Supplementary Information

A Missing Allene of Heavy Group-14 Elements. 2-Germadisilaallene

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Contents

1. Details of X-ray analysis

Table S1. Crystal data and structure refinement for 2-germadisilaallene[a]

Crystal	A	B	B	B	B	C	C
Temperature/K	223	123	173	223	273	93	223
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1(#2)	*P*-1(#2)	*P*-1(#2)	*P*-1(#2)	*P*-1(#2)	*P*-1(#2)	*P*-1(#2)
Unit cell dimensions							
a/Å	11.783(3)	11.709(3)	11.7571(2)	11.777(3)	11.792(2)	11.683(3)	11.787(3)
b/Å	12.317(2)	12.239(2)	12.2792(1)	12.315(3	12.365(2)	12.214(3)	12.318(2)
c/Å	18.638(4)	18.548(4)	18.5740(5)	18.633(5)	18.719(4)	18.607(4)	18.634(4)
α/°	73.548(8)	73.464(7)	73.558(5)	73.588(8)	73.572(6)	73.588(7)	73.594(6)
β/°	87.246(10)	87.139(8)	87.309(7)	87.260(9)	87.166(8)	87.156(8)	87.201(7)
γ/°	72.204(8)	71.999(7)	72.299(5)	72.249(8)	72.153(6)	71.628(7)	72.174(6)
Volume	2467.8(9)	2421.2(9)	2447.83(13)	2466.8(10)	2489.9(8)	2414.8(9)	2468.9(9)
Z	2	2	2	2	2	2	2
Density (calcd)/(mg m^{-3})	1.101	1.123	1.110	1.102	1.092	1.126	1.101
Absorption coeff. (mm^{-1})	0.883	0.900	0.890	0.884	0.875	0.903	0.883
F(000)	888	888	888	888	888	888	888
Crystal size	0.30 mm	0.30 mm	0.30 mm	0.30 mm	0.30 mm	0.30 mm	0.30 mm
(max, mid, min)	0.15 mm	0.30 mm	0.30 mm	0.30 mm	0.30 mm	0.20 mm	0.20 mm
	0.10 mm^3	0.10 mm	0.10 mm	0.10 mm	0.10 mm	0.10 mm	0.10 mm
θ for data collection	3.29 to 27.48°	3.31 to 28.28°	3.30 to 27.48°	3.29 to 27.48°	3.27 to 27.50°	3.31 to 27.48°	3.29 to 27.48°
Index Range	-15<=h<=15,	-15<=h<=15,	-14<=h<=15,	-15<=h<=11,	-15<=h<=15,	-15<=h<=15,	-15<=h<=15,
	-14<=k<=15,	-15<=k<=16,	-15<=k<=15,	-15<=k<=15,	-16<=k<=16,	-15<=k<=15,	-15<=k<=15,
	-23<=l<=24	-24<=l<=24	-19<=l<=24	-24<=l<=22	-24<=l<=23	-24<=l<=24	-24<=l<=24
Reflection Collected	20066	38183	19094	19021	23225	37880	28393
Independent refl. [R(int)]	10288[0.0000]	11049[0.0277]	10527[0.0515]	10558[0.0240]	10992[0.0632]	10992[0.0546]	11079[0.0367]
Completeness to θ=25. 0°	94.6 %	99.7 %	96.6 %	96.4 %	97.7 %	99.7 %	97.8 %
Max./min. transmittion	0.9169/0.7775	0.9154/0.7740	0.9162/0.7760	0.9168/0.7775	0.9176/ 0.7792	0.9152/0.7735	0.9169/0.7776
Data/restraints/parameters	10288/55/443	11049/34/433	10527/55/443	10558/61/ 443	10992/103/443	10992/28/433	11079/61/443
Goodness-of-fit on F^2	1.189	1.137	1.125	1.145	1.204	1.144	1.177
Final R indices [$I>2\sigma(I)$]	R1=0.0938,	R1 = 0.0461,	R1 = 0.0588,	R1 = 0.0706,	R1 = 0.0869,	R1 = 0.0411,	R1 = 0.0760,
	wR2=0.1679	wR2 = 0.0976	wR2 = 0.1262	wR2 = 0.1439	wR2 = 0.1661	wR2 = 0.0815	wR2 = 0.1474
R indices (all data)	R1=0.1362,	R1 = 0.0510,	R1 = 0.0718,	R1 = 0.0880,	R1 = 0.1141,	R1 = 0.0460,	R1 = 0.0973,
	wR2=0.1921	wR2 = 0.1001	wR2 = 0.1338	wR2 = 0.1550	wR2 = 0.1807	wR2 = 0.0838	wR2 = 0.1582
Largest diff. Peak/hole e.$Å^{-3}$	0.361/-0.375	0.788/-0.515	0.604/-0.532	0.449/-0.444	0.324/-0.326	0.419/-0.363	0.408/-0.398

a) Molecular formula: $C_{32}H_{80}GeSi_{10}$; Formula Weight: 818.43; Refinement Method: Full-matrix least-squares on F^2.

