Supporting Information

Unusual Formation of a N-heterocyclic Germylene via Homoleptic Cleavage of a C-C Bond

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Content:

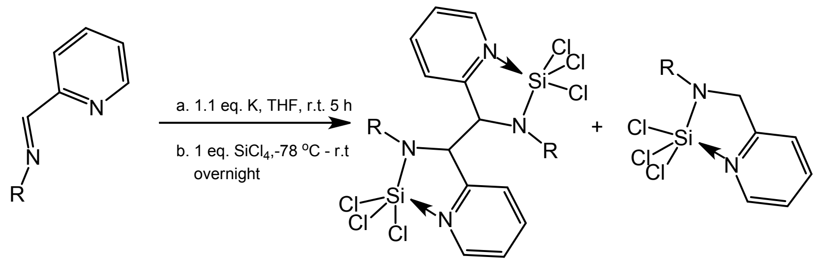
S1 Experimental section

S1.1 Syntheses of compounds 1-4

General Methods. All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box. Ligand IP = (Py)CH(=NR), R= 2,6-$i\text{Pr}_2\text{C}_6\text{H}_3$ was prepared according to literature methods.[S1] GeCl_2(dioxane) was purchased from Sigma Aldrich and used as received. SiCl_4 was distilled and used directly. Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent C_6D_6 was dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

Preparation of $(\text{IPGeCl})_2$ (1). To a mixture of imine IP (5 g, 18.76 mmol) and K (0.77 g, 19.7 mmol) was added THF (50 mL) at room temperature and the suspension was stirred for 5 h. The dark red solution obtained was cooled to -78 °C and then added to a solution of GeCl_2(dioxane) (4.3 g, 18.76 mmol) in 20 mL THF under the same temperature. The mixture was allowed to warm to room temperature and stirred for additional 12 h. All the volatiles were removed under vacuum. The residue was extracted with toluene (50 mL) and filtered. The brown filtrate was evacuated and the residue was extracted with 10 mL *n*-hexane, affording an analytical pure yellow powder (3.6 g). After storing the *n*-hexane solution at 0 °C a yellow crystalline solid of **1** (0.6 g) was obtained. Single crystals suitable for X-ray structure analysis were grown from toluene solution of **1** at -4 °C for 24 h. Total yield: 4.2 g (60 %, based on Ge). Mp: 143 °C (dec). ^{1}H NMR (C_6D_6, 300 MHz, 298 K, ppm): δ 9.32 (m, 2 H, Py*H*), 7.86 (m, 2 H, Py*H*), 7.13-7.06 (m, 6 H, C_6H_3), 6.92 (m, 2 H, Py*H*), 6.21 (m, 2 H, Py*H*), 5.40 (s, 2 H, NC*H*), 4.40 (sept, 2 H, $^3J_{\text{HH}}$ = 6.5 Hz, C*H*Me$_2$), 2.66 (sept, 2 H, $^3J_{\text{HH}}$ = 6.5 Hz, C*H*Me$_2$), 1.48 (d, 6 H, $^3J_{\text{HH}}$ = 6.5 Hz, CH*Me*$_2$), 1.10 (d, 6 H, $^3J_{\text{HH}}$ = 6.5 Hz, CH*Me*$_2$), 1.05 (d, 6 H, $^3J_{\text{HH}}$ = 6.5 Hz, CH*Me*$_2$), 0.62 (d, 6 H, $^3J_{\text{HH}}$ = 6.5 Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 75 MHz, 298 K, ppm): δ 161.1, 150.8, 148.9, 143.82, 140.2, 138.8, 126.7, 125.1 (Ar-*C* and Py-*C*), 76.1 (N*C*H), 29.1, 28.6, 28.2, 27.6, 27.4, 24.1, 23.8. Anal. calcd for $\text{C}_{36}\text{H}_{44}\text{Cl}_2\text{Ge}_2\text{N}_4$ (748.95): C, 57.73; H, 5.92; N, 7.48. Found: C, 57.19; H, 5.94; N, 7.29.

Preparation of IPGe: (**2**). To a mixture of **1** (0.7 g, 0.93 mmol) and KC_8 (0.3 g, 2.32 mmol) toluene (30 mL) was added at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After workup, the suspension was dried under vacuum. The residue was extracted with *n*-hexane (2×30 mL) and filtered. The red filtrate was concentrated and stored at room temperature for 2 days, affording **2** as red blocks. Yield: 0.3 g (48 %, based on **1**). Mp: 115 °C (dec). UV-visible bands at 425 nm. ^{1}H NMR (C_6D_6, 300 MHz, 299 K, ppm): δ 7.87-7.84 (m, 1 H, Py*H*), 7.22-7.13 (m, 3 H, C_6H_3), 6.87-6.83 (m, 1 H, Py*H*), 6.80 (s, 1 H, NC*H*), 6.13-6.07 (m, 1 H, Py*H*), 5.49-5.44 (m, 1 H, Py*H*), 2.78 (sept, 2 H, $^3J_{\text{HH}}$ = 6.9 Hz, C*H*Me$_2$), 1.12 (d, 6 H, $^3J_{\text{HH}}$ = 6.9 Hz, CH*Me*$_2$), 1.09 (d, 6 H, $^3J_{\text{HH}}$ = 6.9 Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 75 MHz, 299 K, ppm): δ 145.1, 141.3, 135.8, 135.4, 127.6, 123.4, 123.1, 120.7, 120.3 (N*C*H), 106.9, 28.1 (*C*HMe$_2$), 26.0, 24.7 (CH*Me*$_2$). Anal. calcd for $\text{C}_{18}\text{H}_{22}\text{GeN}_2$ (339.02): C, 63.77; H, 6.54; N, 8.26. Found: C, 63.54; H,6.92; N, 7.85. EI-MS: *m/z*(%) 340.1 [M^+] (100 %).



3 **4**

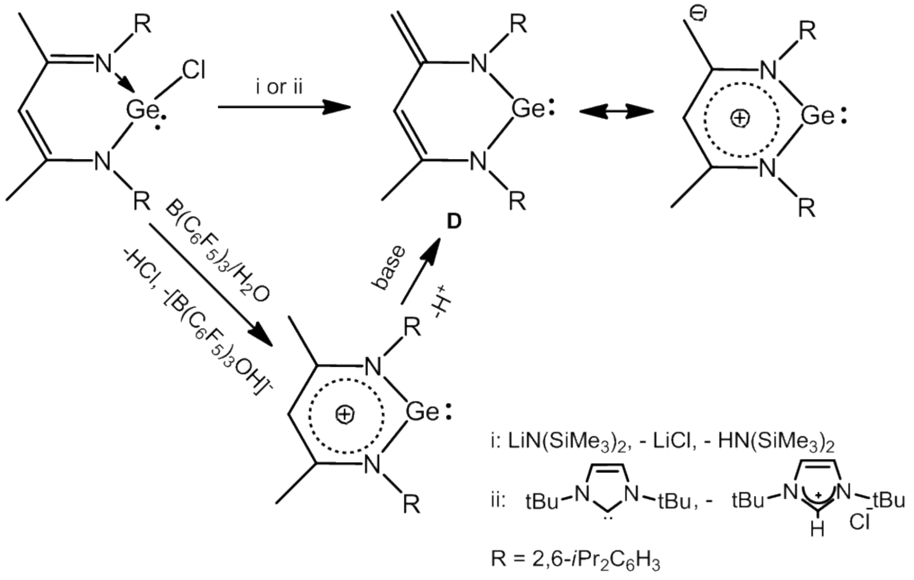
Scheme S1 Syntheses of compounds **3** and **4**.

Preparation of ($(IPSiCl_3)_2$) (3) and ($(IPH)SiCl_3$), (R= 2,6-*i*$Pr_2C_6H_3$) (4) To a mixture of IP (5 g, 18.76 mmol) and K (0.76 g, 19 mmol) THF (50 mL) was added at room temperature and the suspension was stirred for 5 h. The resulting dark red solution was cooled to -78 °C and $SiCl_4$ (9.6 mL, 19 mmol) was added at the same temperature. The mixture was allowed to warm to room temperature and stirred overnight. All the volatiles were removed under vacuum. The residue was extracted with toluene (100 mL) and filtered. A mixture of **3** and **4** as colorless crystals was obtained in toluene solution at -4 °C. By analyzing the ^1H NMR spectrum of the product, the highest yield ratio of **3** and **4** at the early crystallization is 9:4 that declined gradually due to the spontaneous transformation of **3** to **4**. The source of proton at C_{im} in **4** may be from the toluene. During this period, free IP ligand was observed and the yield was increased with the time. After one week, both compounds almost vanished while free IP ligand dominated confirmed by ^1H NMR studies. The corresponding ^1H NMR data of **3** and **4** can be assigned by analyzing the spectra measured at each stage of crystallization.

