Electronic Supplementary Information

Ru-Complexes of an Anionic Germabenzenyl Ligand

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1. General Remarks

All manipulations were performed in an mBraun Lab Master 100 glovebox under an inert atmosphere of purified argon. Solvents used for the reactions were purified by The Ultimate Solvent System (Glass Contour Company)[S1]. Benzene-d_6 and tetrahydrofuran-d_8 were obtained anhydrous by bulb-to-bulb distillation from potassium mirror prior to use. All glassware was oven-dried at 120 ˚C for at least 3 hours prior to use. Germabenzenylpotassium $K^{+}\cdot$ **3**$^{–}$ and $[Cp^{*}RuCl]_4$[S2] were prepared according to the literature procedures. ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance III 800US Plus NMR spectrometer (^{1}H: 800 MHz, ^{13}C: 201 MHz), a JEOL JNM-ECA600 NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz) of the JURC at Institute for Chemical Research, Kyoto University, or a JEOL AL-300 NMR spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz). In ^{1}H NMR signals due to C_6D_5H (7.15 ppm) and $–OCD_2CH(D)–$ in THF-d_7 (1.73 ppm) were used as references, and those due to C_6D_6 (128.0 ppm) and (20.4 ppm), $–OCD_2CD_2–$ in THF-d_8 (25.3 ppm) were used in ^{13}C NMR. Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. For the assignments of the signals, various one- or two-dimensional NMR methods were used, whose details were described in each section. High-resolution mass spectral data were obtained on a Bruker Daltonics micrOTOF focus-Kci with an IonSence DART®-SVP ion source. All melting points were determined on a Yanaco MP-500D micro melting point apparatus and are uncorrected. UV-vis spectra were measured and recorded on a Shimadzu UV-1700 pharmaSpec UV-vis spectrophotometer.

2. Experimental Section

Synthesis of complexes [Cp*Ru{GeC$_5$(*t*-Bu)H$_4$}]$_2$ (1) and [Cp*Ru{GeC$_5$(*t*-Bu)H$_4$}]$_3$ (2)

A THF solution (1 mL) of germabenzenylpotassium $K^+\cdot$ **3**$^-$ (10.2 mg, 0.0438 mmol) was treated with [Cp*RuCl]$_4$ (11.3 mg, 0.0109 mmol) at room temperature, and the solution was stirred for 30 min at the same temperature. After removal of all volatiles, *n*-hexane was added to the residue. The resulting suspension was filtered, and the solvent was removed. Recrystallization of the crude material from benzene afforded **2** as orange crystals (4.3 mg, 3.33 μmol, 23%). Moreover, recrystallization of the residue from *n*-hexane afforded **1** as orange crystals (2.6 mg, 6.04 μmmol, 14%). **1**: m.p. 199 ˚C (dec.); ^{1}H NMR (600 MHz, 25 ˚C, C_6D_6): δ 1.29 (s, 9H, C(CH$_3$)$_3$), 1.62 (s, 15H, CH$_3$-Cp*), 3.05 (ddd, 1H, ^2J = 6.9 Hz, ^2J = 6.2 Hz, ^3J = 1.3 Hz, CH), 5.18 (dd, 1H, ^2J = 5.8 Hz, ^2J = 6.2 Hz, CH), 5.78 (dd, 1H, ^2J = 5.8 Hz, ^3J = 1.3 Hz, CH), 7.04 (d, 1H, ^2J = 6.9 Hz, CH); ^{13}C NMR (151 MHz, 25 ˚C, C_6D_6): δ = 10.27 (CH$_3$-Cp*), 32.21 (C(CH$_3$)$_3$), 36.64 (C(CH$_3$)$_3$), 49.78 (CH), 86.37 (CH), 86.72 (C-Cp*), 96.77 (CH), 141.39 (CH), 142.46 (CH); ^{1}H NMR (800 MHz, 25 ˚C, THF-*d*$_8$): δ 0.96 (s, 9H, C(CH$_3$)$_3$), 1.74 (s, 15H, CH$_3$-Cp*), 2.79 (dd, 1H, ^2J = 7.1 Hz, ^2J = 6.3 Hz, CH), 5.05 (dd, 1H, ^2J = 6.3 Hz, ^2J = 5.8 Hz, CH), 5.68 (d, 1H, ^2J = 5.8 Hz, CH), 6.60 (d, 1H, ^2J = 7.1 Hz, CH); ^{13}C NMR (201 MHz, 25 ˚C, THF-*d*$_8$): δ = 10.45 (CH$_3$-Cp*), 32.29 (C(CH$_3$)$_3$), 36.85 (C(CH$_3$)$_3$), 50.23 (CH), 86.70 (CH), 87.41 (C-Cp*), 97.36 (CH), 141.62 (CH), 142.61 (CH); UV-vis (*n*-hexane): λ 220 (ε 1.2 × 10^5), λ 343 (ε 1.4 × 10^4), λ 423 (ε 9.9 × 10^3) nm; UV-vis (THF): λ 211 (ε 1.3 × 10^5), λ 342 (ε 1.7 × 10^4), λ 419 (ε 1.2 × 10^4) nm; HRMS (DART-TOF, positive mode) *m*/*z* calcd. for $C_{38}H_{57}Ge_2Ru_2$ ([M+H]$^+$): 861.1012, found: 861.1029. **2**: m.p. 147 ˚C (dec.); UV-vis (*n*-hexane): λ 217 (ε 2.3×10^4), λ 263 (ε 8.2×10^3), λ 312 (ε 3.5×10^3), λ 383 (ε 2.0×10^2) nm; UV-vis (THF): λ 216 (ε 2.5×10^4), λ 269 (ε 8.5×10^3), λ 302 (ε 5.0×10^3), λ 376 (ε 2.4×10^2) nm; HRMS (DART-TOF, positive mode) *m*/*z* calcd. for $C_{57}H_{85}O_3Ge_3Ru_3$ ([MO$_3$+H]$^+$): 1339.1333, found: 1339.1331.

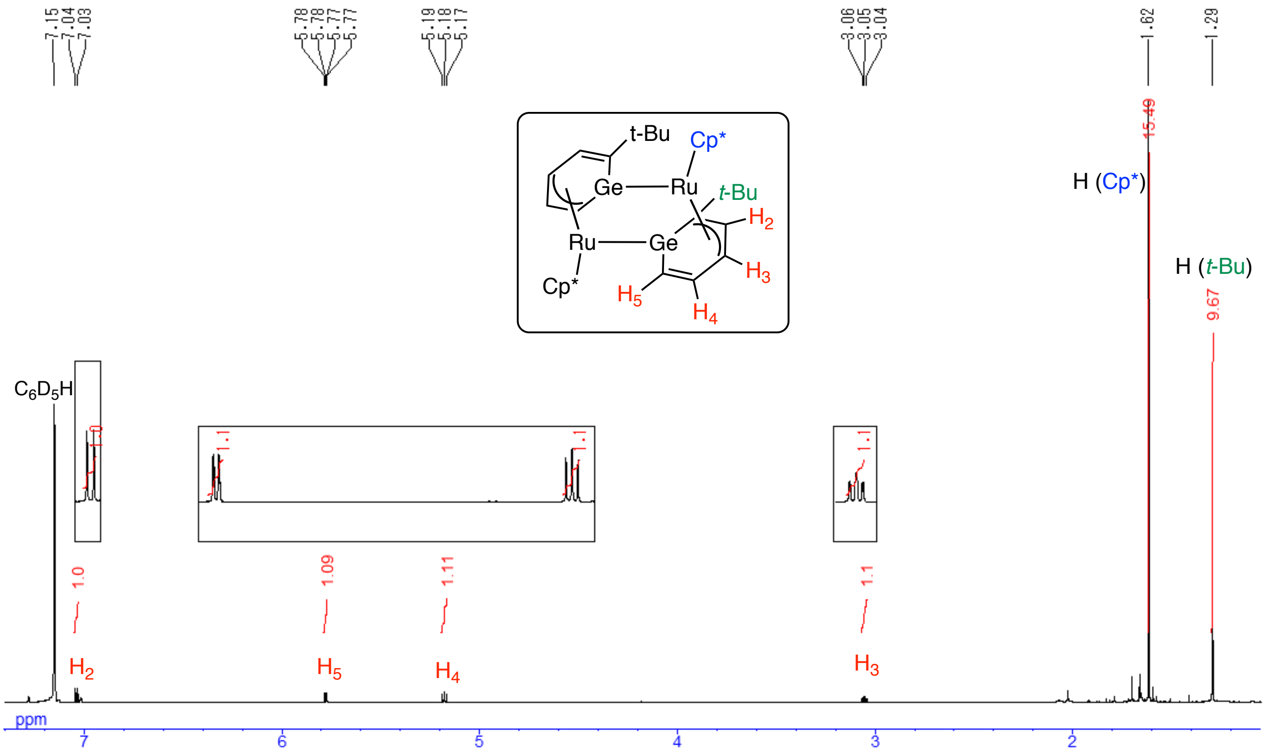

Fig. S1 ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **1**.