2. UV-vis and NMR spectra of 4

1) UV-vis spectrum of 4

UV-vis spectrum of 2-germadisilaallene **4** was measured using a sealed glass apparatus equipped with a quartz cell (light path 10 mm).

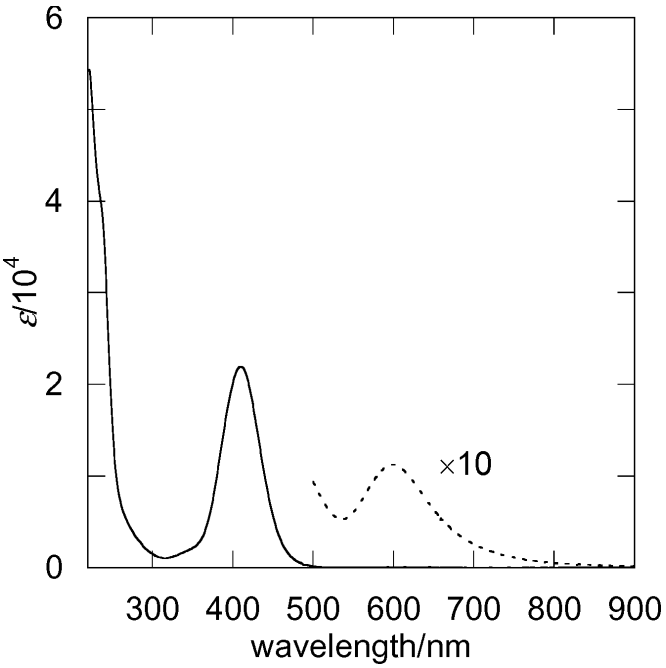
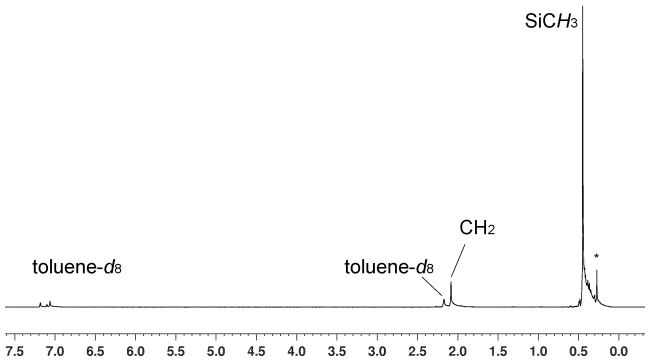


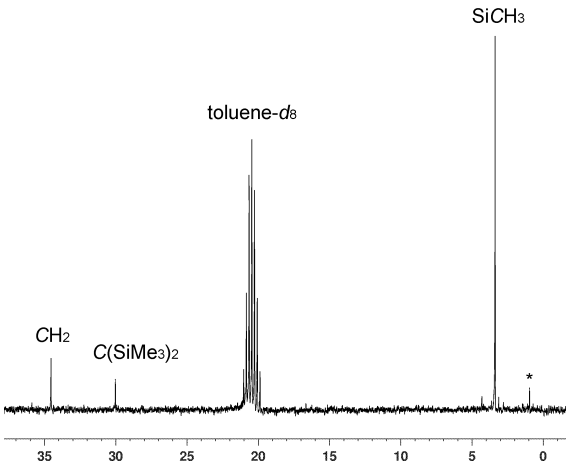
Fig. S1. UV-vis spectrum of **4** in hexane at room temperature.

