Supplementary Information

Silagermylenation of C=O bonds and radical fragmentation of CO_2-expanded bis(germylene) by a cyclic (alkyl)(amino)carbene

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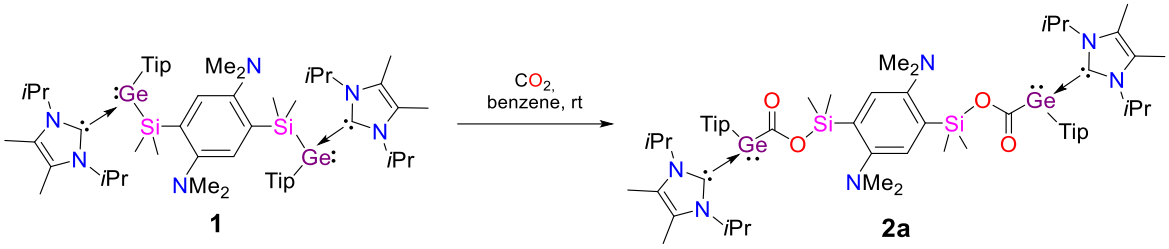
1. General considerations

All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk or glovebox techniques. The glassware was pre-dried in an oven at 125 °C and heated in vacuo prior to use. Solvents were taken from solvent purification systems (Innovative technology PureSolv MD7 or MBraun SPS 5/7; hexane, pentane, thf, benzene). Benzene-d_6 and thf-d_8 were dried over a potassium mirror, degassed through freeze-pump-thaw cycles and condensed under argon prior to use. NHC-bis(germylene) **1**,[S1] 1,3-bis(2,6-diisopropyl)imidazol-2-ylidene (NHC)[S2] and 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene ($CAAC^{Me}$)[S3] were prepared according to published procedures. All other chemicals were obtained commercially and used as received. The NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer at 300 K (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{29}Si: 79.49 MHz) or on a Bruker Avance III HD 300 at 300 K (^{1}H: 300.13 MHz, ^{13}C: 75.56 MHz, ^{29}Si: 59.6 MHz). The ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual proton and natural abundance ^{13}C resonances of the deuterated solvents and chemical shifts were reported relative to SiMe4 (benzene-d_6: δH = 7.16 ppm and δC = 128.06 ppm, thf-d_8: δH = 1.72, 3.58 ppm and δC = 67.21, 25.31 ppm).[S4] The ^{29}Si NMR chemical shifts were referenced to external $SiMe_4$. The following abbreviations were used for the multiplicities: s – singlet, d – doublet, t – triplet, sept – septet, m – multiplet, br – prefix broad. IR data of powder samples was acquired on a Bruker Vertex 70 spectrometer in attenuated total reflectance (ATR) mode. X-band continuous wave (cw) EPR spectra were recorded on a Magnettech MiniScope MS 5000 with a microwave frequency of 9.44 GHz using a modulation amplitude of 100 kHz. For least-square fitting of the data, the Nelder-Mead method was applied and the spectra were simulated with the Easyspin toolbox (version 6.0.6)[S5] for Matlab R2024a[S6] using the resulting fit data. Melting points were determined under argon in sealed NMR tubes. The molten samples were examined by NMR spectroscopy to confirm whether decomposition had occurred upon melting. Elemental analyses were performed in triplicate for each sample using Leco CHN900 analyzer and mean values are reported. Single crystal X-ray diffraction (SC-XRD) was performed on a Bruker D8 Venture diffractometer with a microfocus sealed tube and a Photon II detector. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used. Data were corrected for absorption effects using the multi-scan method. The structures were solved by direct methods using SHELXT[S7] and refined by full matrix least squares calculations on F2 (SHELXL)[S8] in the graphical user interface Shelxle.[S9] Computations were carried out with the Gaussian 16.C01 program package.[S10] Structural optimizations and frequency analyses were performed at the BP86-D3(BJ)/def2-SVP[11,12] or the UB3LYP-D3(BJ)/def2-SVP[12,13] (for paramagnetic compound **3**) level of theory, including the D3 dispersion correction by Grimme with Becke-Johnson damping[S14] and subsequent single-point calculations at the BP86-D3(BJ)/def2-TZVPP[11,12] or the UB3LYP-D3(BJ)/def2-TZVPP[12,13] (for paramagnetic compound **3**) level of theory. For the calculations of EPR parameters, the ORCA quantum chemistry program package (version 5.0.4)[S15] was used at the UB3LYP/def2-TZVPP[12,13] level of theory. Kohn-Sham orbitals and spin densities were visualized with ChemCraft.[S16]

2. Synthetic Procedures

2.1 Synthesis of oxycarbonyl NHC-bis(germylene) 2a

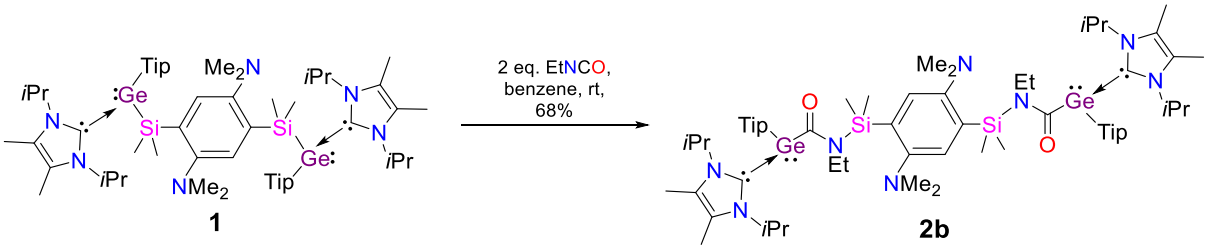


NHC-bis(germylene) **1** (261 mg, 212 µmol, 1 eq.) is suspended in 2.5 mL of benzene. Stirring under CO_2 atmosphere at ambient pressure for 20 minutes results in a colorless solution. The solvent is removed under vacuum to yield NHC-bis(germylene) **2a** (255 mg, 195 µmol, 92%) as a colorless amorphous powder.

^{1}H NMR (400.13 MHz, 300 K, TMS): δ (thf-d$_8$) = 7.59 (s, 2H, Ph*H*), 6.86 (s, 4H, Tip*H*), 5.69 (m, 4H, C*H*(CH$_3$)$_2$ of NHC), 3.74 (sept, 4H, C*H*(CH$_3$)$_2$ of Tip), 2.77 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.52 (s, 12H, N(C*H*$_3$)$_2$), 2.24 (s, 12H, NHC-CC*H*$_3$), 1.37 (d, 12H, CH(C*H*$_3$)$_2$ of NHC), 1.19, 1.19 (each d, overall 12H, CH(C*H*$_3$)$_2$ of NHC), 1.11, 1.08 (d, brd, overall 24H, CH(C*H*$_3$)$_2$ of Tip), 0.96 (d, 12H, CH(C*H*$_3$)$_2$ of Tip), 0.41 (s, 12H, Si(C*H*$_3$)$_2$) ppm. δ (C$_6$D$_6$) = 8.15, 8.15 (overlapping s, overall 2H, Ph*H*), 7.16 (s, 4H, Tip*H*, overlapping with C$_6$D$_6$ peak), 5.93 (m, 4H, C*H*(CH$_3$)$_2$ of NHC), 4.13 (sept, 4H, C*H*(CH$_3$)$_2$ of Tip), 2.91 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.54, 2.53 (overlapping s, overall 12H, N(C*H*$_3$)$_2$), 1.58 (s, 12H, NHC-CC*H*$_3$), 1.44 (d, 12H, CH(C*H*$_3$)$_2$ of NHC), 1.36, 1.34 (each d, overall 12H, CH(C*H*$_3$)$_2$ of NHC), 1.24, 1.21 (each d, overall 24H, CH(C*H*$_3$)$_2$ of Tip), 0.94 (brd, 12H, CH(C*H*$_3$)$_2$ of Tip), 0.88, 0.86, 0.85, 0.84 (each s, overall 12H, Si(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, C$_6$D$_6$, 300 K, TMS): δ = 204.89 (*C*O), 173.44 (NHC-*C*), 158.19, 154.10 (Ph*C*), 149.41, 146.90, 140.07 (Tip*C*), 129.16 (NHC-*C*CH$_3$), 125.48 (Ph*C*), 121.05 (Tip*C*), 52.67 (*C*H(CH$_3$)$_2$ of NHC), 47.15 (N(*C*H$_3$)$_2$), 35.01, 34.74 (*C*H(CH$_3$)$_2$ of NHC), 25.60, 25.22, 24.68, 24.59 (CH(*C*H$_3$)$_2$ of Tip), 21.03, 20.96 (CH(*C*H$_3$)$_2$ of NHC), 9.93 (NHC-C*C*H$_3$), 1.40, 1.28 (Si(*C*H$_3$)$_2$) ppm. **^{29}Si{^{1}H} NMR** (79.49 MHz, 300 K, TMS): δ (thf-d$_8$) = 2.09, 2.05, δ (C$_6$D$_6$) = 2.70 ppm. **Elemental analysis:** Calcd. for (C$_{70}$H$_{114}$Ge$_2$N$_6$O$_4$Si$_2$): C, 64.42; H, 8.80; N, 6.44. Found: C, 64.69; H, 7.72; N, 6.10. **Mp.:** 164°C (under formation of Tip$_2$Ge=GeTip$_2$ and unidentified decomposition products). **IR:** ν(CO) 1613 cm^{-1}.