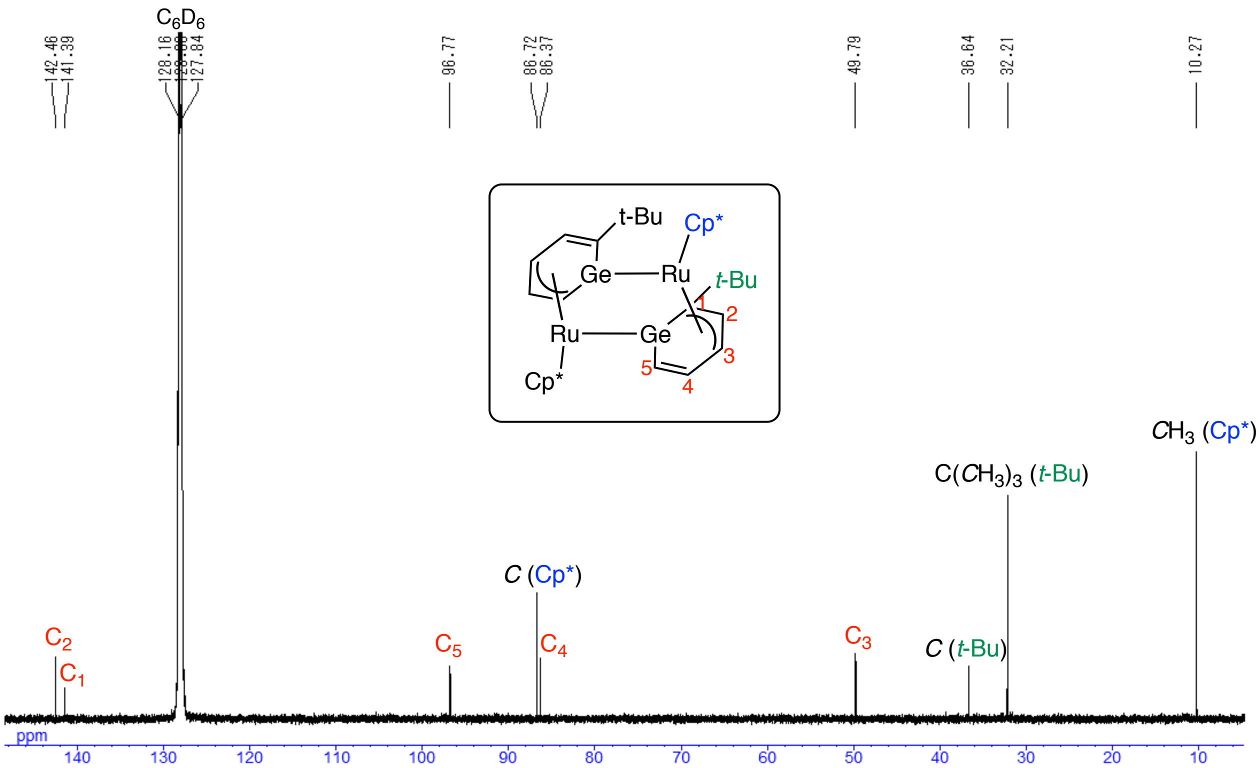

Fig. S2 ^{13}C NMR spectrum (151 MHz, 298 K, C_6D_6) of **1**.

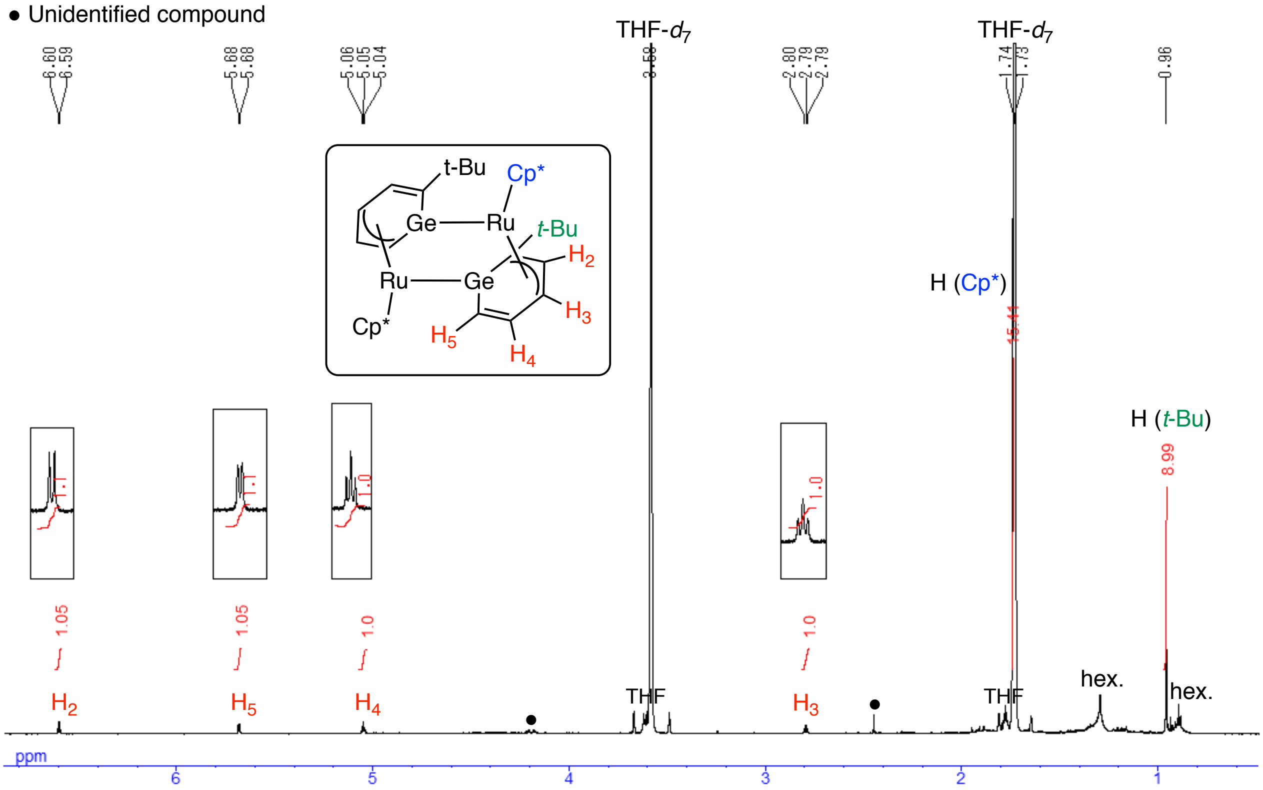

Fig. S3 ^{1}H NMR spectrum (800 MHz, 298 K, THF-d_8) of **1**.

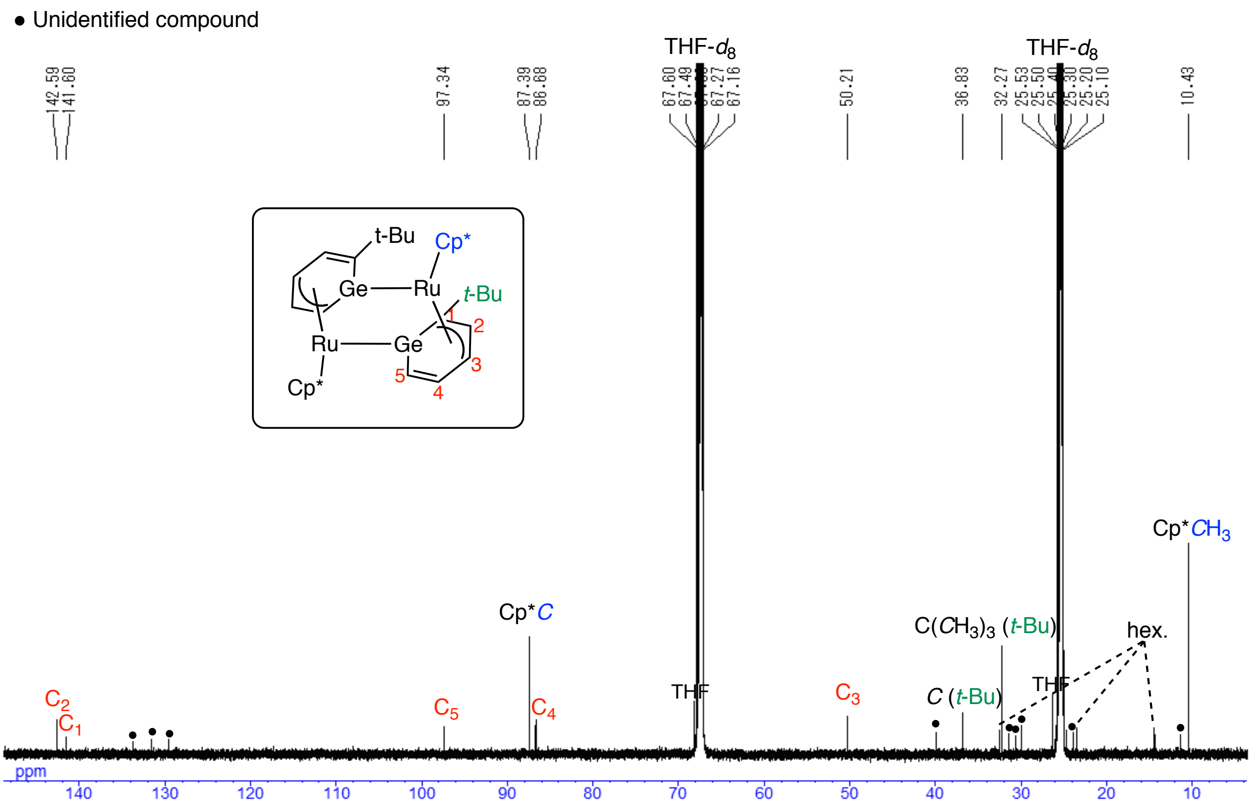

Fig. S4 ^{13}C NMR spectrum (201 MHz, 298 K, THF-d_8) of **1**.

