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A phenyl-substituted germole dianion and its reaction with hafnocene dichloride

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Methods: All reactions were carried out under inert atmosphere using standard Schlenk techniques or a *MBraun* glove box. As inert gas, argon 5.0 or nitrogen 5.0 were used. All glassware was stored at 120°C. Before use, it was evacuated and filled with inert gas three times.

All solvents were dried and stored over molecular sieves (400 pm) or freshly distilled prior to use. Diethyl ether, pentane, hexane, benzene and toluene were dried over sodium/potassium alloys. Tetrahydrofuran was pre-dried over KOH and then dried over sodium/potassium alloy. All other chemicals were prepared by literature procedures or obtained from commercial suppliers and used as delivered.

NMR spectroscopy: All NMR spectra were recorded on Bruker Avance 500 and Bruker Avance III 500 spectrometers. The ^{1}H NMR spectra were calibrated using the residual proton signal of the solvent as internal reference. The central carbon signal of the solvent was used as internal reference for $^{13}C\{^{1}H\}$ NMR spectra. For the ^{29}Si NMR spectra, Me_2SiHCl (δ ^{29}Si = 11.1) was used as an external standard versus $SiMe_4$ (δ ^{29}Si = 0.0). All $^{29}Si\{^{1}H\}$ inverse gated NMR spectra were recorded with a relaxation delay D1 = 10 s. The $^{29}Si\{^{1}H\}$ INEPT NMR spectra were recorded with a combination of D3 = 0.0068 s and D4 = 0.0313 s to enhance the signal intensity caused by $SiMe_3$ groups. All other hetero nuclei NMR spectra were recorded with classical pulse sequences and with ^{1}H decoupling. Temperatures, solvents and spectrometer frequencies for each NMR spectrum can be taken from the experimental part.

Table S1 Internal references for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra.

Solvent	δ^{1}H [ppm]	δ^{13}C [ppm]
C_6D_6	7.16 (C_6D_5**H**)	128.060
$CDCl_3$	7.26 (C**H**Cl_3)	77.16

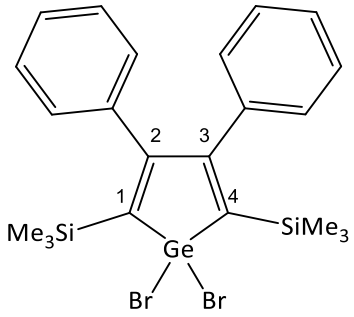
To describe the coupling patterns, common abbreviations (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet) were used. For the characterization of known compounds, the NMR

chemical shifts were compared to literature data. DEPT-135 NMR and 2D NMR experiments such as $^{1}H^{13}C$ HMQC, $^{1}H^{13}C$ HMBC, $^{1}H^{1}H$ COSY, $^{1}H^{29}Si$ HMQC and $^{1}H^{29}Si$ HMBC were used to assign the NMR signals for unknown compounds.

X-ray analyses: Single crystal X-ray analyses were carried out on a Bruker Apex 2 with Mo-Kα radiation. SHELXL-2014[S1] and Crystal Impact Diamond 4.2[S2] were used for solving, refining and visualizing the molecular structures.

Combustion analyses: For combustion analyses (C, H, N, S), an *Euro EA Element Analyzer* with *EuroVector* equipment was used. Inaccuracies of the measured values are due to formation and incomplete combustion of silicon or germanium carbide.

1,1-Dibromo-3,4-diphenyl-2,5-bis(trimethylsilyl)germacyclopentadiene 5[S3]



A solution of *n*-butyllithium (4.31 mmol) in *n*-hexane (2.7 mL) was added to a solution of bis(cyclopentadienyl)zirconium dichloride (600 mg, 2.05 mmol) in abs. *n*-hexane (20 mL) at -90°C. The mixture was stirred for 1 h at that temperature, and a solution of 1-phenyl-2-(trimethylsilyl)acetylene (751 mg, 4.309 mmol) in abs. *n*-hexane (2 mL) was added. After 12 h of stirring while warming to room temperature, $GeBr_4$ (804 mg, 2.05 mmol) dissolved in abs. hexane (2 mL) was added dropwise to the red brown suspension at -40°C, and this was stirred for 12 h while warming to room temperature. After filtration, the solvent was removed *in vacuo*, and the product was isolated by crystallization form hexane at -30°C as colorless solid. Crystals suitable for single crystal X-ray analysis were obtained by storage of a saturated solution of a mixture of hexane isomers at -30°C (yield: 773 mg, 1.33 mmol, 65%).

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ ^{1}H = 0.16 (s, 18 H, $Si(CH_3)_3$), 6.66 – 6.68 (m, 4 H, *o*-CH), 6.77 – 6.78 (m, 6 H, *m*-CH, *p*-CH).

^{13}C {^{1}H} NMR (125.7 MHz, C_6D_6, 298 K): δ ^{13}C = 0.7 (CH_3) ($Si(CH_3)_3$), 127.4 (*p*-CH), 127.6 (*m*-CH), 128.9 (*o*-CH), 138.6 (4°) (C1/4), 139.2 (4°) (*i*-CH), 162.8 (C2/3).

^{29}Si\{^{1}H\} INEPT NMR (99.3 MHZ, C_6D_6, 298 K): $\delta^{29}Si$ = -5.8.

HR/MS (70 eV, EI): calcd.: 579.9308 found: 579.9309

Due to the formation of germanium carbide, the elemental analysis did not give satisfactory results.

EA, % (calcd./found): C (45.47/45.84) H (4.86/5.68)

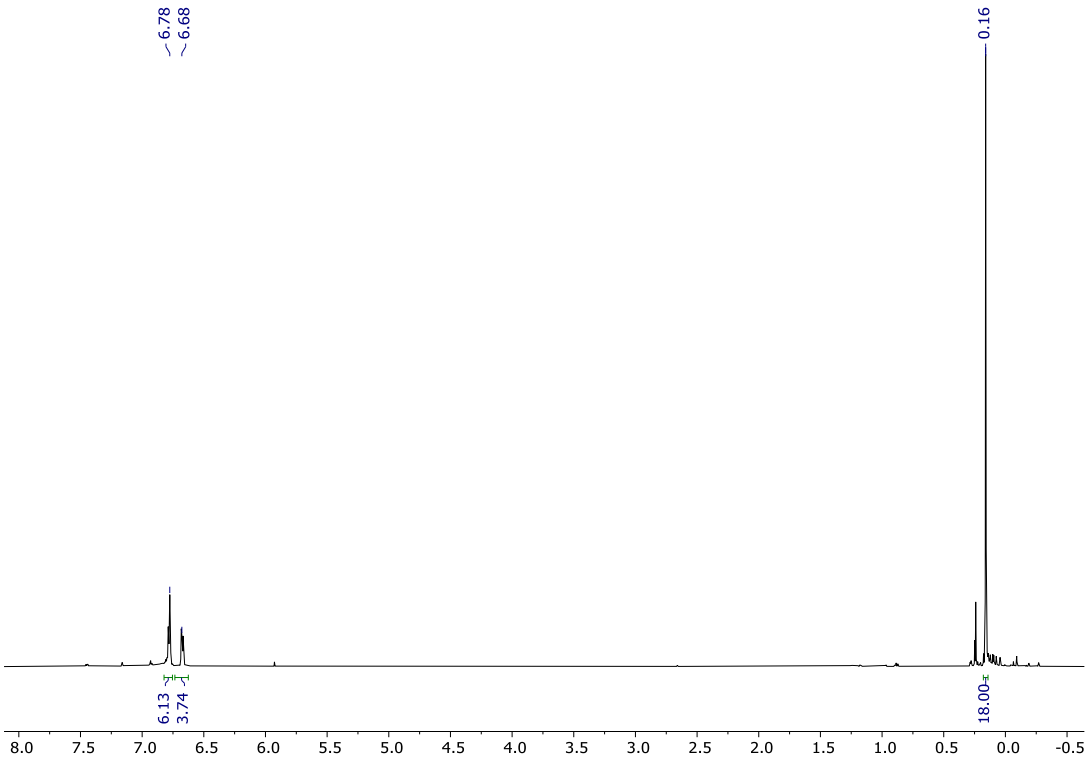


Figure S1. ^{1}H NMR spectrum of dibromide **5**.