For **3**: ^1H NMR (C_6D_6, 500 MHz, 298 K, ppm): δ 8.20-8.15 (m, 2 H, Py*H*), 8.07-8.03 (m, 2 H, Py*H*), 7.11-6.98 (m, 6 H, C_6H_3), 6.86-6.82 (m, 2 H, Py*H*), 6.13-6.08 (m, 2 H, Py*H*), 5.24 (s, 2 H, NC*H*), 3.76 (sept, 2 H, $^3J_{HH}$ = 6.5 Hz, C*H*Me$_2$), 2.86 (sept, 2 H, $^3J_{HH}$ = 6.5 Hz, C*H*Me$_2$), 1.56 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 1.41 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 1.05 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 0.78 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$). ^{29}Si NMR (C_6D_6, 99 MHz, 298 K, ppm): δ -103.5 (*Si*Cl$_3$).

For **4**: ^1H NMR (C_6D_6, 500 MHz, 298 K, ppm): δ 8.50-8.48 (m, 1 H, Py*H*), 8.20-7.09 (m, 3 H, C_6H_3), 6.48-6.45 (m, 1 H, Py*H*), 6.27-6.25 (m, 1 H, Py*H*), 5.85-5.84 (m, 1 H, Py*H*), 4.02 (s, 2 H, NC*H*$_2$), 3.55 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 1.59 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.24 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$). ^{29}Si NMR (C_6D_6, 99 MHz, 298 K, ppm): δ -101.9 (*Si*Cl$_3$).

S1.2 Synthetic routes of a reported germylene D[S2] with altering single-double bonds for comparison with that of compound 2.



Scheme S2 Synthetic ways toward heterofulvene-like germylene **D**.

S2 Crystal structure determination

Suitable crystals for single crystal X-ray diffraction analysis of compounds **1-4** were selected under argon atmosphere and transferred in perfluorated oil on a microscope slide, which was cooled with a nitrogen gas flow by the X-Temp2 device.[S3] Crystals were mounted to the tip of a MiTeGen©MicroMount using a polarizer microscope. The data were collected either on a Bruker D8 three circle diffractometer equipped with a Smart Apex II Quazar detector and an Incoatec Mo or Ag microsource[S4] with mirror optics, or a Bruker TXS-Mo rotating anode with mirror optics and a Smart Apex II Ultra detector. The data were integrated with SAINT[S5] and a semi-empirical absorption correction with SADABS[S6] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods against F^2 (SHELXL-2012)[S7] within the SHELXLE-GUI.[S8] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The disorder in **1** and **2** was refined using distance restraints and restraints for the anisotropic displacement parameter.[S9]

S2.1 Crystal Data and Structure Refinement for Compounds 1-4. S= toluene (Table S1)

	1·2S	**2**	**3**·S	**4**
empirical formula	$C_{93}H_{112}Cl_4Ge_4N_8$	$C_{18}H_{22}GeN_2$	$C_{43}H_{52}Cl_6N_4Si_2$	$C_{18}H_{23}Cl_3N_2Si$
CCDC No.	953613	953614	953615	953616
M [g/mol]	1774.06	338.96	893.76	401.82
crystal system	Triclinic	Monoclinic	Monoclinic	Othorhombic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_12_12_1$

T [K]	100	100	100	100
a [Å]	12.692(2)	24.693(3)	14.149(2)	9.984(2)
b [Å]	12.839(2)	10.903(2)	17.560(2)	13.987(2)
c [Å]	15.409(3)	27.840(3)	17.357(3)	14.110(2)
α [°]	98.61(2)	90	90	90
β [°]	102.61(2)	114.96(2)	94.21(3)	90
γ [°]	113.07(3)	90	90	90
V [Å^3]	2175.6(8)	6795.3(19)	4300.8(11)	1970.4(6)
Z	1	16	4	4
ρ_{calc} [Mg/m^{-3}]	1.354	1.325	1.380	1.355
μ [mm^{-1}]	0.814	0.951	0.492	0.529
F(000)	922	2816	1872	840
crystal size [mm]	0.2 x 0.2 x 0.2	0.156 x 0.15 x 0.096	0.11 x 0.076 x 0.052	0.1 x 0.09 x 0.05
θ-min, max [°]	1.445 - 20.835	1.273 - 20.827	1.443 - 27.099	2.05 - 29.134
max., min. transm.	0.8618, 0.7689	0.8746, 0.7816	0.8620, 0.7966	0.8621, 0.8083
refl. collected	64131	52365	52526	55923
unique refl.	9244	7215	9483	5318
parameters	539	406	511	222
restraints	227	67	1	0
GooF	1.051	1.042	1.033	1.08
$R1$,[a] w$R2$[b][$I>2\sigma(I)$]	0.0258, 0.0608	0.0343, 0.0772	0.034, 0.0716	0.0322, 0.0856
$R1$, $wR2$ (all data)	0.0323, 0.0639	0.0442, 0.0809	0.0529, 0.0787	0.0334, 0.0864
largest diff. peak, hole (e Å^{-3})	0.552, -0.382	1.099, -0.676	0.395, -0.253	0.521, -0.187

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a) $R1 = \frac{\sum \left\| F_o \right| - \left| F_c \right\|}{\sum \left| F_o \right|}$ b) $wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$ with $w = \frac{1}{\sigma^2\left(F_o^2\right) + \left(g_1 P\right)^2 + g_2 P}$; $P = \frac{\left(F_o^2 + 2F_c^2\right)}{3}$.

S2.2 Crystal structures of 1-4

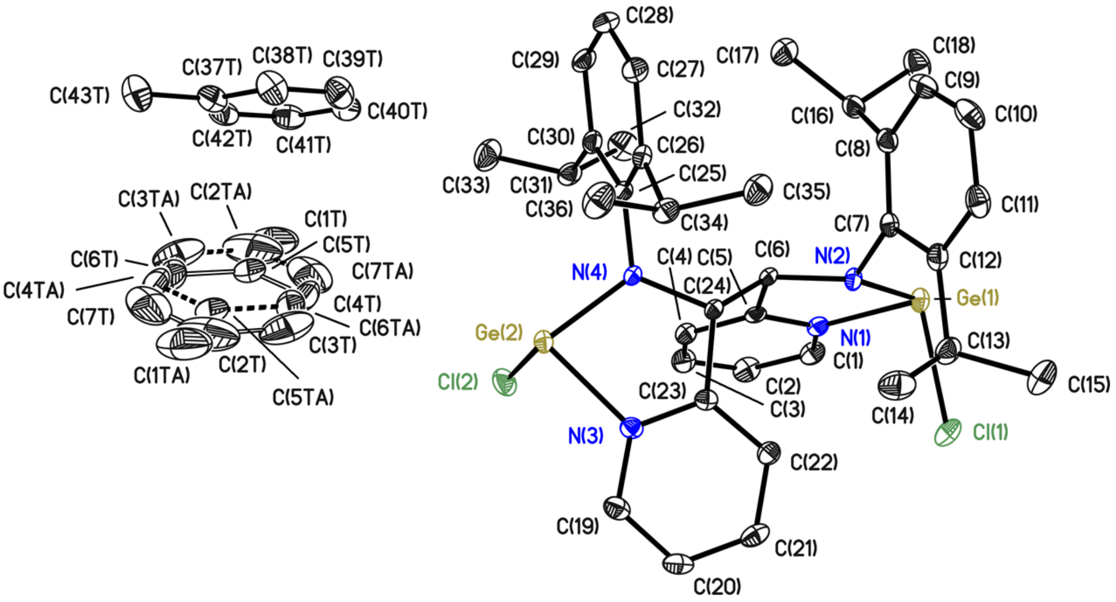


Figure S1 Molecular structure of **1**. Anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

