	188.7
C ¹ –C ²	138.4	136.9	138.1	136.0	138.2	136.0
C ² –C ³	144.2	147.2	147.5	145.3	148.7	149.0
C ³ –C ⁴	137.7	136.9	138.1	136.0	136.1	136.0
α (SiC ₄ /SiGe ₂) ^[c]	68.3	66.6	65.4	79.7	–	–
α (SiC ₄ /Si ₂ Ge ₂) ^[d]	–	–	–	–	58.3	75.8

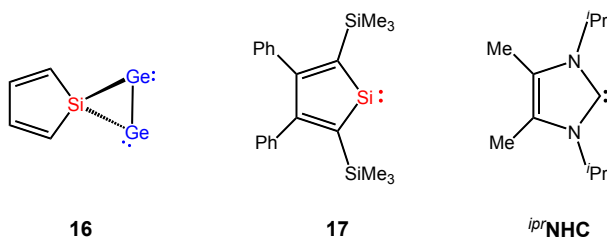
[a] Experimental data from XRD. [b] M06-2X/Def2-TZVP. [c] The angle α is defined as the dihedral angle between the plane of the silole ring (SiC₄) and the plane of the three-membered ring (Si¹Ge¹Ge²). [d] The angle α is defined as the dihedral angle between the plane of the silole ring (SiC₄) and the plane of the four-membered ring (Si¹Ge¹Si⁴Ge²). [e] Sum of the covalent radii expected for Ge–E single bonds: E = Si: 237 pm, E = Ge: 242 pm, E = C: 196 pm.⁵⁶

Computational Details

All quantum chemical calculations were carried out using the Gaussian 09 package.⁵⁷ The NBO analyses⁵⁸ were performed with the Version 6.0 of the NBO program which was implemented in the G09 D.01 version of the Gaussian program.⁵⁹ The AIMALL program was used to perform the QTAIM analysis.⁵¹⁰ For visualization of the natural bond orbitals the program Jmol was used.⁵¹¹

The molecular structure optimizations were performed using the M06-2X functional⁵¹² along with the Def2-TZVP basis set for all elements.⁵¹³⁻⁵¹⁵ Stationary points were verified as minima by subsequent frequency calculations (Number of imaginary frequencies (NIMAG): 0).

Table S5. Calculated absolute energies, E(SCF), and free enthalpies at 298 K, G^{298} , for compounds of interest.



Compound	Method/basis set	E(SCF) [a.u.]	NIMAG ZPVE [kJ mol ⁻¹]	G^{298} [a.u.]
5a	M062X/Def2-TZVP	-6959.07508	0, 2720	-6958.13982
6a		-2264.32771	0, 1926	-2263.67062
7		-4341.33404	0, 1926	-4340.68232
8		-8682.76956	0, 3683	-8681.42540
12		-5050.73082	0, 569	-5050.56376
13		-4393.50404	0, 578	-4393.32978
14		-4757.93073	0, 565	-4757.76379
15		-4678.07293	0, 371	-4677.97454
16		-4598.19693	0, 184	-4598.16133
17		-1723.59513	0, 1132	-1723.22562
18		-4679.29260	0, 410	-4679.17930
19		-4680.51207	0, 454	-4680.38350
20		-4817.59619	0, 367	-4817.49962
21		-2409.37745	0, 201	-2409.33134
22		-5051.91876	0, 607	-5051.73732
23		-5189.00791	0, 525	-5188.85783
24		-2595.07382	0, 278	-2595.00354
25		-5053.16477	0, 692	-5052.95206
26		-5054.35195	0, 729	-5054.12463
GeH ₂		-2078.13937	0, 292	-2078.14947
GeH ₄		-2079.37509	0, 787	-2079.36573
<i>ipr</i> NHC		-540.64147	0, 779	-540.38628
^H NHC		-226.17143	0, 190	-226.12545