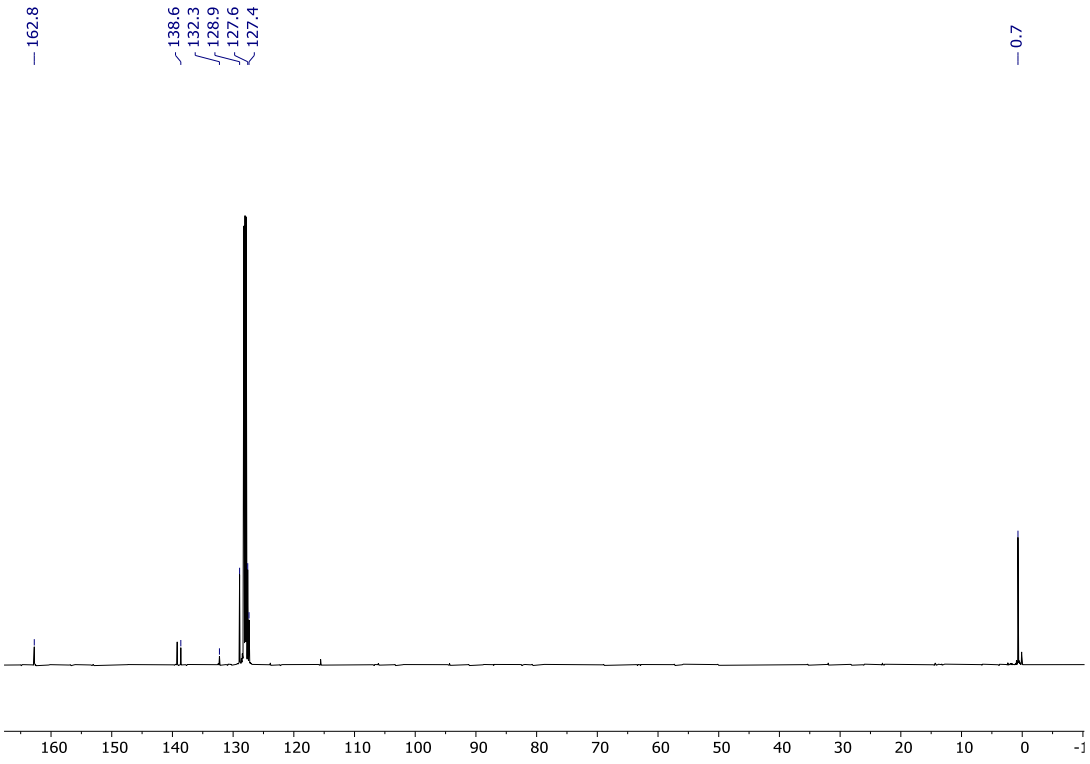


Figure S2. ^{13}C{^{1}H} NMR spectrum of dibromide **5**.

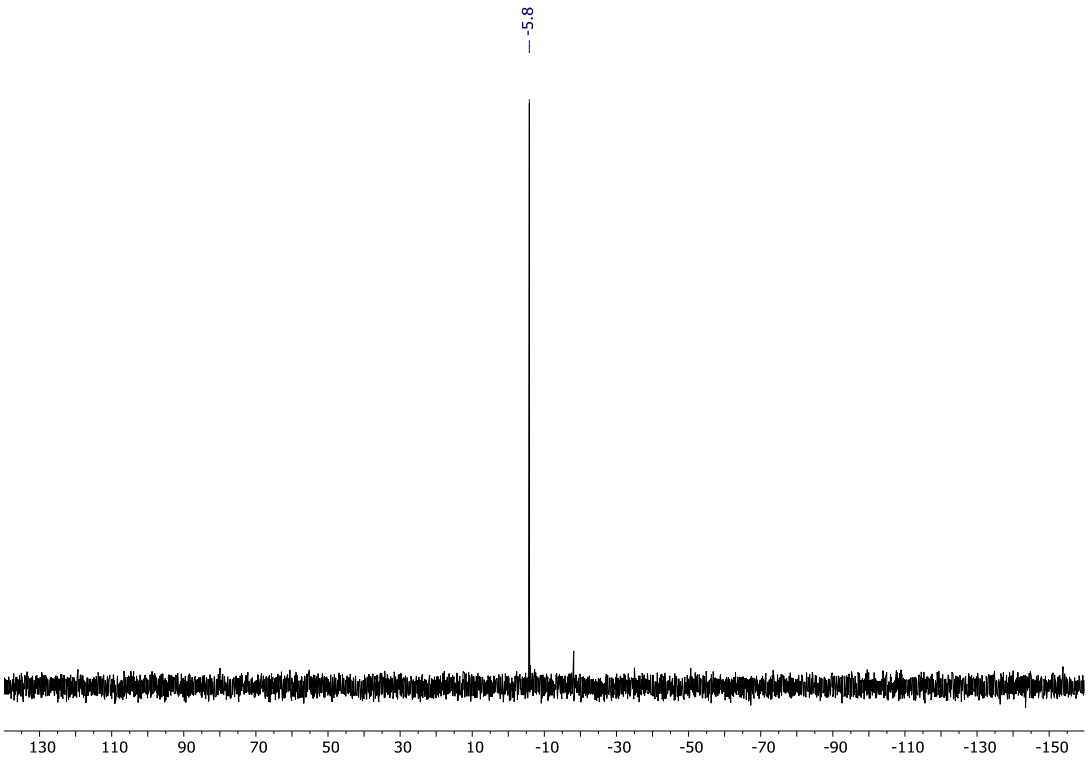
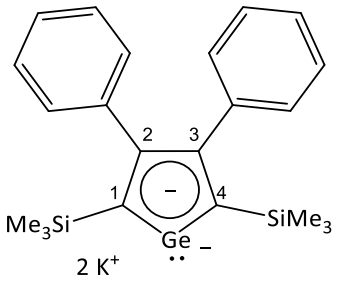


Figure S3. $^{29}Si\{^{1}H\}$ Inept NMR spectrum of dibromide **5**.

Dipotassium 3,4-diphenyl-2,5-bis(trimethylsilyl)germacyclopentadienediide 6[S3]



Potassium metal (134 mg, 3.44 mmol) was added to a solution of compound **5** (200 mg, 0.344 mmol) in abs. THF (6 mL). After 18 h stirring, insoluble materials were removed by filtration. The product was obtained quantitatively as a brown-yellow solution in THF. The crude material is suitable for further reactions. A few crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of THF at room temperature.

^{1}H NMR (500 MHz, C_6D_6/THF, 298 K): δ ^{1}H = 0.25 (s, 18 H, $Si(CH_3)_3$), 6.77 – 6.80 (m, 2 H, *p*-CH), 6.92 – 6.95 (m, 4 H, *m*-CH), 6.95 – 6.98 (m, 4 H, *o*-CH).
^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6/THF, 298 K): δ ^{13}C = 6.3 ($Si(CH_3)_3$), 121.6 (*p*-CH), 126.5 (*m*-CH), 130.8 (*o*-CH), 141.2 (C2/3), 151.1 (*i*-C), 163.0 (C1/4).
^{29}Si {^{1}H} INEPT NMR (99.3 MHZ, C_6D_6/THF, 298 K): δ ^{29}Si = -15.3.