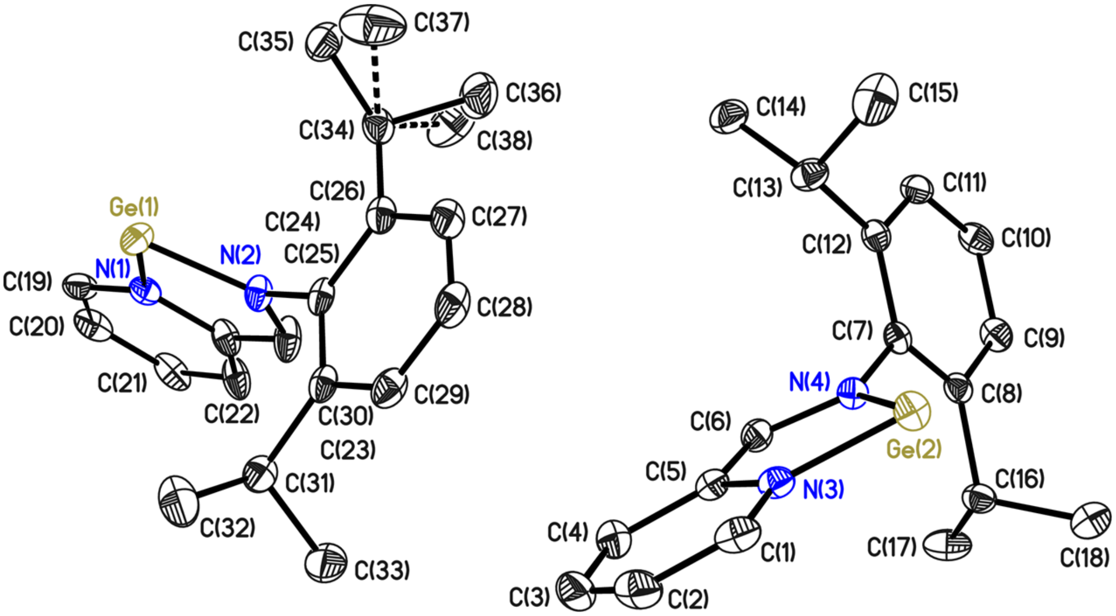


Figure S2 Molecular structure of **2**. Anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

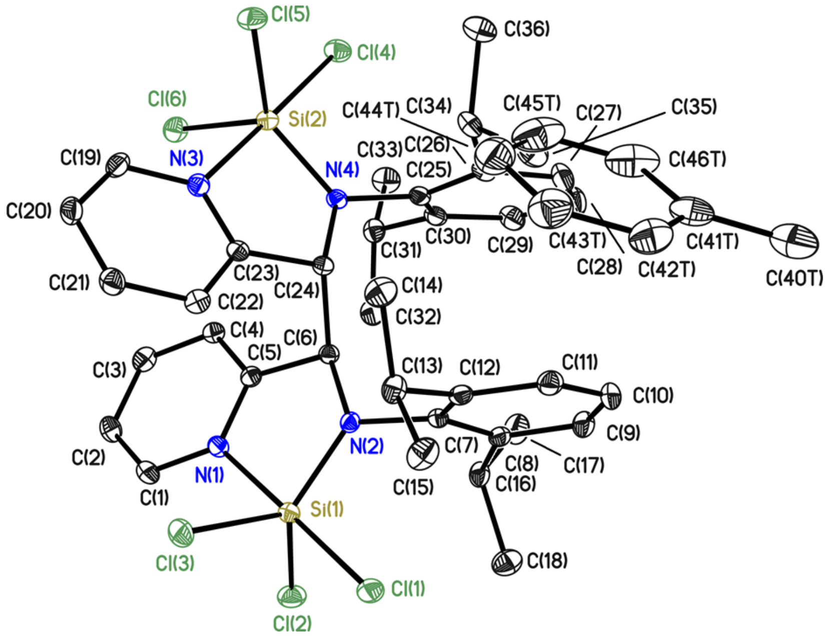


Figure S3 Molecular structure of **3**. Anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

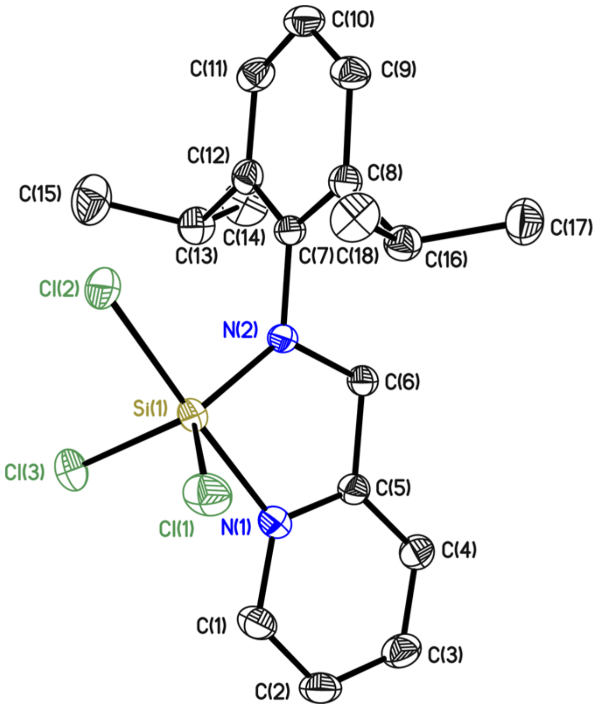
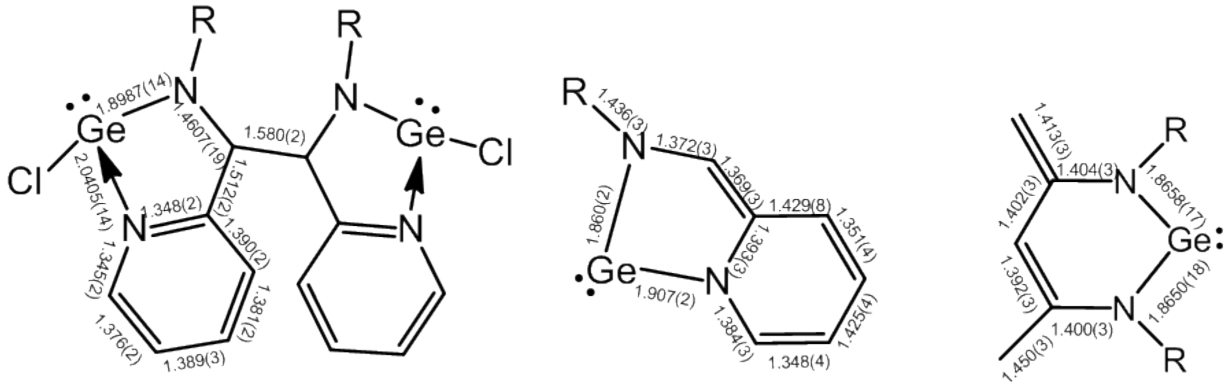


Figure S4 Molecular structure of **4**. Anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

S2.3 Comparison of bond lengths in compounds 1, 2, and D



1 **2** **D**

Scheme S3 Comparison of bond lengths in compounds **1**, **2**, and germylene **D**. (Due to the essential similarity between the two units in the crystal lattice of **2**, only the values for one are shown).

S3 UV-visible spectroscopy

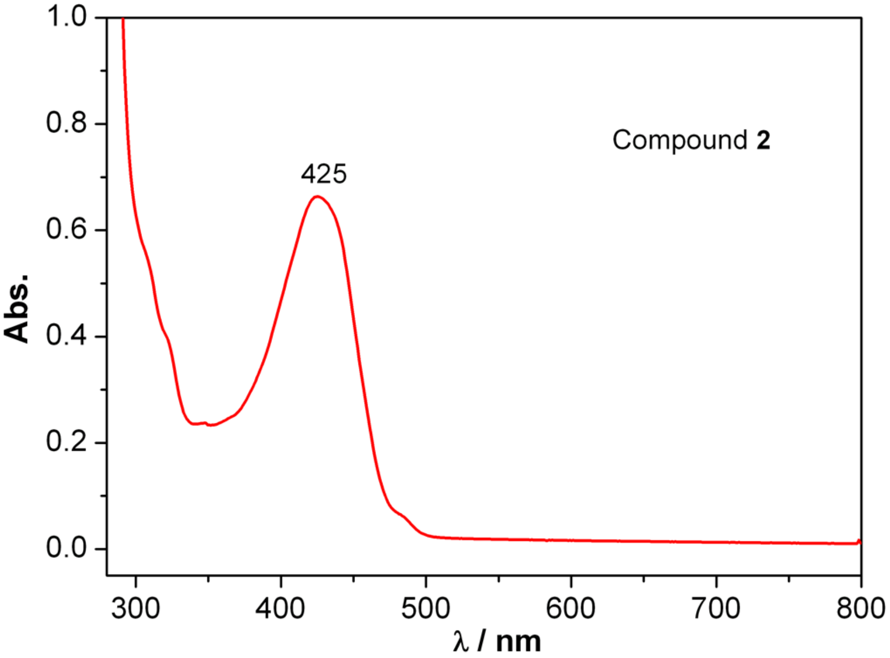


Figure S5 UV-visible spectrum of compound **2** in *n*-hexane

S4 High resolution ICP-MS spectrometry

The measurement for ICP-MS was carried out on a DRC II, made by Perkin Elmer. 3.07 mg of crystal **2** was treated with 1 mL HNO_3 (aq.) The solution was further diluted to a 1/1000 concentration, which was then used for the measurement. The characteristic peaks of elemental germanium and the germanium oxides (GeO_2 and GeO_x) shown in Figure S9 confirms that Ge is the single metal in crystal **2**. The corresponding concentration of Ge is aprox. 50 ppm. Due to the high sensitivity of Bi element in this measurement, the signal of Bi in Figure S9 was caused by the experimental operation.