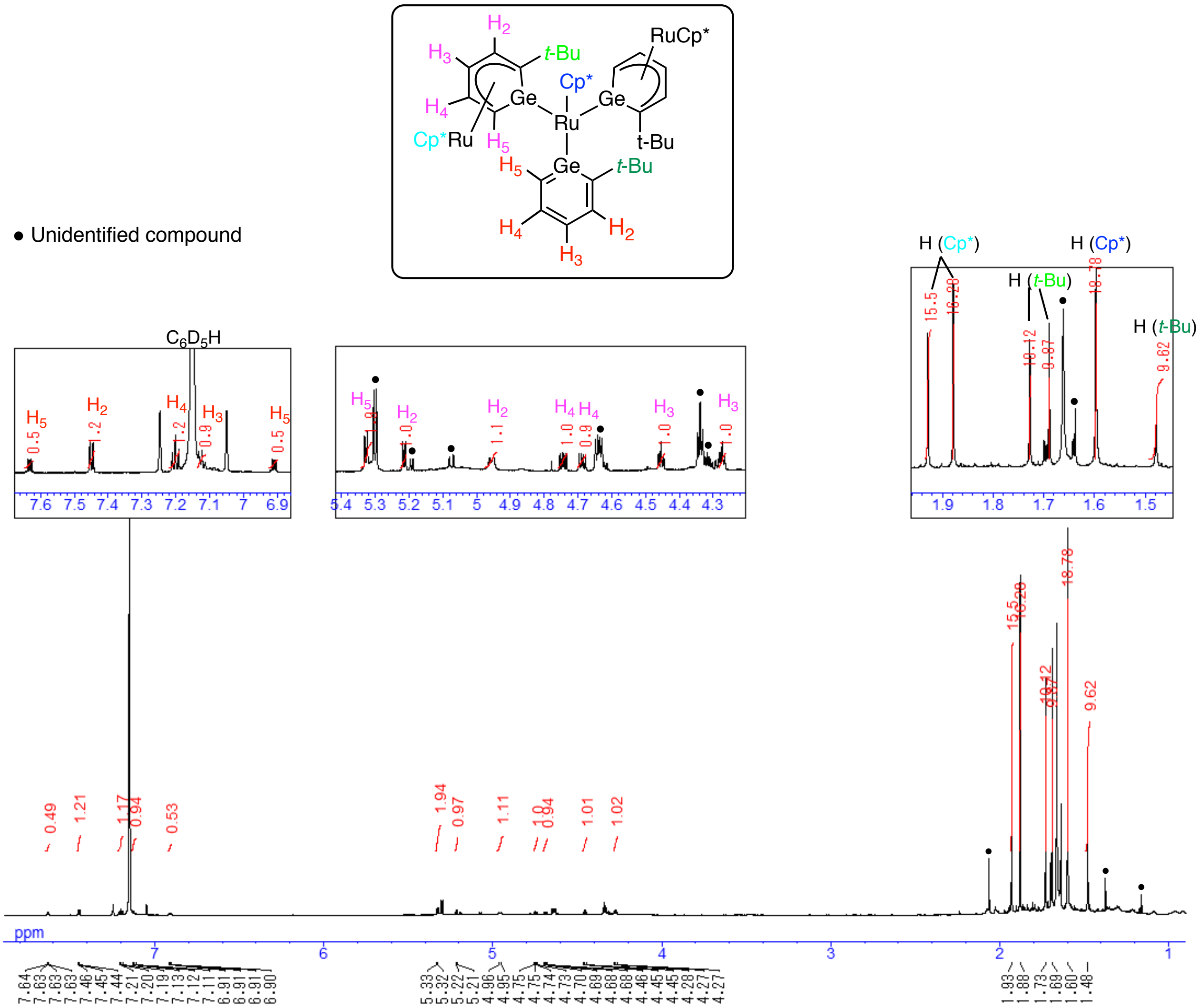

Fig. S5 [1]H NMR spectrum (800 MHz, 298 K, C_6D_6) of **2**.

3. UV-Vis Spectra

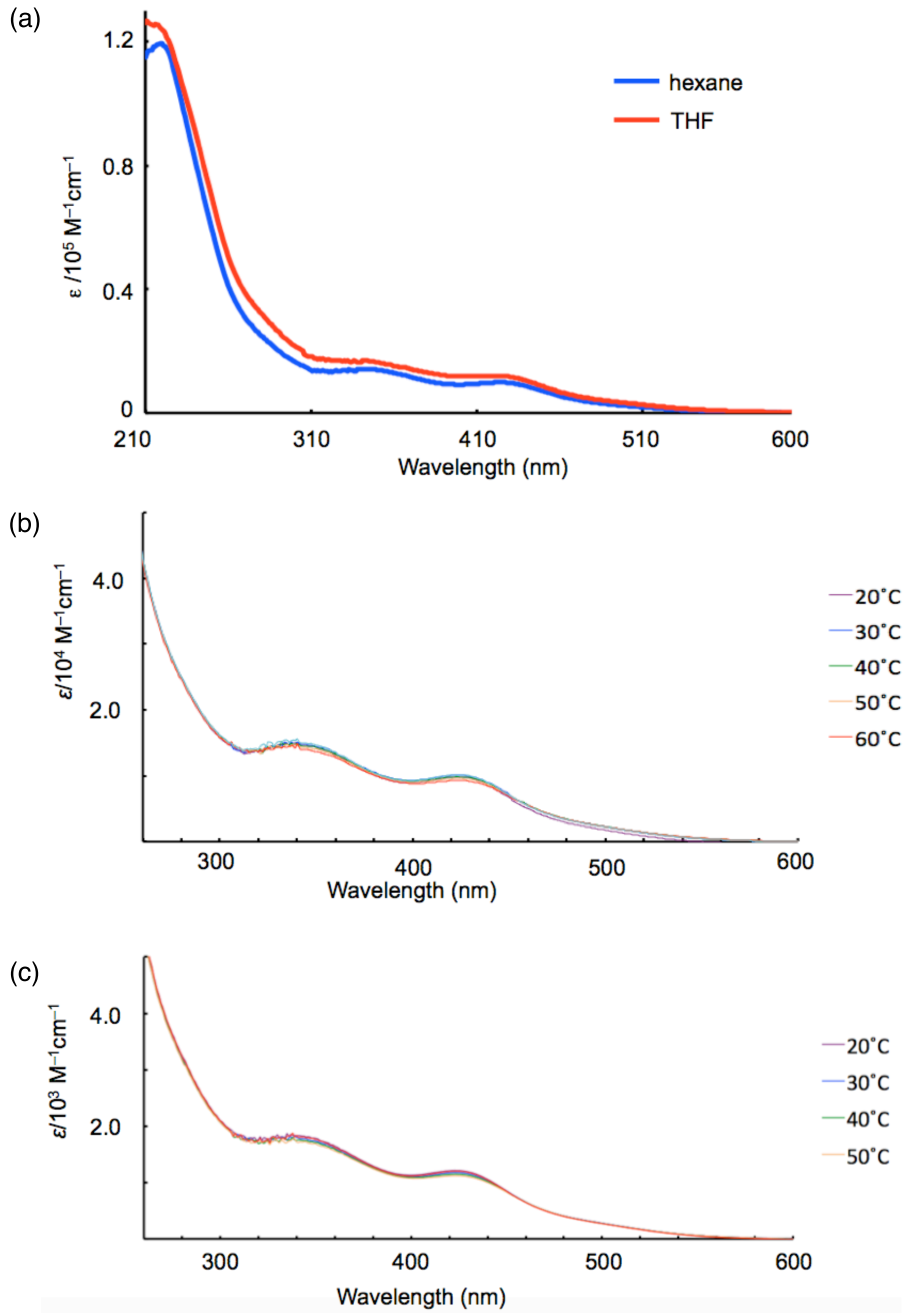

Fig. S6 (a) UV-vis spectra of **1** in *n*-hexane (1.2×10^{-4} M, blue line) and THF (1.2×10^{-4} M, red line) in a cuvette with a path length of 1 mm at 298 K. (b) UV-vis spectra of **1** in *n*-hexane (1.8×10^{-4} M) in a cuvette with a path length of 1 mm at various temperatures. (c) UV-vis spectra of **1** in THF (1.6×10^{-4} M) in a cuvette with a path length of 1 mm at various temperatures.