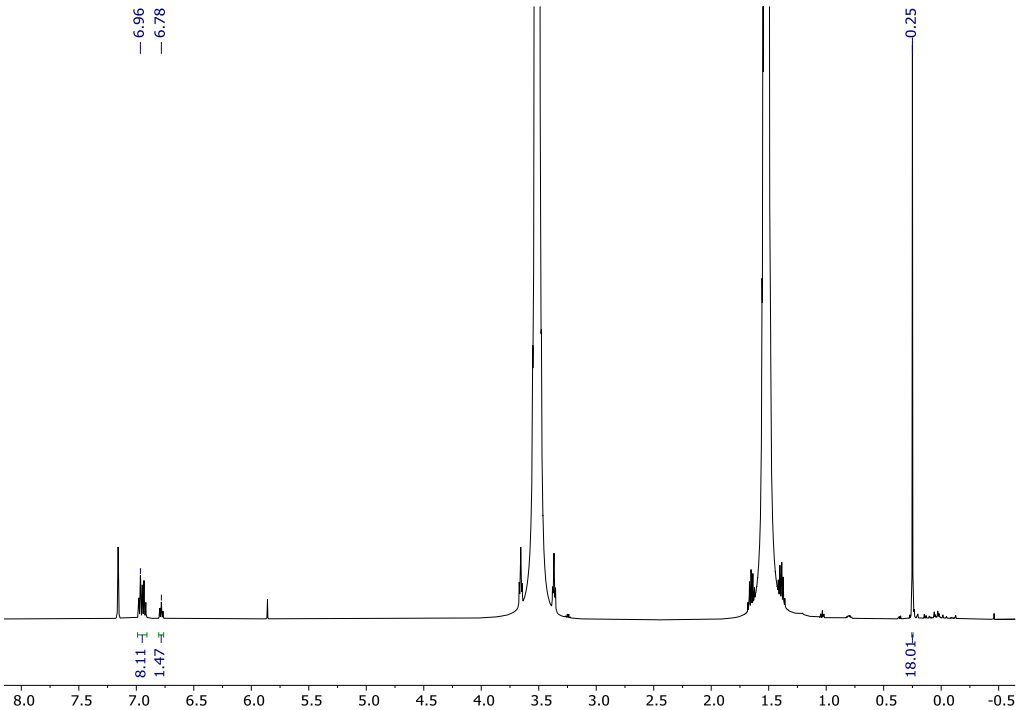


Figure S4. ^{1}H NMR spectrum of **6**.

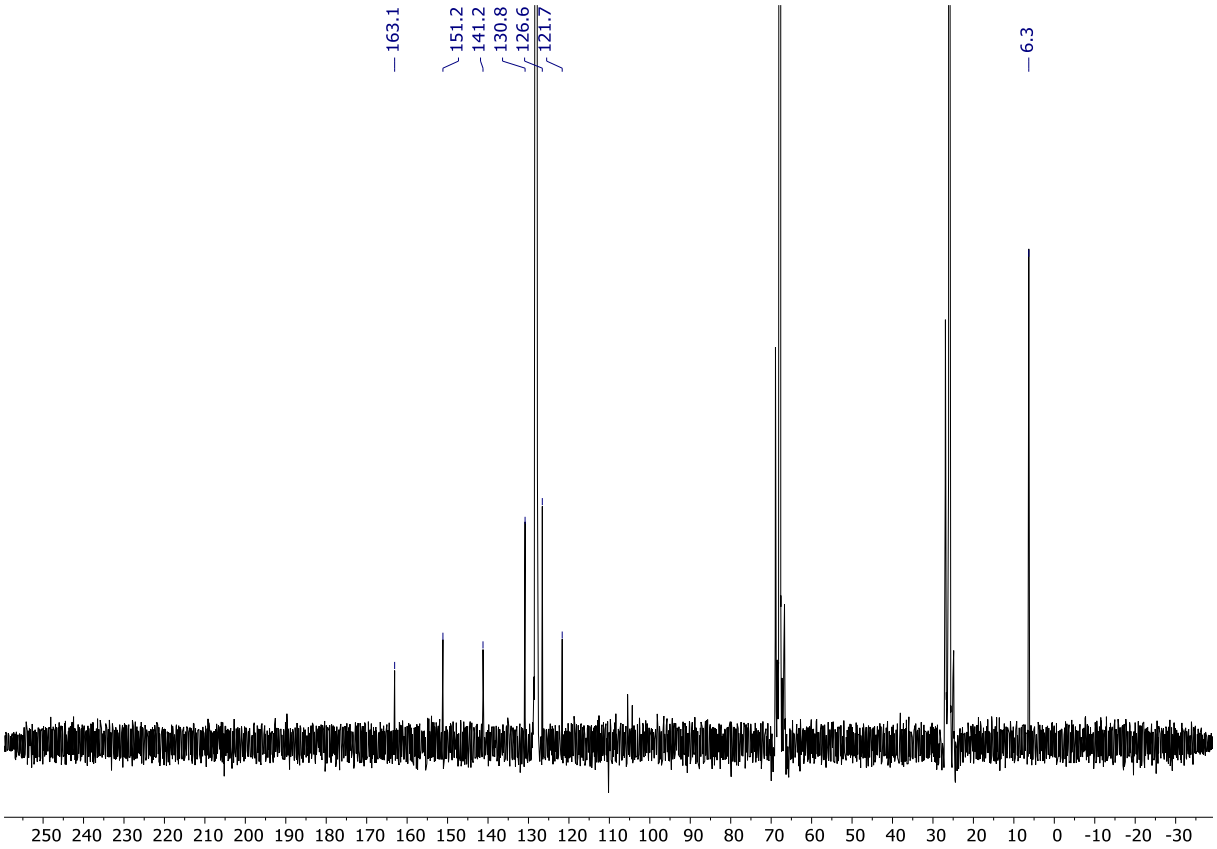


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

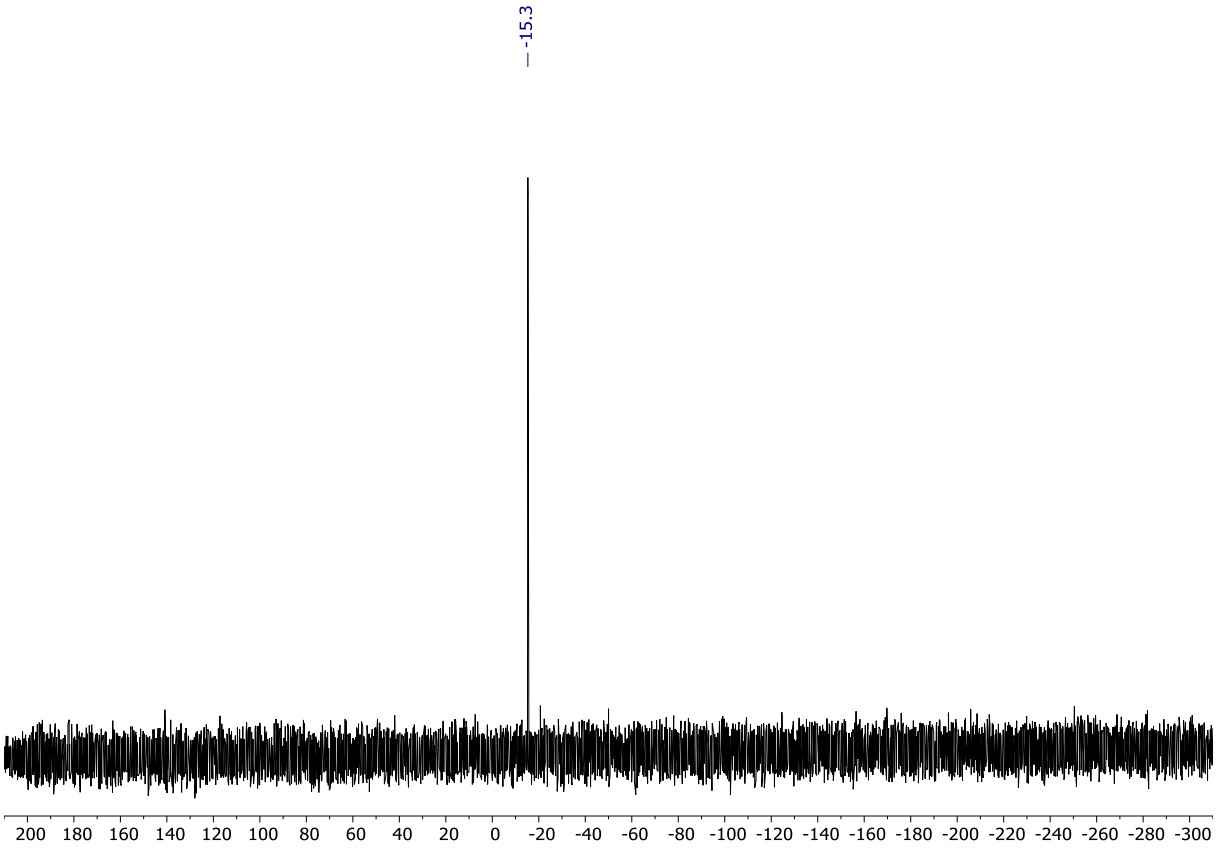
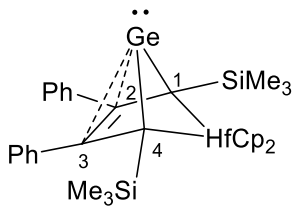


Figure S6. $^{29}Si\{^{1}H\}$ Inept NMR spectrum of compound **6**.