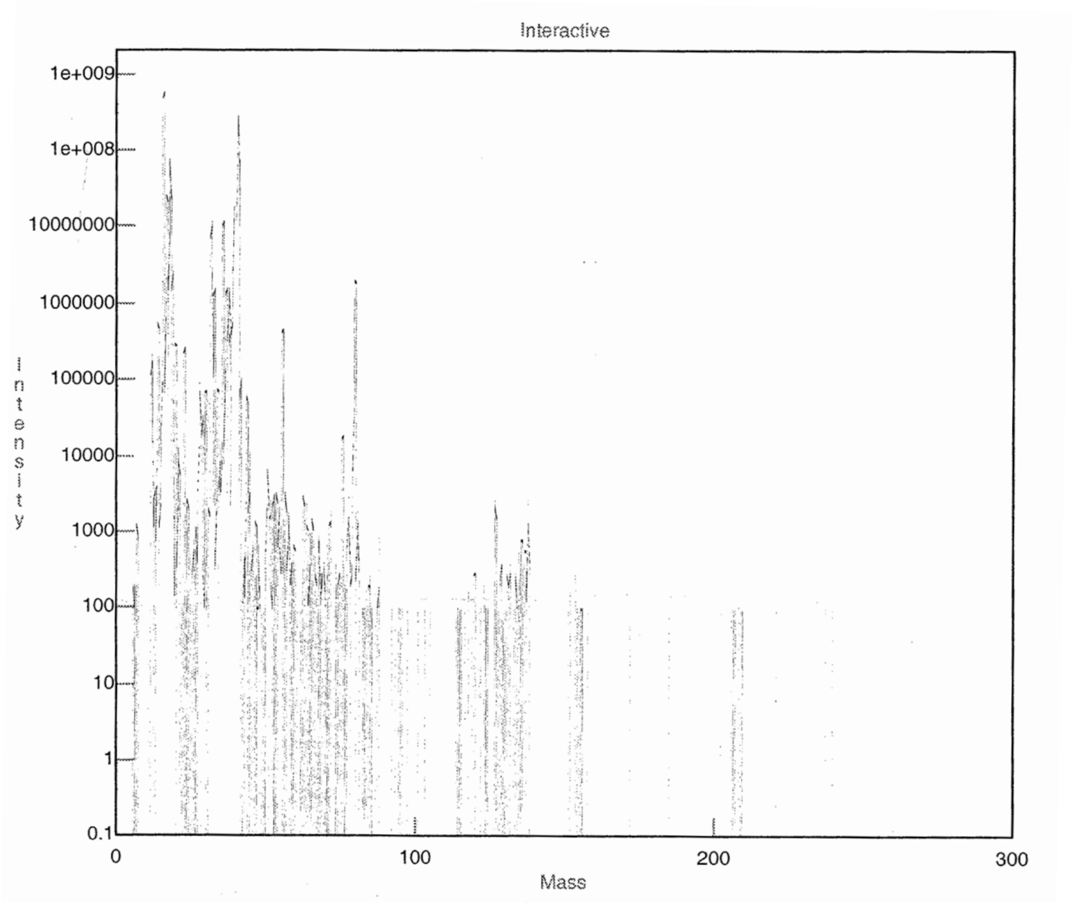


Figure S6 Blank measurement (background)

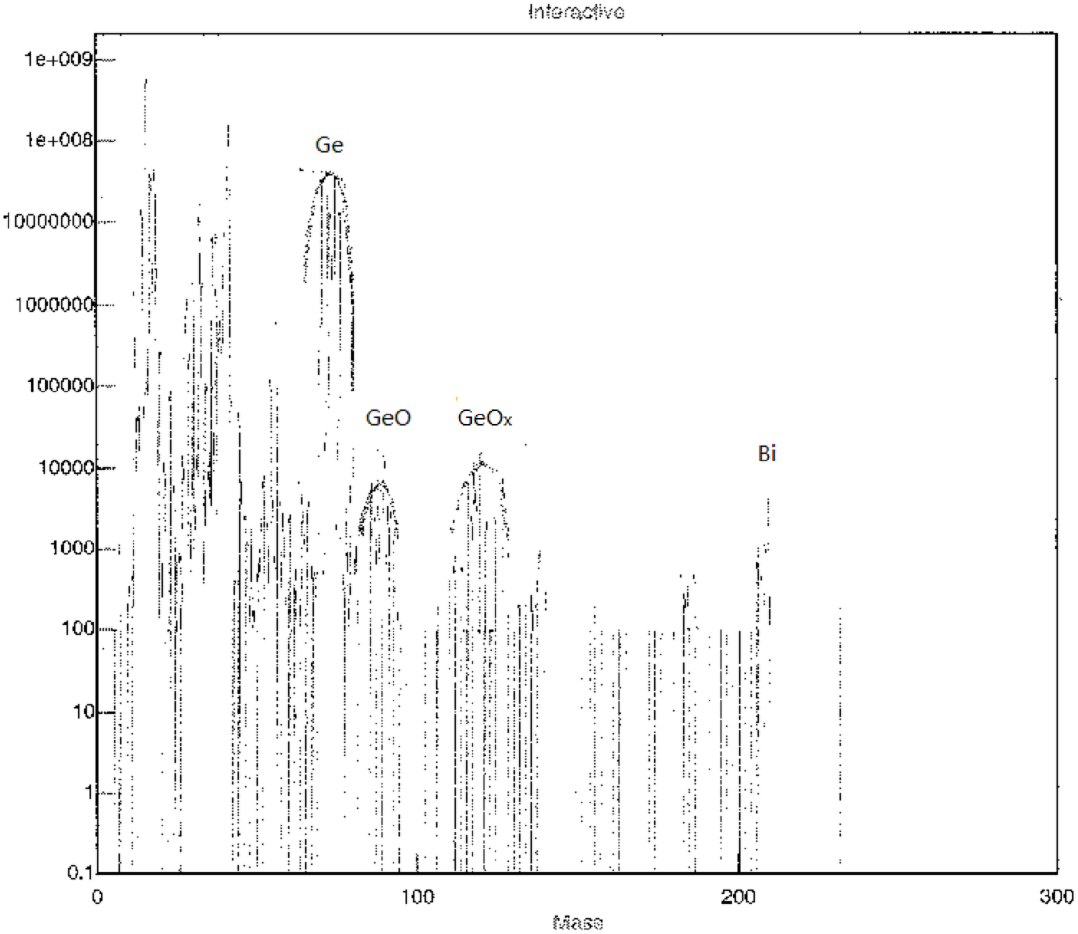


Figure S7 Sample measurement

S5 Theoretical calculations

All molecular structures were optimized at the density functional theory (DFT) level using the B3LYP functional.[S10] and the Karlsruhe def2-TZVP basis set.[S11] The optimized structures were confirmed to be minima through evaluating force constants.[S12] For the larger dimer only the lowest eigenvalues of the Hessian have been calculated confirming a minimum or transition state character. Dispersion effects were taken into account by using the Grimme D3 correction.[S13] Nuclear magnetic shieldings and nucleus independent chemical shift (NICS) values[S14] were calculated using the same functional and basis set. The molecular structure optimizations and the calculation of the nuclear magnetic shieldings were performed with TURBOMOLE version 6.4.[S15] The magnetically induced current density was calculated using the GIMIC method.[S16] GIMIC is an independent program that uses the magnetically perturbed AO-density matrices from nuclear magnetic shielding calculations, the one-electron density matrix, and basis-set information as input data.[S16a] Gauge including atomic orbitals (GIAO) are employed[S17] to obtain accurate gauge independent current densities. The integrated ring-current susceptibility (in nA/T), which is denoted in the following as ring-current strength, can be used as a reliable measure of the degree of molecular aromaticity with respect to the magnetic criterion.[S18] It is also possible to obtain detailed information about the current pathways even in complex molecular ring systems.[S19] The current strengths and current pathways are obtained by numerical integration of the current density passing through cut planes perpendicularly to selected bonds of the molecular system. The ring-current strength for benzene lies for example at 11.8 nA/T at the same level of theory and can be used as reference value for aromatic molecules.[S20] The current pathway picture is obtained with JMOL[S19e] and GIMP.[S21]