2) NMR spectra of 4 at 293 K

(a) ^{1}H NMR



(b) ^{13}C NMR



(c) ^{29}Si NMR

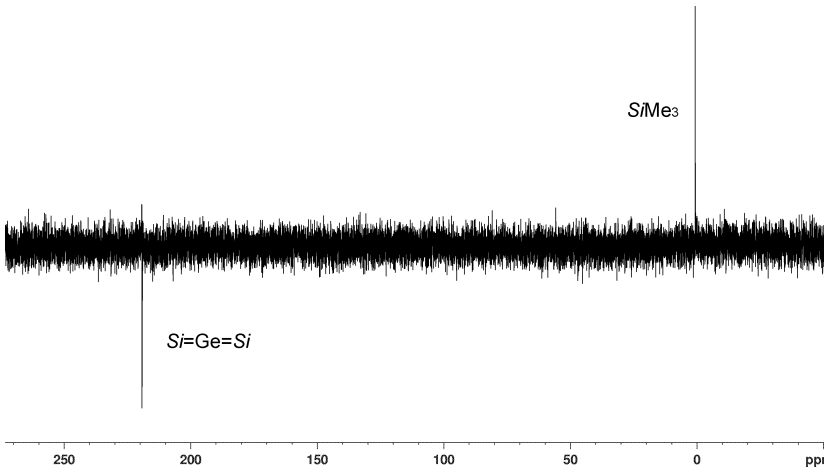
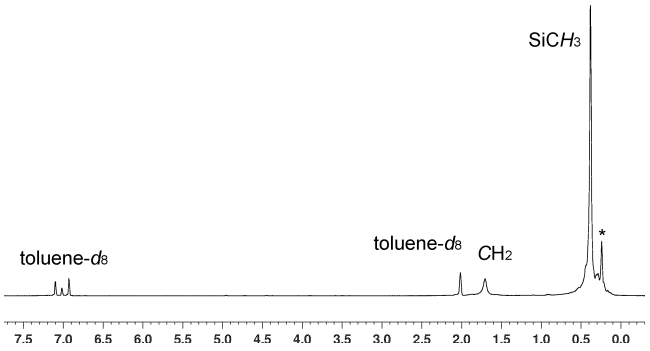


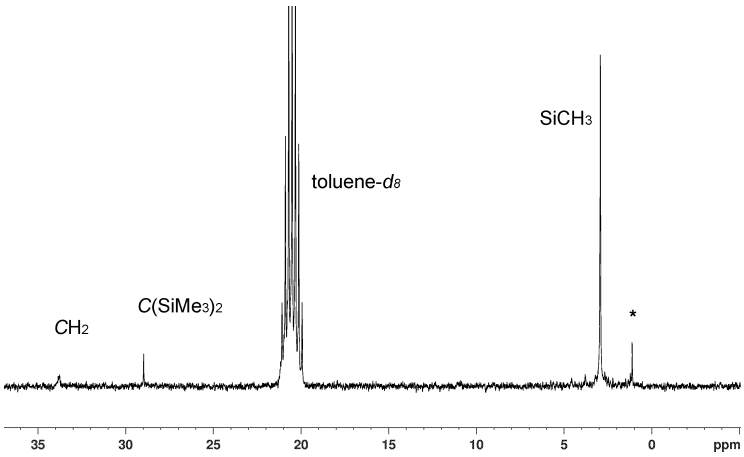
Fig. S2. NMR spectrum of **4** in toluene-d_8 at 293 K. (a) ^{1}H NMR. (b) ^{13}C NMR. (c) ^{29}Si NMR. Signals marked * are due to silicone grease.

3) NMR spectra of 4 at 193 K

(a) ^{1}H NMR



(b) ^{13}C NMR



(c) ^{29}Si NMR

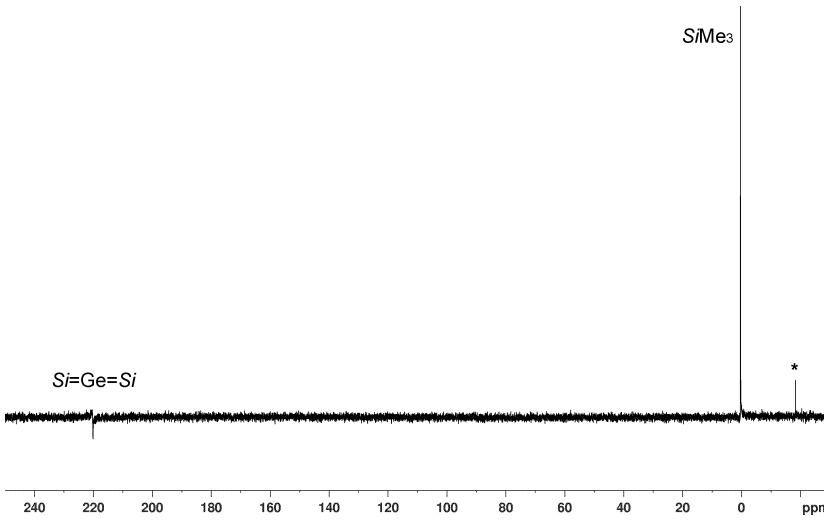


Fig. S3. NMR spectrum of **4** in toluene-d_8 at 193 K. (a) ^{1}H NMR. (b) ^{13}C NMR. (c) ^{29}Si NMR. Signals marked * are due to silicone grease.