6-λ²-Germa-5-hafnocenabicyclo[2.1.1]hex-2-ene 7 [S4]



Bis(cyclopentadienyl)hafnium dichloride (170 mg, 0.45 mmol, 1.00 equiv.) dissolved in THF (2 mL) was added to a solution of freshly prepared dipotassium germacyclopentadienediide **6** (223 mg, 0.45 mmol, 1.00 equiv.) in THF (10 mL) at -80 °C. The red-brown solution was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under reduced pressure, the residue was dissolved in THF/*n*-pentane (4 mL/20 mL). After filtration, the solution was concentrated and was kept at -30 °C overnight to afford an orange solid of germylene **7** (yield: 237 mg, 0.32 mmol, 72%).

^{1}H NMR (499.9 MHz, 305.0 K, C_6D_6): δ^{1}H = -0.01 (s, 18H, $Si(CH_3)_3$), 5.72 (s, 5H, C_5H_5), 5.73 (s, 5H, C_5H_5), 6.79-7.02 (m, 10H, *Ar*-CH).

^{13}C{^{1}H} NMR (125.7 MHz, 305.0 K, C_6D_6): δ^{13}C = 4.3 ($Si(CH_3)_3$), 103.9 (C_5H_5), 104.5 (C_5H_5), 118.6 (C1/4), 126.8, 127.5, 129.3 (3x CH aryl), 141.5 (*ipso*-C aryl), 143.0 (C2/3).

^{29}Si{^{1}H} NMR (99.3 MHz, 305.0 K, C_6D_6): δ^{29}Si = -3.3 ($Si(CH_3)_3$).

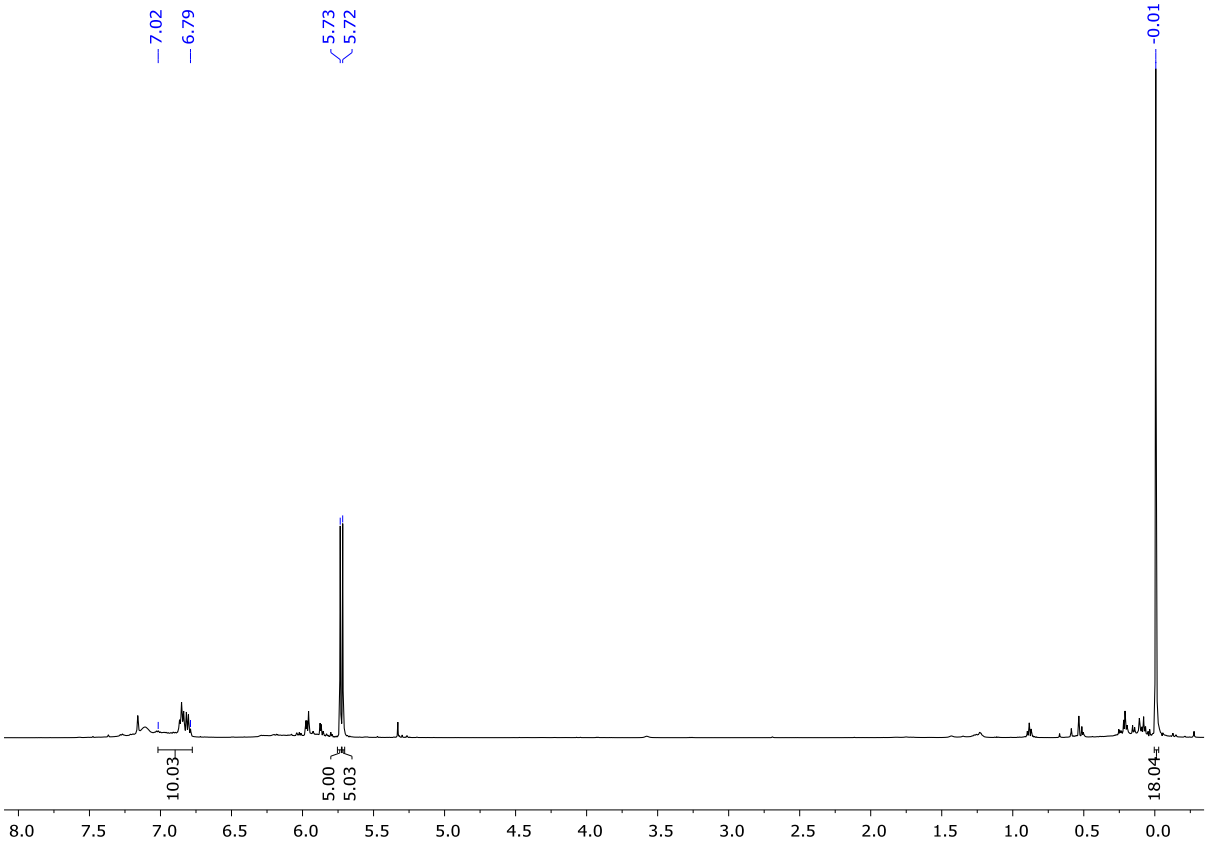


Figure S7. ^{1}H NMR spectrum of germylene **7**.