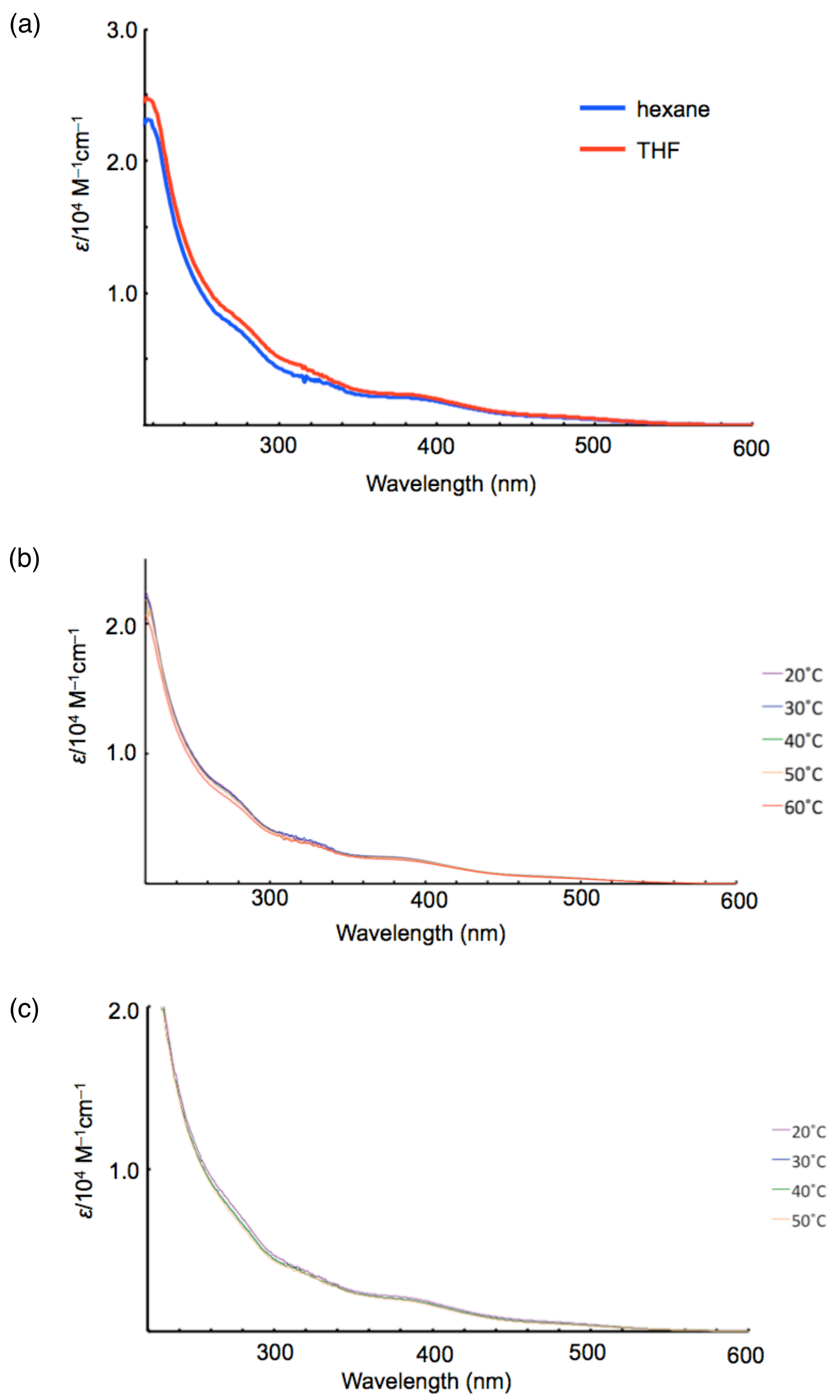

Fig. S7 (a) UV-vis spectra of **2** in *n*-hexane (3.6×10^{-4} M, blue line) and THF (5.4×10^{-4} M, red line) a cuvette with a path length of 1 mm at 298 K. (b) UV-vis spectra of **2** in *n*-hexane (5.4×10^{-4} M) in a cuvette with a path length of 1 mm at various temperatures. (c) UV-vis spectra of **2** in THF (9.5×10^{-4} M) in a cuvette with a path length of 1 mm at various temperatures.

4. X-Ray Diffraction Studies

Single crystals of **1** was obtained from recrystallization in hexane at room temperature in an argon-filled glove box. [**2**·0.5benzene] was obtained from recrystallization in benzene at room temperature in an argon-filled glove box.

The X-ray diffraction data for **1** were collected using synchrotron radiation (λ = 0.800 Å) at SPring-8 (BL38B1) with Rayonix MX225HE at 100 K. Intensity data for [**2**·0.5benzene] were collected on a RIGAKU Saturn70 CCD(system) with VariMax Mo Optic using MoKα radiation (λ = 0.71070 Å) at 103 K. Crystal data are summarized in Table S1. The structures were solved by a direct method (SHELXT[S3]) and refined by a full-matrix least square method on F^2 for all reflections (SHELXL-2016[S3]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC-1827996 (**1**) and CCDC-1827997 ([**2**·0.5benzene]), and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

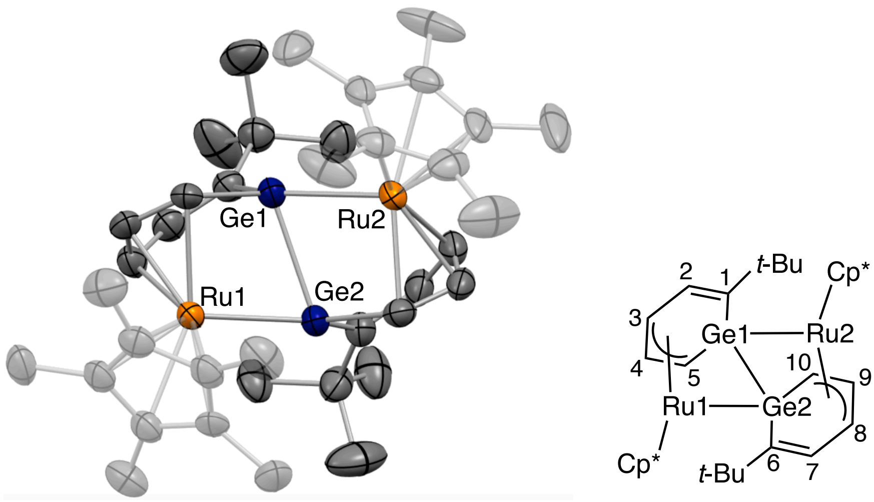

Fig. S8 Molecular structure of **1** (ORTEP drawing; thermal ellipsoids set 50% probability). Hydrogen atoms were omitted for clarity.

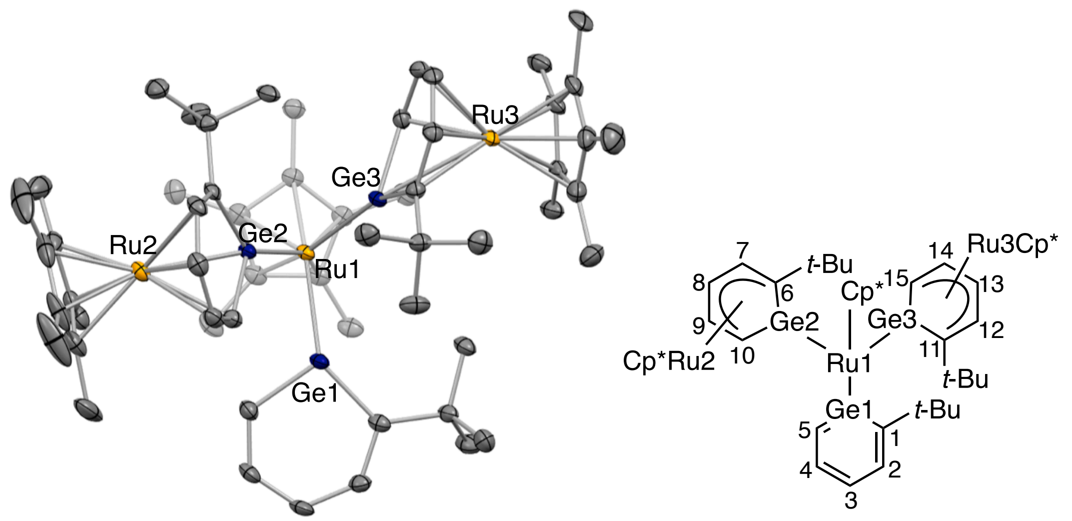

Fig. S9 Molecular structure of [**2**·0.5benzene] (ORTEP drawing; thermal ellipsoids set 50% probability). Hydrogen atoms and benzene molecule were omitted for clarity.

Table S1 Crystallographic data for **1** and [**2**·0.5benzene].

	1	[**2**·0.5benzene]
Empirical formula	$C_{38}H_{56}Ge_2Ru_2$	$C_{57}H_{84}Ge_3Ru_3\cdot0.5(C_6H_6)$
Formula weight	860.14	1329.27
Temperature (K)	100(2)	103(2)
Crystal colour	orange	orange
Crystal size (mm)	0.040×0.020×0.010	0.170×0.060×0.030
Crystal system	triclinic	triclinic
Space group	*P*-1 (#2)	*P*-1 (#2)
a (Å)	11.4301(2)	12.3082(2)
b (Å)	11.9637(2)	13.0253(2)
c (Å)	13.1386(2)	19.5207(3)
α (˚)	87.8950(10)	74.599(2)
β (˚)	84.2490(10)	89.9930(10)
γ (˚)	88.7100(10)	71.829(2)
V (Å^3)	1786.09(5)	2854.97(9)
Z	2	2
D_{calc} (g·cm^{-3})	1.599	1.546
μ (mm^{-1})	3.438	2.368
θ range (˚)	1.755 to 28.750	2.271 to 25.246
Reflections collected	60400	30484
Independent reflections	6488	10073
R_{int}	0.0708	0.0168
No. of restraints	10	0
No. of parameters	421	619
Completeness to θ	99.7	97.3
Goodness of fit	1.116	1.113
R_1 [I>2σ(I)]	0.0444	0.0300
wR_2 [I>2σ(I)]	0.1276	0.0797
R_1 (all data)	0.0487	0.0325
wR_2 (all data)	0.1303	0.0809
Flack parameter	–	–
Largest diff. peak (e·Å^3)	1.502	1.888
Largest diff. hole (e·Å^3)	–1.233	–0.803
CCDC number	1827996	1827997

5. Theoretical Calculations

Theoretical calculations for the geometry optimization and frequency calculations of **1**, **5** (η^6), **6** (η^1), [**6**·thf] (η^1), and [**6**·2thf] (η^1) were carried out on the *Gaussian 09* (Revision E.01) program package.[S4] Geometry optimizations were performed with the B3PW91 levels by using the basis sets of LanL2DZ for Ru, Ge, 6-31G(d) for C, H, O. The frequency calculations confirmed minimum energies for the optimized structures. NMR shielding tensors were calculated with the B3PW91 levels by using the basis sets of TZVP for Ru, Ge, 6-311++G(2df,2p) or 6-311++G(2d,p) for C, H, O using the gauge-independent atomic orbital (GIAO) method towards the aforementioned optimized structures.