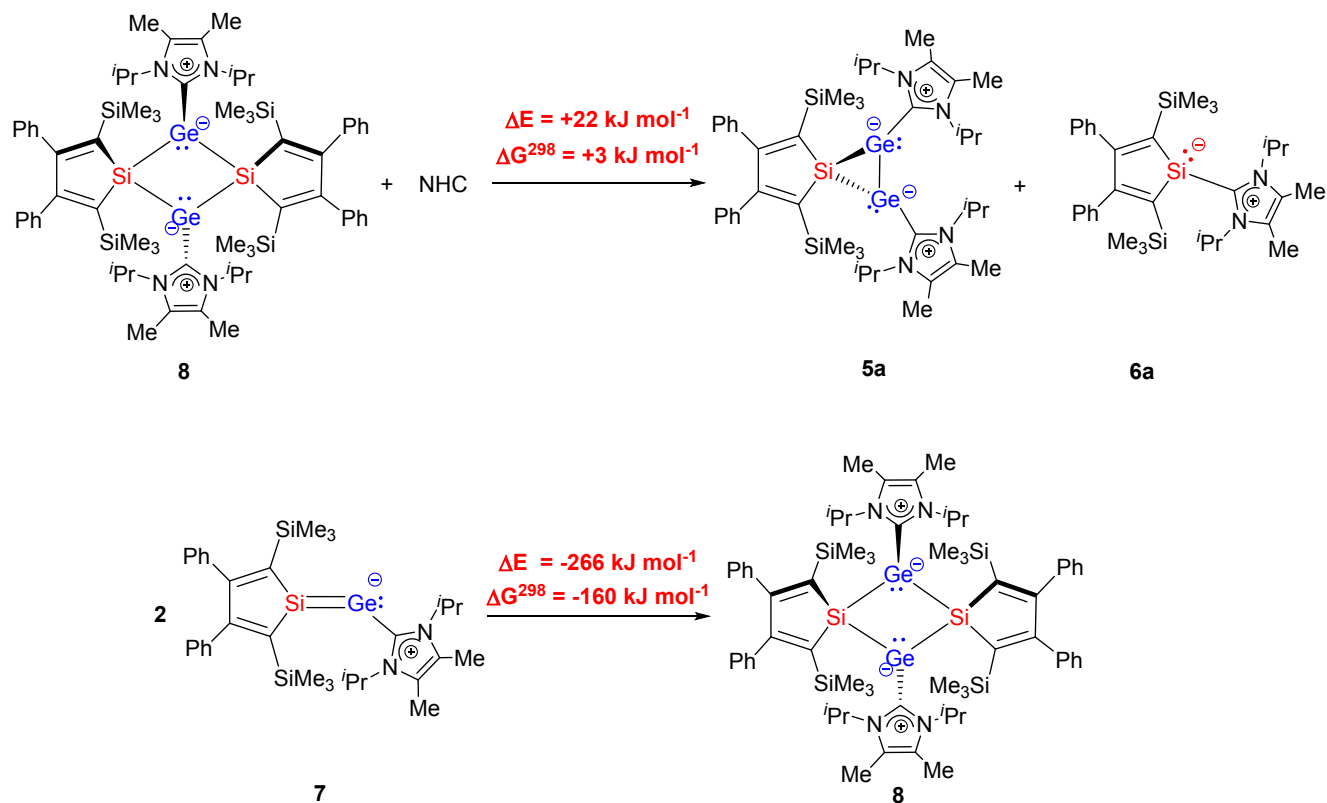


Figure S7. Top: Calculated reaction energies of the reaction of NHC with compound **8**. Bottom: Calculated dimerization energy ΔE and free Gibbs energy ΔG^{298} of silagermenylidene **7** to give disiladigermetane **8** (Energies ΔE and Gibbs energy at 298 K, ΔG^{298} (in $\text{kJ}\cdot\text{mol}^{-1}$, calculated at M062X/Def2-TZVP, see Table S5).

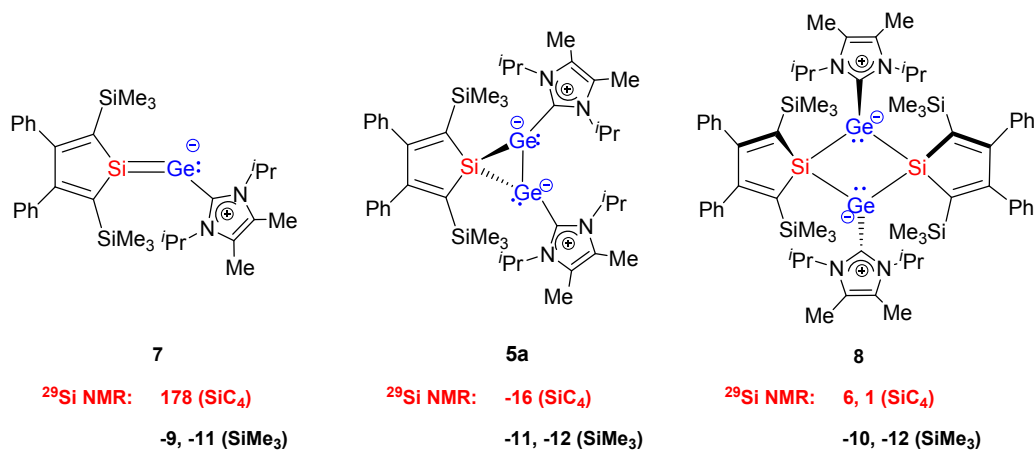


Figure S8. Calculated ^{29}Si NMR Chemical shifts for compounds **5a**, **7** and **8** (M062X/Def2-TZVP).