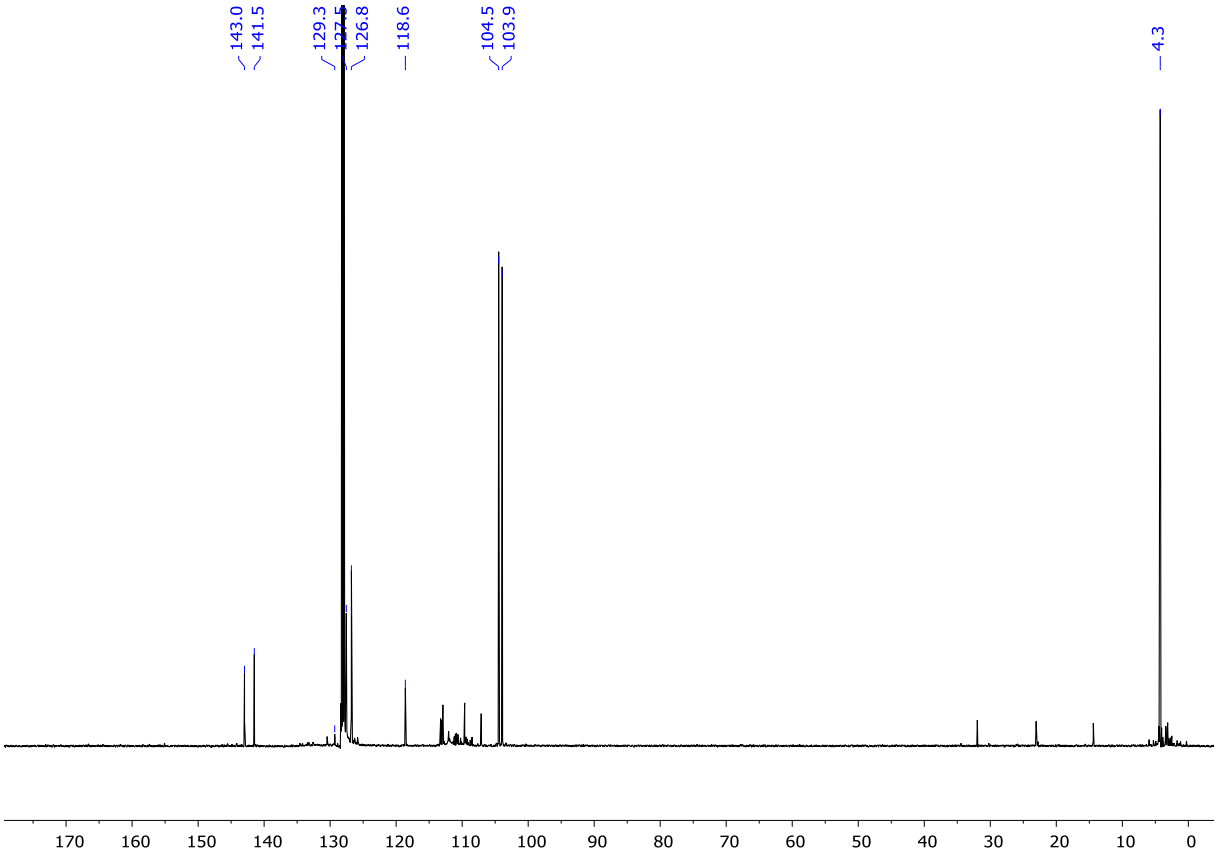


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of germylene **7**.

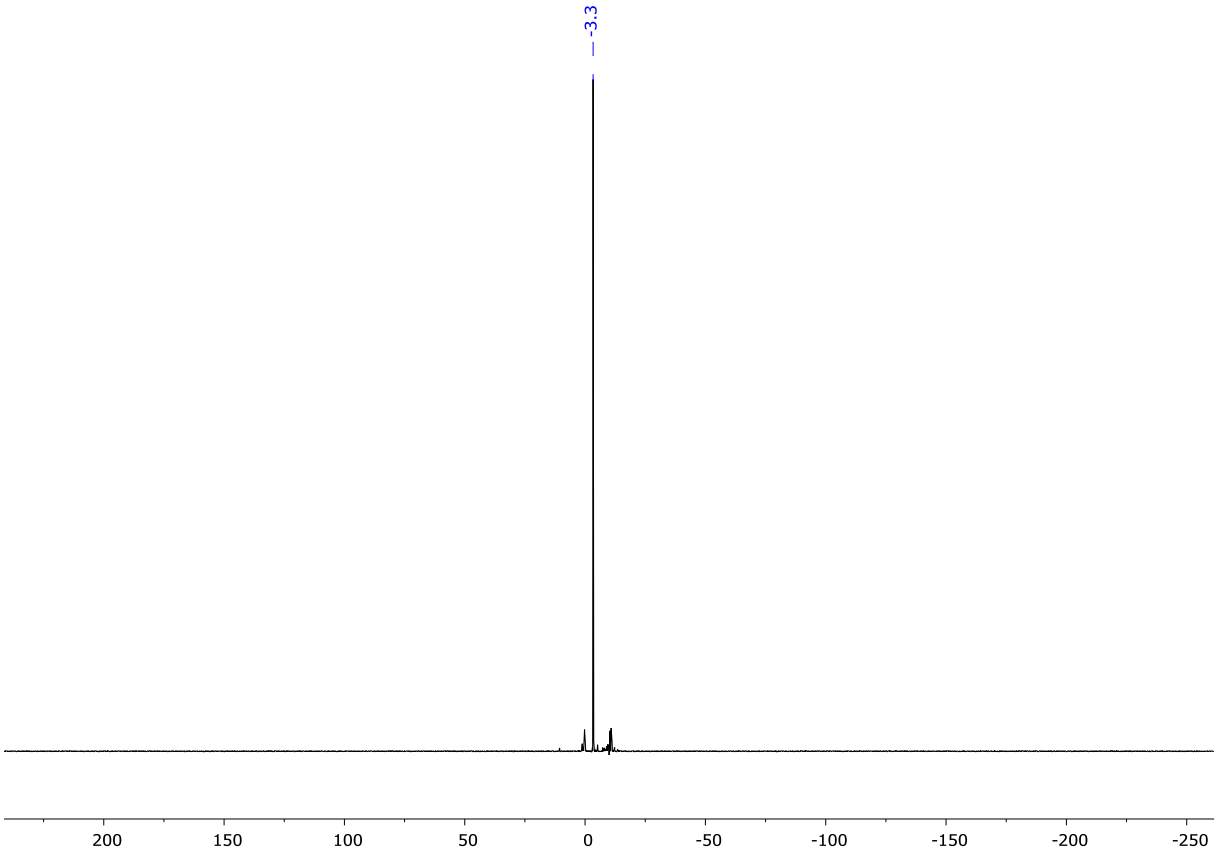
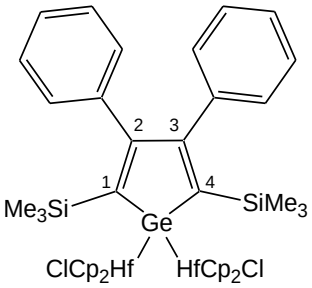


Figure S9. $^{29}Si\{^{1}H\}$ INEPT NMR spectrum of germylene **7**.

1,1-Bis[bis(cyclopentadienyl)chlorohafnium]-3,4-diphenyl-2,5-bis(trimethylsilyl)germacyclopentadiene 8



Bis(cyclopentadienyl)hafnium dichloride (239 mg, 0.630 mmol) dissolved in abs. THF (2 mL) was added to a solution of salt **6** (0.315 mmol) in abs. THF (5.5 mL) at 0°C. The dark brown reaction mixture was stirred for 12 h, and the solvent was removed *in vacuo*. At this point, the reaction was complete according to NMR spectroscopy. The residue was dissolved in abs. *n*-pentane (4 mL) and THF (1 mL), the insoluble components were removed by filtration, and the solution was stored at -30°C overnight to produce small amount of red crystals suitable for single crystal X-ray diffraction analysis (yield: 14 mg, 0.012 mmol, 2%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ^{1}H = 0.09 (s, 18 H, $Si(CH_3)_3$), 5.90 (br. s, 10 H, C_5H_5), 6.27 (br. s, 10 H, C_5H_5), 6.89 – 7.38 (m, 10 H, *Ar*-CH).

^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298 K): δ^{13}C = 4.2 ($Si(CH_3)_3$), 111.9 (br., C_5H_5), 112.2 (br., C_5H_5), 125.9 (*Ar*-CH), 127.3 (*Ar*-CH), 132.0 (br., *Ar*-CH), 146.4 (*i*-C), 166.6 (C2/3), 173.1 (C1/4).

^{29}Si{^{1}H} INEPT NMR (99.3 MHZ, $CDCl_3$, 298 K): δ^{29}Si = -10.4 ($Si(CH_3)_3$).

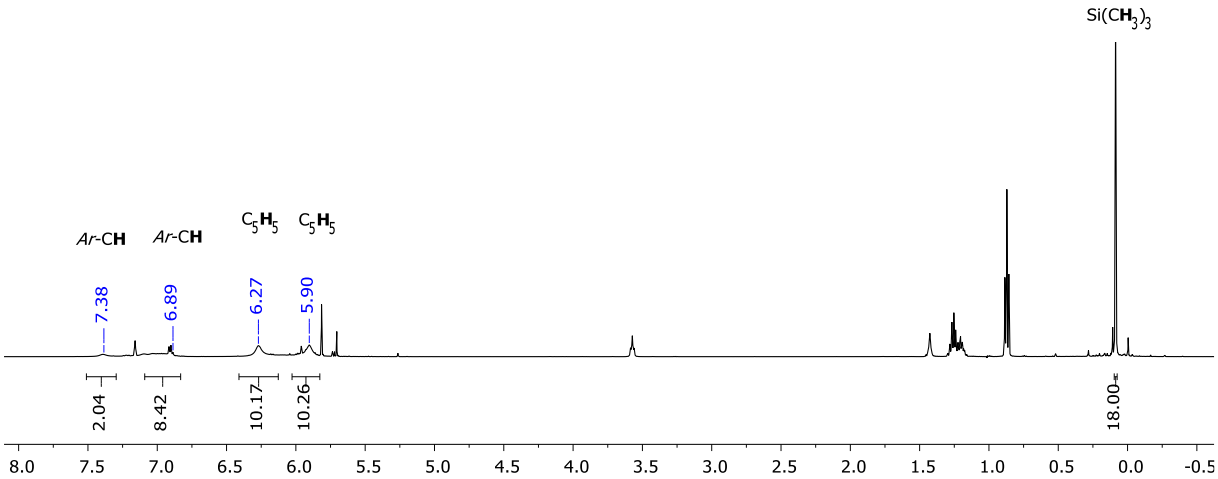


Figure S10. ^{1}H NMR spectrum of germole **8**.