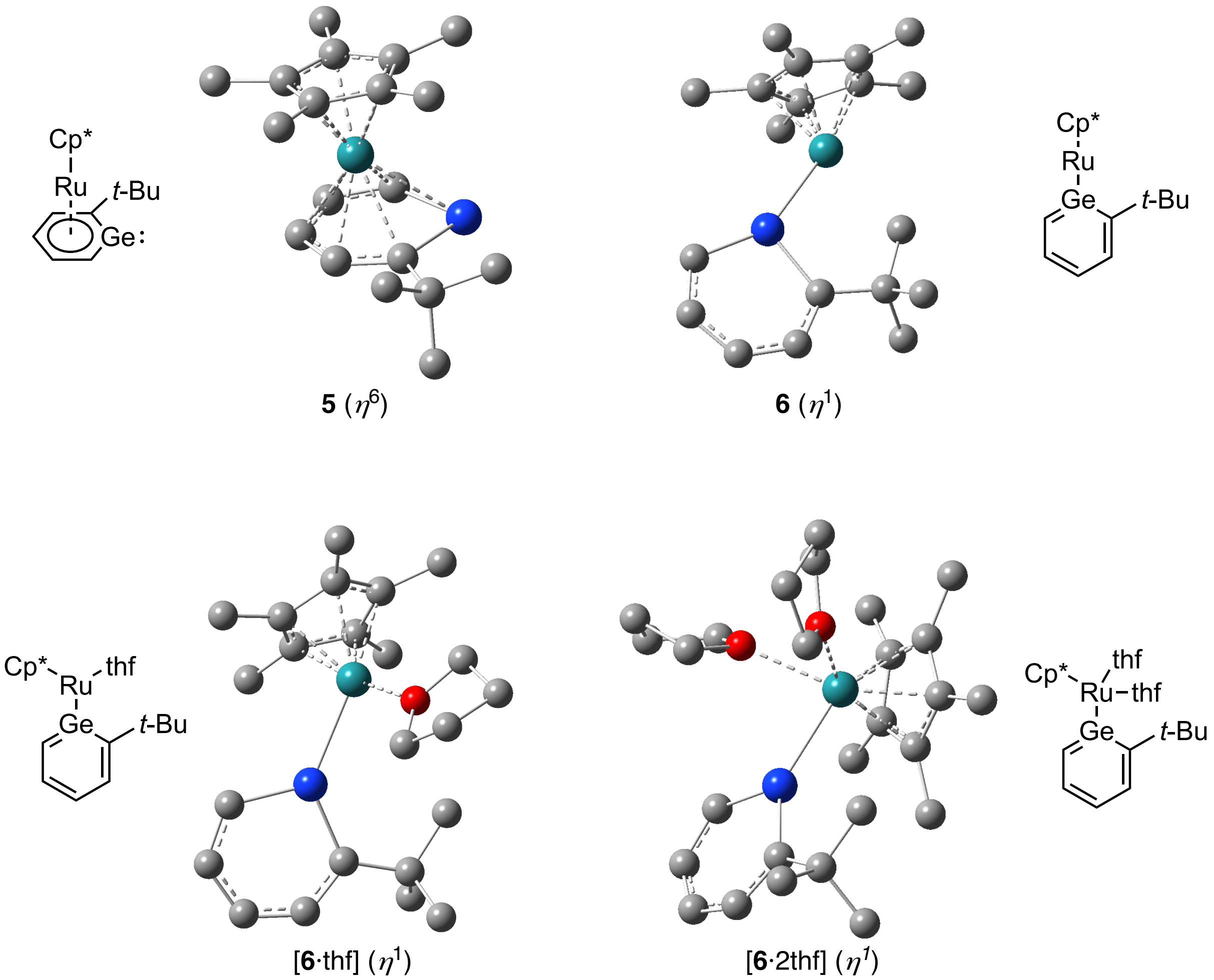

Fig. S10 Optimized structures for **5** (η^6), **6** (η^1), [**6**·thf] (η^1), and [**6**·2thf] (η^1). Hydrogen atoms were omitted for clarity. Grey, carbon; blue, germanium; green, ruthenium, red, oxygen.

5-1. Comparison between the experimentally observed and theoretically calculated structures of 1.

Table S2 Selected bond lengths (Å) and angles (deg). Structural optimization was performed at B3PW91/LanL2DZ(Ge,Ru),6-31G(d)(C,H) level of theory.

	Ge1–C1	C1–C2	C2–C3	C3–C4	C4–C5	Ge1–C5
1 (obsd.)	1.968(5)	1.333(7)	1.469(7)	1.444(8)	1.402(7)	1.932(5)
***1** (calcd.)*	*1.986*	*1.349*	*1.474*	*1.447*	*1.416*	*1.950*
	Ge2–C6	C6–C7	C7–C8	C8–C9	C9–C10	Ge2–C10
1 (obsd.)	1.974(5)	1.335(8)	1.466(7)	1.447(7)	1.395(7)	1.932(5)
***1** (calcd.)*	*1.986*	*1.349*	*1.474*	*1.447*	*1.416*	*1.950*
	Ge1–Ge2	Ge1–Ru1	Ge2–Ru2	Ge1–Ru2	Ge2–Ru1	
1 (obsd.)	2.5053(7)	2.8743(6)	2.8672(6)	2.4454(6)	2.4534(6)	
***1** (calcd.)*	*2.5786*	*2.9524*	*2.9524*	*2.5084*	*2.5084*	
	Ru1–C1	Ru1–C2	Ru1–C3	Ru1–C4	Ru1–C5	
1 (obsd.)	3.687(5)	3.285(5)	2.238(5)	2.110(5)	2.225(5)	
***1** (calcd.)*	*3.746*	*3.317*	*2.255*	*2.131*	*2.233*	
	Ru2–C6	Ru2–C7	Ru2–C8	Ru2–C9	Ru2–C10	
1 (obsd.)	3.685(5)	3.276(5)	2.217(5)	2.100(5)	2.194(5)	
***1** (calcd.)*	*3.746*	*3.317*	*2.255*	*2.131*	*2.233*	
	C1–Ge1–C5	Ge1–C1–C2	C1–C2–C3	C2–C3–C4	C3–C4–C5	Ge1–C5–C4
1 (obsd.)	101.6(2)	111.3(4)	125.9(5)	119.1(5)	120.1(5)	114.5(4)
***1** (calcd.)*	*101.6*	*111.4*	*125.8*	*120.3*	*119.0*	*115.3*
	C6–Ge2–C10	Ge2–C6–C7	C6–C7–C8	C7–C8–C9	C8–C9–C10	Ge2–C10–C9
1 (obsd.)	100.7(2)	111.2(4)	125.8(5)	118.7(4)	118.9(4)	115.5(4)
***1** (calcd.)*	*101.6*	*111.4*	*125.8*	*120.3*	*119.0*	*115.3*

5-2. GIAO calculations

Table S3 Observed and calculated ^{1}H and ^{13}C NMR chemical shifts (ppm) for complexes **1**, **5** (η^6), **6** (η^1), [**6**·thf] (η^1), and [**6**·2thf] (η^1).

	1 (obsd.)	**1** (obsd.)	***1*** *(calcd.)*[a]	***1*** *(calcd.)*[b]	***5*** *(η^6) (calcd.)*[b]	***6*** *(η^1) (calcd.)*[b]	*[**6**·thf] (η^1) (calcd.)*[b]	*[**6**·2thf] (η^1) (calcd.)*[b]
solv.	C_6D_6	THF-d_8	–	–	–	–	–	–
H2	7.04	6.60	*7.00*	*6.80*	*5.31*	*8.00*	*7.95*	*8.12*
H3	3.05	2.79	*2.85*	*2.83*	*4.45*	*6.82*	*6.64*	*6.62*
H4	5.18	5.05	*5.05*	*4.83*	*4.94*	*8.17*	*8.00*	*7.93*
H5	5.78	5.68	*5.34*	*5.54*	*4.76*	*8.98*	*8.81*	*8.08*
C1	141.39	141.62	*153.39*	*153.75*	*160.97*	*202.76*	*188.81*	*196.53*
C2	142.46	142.61	*149.78*	*149.94*	*92.37*	*136.81*	*139.43*	*141.26*
C3	49.78	50.23	*60.37*	*60.38*	*77.84*	*119.26*	*116.18*	*114.33*
C4	86.37	86.70	*92.76*	*91.19*	*91.57*	*139.21*	*139.32*	*137.86*
C5	96.77	97.36	*109.87*	*110.61*	*115.28*	*154.76*	*156.90*	*161.01*

[a] Calculated at the GIAO-B3PW91/TZVP(Ge,Ru),6-311++G(2d,p)//B3PW91/LanL2DZ(Ge,Ru),6-31G(d).
[b] Calculated at the GIAO-B3PW91/TZVP(Ge,Ru),6-311++G(2df,2p)//B3PW91/LanL2DZ(Ge,Ru),6-31G(d).