In solution, slow decomposition is observed, providing an unidentified mixture of products. A characteristic septet at 4.89 ppm in the ^{1}H NMR spectrum (in thf-d$_8$), concomitant with the precipitation of a colorless solid, suggests the formation of poorly soluble NHC–CO$_2$).[S17a]

2.2 Synthesis of aminocarbonyl NHC-bis(germylene) 2b

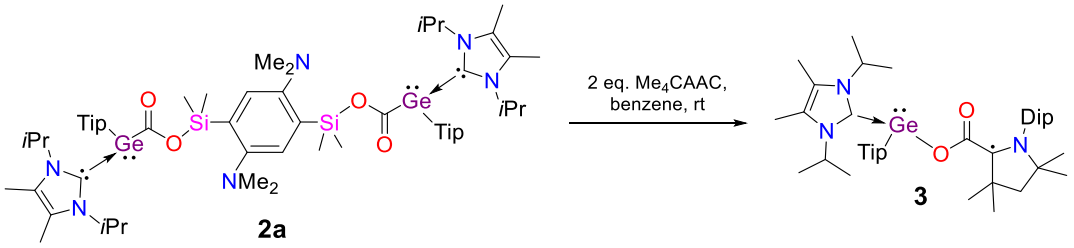


NHC-bis(germylene) **1** (250 mg, 177 µmol, 1 eq.) is suspended in 4 mL of benzene. Dropwise addition of a solution of ethyl isocyanate in benzene (0.41 M, 0.99 mL, 406 µmol, 2.3 eq.) results in complete dissolution of the starting material and subsequent precipitation of a colorless solid. After stirring for one hour, the solvent is removed and the residue is washed with 2 mL of pentane to yield NHC-bis(germylene) **2b** as a colorless powder (176 mg, 121 µmol, 68%). Single crystals of **2b** suitable for SC-XRD anylsis are obtained from a benzene/thf/hexane solution.

^{1}H NMR (400.13 MHz, thf-d$_8$, 300 K, TMS): δ = 7.41 (s, 2H, Ph*H*), 6.86 (s, 4H, Tip*H*), 5.73 (m, 4H, C*H*(CH$_3$)$_2$ of NHC), 3.86 (brsept, 2H, C*H*(CH$_3$)$_2$ of Tip), 3.69 (app. quint, 4H, NC*H*$_2$CH$_3$), 3.51 to 3.40 (m, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.75 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.54 (s, 12H, N(C*H*$_3$)$_2$), 2.18 (s, 12H, NHC-CC*H*$_3$), 1.44 (d, 12H, CH(C*H*$_3$)$_2$ of NHC), 1.27 (brtr, 6H, NCH$_2$C*H*$_3$), 1.19, 1.18, 1.16 (overlapping d, overall 24H, CH(C*H*$_3$)$_2$ of NHC and CH(C*H*$_3$)$_2$ of Tip), 0.93 (brd, 24H, CH(C*H*$_3$)$_2$ of Tip), 0.53, 0.28 (each s, each 6H, Si(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, thf-d$_8$, 300 K, TMS): δ = 212.19, 211.93 (*C*O), 172.49 (NHC-*C*), 156.54, 154.29, 154.24 (Ph*C*), 149.63, 146.66, 139.92 (Tip*C*), 128.64, 128.45 (NHC-*C*CH$_3$), 126.33 (Ph*C*), 121.41 (Tip*C*), 53.03 (*C*H(CH$_3$)$_2$ of NHC), 47.39 (N(*C*H$_3$)$_2$), 42.64 (N*C*H$_2$CH$_3$), 34.93, 34.58 (*C*H(CH$_3$)$_2$ of NHC), 25.83, 25.09, 24.51, 24.39 (CH(*C*H$_3$)$_2$ of Tip), 21.34, 21.13, 20.88 (CH(*C*H$_3$)$_2$ of NHC), 18.80 (NCH$_2$*C*H$_3$), 10.22, 8.18 (NHC-C*C*H$_3$), 1.44, 0.34, 0.21 (Si(*C*H$_3$)$_2$) ppm. **^{29}Si{^{1}H} NMR** (79.49 MHz, thf-d$_8$, 300 K, TMS): δ = −6.27, −6.44 ppm. **Elemental analysis:** Calcd. for (C$_{81}$H$_{131}$Ge$_2$N$_8$O$_2$Si$_2$): C, 67.07; H, 9.12; N, 7.73. Found: C, 67.13; H, 8.12; N, 7.62. **Mp.:** 110°C (under unselective decomposition to unidentified products). **IR:** ν(CO) 1548 cm^{-1}.

In solution, slow decomposition is observed, providing an unidentified mixture of products. A septet at 5.00 ppm in the ^{1}H NMR spectrum (in thf-d$_8$), concomitant with the precipitation of a colorless solid (characteristic for poorly soluble NHC–heteroallene adducts),[S17] suggests the formation of NHC–C(O)NEt.

2.3 Reaction of NHC-bis(germylene) 2a with CAAC^{Me}



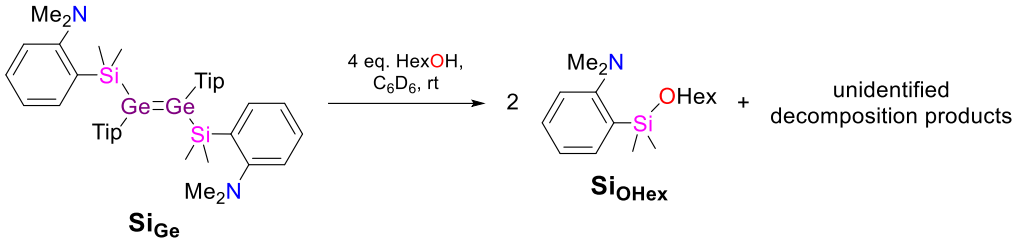
NHC-bis(germylene) **2a** (100 mg, 75.3 µmol, 0.5 eq.) and CAAC^{Me} (43.0 mg, 151 µmol, 1 eq.) are each dissolved in 2 mL of benzene. The germylene solution is added rapidly to the CAAC^{Me} solution *via* syringe. The resulting intensely red solution is concentrated under vacuum and 4 mL of pentane are added prior to filtration. Off-white crystals of germylene **3** (13 mg, 16.7 µmol, 11%) are grown from the concentrated filtrate at +4°C.

EPR (9.44 GHz, 5 dB, 1.5 G modulation amplitude, 100 kHz modulation frequency, C_6D_6, 300 K): *g* 2.0035, *A*(^{14}N) 5.96 G.

*Reasonable elemental analysis and IR spectroscopy of **3** were prevented by its highly sensitive nature.*

2.4 Synthesis of alkoxylated anilinyl silanes for NMR comparison

Reaction of a o-anilino disubstituted silyl digermene[S18] with hexanol

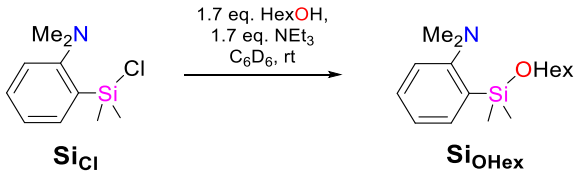


To a solution of digermene **Si$_{Ge}$** (30.0 mg, 33.0 µmol, 1 eq.) in 0.5 mL of C_6D_6 in an NMR tube hexanol (16.8 µL, 134 µmol, 4 eq.) is added *via* syringe at room temperature. Quantitative conversion to siloxane **Si$_{OHex}$** is confirmed *via* multinuclear NMR spectroscopy.