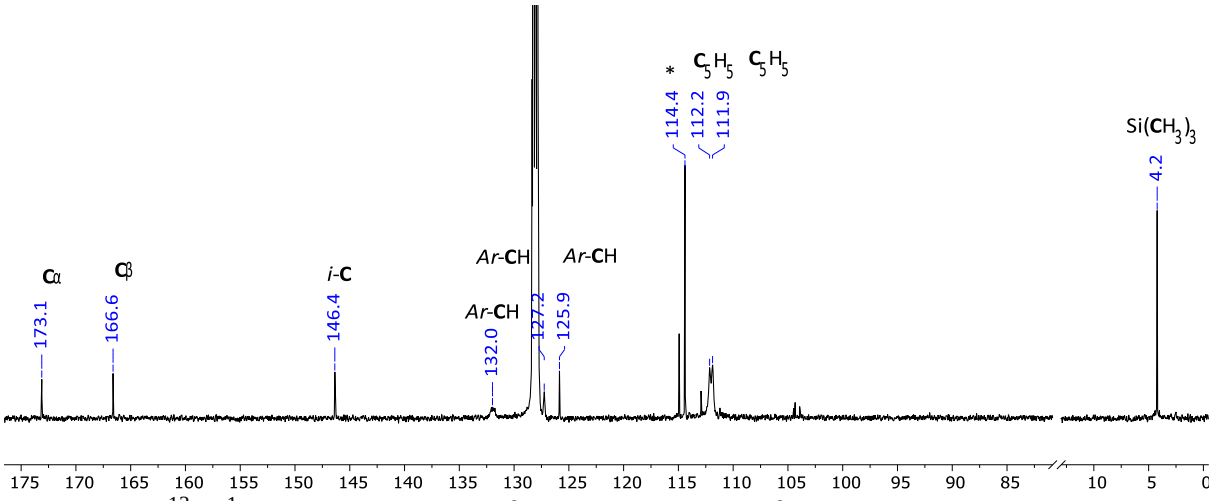


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of germole **8**. Signals from pentane and THF are not shown.

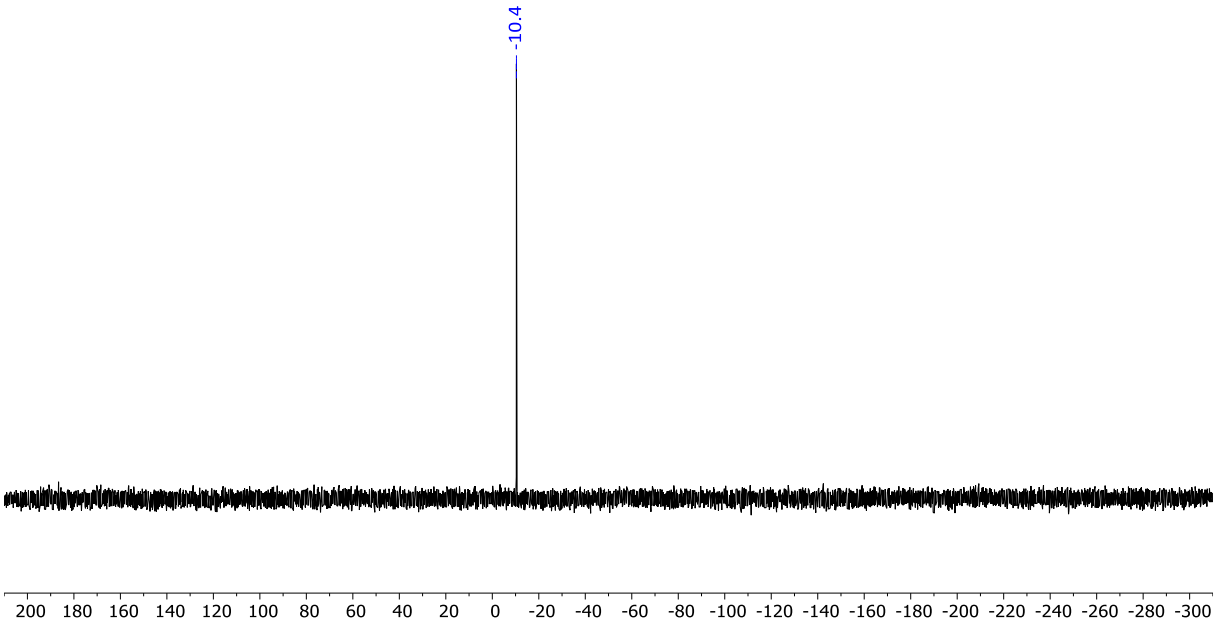
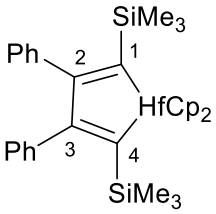


Figure S12. $^{29}Si\{^{1}H\}$ INEPT NMR spectrum of germole **8**.

1,1-Bis(cyclopentadienyl)-3,4-diphenyl-2,5-bis(trimethylsilyl)hafnacyclopentadiene 9 [S4]



Germylene **7** (237 mg, 0.32 mmol) was dissolved in benzene-d_6 (0.6 mL). The solution was exposed to air and stirred at room temperature for 4 h. The color of the mixture changed immediately from orange to red and after stirring to pale yellow. Analysis by NMR spectroscopy showed the formation of hafnacyclopentadiene **9** in quantitative yield.

^{1}H NMR (499.9 MHz, 305.0 K, C_6D_6): δ^1H = -0.14 (s, 18H, Si(CH_3)$_3$), 6.08 (s, 10H,2x C_5H_5), 6.69-6.90 (m, 10H, due to the overlap of the signals of **9** with signals of impurities the integrals show more *Ar*-H atoms than required, *Ar*-CH).

^{13}C{^{1}H} NMR (125.7 MHz, 305.0 K, C_6D_6): δ^{13}C = 3.2 (Si(CH_3)$_3$), 110.8 (C_5H_5), 125.2, 126.8, 130.1 (3x CH aryl), 146.7 (*ipso*-C aryl), 149.6 (C2/3), 203.3 (C1/4).

^{29}Si{^{1}H} NMR (99.3 MHz, 305.0 K, C_6D_6): δ^{29}Si = -13.5 (Si(CH_3)$_3$).