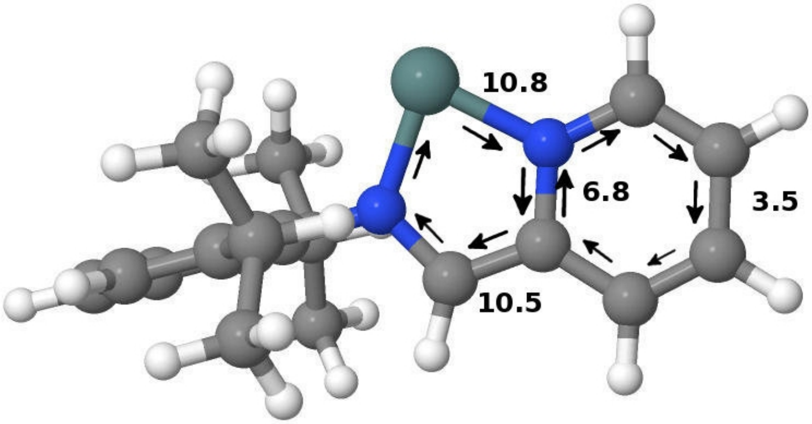


Figure S8 Schematic picture of the calculated current pathways in compound **2**. The numbers in black denote the calculated current strength susceptibility in nA/T for the respective bond, while the black arrows indicate the direction of the currents. Diatropic currents are assumed to circle clockwise paratropic ones anti-clockwise.

S5.1 The investigation of the C-C bond cleavage

The investigation of the C-C bond cleavage of **1** turned out to be nontrivial. It was not possible to isolate the determining transition state for the bond breaking with several tested DFT functionals. When attaching 2K$^+$ ions to the minimum structure of the dimer the system dissociated during the geometry optimization when a triplet occupation was forced. However, this was not the case for the open-shell singlet. A possible transition state was found at a C-C distance of 185 pm through a constrained geometry optimization scan along the C-C bond (only the C-C bond distance was fixed while the rest of the system was relaxed without any constraints). Attaching to this transition structure 2K atoms forced the molecule to dissociate. The electronic energy barrier from the ground state to the transition state was calculated to be 24.3 kJ/mol, which is very low. It is hard to assign a reliable mechanism for the C-C bond cleavage based on the present DFT calculations, since a multireference treatment would be necessary for the problem. However, this is computationally not feasible, because the full germylene dimer is too large. Based on the obtained results it seems very likely that either 2K$^+$ ions attack the chlorines generating KCl and a triplet state is formed, which quickly dissociates into the monomers or two neutral K atoms attach to the two chlorines of a transition state and inject two electrons leading finally to the C-C bond cleavage and KCl.

S5.2 Molecular structures in xyz format

Cartesian coordinates in Å for molecule **2**, optimized at the B3LYP/def2-TZVP level of theory.

S5.2.1 Molecule 2

Ge	0.9797398	2.5962865	10.7877503
N	2.4900467	3.7938020	10.7948620
N	2.0329111	1.6986896	9.4911560
C	3.5176087	3.4263816	9.9115053
C	3.2411289	2.2763750	9.2112819
H	3.9062019	1.8321703	8.4848324
C	2.6390435	4.9263121	11.5577877

H	1.8130244	5.1567303	12.2193815
C	4.8049050	5.3518977	10.5969063
H	5.6905883	5.9709625	10.5381300
C	4.6878636	4.2382683	9.8293907
H	5.4708610	3.9413112	9.1430799
C	1.6474895	0.4938987	8.8144397
C	0.9314908	0.5808021	7.6041289
C	0.5387457	-0.6063020	6.9854059
H	-0.0174768	-0.5628358	6.0569800
C	0.8453527	-1.8408890	7.5353177
H	0.5285431	-2.7505278	7.0395710
C	1.5612782	-1.9078811	8.7200508
H	1.8004964	-2.8768704	9.1408406
C	1.9790816	-0.7526167	9.3812120
C	2.7706501	-0.8772445	10.6759337
H	3.0270764	0.1289424	11.0065944
C	0.5772253	1.9132057	6.9579503
H	1.0054826	2.7046971	7.5725336
C	1.9350031	-1.5240454	11.7918148
H	1.0186379	-0.9601120	11.9761382
H	2.5048805	-1.5572404	12.7236776
H	1.6517933	-2.5483707	11.5381047
C	4.0905728	-1.6364105	10.4668117
H	3.9175832	-2.6723596	10.1659975
H	4.6687473	-1.6529950	11.3938522
H	4.7017882	-1.1631492	9.6959388
C	1.1885363	2.0477680	5.5542427
H	0.7803284	1.3069822	4.8627546
H	2.2721312	1.9180449	5.5802977
H	0.9763222	3.0373242	5.1422303

C	-0.9425802	2.1383750	6.9199700
H	-1.1715768	3.1203847	6.4987298
H	-1.3738132	2.0915344	7.9217035
H	-1.4436429	1.3870805	6.3048776
C	3.7442969	5.7072964	11.4911659
H	3.8147476	6.5892315	12.1122898

S5.2.2 Molecule 1

Ge	-2.7076499	-0.2846426	2.6642526
C	-1.9248691	-3.1875789	3.1407815
H	-2.7237457	-3.1133206	3.8671581
N	-1.6463978	-2.0719958	2.4504429
Cl	-4.5734109	-1.2697205	1.5936141
Ge	1.4647951	-2.3600131	-2.6072091
N	-1.5426256	0.1716610	1.2048802
C	-1.2451349	-4.3652947	2.9130088
H	-1.4909418	-5.2512282	3.4817050
Cl	1.9203035	-4.3840115	-1.4706002
C	-0.6918324	-2.0565183	1.5066223
C	0.0147405	-3.2197917	1.2208838
H	0.7512905	-3.2310676	0.4353858
N	1.0966771	-1.1201382	-1.1848812
C	-0.2624394	-4.3775549	1.9251562
H	0.2810725	-5.2841288	1.6911006
N	-0.5837132	-2.6776802	-2.3449244
C	-0.4799660	-0.7394634	0.8041503
H	0.4981669	-0.3584729	1.1264026
C	0.3890873	1.8117753	2.7666437
H	0.2630910	0.7298641	2.8021623
C	-1.3981743	1.5700963	0.9215998

C	1.8816612	2.0987121	2.5696766
H	2.4711434	1.5992198	3.3415513
H	2.0929870	3.1680025	2.6352485
H	2.2280589	1.7502833	1.5991485
C	-0.3731718	3.7219947	1.3428844
H	0.3454457	4.3306926	1.8769871
C	-0.0995847	2.3555963	4.1197183
H	0.4815550	1.9201875	4.9367021
H	-1.1523969	2.1208684	4.2855352
H	0.0136184	3.4409583	4.1669784
C	-0.4613644	2.3607611	1.6297585
C	-4.7497368	1.9113548	-0.3993531
H	-5.5052707	1.2897879	-0.8848992
H	-4.9002778	2.9438574	-0.7238717
H	-4.9233760	1.8624673	0.6762027
C	-2.2687519	2.1847024	-0.0081326
C	-2.1602493	3.5563101	-0.2369327
H	-2.8253161	4.0281004	-0.9496878
C	-1.2106300	4.3221139	0.4162508
H	-1.1303126	5.3833630	0.2148408
C	-3.1201683	1.4147730	-2.2697291
H	-3.8781257	0.8035734	-2.7654539
H	-2.1394786	1.0155024	-2.5343076
H	-3.1836365	2.4248762	-2.6803472
C	-3.3428650	1.4086511	-0.7510753
H	-3.2885174	0.3807792	-0.4120642
C	-2.6124920	-3.8477263	-2.7315852
H	-3.1466367	-4.6229188	-3.2630554
C	-1.2757626	-3.6289978	-2.9889517
H	-0.7203430	-4.2238768	-3.7023851