5-3. AIM calculations

AIM (Atoms in Molecules) calculations for complexes **1** and **2** were performed by AIMAll program. Wavefunction files were created by Gaussian 09 program with the basis sets of TZVP for Ru, Ge, 6-311++G(2df,2p) for C, H. Found bond critical points (BCPs) and bond paths (BPs) were shown in Figs. S11 and S12.

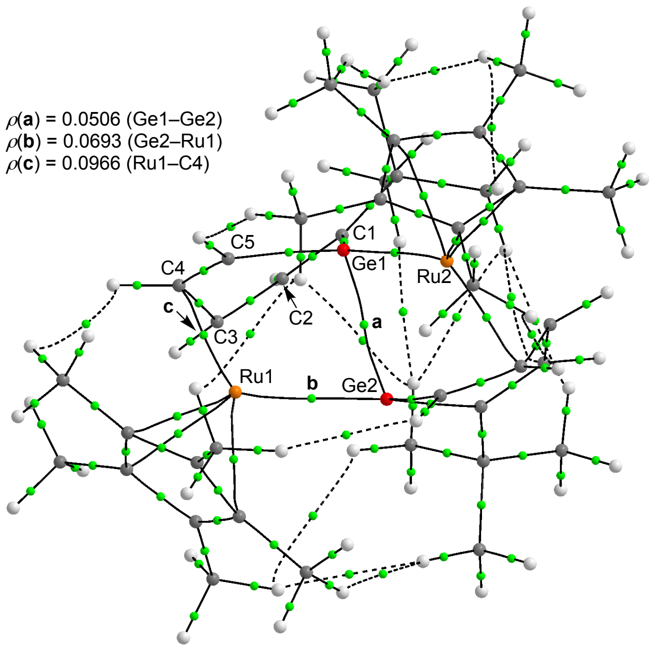

Fig. S11 BCPs (green) and BPs (black line) in complex **1**.

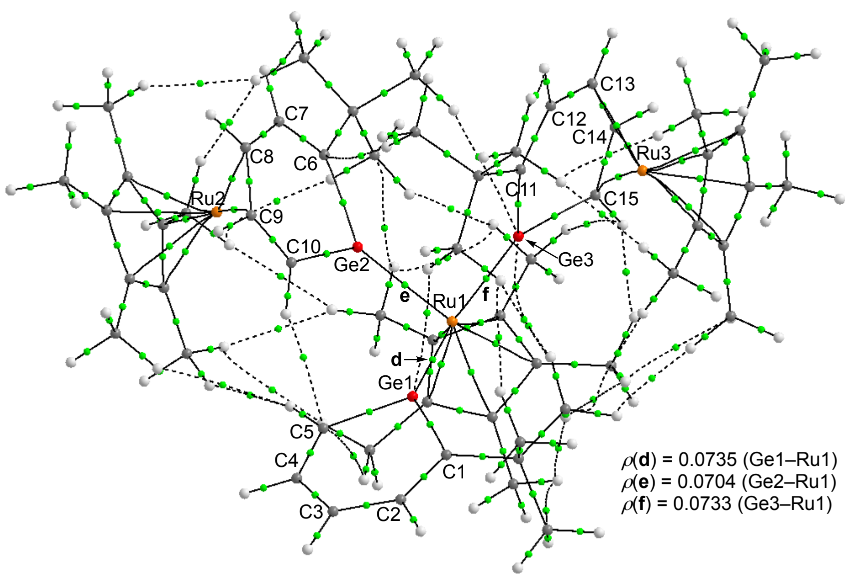

Fig. S12 BCPs (green) and BPs (black line) in complex **2**.

5-4. NBO calculations

NBO calculations for complex **2** were performed by NBO 6.0 program with the basis sets of TZVP for Ru, Ge, 6-311G(2df,2p) for C, H. The results for the Ge-containing bonds are summarized in Table S4.

Table S4 The results of NBO analysis for Complex **2**.

Ge–X		Occupancy	Ge					X				
			coefficients/%	s (%)	p (%)	d (%)	hybrids	coefficients/%	s (%)	p (%)	d (%)	hybrids
Ge1–C1	σ	1.93434	0.5108/26.09	30.35	69.53	0.12	$sp^{2.29}$	0.8597/73.91	29.92	69.90	0.15	$sp^{2.34}d^{0.01}$
Ge1–C5	σ	1.94553	0.5097/25.98	26.11	73.76	0.12	$sp^{2.82}$	0.8604/74.02	34.59	65.21	0.18	$sp^{2.82}$
	π	1.52409	0.5335/28.47	0.05	99.85	0.10	$sp^{99.99}d^{2.08}f^{0.02}$	0.8458/71.53	0.02	99.92	0.03	$sp^{99.99}d^{1.26}f^{1.31}$
Ge2–C10	σ	1.81426	0.4909/24.10	28.09	71.78	0.13	$sp^{2.56}$	0.8712/75.90	39.04	60.71	0.23	$sp^{1.56}d^{0.01}$
Ge1–Ru1	σ	1.78474	0.7307/53.39	44.64	55.34	0.02	$sp^{1.24}$	0.6827/46.61	28.37	0.45	71.15	$sp^{0.02}d^{2.51}$
Ge2–Ru1	σ	1.81803	0.8028/64.45	64.19	35.80	0.01	$sp^{0.56}$	0.5962/35.55	34.66	0.39	64.91	$sp^{0.01}d^{1.87}$
Ge3–Ru1	σ	1.85346	0.8163/66.64	76.88	23.11	0.00	$sp^{0.30}$	0.5776/33.36	35.70	0.44	63.81	$sp^{0.01}d^{1.79}$

5-5. Coordinates for the optimized structures

1 (C_2 symmetry)

Ru	-0.45474	2.18791	-0.56737
Ge	-1.17891	-0.52203	0.35362
C	-2.54141	1.92178	-0.22811
C	-2.11186	0.71439	-0.83137
C	-2.00637	2.29031	1.06508
C	-1.88724	0.01748	2.12931
C	-2.27721	-0.96899	3.22585
C	-2.08477	1.3498	2.19671
C	-1.11686	-1.9217	3.55499
C	1.39783	3.1412	-1.50677
C	-0.60079	4.27794	-1.25719
C	0.70952	4.11158	-0.69461
C	0.53132	2.72005	-2.57204
C	-0.70952	3.4162	-2.41221
C	-3.46964	-1.80405	2.71613
C	2.86818	2.85517	-1.43565
C	0.9135	1.85143	-3.72878
C	-1.613	5.28744	-0.81348
C	1.30784	4.93012	0.40685
C	-1.86236	3.36545	-3.36554
Ru	0.45474	-2.18791	-0.56737
Ge	1.17891	0.52203	0.35362
C	2.54141	-1.92178	-0.22811
C	2.11186	-0.71439	-0.83137
C	2.00637	-2.29031	1.06508
C	1.88724	-0.01748	2.12931
C	2.27721	0.96899	3.22585
C	2.08477	-1.3498	2.19671
C	1.11686	1.9217	3.55499
C	-1.39783	-3.1412	-1.50677
C	0.60079	-4.27794	-1.25719
C	-0.70952	-4.11158	-0.69461
C	-0.53132	-2.72005	-2.57204
C	2.71283	0.26364	4.51929
C	0.70952	-3.4162	-2.41221
C	3.46964	1.80405	2.71613
C	-2.86818	-2.85517	-1.43565
C	-0.9135	-1.85143	-3.72878
C	1.613	-5.28744	-0.81348
C	-1.30784	-4.93012	0.40685

C	1.86236	-3.36545	-3.36554
H	-3.17588	2.61973	-0.77589
H	-2.42824	0.49374	-1.84842
H	-2.20948	3.32193	1.35138
H	-2.41746	1.8039	3.13387
H	-0.7553	-2.43656	2.65751
H	-1.43627	-2.67765	4.28499
H	-0.26903	-1.37271	3.97549
H	-4.32077	-1.16182	2.46217
H	-3.79434	-2.52628	3.47713
H	-3.19644	-2.37039	1.81712
H	3.11568	1.84924	-1.78292
H	3.26116	2.96341	-0.42118
H	3.40867	3.56937	-2.07316
H	1.35737	2.4458	-4.54118
H	0.04607	1.32835	-4.14153
H	1.64612	1.09374	-3.43794
H	-1.45803	6.2449	-1.32972
H	-1.54346	5.47881	0.26151
H	-2.63663	4.96388	-1.02709
H	1.79475	5.83361	0.01052
H	2.05983	4.36657	0.96611
H	0.5477	5.25297	1.12447
H	-1.71339	4.072	-4.19361
H	-2.80655	3.63058	-2.87996
H	-1.98061	2.36801	-3.80085
H	3.17588	-2.61973	-0.77589
H	2.42824	-0.49374	-1.84842
H	2.20948	-3.32193	1.35138
H	2.41746	-1.8039	3.13387
H	0.7553	2.43656	2.65751
H	1.43627	2.67765	4.28499
H	0.26903	1.37271	3.97549
H	1.91092	-0.36494	4.92386
H	2.96876	1.00905	5.28235
H	3.59556	-0.36714	4.3624
H	4.32077	1.16182	2.46217
H	3.79434	2.52628	3.47713
H	3.19644	2.37039	1.81712
H	-3.11568	-1.84924	-1.78292
H	-3.26116	-2.96341	-0.42118
H	-3.40867	-3.56937	-2.07316
H	-1.35737	-2.4458	-4.54118
H	-0.04607	-1.32835	-4.14153
H	-1.64612	-1.09374	-3.43794
H	1.45803	-6.2449	-1.32972