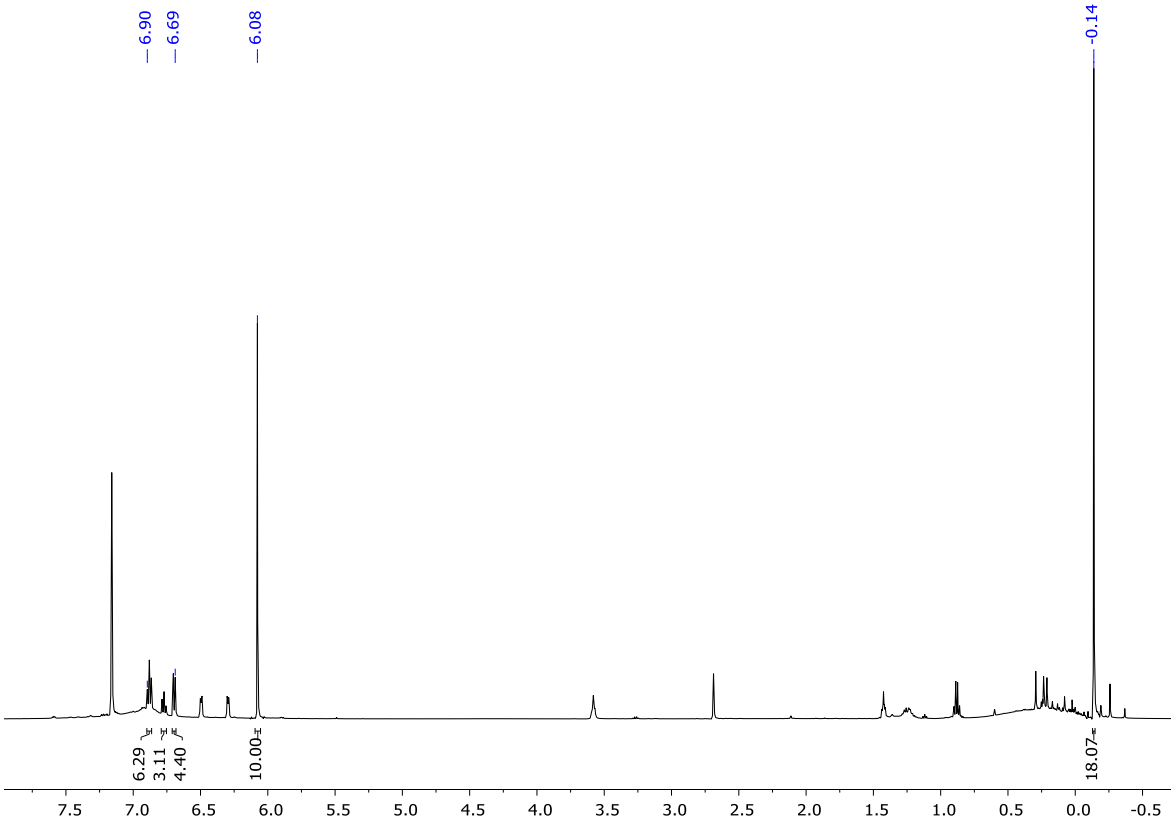


Figure S13. ^{1}H NMR spectrum of hafnacyclopentadiene **9**.

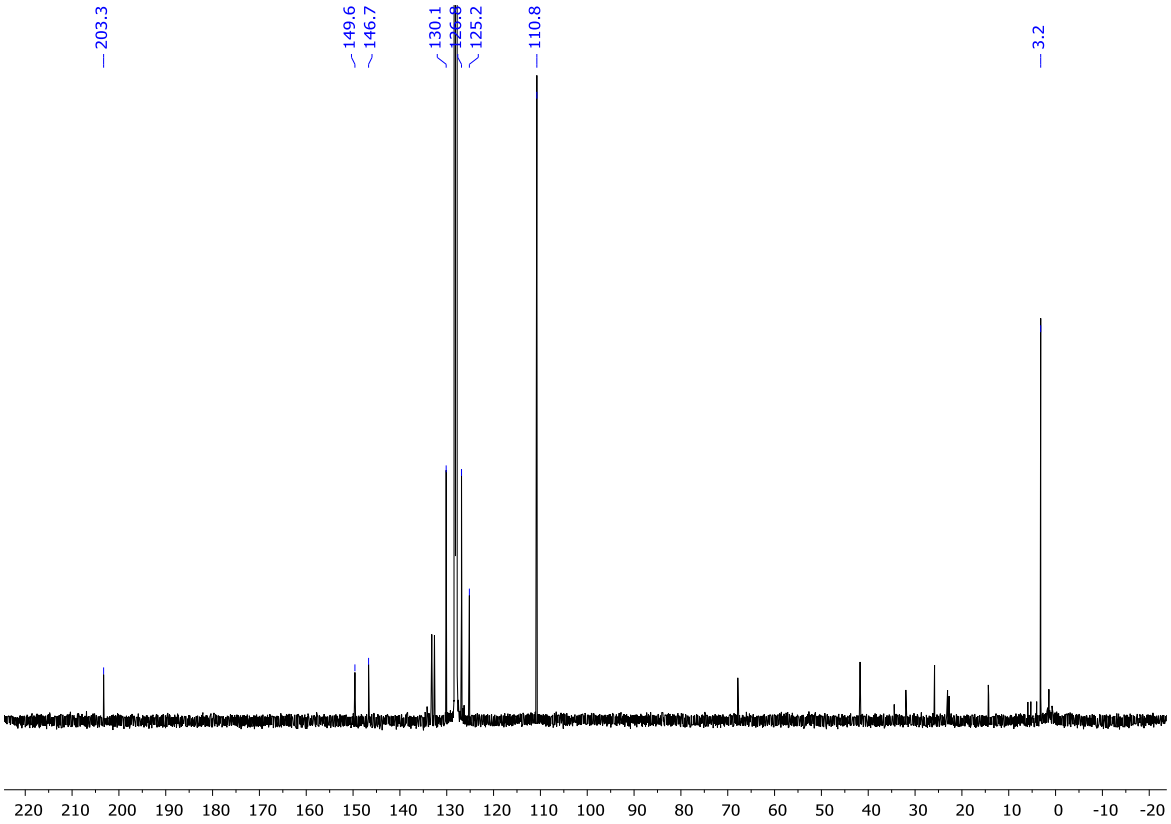


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of hafnacyclopentadiene **9**.

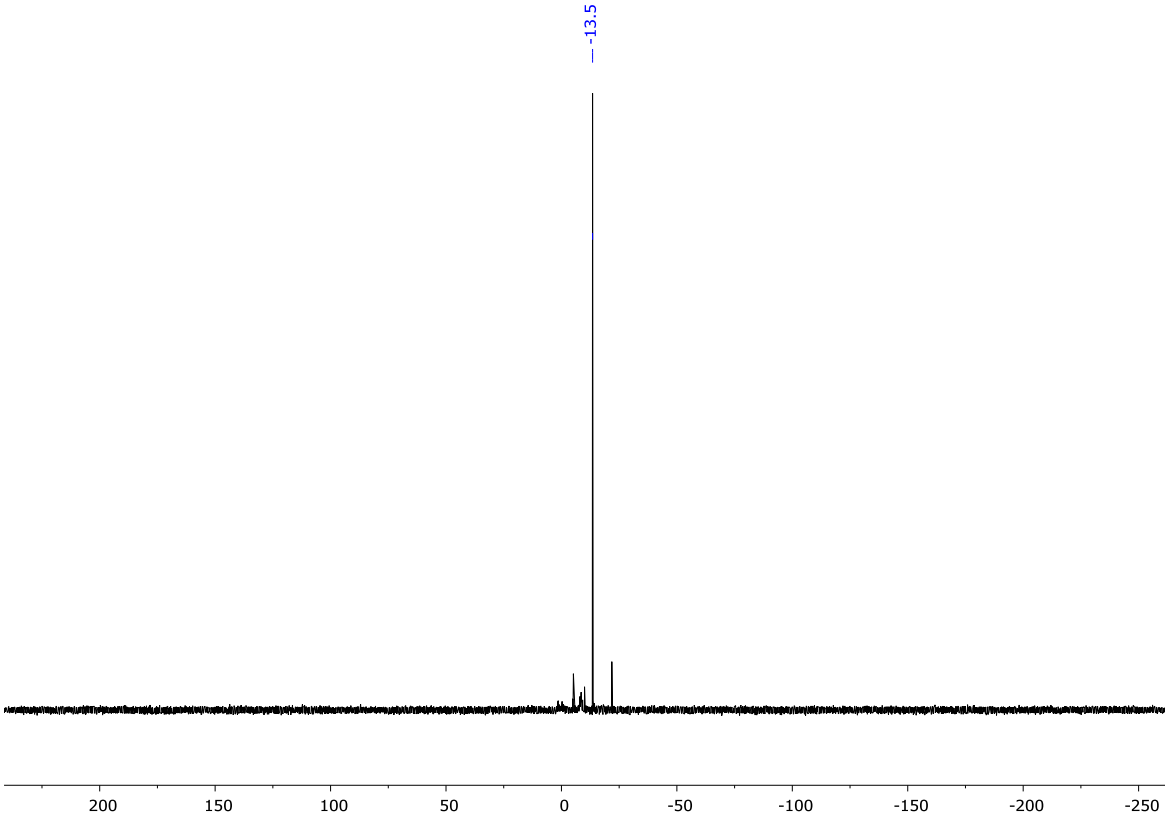
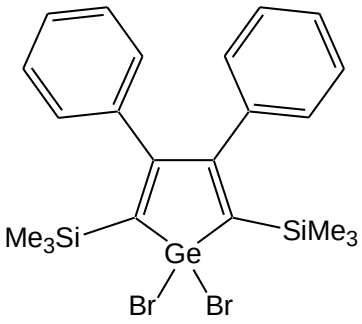