C	-3.2334438	-3.0617209	-1.7628802
H	-4.2744417	-3.2121451	-1.5064542
C	-2.5079253	-2.0840056	-1.1064773
H	-2.9741310	-1.4945560	-0.3352652
C	-1.1659771	-1.8976423	-1.4204354
C	-0.2761826	-0.8694261	-0.7693708
H	-0.6131087	0.1145306	-1.1212965
C	2.0854013	-0.1075065	-0.9540079
C	4.5061058	-2.4230038	0.4120154
H	4.5171203	-3.3831581	0.9324890
H	5.4028838	-1.8697880	0.7011865
H	4.5604533	-2.6270309	-0.6579714
C	2.0847244	1.0916673	-1.7064726
C	3.1175417	-1.4155552	2.2713358
H	3.1392111	-2.3704813	2.8019068
H	2.1890177	-0.9054918	2.5337657
H	3.9429093	-0.8059702	2.6459420
C	3.0816546	2.0369863	-1.4709461
H	3.0833611	2.9584703	-2.0393624
C	1.0998619	1.3553307	-2.8367020
H	0.3468500	0.5676629	-2.8306310
C	4.0933562	1.8081810	-0.5521276
H	4.8629821	2.5531803	-0.3910114
C	1.8068227	1.2767158	-4.2002291
H	1.0867966	1.4172106	-5.0105631
H	2.2948466	0.3105677	-4.3395962
H	2.5695596	2.0535311	-4.2889025
C	4.1198603	0.6133861	0.1454048
H	4.9191357	0.4281604	0.8523821
C	0.3717087	2.6942724	-2.6755074

H	-0.4019901	2.8019434	-3.4388351
H	1.0588468	3.5361129	-2.7829685
H	-0.1012824	2.7739649	-1.6990416
C	3.1289591	-0.3521519	-0.0314623
C	3.2283432	-1.6462598	0.7579859
H	2.3958407	-2.2707250	0.4561170

S5.2.3 Molecule 1 radical

Ge	-2.4746646	-0.3426325	3.2375823
C	-1.9007887	-3.3261387	3.0911733
H	-2.4961978	-3.3523313	3.9959513
N	-1.7146069	-2.1146124	2.5395137
Cl	-4.5128366	-0.6618061	2.2289802
N	-1.4720404	0.2922029	1.6081958
C	-1.3780024	-4.4707753	2.5413488
H	-1.5535532	-5.4262905	3.0138146
C	-0.9852589	-1.9873807	1.3749757
C	-0.4250332	-3.1376046	0.7755459
H	0.1477108	-3.0267773	-0.1360315
C	-0.6192625	-4.3654977	1.3513953
H	-0.1978302	-5.2531814	0.8976295
C	-0.8729658	-0.6725670	0.9031883
H	-0.3107811	-0.4336483	0.0087061
C	0.4000043	2.0530209	2.9793260
H	0.2573733	0.9785668	3.0991493
C	-1.3997644	1.6578414	1.1937102
C	1.8778837	2.2689980	2.6207123
H	2.5224903	1.8603545	3.4025862
H	2.1132582	3.3304881	2.5168097
H	2.1297189	1.7779031	1.6786065

C	-0.4876123	3.8649557	1.4714658
H	0.1802638	4.5515991	1.9767146
C	0.0515092	2.7150070	4.3200216
H	0.6924941	2.3281254	5.1158690
H	-0.9867013	2.5211230	4.5951742
H	0.1904328	3.7975773	4.2739675
C	-0.5201193	2.5278643	1.8651411
C	-4.6144268	1.7061935	-0.5867326
H	-5.2765623	0.9821359	-1.0663983
H	-4.7125769	2.6538427	-1.1214615
H	-4.9612562	1.8475810	0.4369597
C	-2.2224571	2.1102652	0.1441518
C	-2.1395584	3.4543300	-0.2184449
H	-2.7588522	3.8230244	-1.0264500
C	-1.2874790	4.3283412	0.4386563
H	-1.2457439	5.3701010	0.1448035
C	-2.6842434	0.9521028	-2.0430893
H	-3.3453846	0.2521977	-2.5595096
H	-1.6732280	0.5386503	-2.0581849
H	-2.6693578	1.8843408	-2.6132083
C	-3.1706507	1.1871664	-0.6046278
H	-3.1818361	0.2254353	-0.0961331

S5.2.4 Transition state

Ge	-3.4725406	-0.8893694	0.7673540
C	-2.1098917	-3.2845626	2.0655728
H	-3.1302648	-3.6416533	2.1157483
N	-1.9300600	-2.0831105	1.4956931
Cl	-3.8076611	-2.4210113	-0.9986014
Ge	3.4706839	-0.8954255	-0.7671006

N	-1.9322526	0.1543956	0.2384201
C	-1.0478039	-4.0234595	2.5387184
H	-1.2199534	-4.9906195	2.9899205
Cl	3.8024634	-2.4284829	0.9983372
C	-0.6997646	-1.5557847	1.3565199
C	0.4115315	-2.2593262	1.8140171
H	1.4015667	-1.8604034	1.6717147
N	1.9320612	0.1509732	-0.2387442
C	0.2378099	-3.4957404	2.4037852
H	1.1041998	-4.0492847	2.7422506
N	1.9265054	-2.0863882	-1.4962545
C	-0.6378842	-0.2450186	0.6703694
H	-0.1308940	0.4972270	1.2908199
C	-1.9834175	2.3292078	2.2520371
H	-1.6749480	1.2978333	2.4206697
C	-2.1200387	1.5098653	-0.1855109
C	-0.9589972	3.2373856	2.9416044
H	-0.8360676	2.9420672	3.9856790
H	-1.2784309	4.2815517	2.9345937
H	0.0129647	3.1814167	2.4540252
C	-2.2419804	3.8747696	0.2967027
H	-2.2042969	4.6927848	1.0042990
C	-3.3711045	2.4889698	2.8961360
H	-3.3207888	2.2825365	3.9682128
H	-4.0991330	1.8088477	2.4502757
H	-3.7412885	3.5087006	2.7640467
C	-2.0779682	2.5683207	0.7520182
C	-4.0307687	0.5912030	-3.0518376
H	-4.1570449	-0.2545983	-3.7306947
H	-4.3288816	1.5020210	-3.5772749

H	-4.7123154	0.4440620	-2.2130359
C	-2.4079743	1.7813165	-1.5413068
C	-2.5936600	3.1048139	-1.9406554
H	-2.8154412	3.3179174	-2.9791577
C	-2.4892095	4.1493402	-1.0391575
H	-2.6182809	5.1725355	-1.3704236
C	-1.6127069	0.8104494	-3.7580212
H	-1.7484974	-0.0289387	-4.4435984
H	-0.5708178	0.8133642	-3.4338195
H	-1.7838144	1.7307777	-4.3202005
C	-2.5753339	0.6773194	-2.5712149
H	-2.3557855	-0.2617953	-2.0756188
C	1.0413390	-4.0257597	-2.5386232
H	1.2120880	-4.9930655	-2.9900414
C	2.1046036	-3.2879977	-2.0663552
H	3.1245187	-3.6463071	-2.1171684
C	-0.2436132	-3.4967579	-2.4024753
H	-1.1108776	-4.0494033	-2.7401683
C	-0.4155546	-2.2601628	-1.8125661
H	-1.4051179	-1.8603578	-1.6692994
C	0.6969014	-1.5576649	-1.3562500
C	0.6370003	-0.2467230	-0.6702118
H	0.1311600	0.4960539	-1.2909945
C	2.1216063	1.5060968	0.1855727
C	4.0329752	0.5853962	3.0514563
H	4.1588634	-0.2608412	3.7298438
H	4.3313206	1.4957891	3.5774800
H	4.7145944	0.4385562	2.2126461
C	2.0800462	2.5650008	-0.7514902
C	1.6147363	0.8049225	3.7572682

H	1.7502386	-0.0347280	4.4425814
H	0.5729251	0.8080963	3.4327842
H	1.7857952	1.7250526	4.3197785
C	2.2449861	3.8711475	-0.2956373
H	2.2077752	4.6895339	-1.0028154
C	1.9858969	2.3264935	-2.2516206
H	1.6750174	1.2959444	-2.4208228
C	2.4928560	4.1449396	1.0402600
H	2.6225227	5.1679104	1.3719782
C	3.3746025	2.4830563	-2.8943596
H	3.3248983	2.2771249	-3.9665634
H	4.1005200	1.8010336	-2.4479753
H	3.7471010	3.5018532	-2.7614886
C	2.5972376	3.0999340	1.9411748
H	2.8194772	3.3124440	2.9797014
C	0.9644702	3.2375021	-2.9418750
H	0.8415727	2.9425605	-3.9860561
H	1.2867944	4.2807714	-2.9346124
H	-0.0080402	3.1841437	-2.4550729
C	2.4105747	1.7767285	1.5413053
C	2.5776581	0.6721774	2.5706356
H	2.3581578	-0.2666334	2.0744728

S5.3 Harmonic frequencies

Harmonic frequencies calculated at the B3LYP/def2-TZVP level.