^{1}H NMR (300.13 MHz, C_6D_6, 300 K, TMS): δ = 7.88 (ddd, 1H, Me_2N-Ph*H*), 7.25 (ddd, 1H, Me_2N-Ph*H*), 7.13 (ddd, 2H, Me_2N-Ph*H*, overlapping with peaks of unidentified by-products), 3.71 (t, 2H, $OCH_2(CH_2)_4CH_3$), 2.46 (s, 6H, $N(CH_3)_2$), 1.65 (tt, 2H, $OCH_2CH_2(CH_2)_3CH_3$), 1.44 to 1.12 (m, 6H, $O(CH_2)_2(CH_2)_3CH_3$ overlapping with peaks of unidentified by-products), 0.89 (t, 3H, $O(CH_2)_5CH_3$ of HexOH), 0.51 (s, 6H, $Si(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75.47 MHz, C_6D_6, 300 K, TMS): δ = 161.19, 136.58 (PhC_{quart}), 136.20, 131.07, 125.16, 121.30 (Ph*C*), 63.04 ($OCH_2(CH_2)_4CH_3$ of HexOH), 46.67 ($N(CH_3)_2$), 33.38 ($OCH_2CH_2(CH_2)_3CH_3$ of HexOH), 32.13 ($O(CH_2)_2CH_2(CH_2)_2CH_3$ of HexOH), 26.14 ($O(CH_2)_3CH_2CH_2CH_3$ of HexOH), 23.12 ($O(CH_2)_4CH_2CH_3$ of HexOH), 14.33 ($O(CH_2)_5CH_3$ of HexOH), −0.33 ($Si(CH_3)_2$) ppm. **^{29}Si{^{1}H} NMR** (59.63 MHz, C_6D_6, 300 K, TMS): δ = 3.59 ppm.

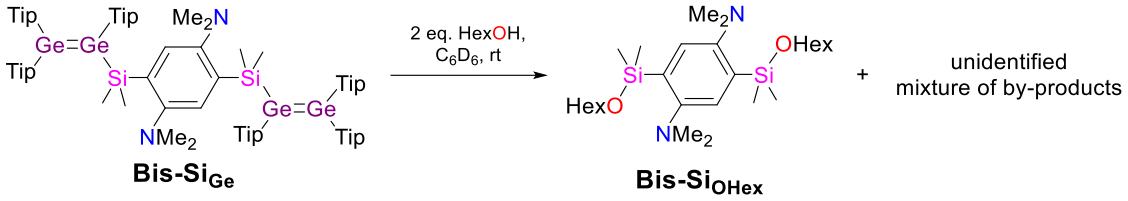
In the ^{29}Si-^{1}H-HMBC NMR spectrum (Figure S19), a cross peak of the ^{29}Si resonance (3.59 ppm) with the ^{1}H resonance of the OCH_2 group (3.71 ppm) further corroborates the HexO-substitution at silicon.

The reaction of chlorosilane **Si$_{Cl}$**[S19] with hexanol providing the same product according to multinuclear NMR spectroscopy serves as additional proof of the identity of **Si$_{OHex}$**:



Chlorosilane **Si$_{Cl}$** (50.0 mg, 234 µmol, 1 eq.) is dissolved in 0.5 mL of C_6D_6 and hexanol (0.05 mL,401 µmol, 1.7 eq.) as well as triethylamine (0.02 mL, 398 µmol, 1.7 eq.) are added *via* syringe. A viscous opaque suspension results which is filtrated and washed with circa 0.3 mL of hexane. All volatile species are removed *in vacuo* and the residue is dissolved in C_6D_6. The formation of siloxane **Si$_{OHex}$** is confirmed by multinuclear NMR spectroscopy.

Reaction of a silylenephenylene bridged bis(digermene)[S18] with hexanol



Bis-Si$_{Ge}$ **Bis-Si$_{OHex}$**

To a solution of bis(digermene) **Bis-Si$_{Ge}$** (50.0 mg, 26.2 µmol, 1 eq.) in 0.5 mL of C_6D_6 in an NMR tube hexanol (6.6 µL, 52.4 µmol, 2 eq.) is added. Quantitative conversion to the bis(siloxane) **Bis-Si$_{OHex}$** is confirmed by multinuclear NMR spectroscopy.

^{1}H NMR (300.13 MHz, C_6D_6, 300 K, TMS): δ = 7.92 (s, 2H, Me_2N-Ph*H*), 3.78 (t, 4H, OC*H*$_2$(CH$_2$)$_4$CH$_3$), 2.56 (s, 12H, N(C*H*$_3$)$_2$), 1.83 to 1.67 (m, 4H, OCH$_2$C*H*$_2$(CH$_2$)$_3$CH$_3$ overlapping with peaks of unidentified by-products), 1.55 to 1.23 (m, 12H, O(CH$_2$)$_2$(C*H*$_2$)$_3$CH$_3$ overlapping with peaks of unidentified by-products), 1.21 to 1.17 (m, 4H, O(CH$_2$)$_5$C*H*$_3$ overlapping with peaks of unidentified by-products), 0.95 to 0.83 (m, 6H, O(CH$_2$)$_5$C*H*$_3$ overlapping with signals of decomposition products of Tip$_2$Ge=GeHTip), 0.54 (s, 12H, Si(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (75.47 MHz, C_6D_6, 300 K, TMS): δ = 157.97, 139.91 (Ph*C*$_{quart}$), 129.30 (Ph*C*), 63.08 (O*C*H$_2$(CH$_2$)$_4$CH$_3$), 47.00 (N(*C*H$_3$)$_2$), 34.84, 34.66 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_3$), 26.30, 26.14 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$CH$_3$), 24.22, 24.10 (O(CH$_2$)$_3$*C*H$_2$CH$_2$CH$_3$), 23.19, 23.12 (O(CH$_2$)$_4$*C*H$_2$CH$_3$), 14.35, 14.29 (O(CH$_2$)$_5$*C*H$_3$), −0.32 (Si(*C*H$_3$)$_2$) ppm. **^{29}Si{^{1}H} NMR** (59.63 MHz, C_6D_6, 300 K, TMS): δ = 3.54 ppm.

In the ^{29}Si-^{1}H-HMBC NMR spectrum (Figure S23), a cross peak of the ^{29}Si resonance (3.54 ppm) with the ^{1}H resonance of the OCH$_2$ group (3.76 ppm) further corroborates the HexO-substitution at silicon.