3. Plots of ln([4X]/[4A]) vs 1/T

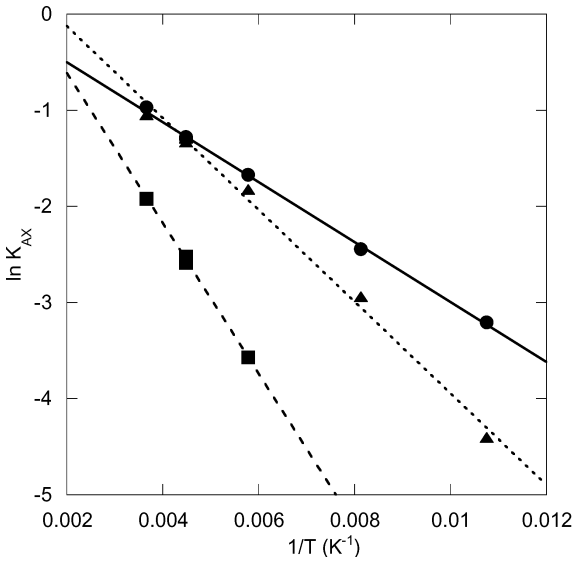


Figure S4. van't Hoff plot (ln K_{AX} vs 1/T) for the equilibrium between isomer **4A** and **4X** (X = B, C or D) in the crystals of 2-germadisilaallene **4**; K_{AX} = [**4X**]/[**4A**]. K_{AX} values is the ratio of the site occupancy factor (sof) of Ge1X (X=B, C, or D) to that of Ge1A. The data of ln K_{AB} are represented by solid circles, K_{AC} by solid triangles, and K_{AD} by solid squares. The linear lines are obtained by the least squares fitting (the correlation coefficients R are 0.999 (K_{AB}), 0.997 (K_{AC}), and 0.999 (K_{AD}), respectively).

Table S2. Relative Enthalpy (ΔH_{AX}) and Entropy (ΔS_{AX}) among Isomers **4A**-**4D**

Isomer	ΔH_{AX} (kcal mol^{-1})	ΔS_{AX} (cal mol^{-1} K^{-1})
4A	0.00	0.00
4B	0.52	0.25
4C	0.95	1.65
4D	1.55	1.89

4. Experimental details of the reaction of dialkylsilylene 2 with $GeCl_4$

A mixture of THF (15 ml) and germanium tetrachloride (1.80 g, 8.40 mmol) was added through vacuum line to dialkylsilylene **5** (0.90 g, 2.41 mmol) in a Schlenk flask. The resulting solution was stirred for 3 hours at –30 °C. After removal of the volatiles, recrystallization from hexane gave 1-chloro-2,2,5,5-tetrakis(trimethylsilyl)-1-trichloro-germyl-1-silacyclopentane (**7**, 1.03g, 1.76 mmol, 73% yield).

7: colourless crystals; mp 78–80 °C (dec); δ_H (C_6D_6, 400 MHz) 0.24 (s, 18 H, $SiMe_3$), 0.29 (s, 18 H, $SiMe_3$), 1.80-1.90 (m, 4 H, CH_2), δ_C (C_6D_6, 100 MHz) 3.6 ($Si(\underline{C}H_3)_3$), 4.0 ($Si(\underline{C}H_3)_3$), 14.0 ($\underline{C}(SiMe_3)_2$), 32.7 ($\underline{C}H_2$), δ_{Si} (C_6D_6, 79 MHz) 3.9 ($\underline{Si}Me_3$), 7.5 ($\underline{Si}Me_3$), 45.9 ($\underline{Si}$), *m*/*z* 572 (M^+-15, 7%), 407 (70), 73 (100). Found: C, 32.68; H, 6.80. Calc. for $C_{16}H_{40}Cl_4GeSi_{10}$: C, 32.72; H, 6.86%.

5. Details of a theoretical study of tetramethyl-2-germadisilaallene 8

All DFT calculations were carried out using a Gaussian 98 program. Geometry optimization was carried out at the B3LYP level using 6-31+G(d,p) basis set. During optimization of **8B**, the coordinates of allenic silicon and germanium atoms and carbon atoms bound to the allenic silicon atoms were fixed to the value observed by X-ray analysis of compound **4**. Relative energies are shown in Table S3. Molecular structures and atomic coordinates of optimized structures of **8L**, **8B**, **8Z'**, **8Z**, and **8C** are shown in Figures S5-S9 and Tables S4-S8, respectively. No imaginary frequencies were found at the optimized structures of **8Z**, **8Z'**, and **8C**, while **8B** and **8L** have one and two imaginary frequencies at the optimized structure, respectively The corresponding important structural parameters are given in Table S3.