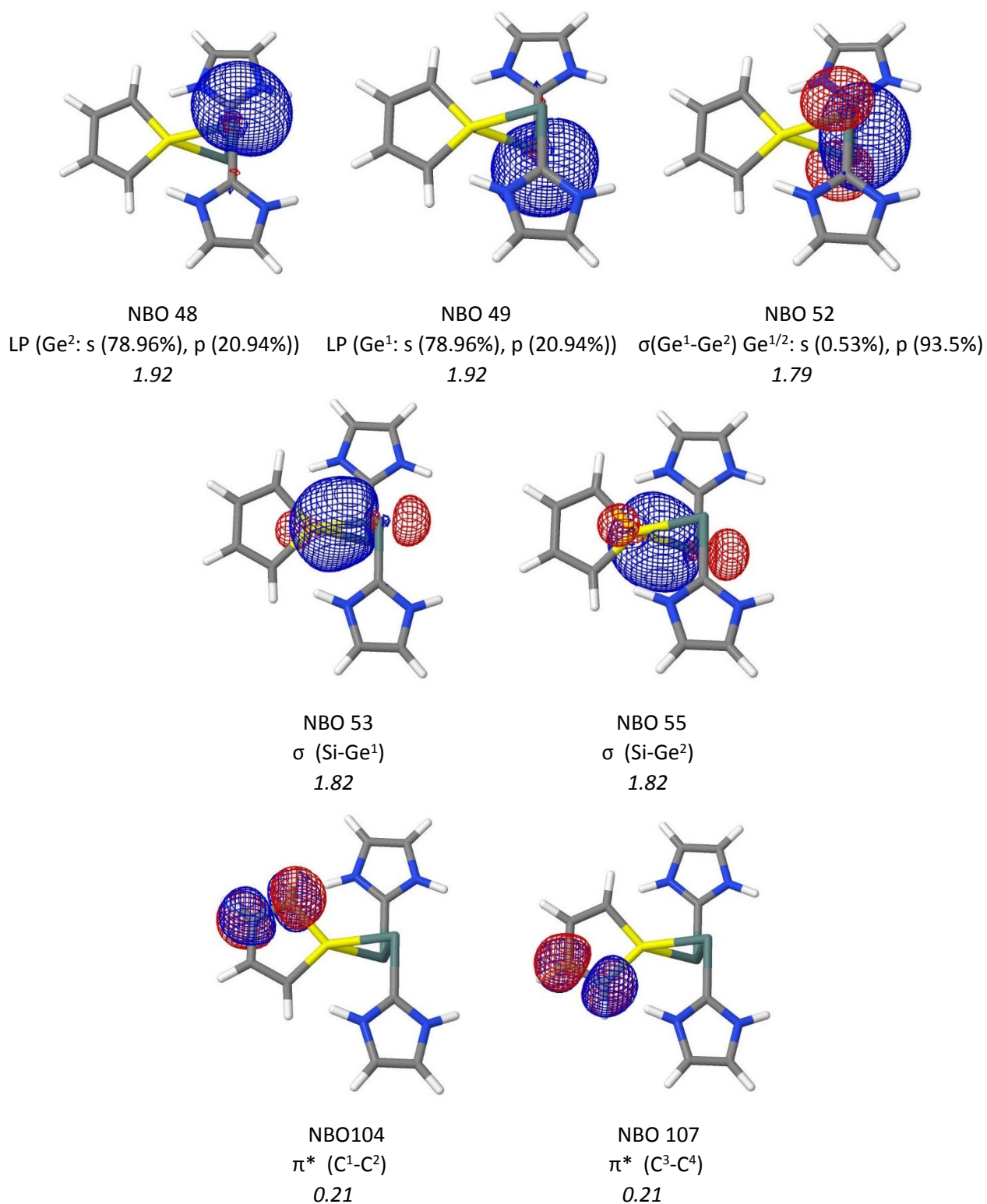
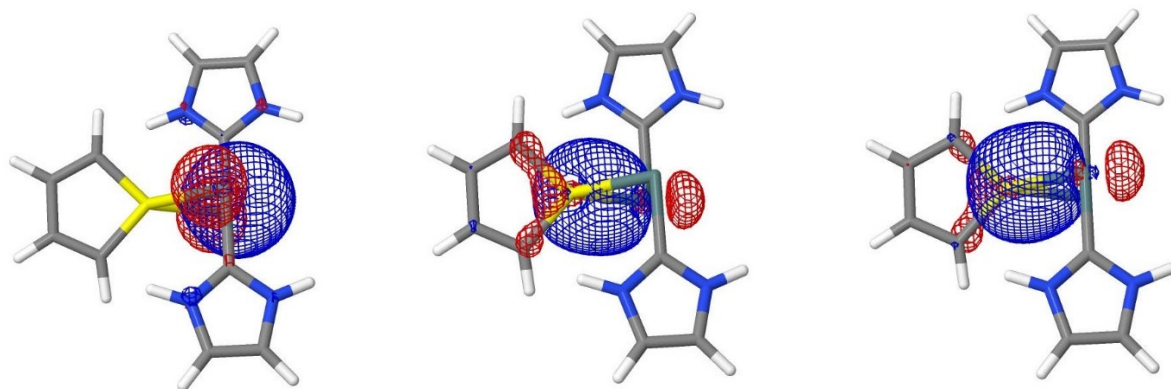