3. Characterization

3.1 X-Ray crystallographic data

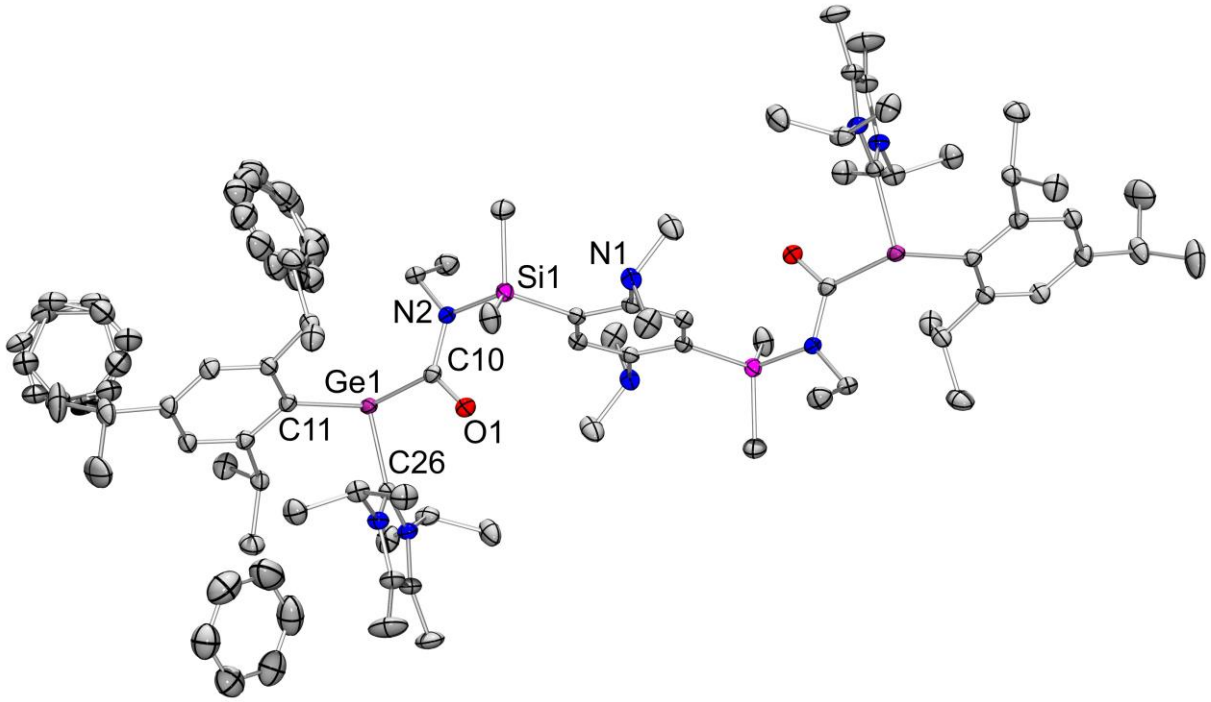


Figure S1. Molecular structure of NHC-bis(germylene) **2b** in the solid state. Hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (in Å) and angles (in °): Ge1–C26 2.078(2), Ge1–C10 2.066(2), N2–C10 1.382(3), C10–O1 1.239(2), Si1–O1 2.788(2), C10-Ge1-C26 90.79(8), C26-Ge1-C11 95.31(8), C11-Ge1-C10 109.92(8), Σ°(Ge1) 296.0(2), C9-N2-Si1 123.8(1), C9-N2-C10 119.6(2), C10-N2-Si1 116.6(2), Σ°(N2) 360.0(5), Si1-N2-C10-O1 9.1(2), C11-Ge1-C10-O1 79.3(2), C26-Ge1-C10-O1 4.8(2).

All non H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH_2) or 1.5 (CH_3). *Disorder*: two co-crystallized benzene molecules are disordered across two positions each (fvar 2: 0.60/0.40 and fvar 3: 0.78/0.22).

Table S1. Crystal Data and Structure Refinement for NHC-bis(germylene) **2b** (CCDC 2427550).[S22]

Identification code	sh5583_a	
Empirical formula	C108 H158 Ge2 N8 O2 Si2	
Formula weight	1801.77	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P−1	
Unit cell dimensions	a = 12.0604(6) Å	α = 84.472(2)°.
	b = 12.6790(6) Å	β = 73.288(2)°.
	c = 19.5103(10) Å	γ = 66.037(2)°.
Volume	2610.4(2) Å^3	
Z	1	
Density (calculated)	1.146 Mg/m^3	
Absorption coefficient	0.649 mm^{-1}	
F(000)	970	
Crystal size	0.180 x 0.100 x 0.010 mm^3	
Theta range for data collection	1.921 to 27.171°.	
Index ranges	−15≤h≤15, −16≤k≤16, −25≤l≤25	
Reflections collected	95589	
Independent reflections	11547 [R(int) = 0.0796]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6765	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11547 / 606 / 677	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0792	
R indices (all data)	R1 = 0.0614, wR2 = 0.0876	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.345 and −0.552 e.Å^{-3}	

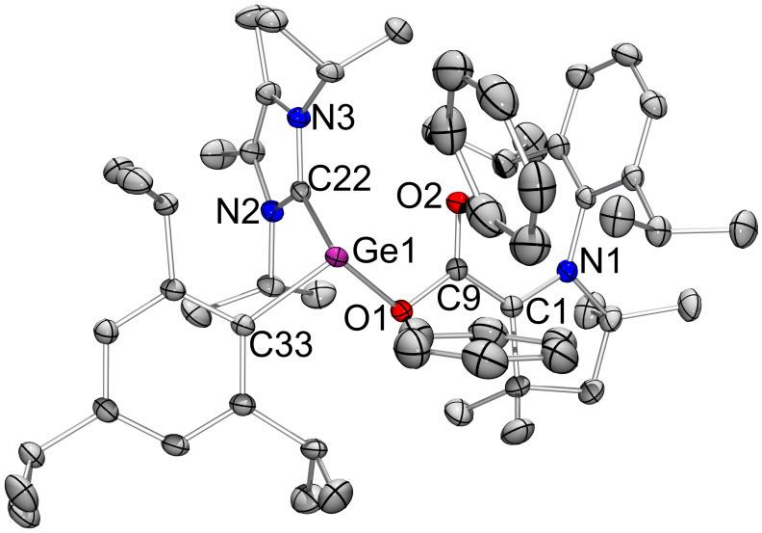


Figure S2. Molecular structure of germylene radical **3** in the solid state. Hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (in Å) and angles (in °): Ge1–C22 2.094(1), Ge1–O1 1.9528(7), Ge1–O2 2.8139(8), C9–O1 1.339(1), C9–O2 1.238(1), C1–N1 1.376(1), C1–C9 1.441(1), O1-Ge1-C22 91.10(3), O1-Ge1-C33 101.76(4), C33-Ge1-C22 95.37(4), Σ°(Ge1) 288.2(1), Ge1-O1-C9-O2 10.5(1).

All non H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH_2) or 1.5 (CH_3).

Table S2. Crystal Data and Structure Refinement for germylene radical **3** (CCDC 2427551).[S22]

Identification code	sh5323_a	
Empirical formula	C56 H83 Ge N3 O2	
Formula weight	902.84	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7231(3) Å	α = 103.0580(10)°.
	b = 12.9550(3) Å	β = 94.8140(10)°.
	c = 16.3893(4) Å	γ = 95.9220(10)°.
Volume	2601.43(11) Å^3	
Z	2	
Density (calculated)	1.153 Mg/m^3	
Absorption coefficient	0.630 mm^{-1}	
F(000)	976	
Crystal size	0.400 x 0.300 x 0.200 mm^3	
Theta range for data collection	2.146 to 28.737°.	
Index ranges	−17≤h≤17, −17≤k≤17, −22≤l≤22	
Reflections collected	114365	
Independent reflections	13482 [R(int) = 0.0358]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.7150	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13482 / 0 / 579	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0633	
R indices (all data)	R1 = 0.0298, wR2 = 0.0656	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.296 and -0.308 e.Å^{-3}	

3.2 NMR spectroscopic data

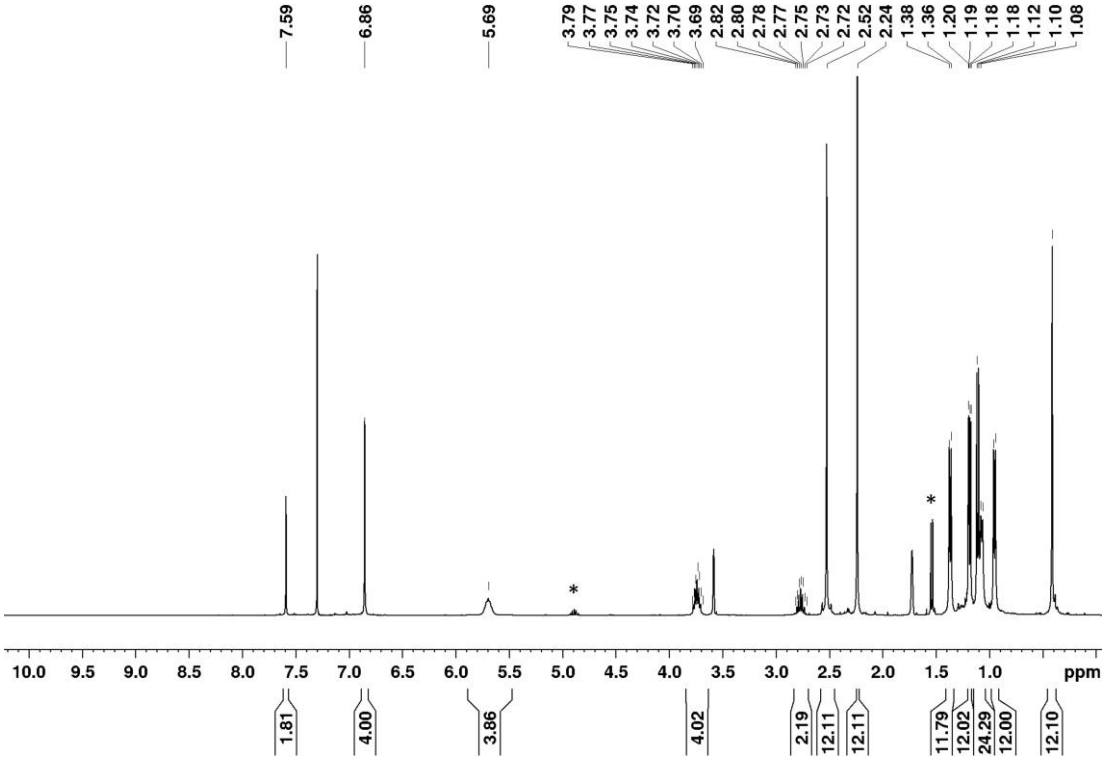


Figure S3. ^{1}H NMR spectrum of oxycarbonyl substituted NHC-bis(germylene) **2a** in thf-d_8 (*: peaks of NHC-CO_2 resulting from beginning decomposition).