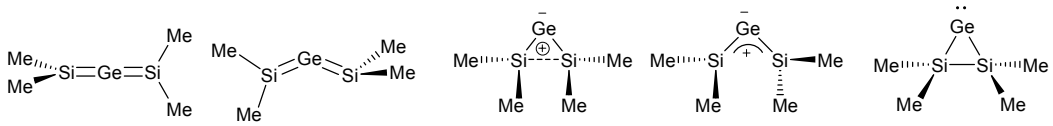


Table S3. Relative Energies among Isomers of Tetramethyl-2-germadisilaallene (**8**) Calculated at the B3LYP/6-31+G(d,p) Level

Compound	E(+ZPE)/a.u.[a]	Δ*E*/(kcal/mol)	Si–Ge distance/Å	angle Si–Ge–Si/°	δ_{Si}[b]
8L (D_{2d})	–2813.497619	+16.6	2.151	180.00	+98.4
8B (C_1)	–2813.502148	+13.8	2.228, 2.230	134.08	+231.4, +231.0
8Z' (C_s)	–2813.522378	+1.1	2.312	70.48	+184.5
8Z (C_2)	–2813.523212	+0.6	2.290	93.22	+378.5
8C (C_2)	–2813.524120	+0.0	2.496	54.18	-50.0

a) including zero-point energy. b) GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p) level.

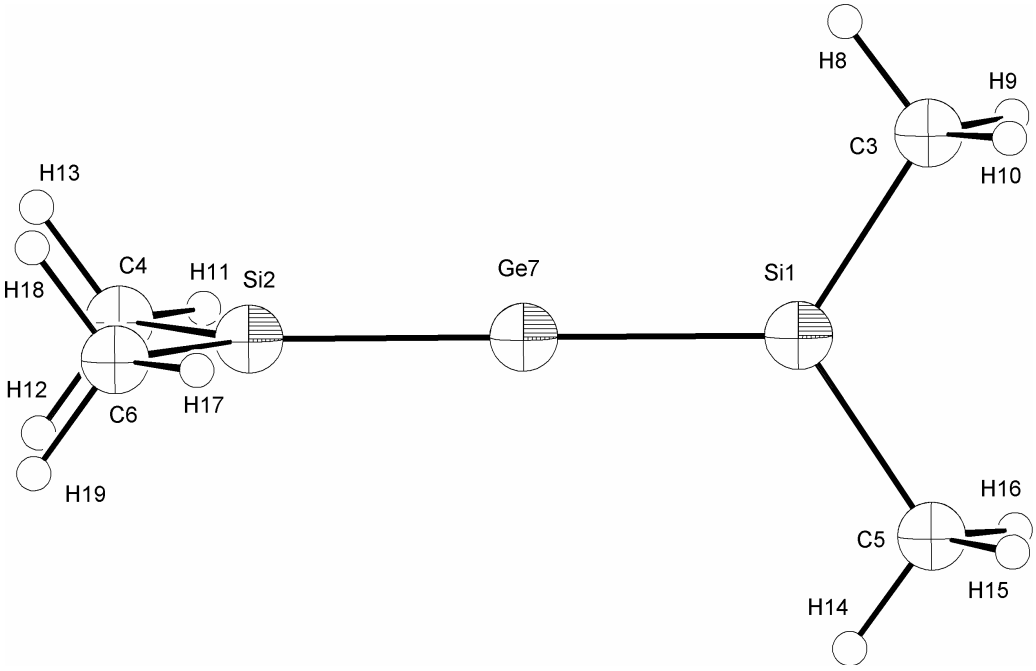


Figure S5. Molecular structure of **8L** (D_{2d} symmetry).