Figure S15. $^{29}Si\{^{1}H\}$ INEPT NMR spectrum of hafnacyclopentadiene **9**.

Details of the X-ray diffraction analyses



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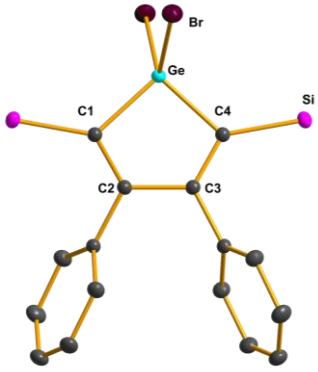
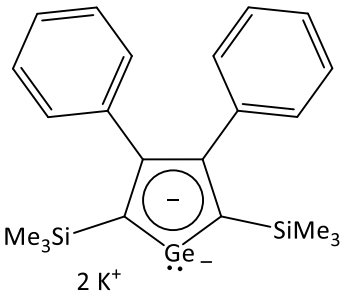


Figure S16. Molecular structure of germole **5** in the crystal. Selected bond lengths (pm) and angles (deg): C1–C2/ C3–C4 135.42(9), C2–C3 152.74(9), Ge–C1/Ge–C4 193.82(6), Ge–Br 230.51 (3), , Σα(germole ring) = 539.8. (thermal ellipsoids at 50% probability, all hydrogen atoms and methyl groups of Me_3Si are omitted for clarity).

Empirical formula	C22 H28 Br2 Ge Si2	
Formula weight	581.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.4104(7) Å	α = 90°.
	b = 10.4473(3) Å	β = 97.5853(16)°.
	c = 11.4731(4) Å	γ = 90°.
Volume	2425.04(14) $Å^3$	
Z	4	
Density (calculated)	1.591 Mg/m^3	
Absorption coefficient	4.663 mm^{-1}	
F(000)	1160	
Crystal size	0.350 x 0.350 x 0.250 mm^3	
Theta range for data collection	2.013 to 40.249°	
Index ranges	-37<=h<=37, -18<=k<=18, -20<=l<=20	
Reflections collected	95517	
Independent reflections	7624 (R(int) = 0.0254)	
Observed reflections (I > 2(I))	6605	
Completeness to theta = 40.249°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.4824 and 0.2902	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7624 / 0 / 126	
Goodness-of-fit on F^2	1.057	
Final R indices (I>2sigma(I))	R1 = 0.0177, wR2 = 0.0421	
R indices (all data)	R1 = 0.0247, wR2 = 0.0439	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.593 and -0.309 e.$Å^{-3}$	



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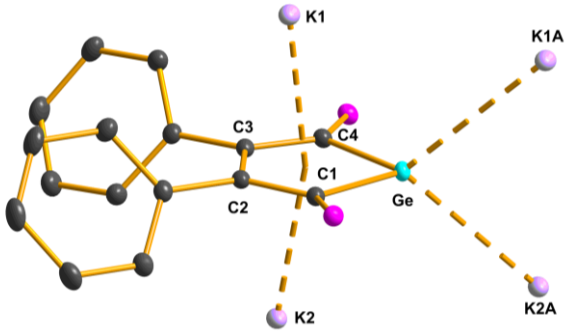
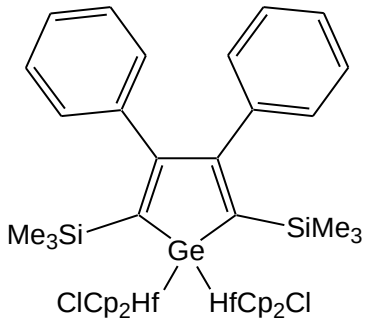


Figure S17. Molecular structure of the ion pair **6** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms and methyl groups of Me_3Si are omitted for clarity).

Empirical formula	C30 H44 Ge K2 O2 Si2	
Formula weight	643.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4092(8) Å	α = 69.1808(19)°.
	b = 11.8887(10) Å	β = 70.9322(18)°.
	c = 15.1092(13) Å	γ = 79.8943(19)°.
Volume	1648.1(2) $Å^3$	
Z	2	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	1.279 mm^{-1}	
F(000)	676	
Crystal size	0.400 x 0.080 x 0.050 mm^3	
Theta range for data collection	1.505 to 33.728°	
Index ranges	-16<=h<=16, -18<=k<=18, -23<=l<=23	
Reflections collected	82581	
Independent reflections	13191 (R(int) = 0.0697)	
Observed reflections (I > 2(I))	9743	
Completeness to theta = 33.728°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9700 and 0.7355	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13191 / 0 / 340	
Goodness-of-fit on F^2	1.020	
Final R indices (I>2sigma(I))	R1 = 0.0355, wR2 = 0.0697	
R indices (all data)	R1 = 0.0632, wR2 = 0.0781	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.573 and -0.703 $e.Å^{-3}$	



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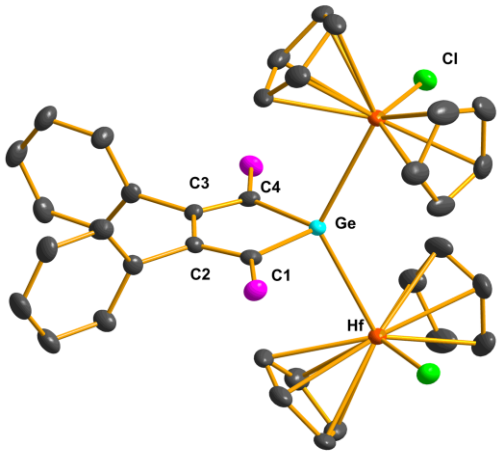

Figure S18. Molecular structure of germole **8** in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms and methyl groups of Me_3Si are omitted for clarity).

Empirical formula	C42 H48 Cl2 Ge Hf2 Si2	
Formula weight	1109.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	$P3_221$	
Unit cell dimensions	a = 11.7949(2) Å	α = 90°.
	b = 11.7949(2) Å	β = 90°.
	c = 25.3318(7) Å	γ = 120°.
Volume	3052.03(14) $Å^3$	
Z	3	
Density (calculated)	1.811 Mg/m^3	
Absorption coefficient	6.042 mm^{-1}	
F(000)	1614	
Crystal size	0.250 x 0.200 x 0.150 mm^3	
Theta range for data collection	1.994 to 30.033°	
Index ranges	-16<=h<=16, -16<=k<=16, -35<=l<=35	
Reflections collected	101559	
Independent reflections	5979 (R(int) = 0.0631)	
Observed reflections (I > 2(I))	5668	
Completeness to theta = 30.033°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6312	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5979 / 0 / 225	
Goodness-of-fit on F^2	1.123	
Final R indices (I>2sigma(I))	R1 = 0.0269, wR2 = 0.0583	
R indices (all data)	R1 = 0.0305, wR2 = 0.0596	
Absolute structure parameter	-0.010(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.081 and -1.003 $e.Å^{-3}$	

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