Figure S9. Calculated natural bond orbitals (NBOs) of model compound **12**. (M06-2X/Def2-TZVP, at an isodensity value of 0.04; LP: lone pair; the orbital occupancy is given in italic.)

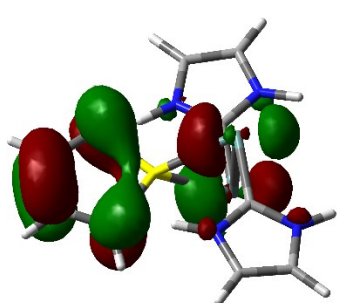


NLMO 52
 σ (Ge¹-Ge²)
1.92

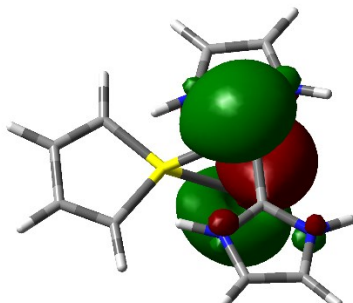
NLMO 53
 σ (Si-Ge²)
1.82

NLMO 55
 σ (Si-Ge²)
1.82

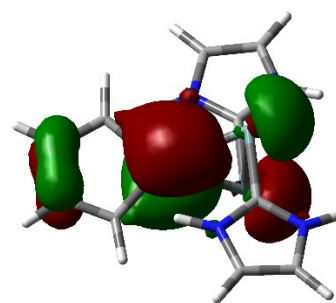
Figure S10. Calculated natural localized molecular orbitals (NLMOs) of model compound **12**. (M06-2X/Def2-TZVP, at an isodensity value of 0.04; the orbital occupancy is given in *italic*.)



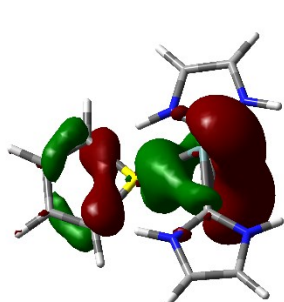
LUMO (-0.05 eV)



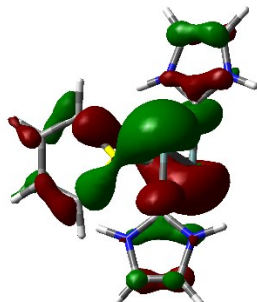
HOMO (-4.97 eV)



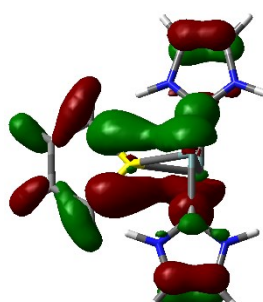
HOMO-1 (-5.03 eV)



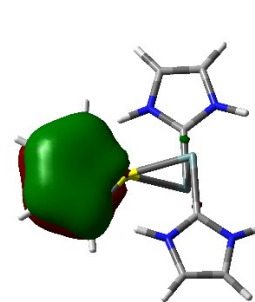
HOMO-2 (-6.72 eV)



HOMO-4 (-8.18 eV)



HOMO-8 (-9.45 eV)



HOMO-9 (-10.16 eV)

Figure S11. Surface diagrams of the frontier orbitals of model compound **12**. (M06-2X/Def2-TZVP, at an isodensity value of 0.04)

Ring strain in sila-di- λ^3 -germiranes. The set of isodesmic reactions eq. 1-5 is used to estimate the ring strain in the three-membered cycles. Comparison of the results of eqs 1 and 2 suggests for siladigermirane **18** a ring strain of 159 kJ mol⁻¹. This is in agreement with the results of previous calculations of the ring strain in heavy cyclopropanes (Ge₃H₆: 165 kJ mol⁻¹; SiGe₂H₆ 162 kJ mol⁻¹).^{S16-S17} Likewise eqs 3 and 4 predict for sila- λ^3 - λ^3 -digermirane **12** a ring strain of 127 kJ mol⁻¹. Therefore, the integration of two λ^3 -germanium atoms decreases the strain in the three-membered ring by 32 kJ mol⁻¹. Comparison of eq. 1 with eq. 5 indicates that the cross-hyperconjugation with the butadiene part of the silole ring has no influence on the ring strain.