S5.3.1 Molecule 2

# mode	symmetry	wave number	IR intensity
#		cm**(-1)	km/mol
1		0.00	0.00000

2		0.00	0.00000
3		0.00	0.00000
4		0.00	0.00000
5		0.00	0.00000
6		0.00	0.00000
7	a	22.25	0.09105
8	a	32.57	0.02591
9	a	40.16	0.02783
10	a	46.80	0.00999
11	a	50.01	0.00096
12	a	96.24	0.38914
13	a	122.74	0.01154
14	a	127.11	0.00054
15	a	129.50	0.10914
16	a	161.07	1.55105
17	a	206.26	0.60970
18	a	226.36	0.14284
19	a	229.60	1.23847
20	a	234.58	0.45547
21	a	240.50	0.02477
22	a	245.05	0.15680
23	a	260.90	1.15791
24	a	267.81	0.56745
25	a	290.38	0.38530
26	a	296.30	0.33025
27	a	316.63	0.00202
28	a	359.08	1.71358
29	a	371.48	8.46460
30	a	417.97	4.60415
31	a	425.07	14.50581

32	a	442.29	0.28697
33	a	466.38	3.74538
34	a	503.62	3.05500
35	a	540.68	7.11166
36	a	568.67	3.12445
37	a	569.26	5.27519
38	a	610.94	4.13699
39	a	624.65	1.38875
40	a	635.39	5.76288
41	a	645.20	0.03582
42	a	671.45	3.20321
43	a	702.13	2.27357
44	a	723.90	0.62292
45	a	741.03	18.31689
46	a	780.45	46.15554
47	a	782.91	31.24423
48	a	812.35	2.17978
49	a	833.46	4.59561
50	a	835.12	5.57982
51	a	843.45	0.63574
52	a	889.21	0.15368
53	a	920.13	0.02867
54	a	933.25	0.23277
55	a	934.68	0.19038
56	a	940.52	4.00839
57	a	944.28	8.54358
58	a	949.86	0.13958
59	a	961.12	0.18374
60	a	963.60	0.03571
61	a	967.08	0.01042

62	a	969.51	0.93355
63	a	1013.32	14.66143
64	a	1029.89	0.67608
65	a	1065.26	1.55435
66	a	1077.09	14.75783
67	a	1119.29	1.08801
68	a	1121.12	0.22014
69	a	1125.55	17.55141
70	a	1149.46	4.57905
71	a	1173.48	3.43156
72	a	1176.18	15.86547
73	a	1187.04	0.94302
74	a	1188.54	2.19680
75	a	1203.49	5.18022
76	a	1225.47	55.20482
77	a	1254.12	4.58799
78	a	1276.90	25.35835
79	a	1277.36	6.10253
80	a	1284.47	1.07543
81	a	1309.10	26.36643
82	a	1341.42	98.97803
83	a	1352.08	3.29103
84	a	1352.70	11.06205
85	a	1360.06	81.24232
86	a	1382.60	0.94556
87	a	1399.00	8.65017
88	a	1400.05	9.35720
89	a	1420.08	4.73019
90	a	1420.79	5.00616
91	a	1422.05	10.94822

92	a	1476.41	26.58728
93	a	1483.04	11.60377
94	a	1486.09	0.22284
95	a	1486.66	0.45306
96	a	1489.99	2.38833
97	a	1490.64	3.62958
98	a	1494.77	4.31621
99	a	1501.84	6.30710
100	a	1502.52	4.22691
101	a	1508.05	18.32905
102	a	1511.01	4.54501
103	a	1544.25	51.91374
104	a	1573.87	10.74100
105	a	1618.46	4.68470
106	a	1629.09	0.24860
107	a	1657.18	18.94475
108	a	3022.60	18.78880
109	a	3022.79	29.20812
110	a	3026.73	61.61971
111	a	3027.04	11.26158
112	a	3066.42	1.90750
113	a	3066.82	6.52850
114	a	3080.78	0.11868
115	a	3080.80	0.33816
116	a	3090.36	91.93663
117	a	3090.71	13.98535
118	a	3090.97	11.10773
119	a	3091.50	15.88607
120	a	3098.74	2.91128
121	a	3099.41	91.64402

122	a	3160.92	0.30817
123	a	3172.41	18.62276
124	a	3173.89	1.98803
125	a	3177.47	1.31046
126	a	3185.25	26.95551
127	a	3191.88	14.65203
128	a	3206.66	10.76660
129	a	3208.41	7.67765

S5.3.2 Molecule 1 radical

# mode	symmetry	wave number	IR intensity
#		cm**(-1)	km/mol
1		0.00	0.00000
2		0.00	0.00000
3		0.00	0.00000
4		0.00	0.00000
5		0.00	0.00000
6		0.00	0.00000
7	a	18.59	0.77431
8	a	40.24	0.02334
9	a	46.92	0.10898
10	a	52.63	0.04781
11	a	60.04	0.46281
12	a	71.21	0.29357
13	a	93.80	1.34785
14	a	96.96	0.22952
15	a	126.28	0.03262
16	a	128.61	1.12426
17	a	134.87	0.07471
18	a	180.16	0.53944

19	a	202.52	6.72703
20	a	206.84	3.31828
21	a	236.52	0.19178
22	a	243.00	1.08798
23	a	248.22	0.13078
24	a	255.01	0.01591
25	a	255.84	0.15178
26	a	278.56	1.38942
27	a	286.64	0.08332
28	a	296.75	9.18301
29	a	309.83	56.69874
30	a	324.54	1.53352
31	a	328.21	5.96978
32	a	351.63	19.31386
33	a	399.70	5.06876
34	a	423.39	11.14431
35	a	454.57	0.15986
36	a	456.05	6.16194
37	a	490.53	0.46019
38	a	517.08	12.50623
39	a	552.09	0.41867
40	a	563.79	7.27516
41	a	595.27	0.12135
42	a	612.66	1.05674
43	a	641.52	3.61068
44	a	649.61	0.73844
45	a	666.74	6.00602
46	a	721.20	0.42644
47	a	722.27	0.71786
48	a	745.61	37.54587

49	a	782.93	27.31437
50	a	809.72	20.99467
51	a	818.35	0.36197
52	a	836.82	11.04739
53	a	850.54	0.13896
54	a	858.01	5.88414
55	a	894.71	0.19598
56	a	923.94	0.07794
57	a	931.70	16.54845
58	a	946.28	0.16783
59	a	948.88	2.06182
60	a	949.63	7.59599
61	a	961.68	0.15518
62	a	966.77	0.50678
63	a	972.52	0.51063
64	a	976.30	0.41193
65	a	979.79	0.04161
66	a	1025.16	14.73145
67	a	1038.87	15.24083
68	a	1070.72	1.64072
69	a	1085.43	10.41590
70	a	1124.72	1.56126
71	a	1126.59	0.89985
72	a	1131.61	17.50381
73	a	1149.58	6.01118
74	a	1179.81	0.61063
75	a	1188.69	19.39560
76	a	1195.22	3.12769
77	a	1199.39	17.53939
78	a	1212.25	4.18621