H	1.54346	-5.47881	0.26151
H	2.63663	-4.96388	-1.02709
H	-1.79475	-5.83361	0.01052
H	-2.05983	-4.36657	0.96611
H	-0.5477	-5.25297	1.12447
H	1.71339	-4.072	-4.19361
H	2.80655	-3.63058	-2.87996
H	1.98061	-2.36801	-3.80085
C	-2.71283	-0.26364	4.51929
H	-3.59556	0.36714	4.3624
H	-2.96876	-1.00905	5.28235
H	-1.91092	0.36494	4.92386

2 (*C*$_1$ symmetry)

Ge	-0.4328	2.76215	-0.50938
C	0.53081	4.09429	-1.51052
C	-0.2287	5.02445	-2.23544
H	0.33906	5.75607	-2.81757
C	-1.61385	5.1884	-2.32423
H	-1.98074	5.99887	-2.95162
C	-2.54829	4.39685	-1.65031
H	-3.60337	4.65463	-1.78349
C	-2.21398	3.32783	-0.83116
H	-3.02789	2.78616	-0.34811
C	2.05786	4.26835	-1.60517
C	2.81102	3.23563	-0.76555
H	2.50147	3.26115	0.28367
H	3.88923	3.43995	-0.81117
H	2.63545	2.21457	-1.11875
Ru	-0.10523	1.0855	1.29865
C	2.53259	4.12127	-3.06578
H	2.25805	3.13818	-3.46416
H	3.62433	4.23	-3.13424
H	2.08411	4.87811	-3.7181
C	2.46639	5.6651	-1.0888

H	2.00015	6.4688	-1.6681
H	3.55568	5.79775	-1.1513
H	2.16563	5.7958	-0.04304
C	0.28121	2.87814	2.64217
C	-1.09843	2.48168	2.76871
C	-1.11891	1.17563	3.36465
C	0.22809	0.74251	3.57535
C	1.09411	1.7997	3.11239
C	0.75513	4.27719	2.39593
H	0.72558	4.84354	3.33909
H	0.13198	4.80581	1.66956
H	1.78503	4.30452	2.03092
C	-2.27875	3.3923	2.63788
H	-3.20139	2.82883	2.47454
H	-2.16915	4.08355	1.79788
H	-2.40872	3.98537	3.55632
C	-2.35933	0.54546	3.91979
H	-2.74481	1.15924	4.74606
H	-2.17447	-0.45485	4.31471
H	-3.14751	0.46938	3.16622
C	0.66305	-0.44732	4.37554
H	0.92645	-0.15057	5.40147
H	1.53544	-0.94148	3.93984
H	-0.12764	-1.19844	4.44646
C	2.56703	1.90935	3.36557
H	3.09745	2.35249	2.51858
H	3.01873	0.93737	3.5754
H	2.75095	2.54677	4.24295
Ge	1.5865	-0.42872	0.39557
C	2.11935	-1.57432	-1.14124
C	2.71908	-2.83867	-0.92807
H	2.85625	-3.48693	-1.79348
C	3.23589	-3.37774	0.28375
H	3.68999	-4.36477	0.24817

C	3.33166	-2.6276	1.4844
H	3.88709	-3.07657	2.30863
C	2.85753	-1.3026	1.58152
H	3.14453	-0.78689	2.49485
C	1.66925	-1.31643	-2.59873
C	1.24453	0.13759	-2.81361
H	0.89234	0.28671	-3.84167
H	2.08533	0.81838	-2.6462
H	0.43443	0.43621	-2.14188
C	0.4647	-2.2343	-2.88839
H	-0.34923	-2.05991	-2.17952
H	0.74423	-3.29306	-2.82427
H	0.07892	-2.04775	-3.89891
C	2.76512	-1.62231	-3.63358
H	3.10068	-2.66476	-3.61498
H	3.63569	-0.98336	-3.46633
H	2.38447	-1.42311	-4.64338
Ru	4.35522	-1.52238	-0.12299
C	5.91391	0.03877	0.14992
C	6.30373	-1.19098	0.7922
C	6.43169	-2.20155	-0.22762
C	6.12278	-1.59753	-1.49578
C	5.80134	-0.21439	-1.25754
C	5.83229	1.37587	0.81577
H	5.51789	1.28815	1.85932
H	5.12468	2.03642	0.31093
H	6.81564	1.86824	0.80708
C	6.64745	-1.34331	2.24168
H	7.68471	-1.03429	2.4312
H	6.54758	-2.3809	2.57441
H	5.99992	-0.728	2.87442
C	6.92055	-3.60205	-0.02162
H	6.48934	-4.29038	-0.75497
H	6.66402	-3.97516	0.97465

H	8.01369	-3.65313	-0.12197
C	6.3064	-2.25654	-2.8275
H	7.36138	-2.2132	-3.13331
H	5.71819	-1.77286	-3.61041
H	6.01624	-3.31152	-2.80152
C	5.57847	0.83422	-2.30209
H	4.82729	1.5641	-1.99195
H	5.25171	0.40446	-3.25222
H	6.51391	1.37853	-2.49494
Ge	-1.66325	-0.36835	0.05401
C	-2.30163	-2.25299	0.04438
C	-2.88459	-2.83239	-1.10621
H	-3.1662	-3.88286	-1.05817
C	-3.23147	-2.20137	-2.33308
H	-3.71593	-2.80831	-3.09385
C	-3.08789	-0.80977	-2.56216
H	-3.50254	-0.41213	-3.48907
C	-2.56061	0.06686	-1.60053
H	-2.63006	1.12491	-1.84406
C	-2.02025	-3.23373	1.20202
C	-1.99338	-2.49887	2.54115
H	-1.69784	-3.17977	3.35012
H	-2.98161	-2.09375	2.77904
H	-1.28216	-1.66815	2.51345
C	-0.63249	-3.85649	0.94696
H	0.15293	-3.09437	0.92333
H	-0.60893	-4.38906	-0.01102
H	-0.38491	-4.57296	1.74161
C	-3.04202	-4.38005	1.32199
H	-2.97002	-5.10995	0.50763
H	-4.06588	-3.9932	1.34346
H	-2.86556	-4.93152	2.25354
Ru	-4.33382	-1.14186	-0.74479
C	-5.92103	-1.15431	0.82965

C	-5.78148	0.17822	0.30997
C	-6.07142	0.13376	-1.09992
C	-6.41151	-1.22426	-1.44151
C	-6.31573	-2.02208	-0.24883
C	-5.85897	-1.53094	2.27675
H	-6.84253	-1.39416	2.74825
H	-5.14203	-0.91316	2.82397
H	-5.57033	-2.5762	2.41777
C	-5.5765	1.42557	1.10983
H	-6.54432	1.89779	1.33203
H	-4.96541	2.15764	0.57575
H	-5.08681	1.21759	2.06424
C	-6.13015	1.32019	-2.01096
H	-7.09832	1.83188	-1.92003
H	-6.00806	1.03037	-3.05871
H	-5.34527	2.04493	-1.77598
C	-6.88726	-1.69852	-2.77931
H	-6.66929	-2.75978	-2.93253
H	-6.4183	-1.14005	-3.59499
H	-7.9743	-1.56796	-2.87247
C	-6.70732	-3.46263	-0.13281
H	-6.22184	-3.94847	0.71766
H	-6.44036	-4.02786	-1.0311
H	-7.79291	-3.55993	0.00877

5 (η^6) (C_1 symmetry)

C	-1.85396	-0.08515	-0.53026
C	-1.18397	0.24533	-1.72622
H	-1.39866	1.19951	-2.20843
C	-0.16183	-0.50968	-2.37052
H	0.28815	-0.08808	-3.26572
C	0.36014	-1.73025	-1.86627
H	1.21463	-2.1515	-2.39848
C	-0.07994	-2.30839	-0.66163
H	0.53259	-3.14345	-0.31458
C	-2.95722	0.89062	-0.06672
C	-3.28137	0.73238	1.42705
H	-4.07702	1.43131	1.71525
H	-2.40496	0.93943	2.05044
H	-3.62421	-0.27967	1.666
C	-4.22271	0.52456	-0.87246
H	-4.50948	-0.51874	-0.69824
H	-4.05884	0.65198	-1.94913
H	-5.06472	1.16459	-0.57746
C	-2.63242	2.37405	-0.31729
H	-2.55492	2.6219	-1.38156
H	-1.68979	2.65294	0.16408
H	-3.42646	3.00677	0.0981
Ru	0.55295	-0.13666	-0.30795
C	1.17891	1.18775	1.36573
C	1.80568	-0.09911	1.50276
C	1.62023	1.77509	0.12604
C	0.37116	1.86971	2.42421
H	1.03179	2.41694	3.11163
H	-0.20221	1.15169	3.0166
H	-0.3326	2.59072	2.0012
C	1.3307	3.16497	-0.34811
H	0.36787	3.52923	0.0195
H	1.30957	3.223	-1.44057
H	2.10322	3.86254	0.00506
C	2.51882	0.84857	-0.50506
C	2.63218	-0.31165	0.34058
C	3.28501	1.08889	-1.76918
H	2.74387	1.75474	-2.44798
H	4.25587	1.55576	-1.55258
H	3.48182	0.15583	-2.3062
C	3.54032	-1.48066	0.11778
H	3.714	-1.66042	-0.94765
H	4.51809	-1.30898	0.58856