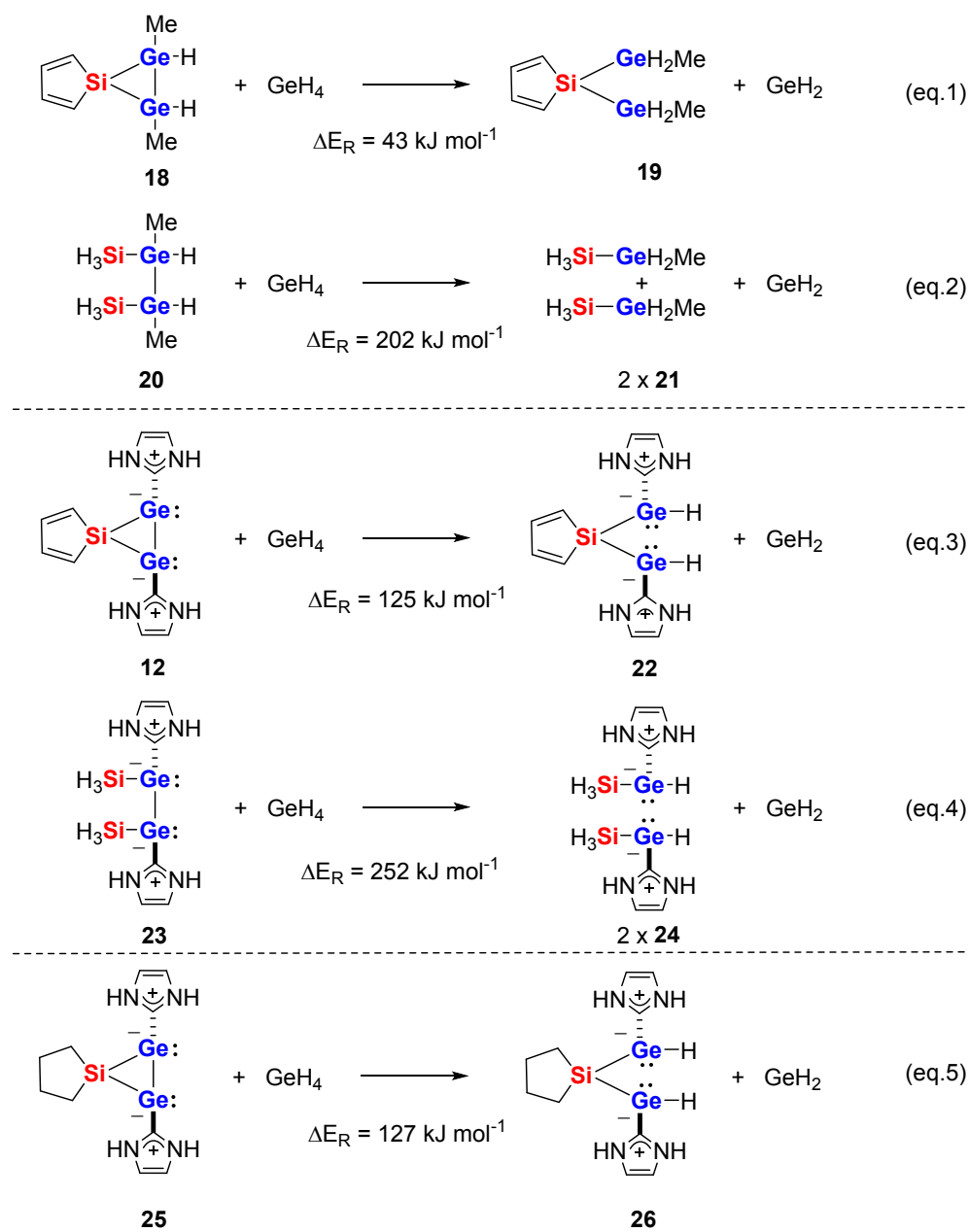


Figure S12. Calculation of the ring strain in siladigermiranes **12**, **18** and **25**.

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