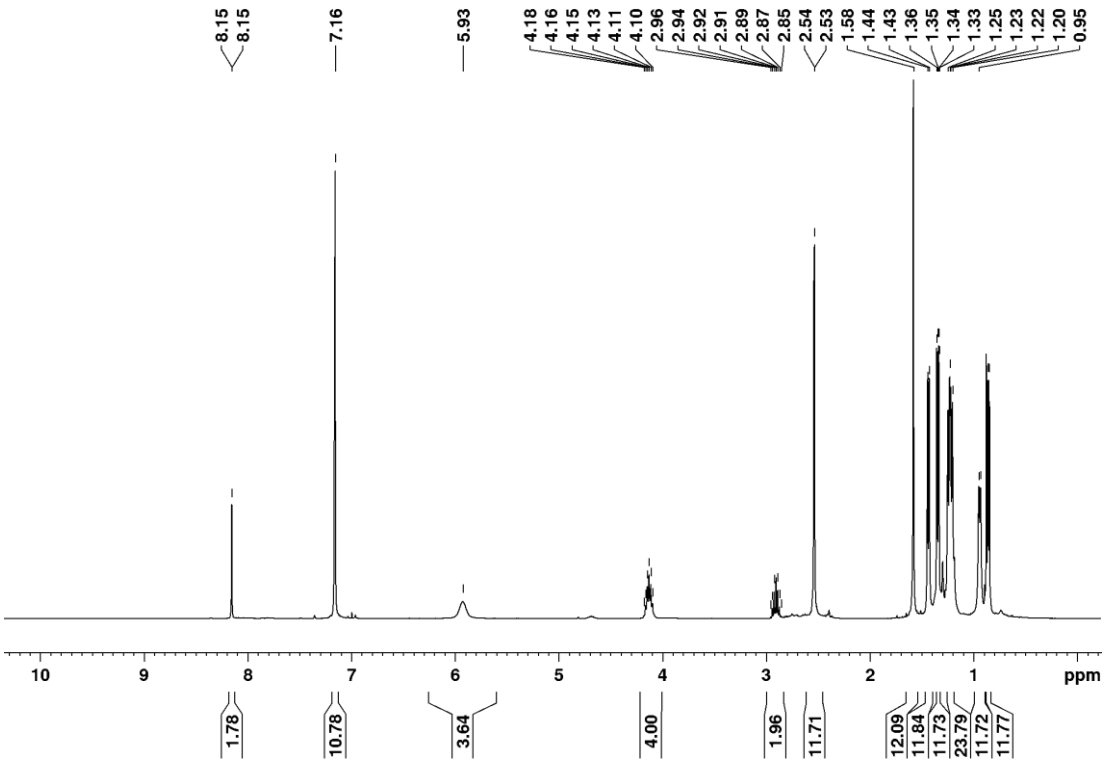


Figure S4. ^{1}H NMR spectrum of oxycarbonyl substituted NHC-bis(germylene) **2a** in C_6D_6.

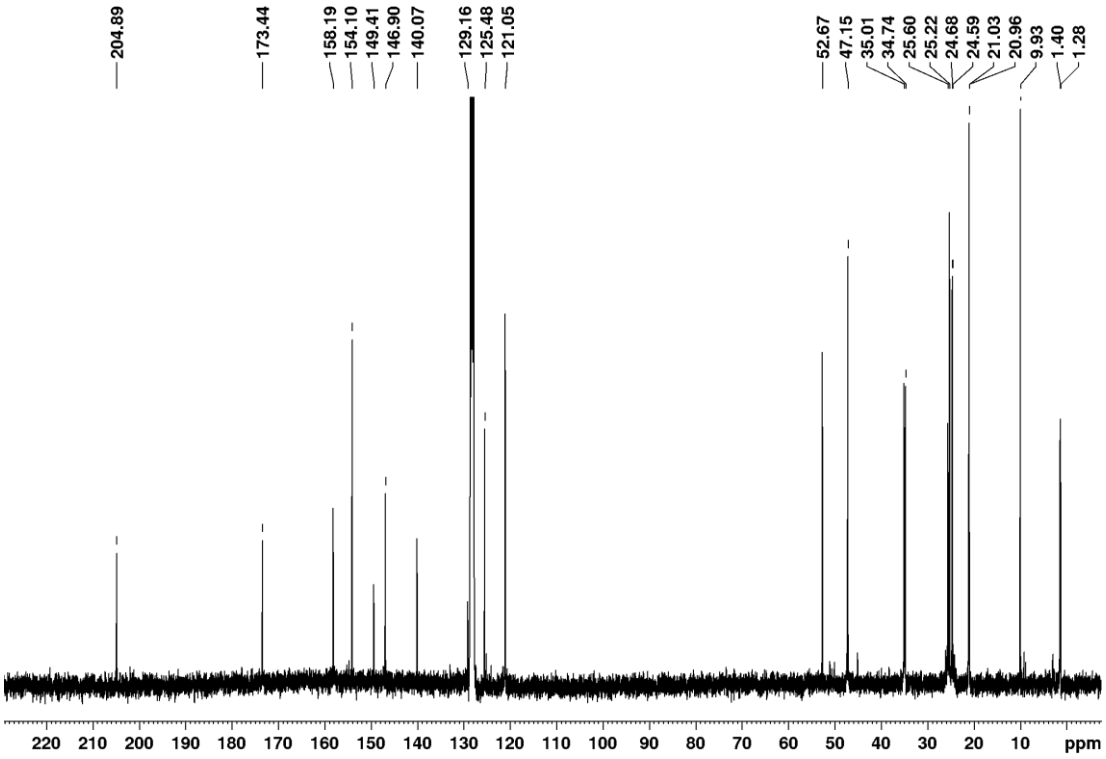


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of oxycarbonyl substituted NHC-bis(germylene) **2a** in C_6D_6.

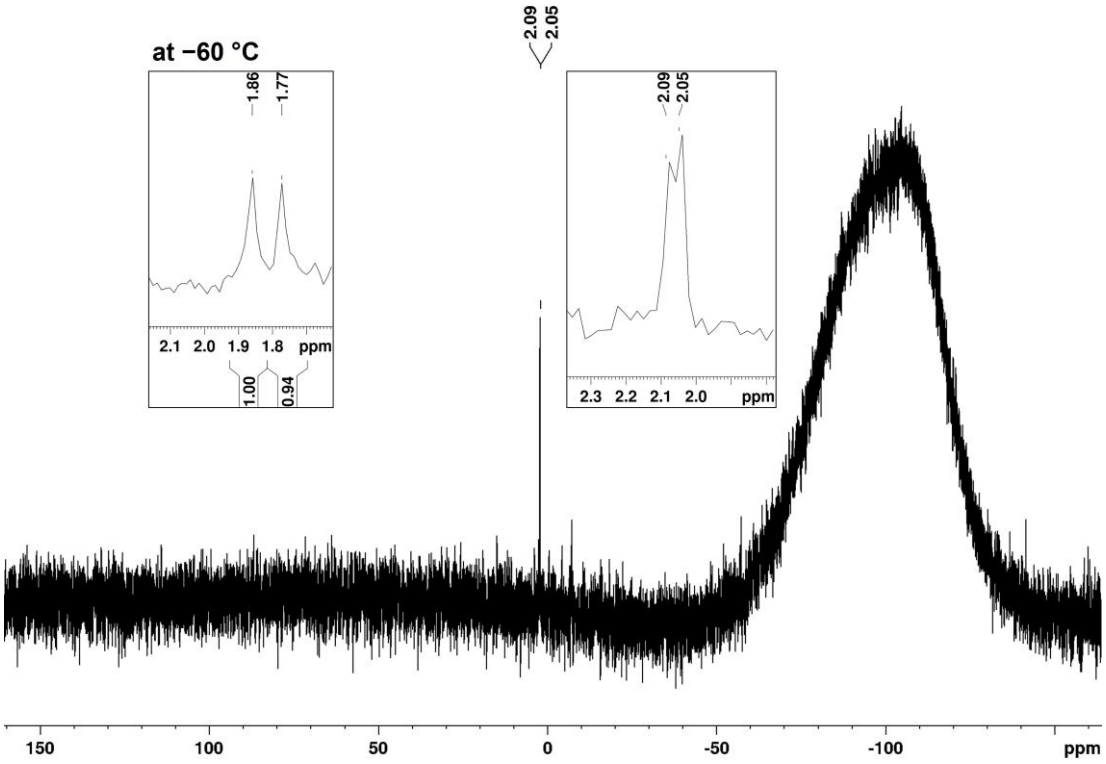


Figure S6. $^{29}Si\{^{1}H\}$ NMR spectrum of a diastereomeric mixture of oxycarbonyl substituted NHC-bis(germylene) **2a** in thf-d_8 and an excerpt from the ^{29}Si NMR spectrum at −60°C.