Table S4. Atomic Coordinates of **8L** (D_{2d} symmetry)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.000000	0.000000	-2.151253
2	14	0	0.000000	0.000000	2.151253
3	6	0	0.000000	1.583382	-3.181675
4	6	0	-1.583382	0.000000	3.181675
5	6	0	0.000000	-1.583382	-3.181675
6	6	0	1.583382	0.000000	3.181675
7	32	0	0.000000	0.000000	0.000000
8	1	0	0.000000	2.463110	-2.533310
9	1	0	-0.886575	1.625370	-3.824708
10	1	0	0.886575	1.625370	-3.824708
11	1	0	-2.463110	0.000000	2.533310
12	1	0	-1.625370	-0.886575	3.824708
13	1	0	-1.625370	0.886575	3.824708
14	1	0	0.000000	-2.463110	-2.533310
15	1	0	0.886575	-1.625370	-3.824708
16	1	0	-0.886575	-1.625370	-3.824708
17	1	0	2.463110	0.000000	2.533310
18	1	0	1.625370	0.886575	3.824708
19	1	0	1.625370	-0.886575	3.824708

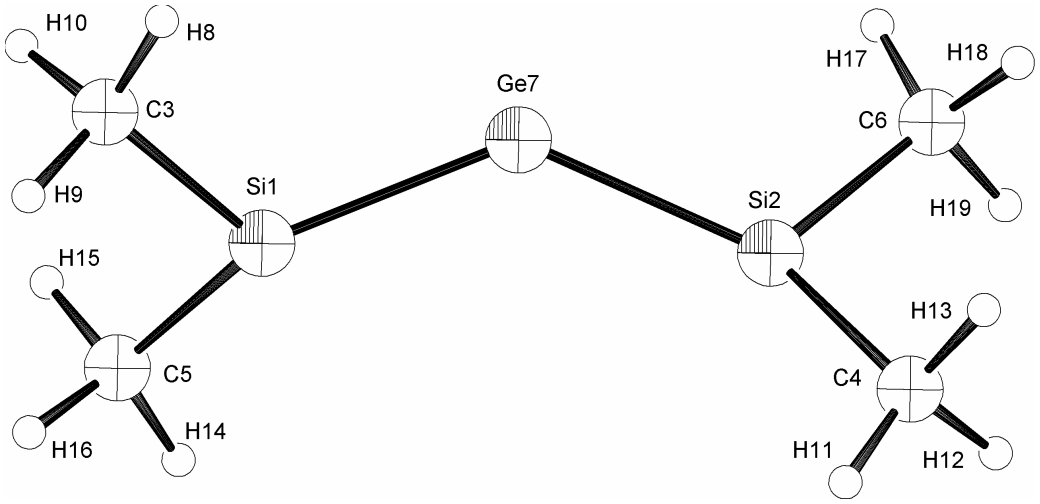


Figure S6. Molecular structure of **8B** (C1 symmetry).

Table S5. Atomic Coordinates of **8B** (C1 symmetry)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-2.051954	0.288991	-0.050671
2	14	0	2.051792	0.291614	0.050764
3	6	0	-3.346596	-0.756055	-0.957757
4	6	0	3.187371	1.341943	-1.050812
5	6	0	-3.186232	1.334216	1.060507
6	6	0	3.340972	-0.766543	0.958795
7	32	0	0.001541	-0.579230	-0.003188
8	1	0	-2.908430	-1.508739	-1.619185
9	1	0	-3.957544	-0.081671	-1.571543
10	1	0	-4.023743	-1.261011	-0.257796
11	1	0	2.674682	2.088151	-1.663116
12	1	0	3.894969	1.856523	-0.389987
13	1	0	3.764102	0.682755	-1.709866
14	1	0	-2.672679	2.076120	1.677281
15	1	0	-3.762508	0.670722	1.715603
16	1	0	-3.894041	1.853375	0.403539
17	1	0	2.894434	-1.521490	1.611908
18	1	0	4.019158	-1.269796	0.258659
19	1	0	3.951478	-0.099421	1.580835