79	a	1259.78	36.49196
80	a	1260.89	5.44427
81	a	1280.78	4.30439
82	a	1289.36	1.04796
83	a	1304.45	25.27114
84	a	1327.04	21.80792
85	a	1335.18	92.12446
86	a	1354.23	12.22250
87	a	1358.46	10.50533
88	a	1367.12	139.36014
89	a	1394.05	10.62856
90	a	1405.87	3.63761
91	a	1406.14	12.49837
92	a	1427.35	5.10986
93	a	1427.66	4.65186
94	a	1448.07	119.99292
95	a	1481.16	50.89843
96	a	1485.77	0.60135
97	a	1486.80	0.52401
98	a	1492.76	3.84806
99	a	1493.03	2.07098
100	a	1496.64	7.74548
101	a	1497.49	69.26596
102	a	1504.08	4.20681
103	a	1504.67	4.63502
104	a	1510.19	32.94568
105	a	1513.55	2.17797
106	a	1550.86	39.48388
107	a	1575.12	86.36938
108	a	1619.14	23.88737

109	a	1619.50	6.77155
110	a	1631.03	0.22320
111	a	3019.42	27.36567
112	a	3022.03	24.45976
113	a	3025.64	37.19091
114	a	3028.75	31.27555
115	a	3057.30	2.43997
116	a	3076.55	23.97784
117	a	3082.05	2.36422
118	a	3082.34	0.38673
119	a	3084.48	40.97563
120	a	3089.33	41.99771
121	a	3092.82	31.81869
122	a	3097.88	48.82895
123	a	3108.24	21.31281
124	a	115.57	21.93262
125	a	3160.85	0.53432
126	a	3173.90	18.12843
127	a	3174.01	11.32765
128	a	3175.54	2.91062
129	a	3179.29	0.79076
130	a	3186.32	27.33258
131	a	3194.80	9.90633
132	a	3213.19	4.97971

S5.3.3 Molecule 1

The lowest eigenvalues of the Hessian of the dimer (1).

# mode	symmetry	wave number
1	a	14.92
2	a	36.82

3	a	38.52

S5.3.4 Transition state

The lowest eigenvalues of the Hessian of the transition state.

# mode	symmetry	wave number
1	a	-57.36
2	a	30.12
3	a	37.20

S5.4 NMR shieldings

Nuclear magnetic shieldings calculated at the B3LYP/def2-TZVP level.

S5.4.1 Molecule 2

#NO.	TYPE	ISOTROPIC
1	ge	1137.61495721
2	n	-24.52778361
3	n	-11.37021209
4	c	41.40525228
5	c	59.45373796
6	h	25.04140882
7	c	40.25706811
8	h	23.20325454
9	c	57.97317978
10	h	25.33542020
11	c	53.16516082
12	h	24.55151793
13	c	34.08042765
14	c	29.78977492
15	c	54.40698007

16	h	24.48861420
17	c	51.31984330
18	h	24.37109306
19	c	55.75796043
20	h	24.49482053
21	c	29.58591557
22	c	149.41697532
23	h	29.36308295
24	c	150.07745345
25	h	29.33255013
26	c	156.17391515
27	h	30.76185737
28	h	30.86313342
29	h	30.76298021
30	c	156.87478519
31	h	30.69235675
32	h	30.82910053
33	h	30.84844393
34	c	156.46511697
35	h	30.65222654
36	h	30.83697322
37	h	30.81688241
38	c	155.68293556
39	h	30.84810628
40	h	30.76316527
41	h	30.75684905
42	c	74.15608040
43	h	25.92576116

S5.5 NICS values

The reported NICS values are calculated at the B3LYP/def2-TZVP level. The label NICS(-1) means that the dummy atom was placed 1 Å below the ring, while for NICS(1) it was placed 1 Å above the ring. Ring 1 is the phenyl ring oriented perpendicular to the germylene heterocycles. Ring 2 is the Ge containing five-membered ring and ring 3 labels the neighboring six-membered pyridinyl ring. Negative NICS values assign an aromatic character of the respective ring.

	Ring 1	Ring 2	Ring 3
NICS(0)	-7.9	-10.2	0.4
NICS(1)	-9.1	-9.0	-2.4
NICS(-1)	-9.1	-8.8	-2.2
NICS(1)zz	-7.5	-9.9	-3.6
NICS(-1)zz	-7.9	-11.2	-2.4

S6 References

S1 H. P. Nayek, N. Arleth, I. Trapp, M. Löble, P. Oña-Burgos, M. Kuzdrowska, Y. Lan, A. K. Powell, F. Breher and P. W. Roesky, *Chem. Eur. J.*, 2011, **17**, 10814-10819.

S2 (*a*) M. Driess, S. Yao, M. Brym and C. van. Wüllen, *Angew. Chem. Int. Ed.*, 2006, **45**, 4349-4352; *Angew. Chem.*, 2006, **118**, 4455-4458; (*b*) W. Wang, S. Inoue, S. Yao and M. Driess, *Organometallics*, 2011, **30**, 6490−6494.

S3 (*a*) T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615-619; (*b*) T. Kottke, R. J. Lagow and D. Stalke, *J. Appl. Crystallogr.*, 1996, **29**, 465-468; (*c*) D. Stalke, *Chem. Soc. Rev.*, 1998, **27**, 171-178.

S4 T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr*., 2009, **42**, 885-891.

S5 SAINT v7.68A in Bruker APEX2 v2012.2-0, Bruker AXS Inst. Inc., Madison, USA, 2012.

S6 G. M. Sheldrick, SADABS-2012/1, Universität Göttingen, Germany, 2012.

S7 G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112-122.

S8 C. B. Huebschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.*, 2011, **44**, 1281-1284.

S9 P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider and M. R. Sawaya, in Crystal StructureRefinement - A Crystallographer's Guide to SHELXL, IUCr Texts on Crystallography, Vol. 8
(Ed.: Müller P.), Oxford University Press, Oxford, UK, 2006.

S10 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

S11 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

S12 P. Deglmann and F. Furche, *Chem. Phys. Letters*, 2002, **362**, 511 – 518.

S13 S. Grimme and J. Antony and S. Ehrlich and H. Krieg, *J. Chem. Phys*, 2010, **132**, 154104-1-15104-19.

S14 P. von Ragué Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317-6318.

S15 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Letters*, 1989, **162**, 165-169.

S16 (*a*) J. Jusélius, D. Sundholm and J. Gauss, *J. Chem. Phys.*, 2004, **121**, 3952-3963.; (*b*) S. Taubert, D. Sundholm and J. Jusélius, *J. Chem. Phys.*, 2011, **134**, 054123:1-12; (*c*) H. Fliegl, S. Taubert, O. Lehtonen and D. Sundholm, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20500-20518.

S17 (*a*) F. London, *J. Phys. Radium*, 1937, **8**, 397-409; (*b*) H. F. Hameka, *Mol. Phys.*, 1958, **1**, 203-215; (*c*) R. Ditchfield, *Mol. Phys.*,1974, **27**, 789-807; (*d*) K. Wolinski and J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251-8260.

S18 (*a*) M. P. Johansson, J. Jusélius and D. Sundholm, *Angew. Chem. Int. Ed.*, 2005, **44**, 1843-1846; (b)

J. Jusélius and D. Sundholm, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6630 – 6634; (*c*) Y. C. Lin, J. Jusélius, D. Sundholm and J. Gauss, *J. Chem. Phys.*, 2005, **122**, 214308:1-9; (*d*) S. Taubert, D. Sundholm and F. Pichierri, *J. Org. Chem.* 2009, **74**, 6495-6502; (*e*) H. Fliegl, D. Sundholm, S. Taubert, J. Jusélius, W. Klopper, *J. Phys. Chem. A*, 2009, **113**, 8668-8676; (*f*) H. Fliegl, O. Lehtonen, M. Patzschke, D. Sundholm, Y. C. Lin, *Theoret. Chem. Acc.*, 2011, **129**, 701-713; (*g*) D. Sundholm, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9025-9028.

S19 (*a*) M. Kaipio, M. Patzschke, H. Fliegl, F. Pichierri and D. Sundholm, *J. Phys. Chem. A*, 2012, **116**, 10257-10268; (*b*) H. Fliegl, D. Sundholm, S. Taubert and F. Pichierri, *J. Phys. Chem. A*, 2010, **114**, 7153-7161; (c) H. Fliegl, D. Sundholm and F. Pichierri, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20659-20665; (d) H. Fliegl, N. Özcan, R. Mera-Adasme, F. Pichierri, J. Jusélius and D. Sundholm, *Mol. Phys.*, 2013, **111**, 1364-1372.

S20 JMOL: an open-source Java viewer for chemical structures in 3D., http://www.jmol.org.

S21 GIMP: GNU Image Manipulation Program, http://www.gimp.org.