H	3.12374	-2.39757	0.54514
C	1.73988	-0.98782	2.70637
H	1.8753	-2.03926	2.43821
H	2.52858	-0.7216	3.42459
H	0.77614	-0.90493	3.21558
Ge	-1.5284	-1.74428	0.53493

6 (η^1) (C_1 symmetry)

Ge	-1.35774	-0.87967	-0.00421
C	-3.79347	-2.3459	0.00152
C	-2.40799	-2.44267	0.00211
C	-4.54253	-1.15705	-0.00207
C	-2.67915	0.49692	-0.00729
C	-2.26091	1.96322	-0.00708
C	-4.02919	0.14626	-0.00572
C	-0.72771	2.12878	-0.01188
C	-2.79217	2.67185	1.2562
Ru	0.85439	0.18608	-0.01286
C	2.21858	-1.43181	0.24981
C	2.93374	0.79255	0.51856
C	2.49418	-0.3976	1.22172
C	2.39563	-0.84559	-1.05515
C	2.85721	0.52428	-0.87695
C	1.92762	-2.86805	0.55061
C	2.27341	-1.5561	-2.36508
C	3.40767	2.05671	1.16373
C	2.46291	-0.56762	2.70667
C	3.22157	1.45763	-1.98748
H	-4.371	-3.27341	0.00444
H	-1.96856	-3.4391	0.00567
H	-5.62641	-1.25858	-0.00147
H	-4.78049	0.9425	-0.00674
H	-0.27799	1.69664	0.92028
H	-0.43542	3.18511	-0.00783
H	-0.28322	1.70383	-0.94931
H	-3.88536	2.62894	1.29706
H	-2.4966	3.72952	1.2726
H	-2.40802	2.18865	2.16207
H	1.35959	-3.33871	-0.25632
H	1.34416	-2.97508	1.46925
H	2.86297	-3.43209	0.67668
H	3.24253	-1.97489	-2.67288

H	1.93632	-0.88119	-3.15775
H	1.55392	-2.37692	-2.30437
H	4.47571	1.99191	1.41509
H	2.86692	2.26377	2.09291
H	3.27815	2.92158	0.50595
H	3.44343	-0.89554	3.08103
H	1.72243	-1.31504	3.00477
H	2.21171	0.36976	3.2125
H	4.26019	1.2965	-2.30901
H	3.12897	2.5047	-1.68389
H	2.58122	1.30701	-2.86246
C	-2.80179	2.6778	-1.26264
H	-3.89532	2.63621	-1.29492
H	-2.50556	3.73531	-1.27641
H	-2.42533	2.19867	-2.17384

[**6**·thf] (η^1) (C_1 symmetry)

Ge	-1.35865	-0.55429	-0.57458
C	-3.31873	-1.87315	-2.20386
C	-1.96384	-1.66775	-1.97226
C	-4.35541	-1.31749	-1.44542
C	-3.00434	0.0188	0.21438
C	-3.11385	0.93669	1.44328
C	-4.19066	-0.46423	-0.34699
C	-1.73845	1.38858	1.9529
C	-3.81753	0.19482	2.59796
Ru	1.04452	-0.15602	0.03507
C	1.437	-2.22032	0.48089
C	2.93651	-0.53979	1.15908
C	1.83839	-1.39126	1.5877
C	2.20061	-1.78924	-0.66572
C	3.15266	-0.77977	-0.22429
C	0.50876	-3.39237	0.53643
C	2.15919	-2.4033	-2.02773
C	3.70878	0.37943	2.05225
C	1.32673	-1.49493	2.98885
C	4.18961	-0.15319	-1.10185
H	-3.61448	-2.51729	-3.0363
H	-1.25747	-2.15204	-2.64744
H	-5.37691	-1.56701	-1.72743
H	-5.12765	-0.14433	0.11957
H	-1.11865	0.53038	2.24165

H	-1.84908	2.03805	2.83174
H	-1.18827	1.94975	1.18789
H	-4.82722	-0.12413	2.31835
H	-3.90271	0.8395	3.48369
H	-3.2535	-0.70218	2.87949
H	-0.03049	-3.52782	-0.40509
H	-0.24526	-3.27294	1.31963
H	1.0713	-4.31363	0.74608
H	2.87326	-3.23661	-2.10158
H	2.41517	-1.67614	-2.80484
H	1.16346	-2.79393	-2.25353
H	4.47362	-0.1713	2.61784
H	3.05712	0.87014	2.78351
H	4.22342	1.16194	1.4859
H	1.95376	-2.17527	3.58291
H	0.30371	-1.87975	3.00834
H	1.32607	-0.52182	3.49061
H	5.02557	-0.84534	-1.27399
H	4.60537	0.75644	-0.65783
H	3.77716	0.10942	-2.08229
C	-3.92164	2.20261	1.09082
H	-4.93459	1.95678	0.75501
H	-4.00889	2.86638	1.96191
H	-3.43392	2.76058	0.28216
C	1.98733	2.91382	-0.18045
C	1.46699	4.28167	-0.59365
C	0.68614	3.94146	-1.86613
C	0.06536	2.58688	-1.5317
H	2.89389	2.63628	-0.73402
H	2.17619	2.8091	0.89028
H	0.79761	4.68196	0.17653
H	2.27214	5.00385	-0.75926
H	-0.07253	4.68763	-2.11932
H	1.37011	3.85314	-2.71837
H	-0.93278	2.67156	-1.09238
H	0.01343	1.90557	-2.38351
O	0.93282	1.99845	-0.52367

[**6**·2thf] (η^1) (C_1 symmetry)

Ge	-1.45817	-0.57696	0.08474
C	-3.28012	-0.02725	-0.19083
C	-4.28051	-0.99154	-0.01096
H	-5.31071	-0.65831	-0.16793
C	-4.16889	-2.33757	0.35305
H	-5.09314	-2.90688	0.43663
C	-2.96486	-2.99706	0.6187
H	-3.03318	-4.05183	0.90056
C	-1.71385	-2.39805	0.55449
H	-0.85218	-3.02009	0.80253
C	-3.75563	1.38569	-0.57729
C	-2.58247	2.32607	-0.86604
H	-1.87411	2.3552	-0.03155
H	-2.94023	3.34732	-1.05344
H	-2.03082	1.99487	-1.75123
Ru	0.91678	0.23609	0.42304
C	-4.62672	1.34564	-1.85057
H	-4.06984	0.90163	-2.68429
H	-4.93157	2.36018	-2.14211
H	-5.53808	0.75563	-1.71026
C	-4.58263	1.99003	0.5761
H	-5.4573	1.3729	0.80883
H	-4.93919	2.9971	0.31832
H	-3.98062	2.06304	1.48939
C	0.34088	1.16029	2.2791
C	1.10747	-0.03541	2.54622
C	2.45534	0.19522	2.05234
C	2.50416	1.47376	1.44249
C	1.17717	2.05885	1.52805
C	-0.99619	1.48723	2.86708
H	-0.8577	1.97835	3.84161
H	-1.60642	0.59387	3.02453
H	-1.56987	2.16695	2.23177
C	0.66627	-1.17201	3.41538
H	1.24047	-2.08237	3.21321
H	-0.38814	-1.4109	3.24917
H	0.80098	-0.93168	4.48029
C	3.62742	-0.71127	2.26488
H	4.17274	-0.41986	3.17379
H	4.33546	-0.6718	1.43047
H	3.31986	-1.75187	2.39671
C	3.72214	2.1672	0.91863
H	4.17792	2.79229	1.70053

H	3.48448	2.83139	0.08082
H	4.48875	1.45947	0.5856
C	0.83238	3.4528	1.10606
H	-0.24744	3.58827	1.00262
H	1.28887	3.70167	0.14214
H	1.19126	4.18688	1.84222
C	2.06091	-2.86706	-0.00902
C	1.56368	-3.54828	-2.23797
C	1.71977	-4.11423	-0.82465
H	1.62271	-2.87654	0.99247
H	3.14369	-2.71778	0.0787
H	0.95369	-4.18053	-2.89022
H	2.54379	-3.40781	-2.71109
H	0.76943	-4.54189	-0.48736
H	2.49093	-4.88664	-0.745
C	2.72508	0.82332	-2.2999
C	1.3151	1.48606	-4.07896
C	2.73803	1.69055	-3.55182
H	2.93245	-0.22924	-2.53597
H	3.42076	1.14386	-1.52326
H	1.24685	0.53945	-4.62884
H	0.97852	2.28565	-4.74567
H	3.51343	1.39097	-4.26366
H	2.90288	2.74209	-3.28753
C	0.49668	1.42226	-2.79062
H	0.13719	2.41053	-2.48298
H	-0.35785	0.74172	-2.84465
C	0.90371	-2.2084	-1.95083
H	1.07703	-1.44917	-2.71599
H	-0.17559	-2.31078	-1.78724
O	1.39589	0.93942	-1.77505
O	1.51872	-1.74714	-0.73206

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