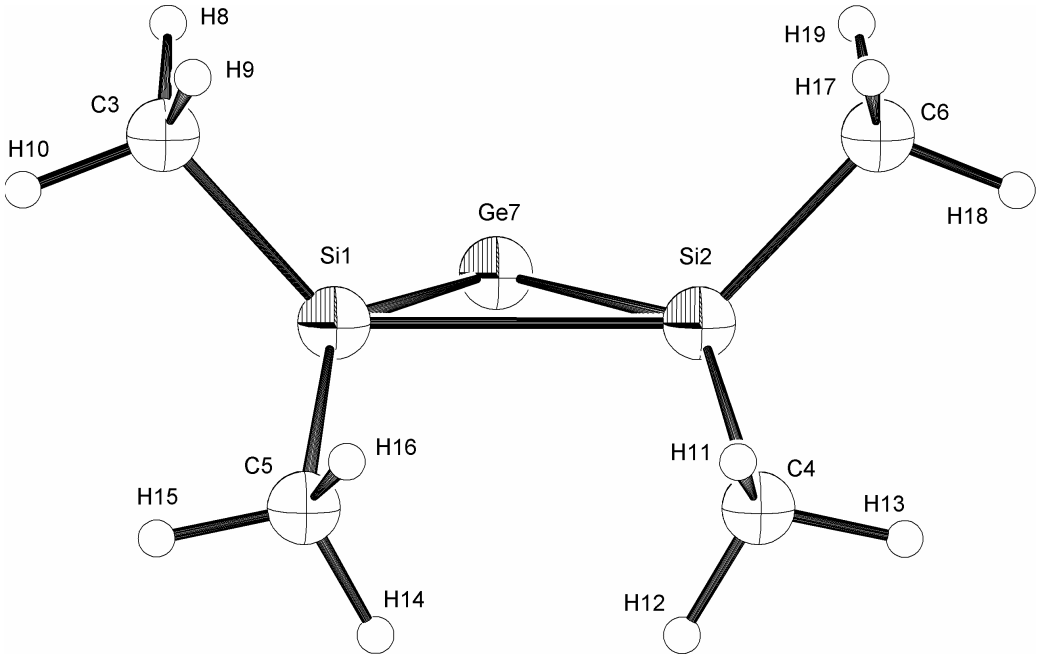


Figure S7. Molecular structure of **8Z'** (C_s symmetry).

Table S6. Atomic Coordinates of **8Z'** (C_s symmetry)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.080430	-0.304643	1.335024
2	14	0	-0.080430	-0.304643	-1.335024
3	6	0	1.322253	-0.425552	2.613630
4	6	0	-1.216332	-1.800913	-1.662152
5	6	0	-1.216332	-1.800913	1.662152
6	6	0	1.322253	-0.425552	-2.613630
7	32	0	0.000000	1.581221	0.000000
8	1	0	2.016789	0.413548	2.518196
9	1	0	1.888516	-1.355444	2.478635
10	1	0	0.919756	-0.430911	3.634887
11	1	0	-0.730044	-2.755729	-1.431068
12	1	0	-2.161981	-1.748341	-1.120693
13	1	0	-1.442545	-1.798872	-2.735949
14	1	0	-2.161981	-1.748341	1.120693
15	1	0	-1.442545	-1.798872	2.735949
16	1	0	-0.730044	-2.755729	1.431068
17	1	0	1.888516	-1.355444	-2.478635
18	1	0	0.919756	-0.430911	-3.634887
19	1	0	2.016789	0.413548	-2.518196

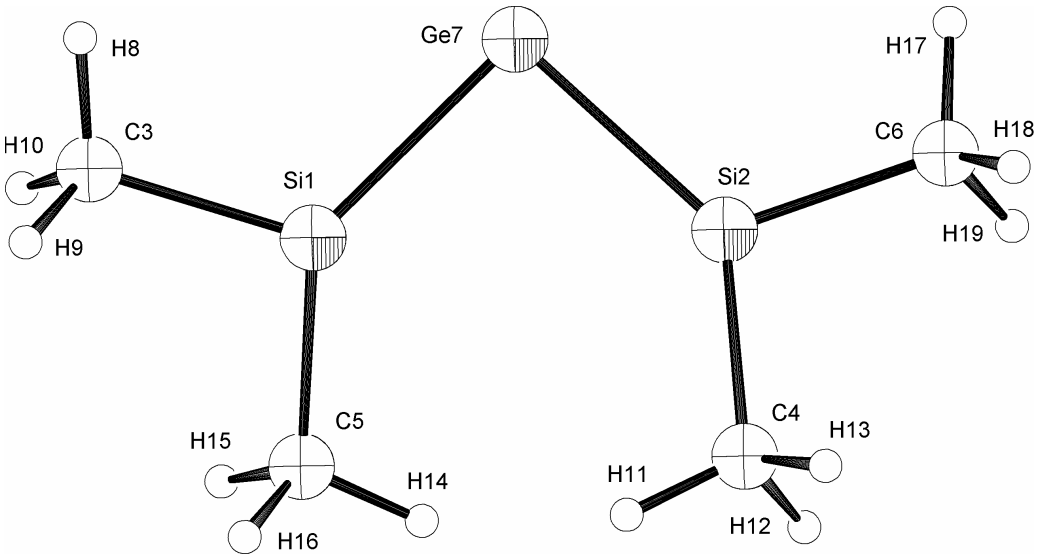


Figure S8. Molecular structure of **8Z** (C_2 symmetry).