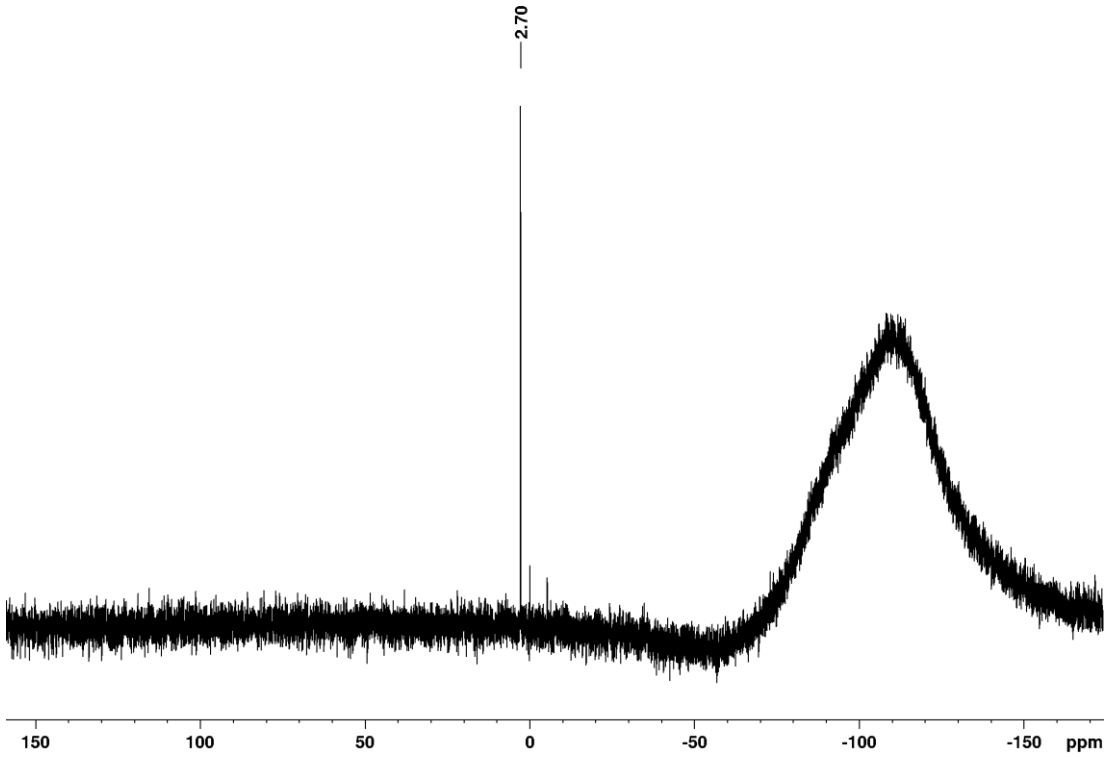


Figure S7. $^{29}Si\{^{1}H\}$ NMR spectrum of oxycarbonyl substituted NHC-bis(germylene) **2a** in C_6D_6.

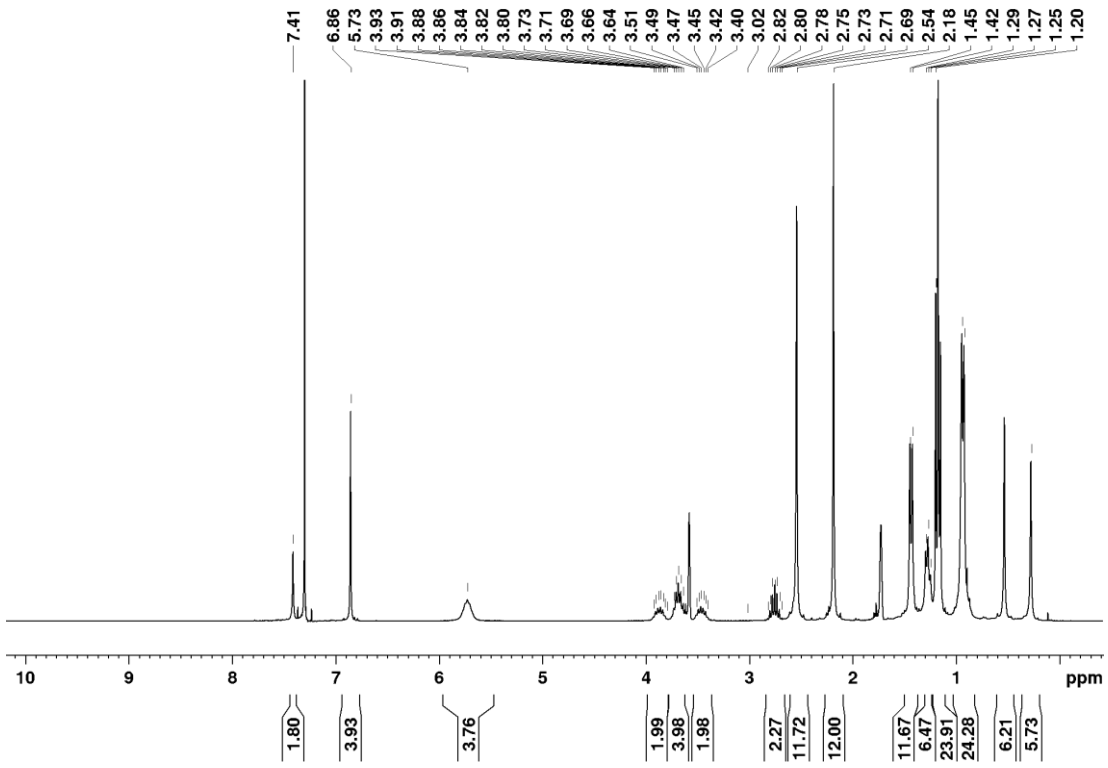


Figure S8. ^{1}H NMR spectrum of aminocarbonyl substituted NHC-bis(germylene) **2b** in thf-d_8.

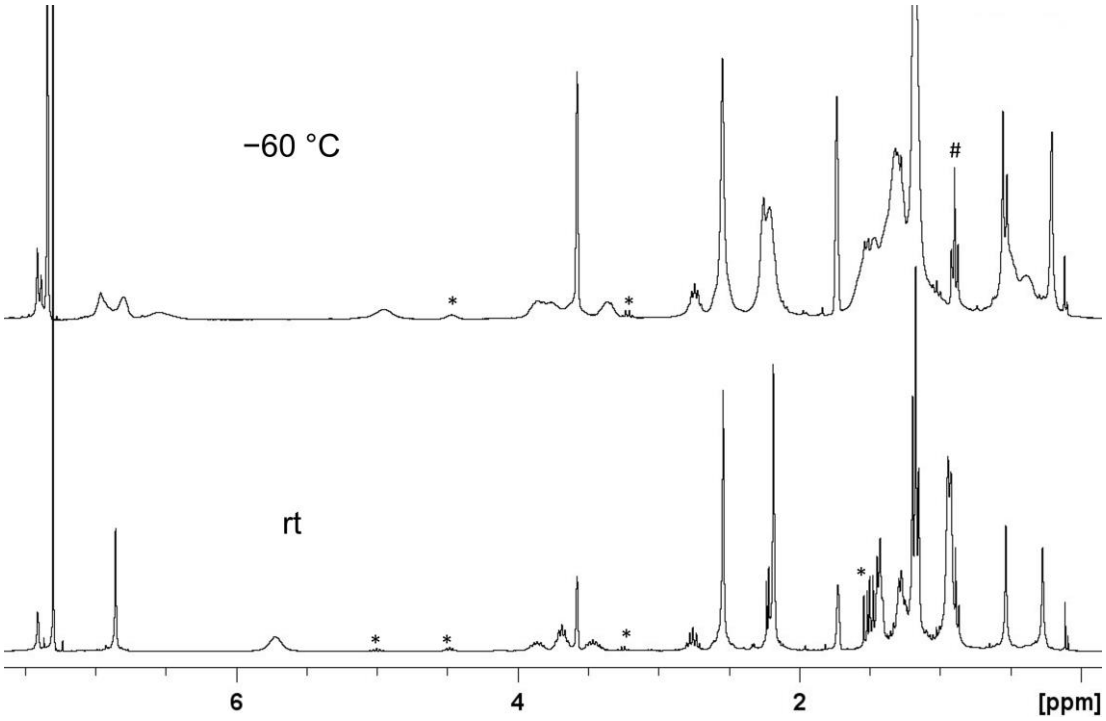


Figure S9. ^{1}H NMR spectra of aminocarbonyl substituted NHC-bis(germylene) **2b** in thf-d_8 at different temperatures (*: peaks of products from beginning decomposition, #: peak of residue hexane).

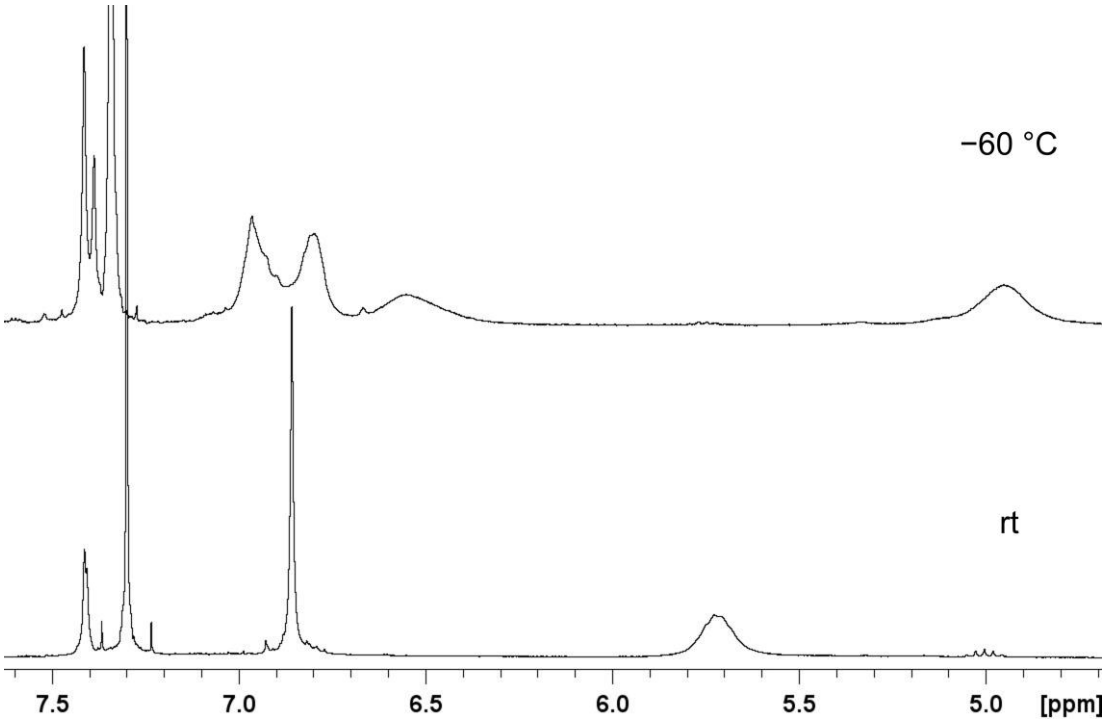


Figure S10. Excerpts of the ^{1}H NMR spectra of aminocarbonyl substituted NHC-bis(germylene) **2b** in thf-d_8 at different temperatures showing the phenylene proton (7.4 ppm at rt), Tip-proton (6.9 ppm at rt) and NHC-methine proton (5.7 ppm at rt) resonances.

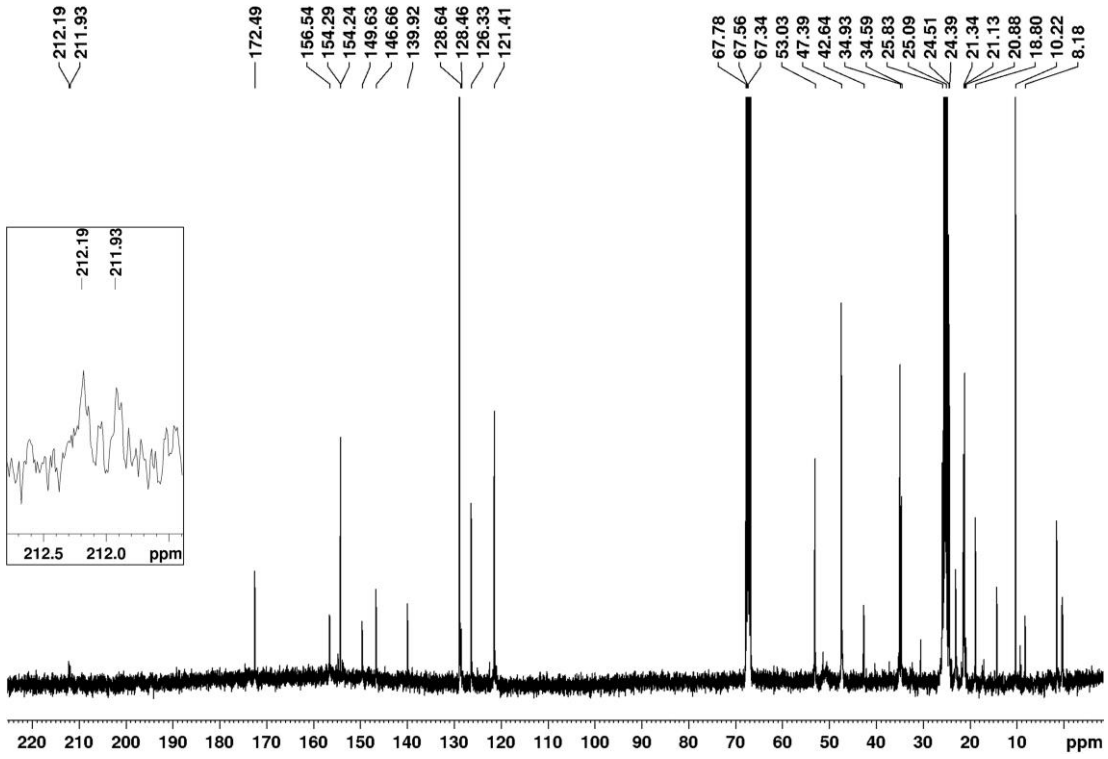


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of aminocarbonyl substituted NHC-bis(germylene) **2b** in thf-d_8.