Table S7. Atomic Coordinates of **8Z** (C_2 symmetry)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.000000	1.664022	-0.273524
2	14	0	0.000000	-1.664022	-0.273524
3	6	0	-0.231843	3.453223	0.314808
4	6	0	-0.471327	-1.809727	-2.111636
5	6	0	0.471327	1.809727	-2.111636
6	6	0	0.231843	-3.453223	0.314808
7	32	0	0.000000	0.000000	1.299598
8	1	0	-0.516238	3.496680	1.369844
9	1	0	-1.012787	3.950716	-0.275073
10	1	0	0.689541	4.035173	0.181564
11	1	0	-0.743216	-0.856055	-2.566960
12	1	0	0.357134	-2.249290	-2.682410
13	1	0	-1.325918	-2.491536	-2.210223
14	1	0	0.743216	0.856055	-2.566960
15	1	0	1.325918	2.491536	-2.210223
16	1	0	-0.357134	2.249290	-2.682410
17	1	0	0.516238	-3.496680	1.369844
18	1	0	-0.689541	-4.035173	0.181564
19	1	0	1.012787	-3.950716	-0.275073

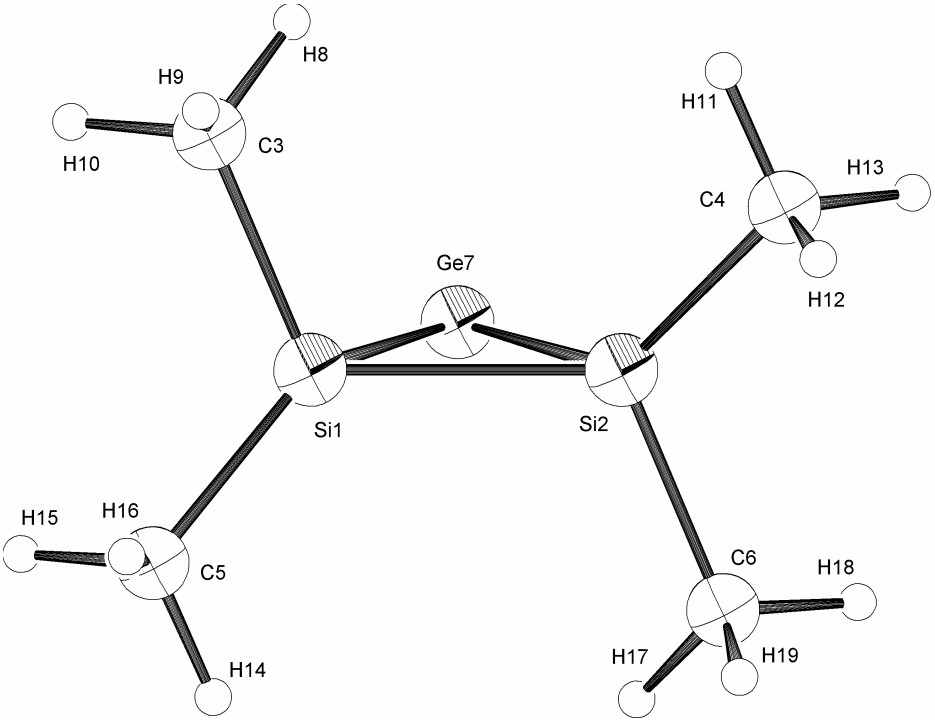


Figure S9. Molecular structure of **8C** (C_2 symmetry).

Table S8. Atomic Coordinates of **8C** (C_2 symmetry)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	1.012884	0.516114	-0.578215
2	14	0	-1.012884	-0.516114	-0.578215
3	6	0	0.883221	2.418880	-0.668968
4	6	0	-2.645873	0.125071	-1.298065
5	6	0	2.645873	-0.125071	-1.298065
6	6	0	-0.883221	-2.418880	-0.668968
7	32	0	0.000000	0.000000	1.644127
8	1	0	0.000000	2.802126	-0.145039
9	1	0	0.816185	2.754643	-1.710372
10	1	0	1.765704	2.883305	-0.214817
11	1	0	-2.698176	1.216588	-1.241997
12	1	0	-2.743147	-0.165214	-2.350761
13	1	0	-3.498638	-0.285647	-0.745641
14	1	0	2.698176	-1.216588	-1.241997
15	1	0	3.498638	0.285647	-0.745641
16	1	0	2.743147	0.165214	-2.350761
17	1	0	0.000000	-2.802126	-0.145039
18	1	0	-1.765704	-2.883305	-0.214817
19	1	0	-0.816185	-2.754643	-1.710372