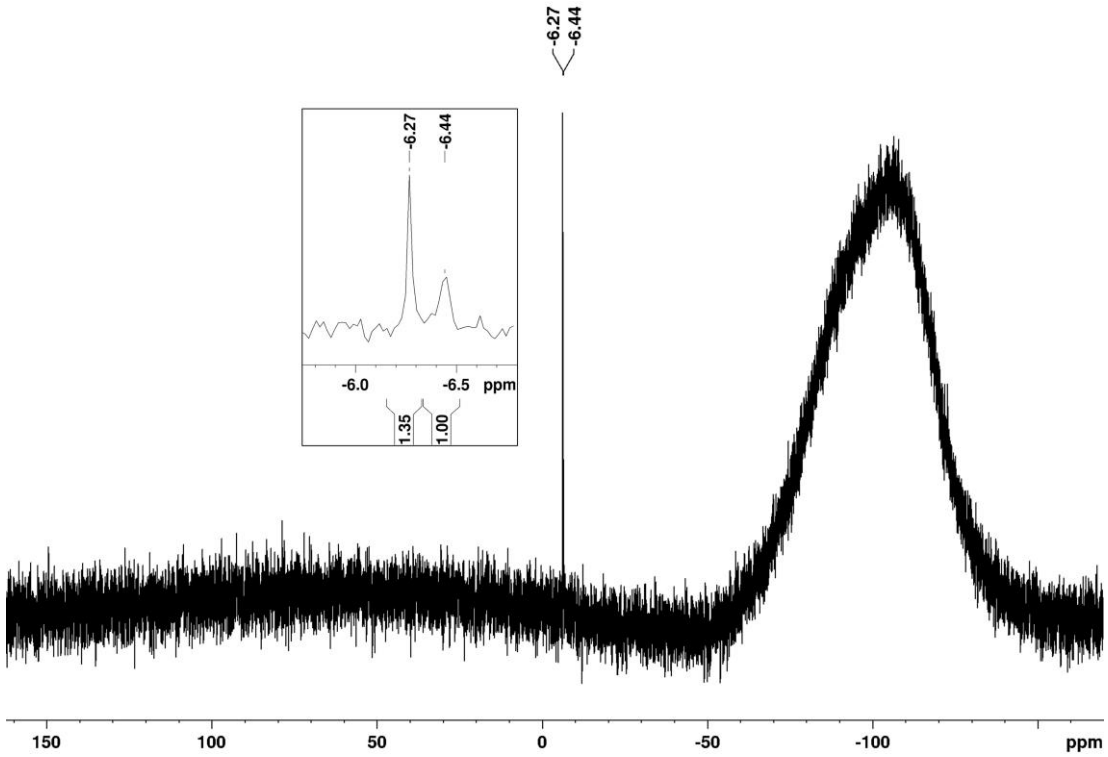


Figure S12. $^{29}Si\{^{1}H\}$ NMR spectrum of aminocarbonyl substituted NHC-bis(germylene) **2b** in thf-d_8.

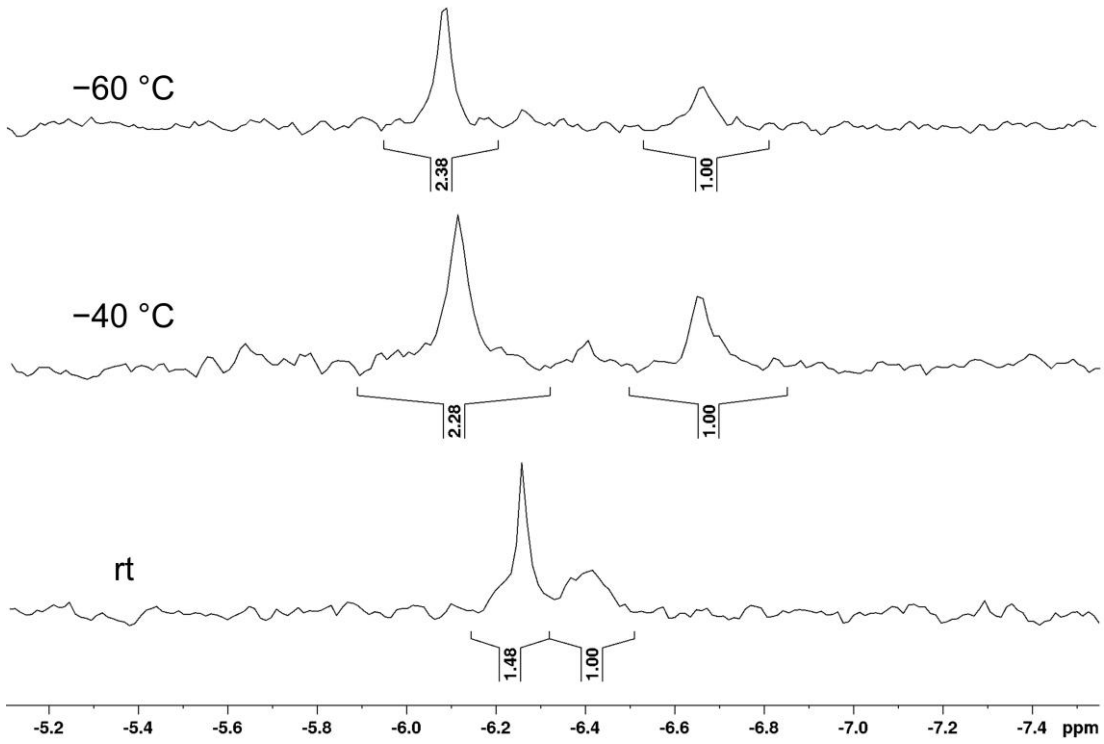


Figure S13. $^{29}Si\{^{1}H\}$ NMR spectra of aminocarbonyl substituted NHC-bis(germylene) **2b** in thf-d_8 at different temperatures.

High temperature experiments for the determination of the coalescence temperature (> rt) were prevented by the limited stability of NHC-bis(germylene) **2b**. Hence, for the determination of the rotational barrier of the C–N bond, the following approach was used according to reference [S20].

The rate constant k_{298} of the conformational change at a temperature below the coalescence temperature (*i.e.* here at 298 K, where the peaks overlap slightly) is estimated *via*:

$$k_{298} = \frac{\pi}{\sqrt{2}} \left(\Delta\vartheta_0{}^2 - \Delta\vartheta_{298}{}^2\right)^{1/2}$$

where $\Delta\nu_0$ is the peak separation at slow exchange (*i.e.* at low temperature, here at 213 K) in Hz and $\Delta\nu_{298}$ is the peak separation at 298 K.

The Eyring equation[S21] was used for the determination of the Gibbs free energy barrier $\Delta G^{\ddagger}$ of the rotation:

$$\Delta G^{\ddagger} = -RT \left(\ln\frac{k}{T} - \ln\frac{k_B}{h}\right)$$

where R is the molar gas constant, T the temperature, k the corresponding rate constant, k_B the Boltzmann constant and h the Planck constant.

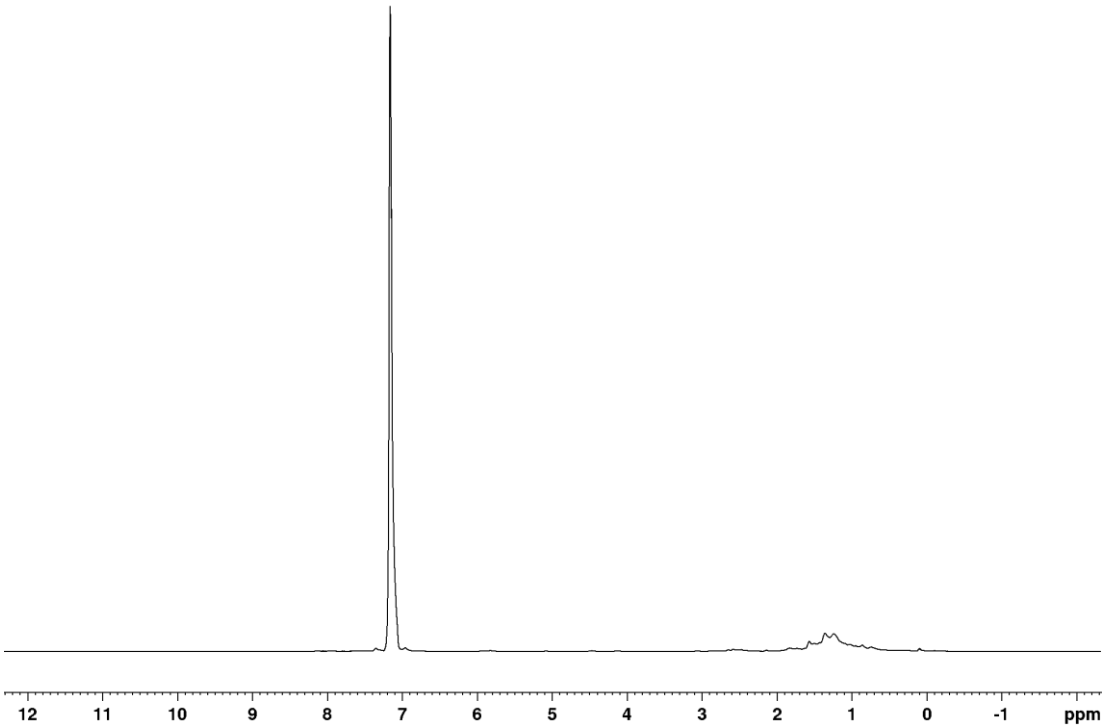


Figure S14. ^{1}H NMR spectrum of germylene radical **3** in C_6D_6.

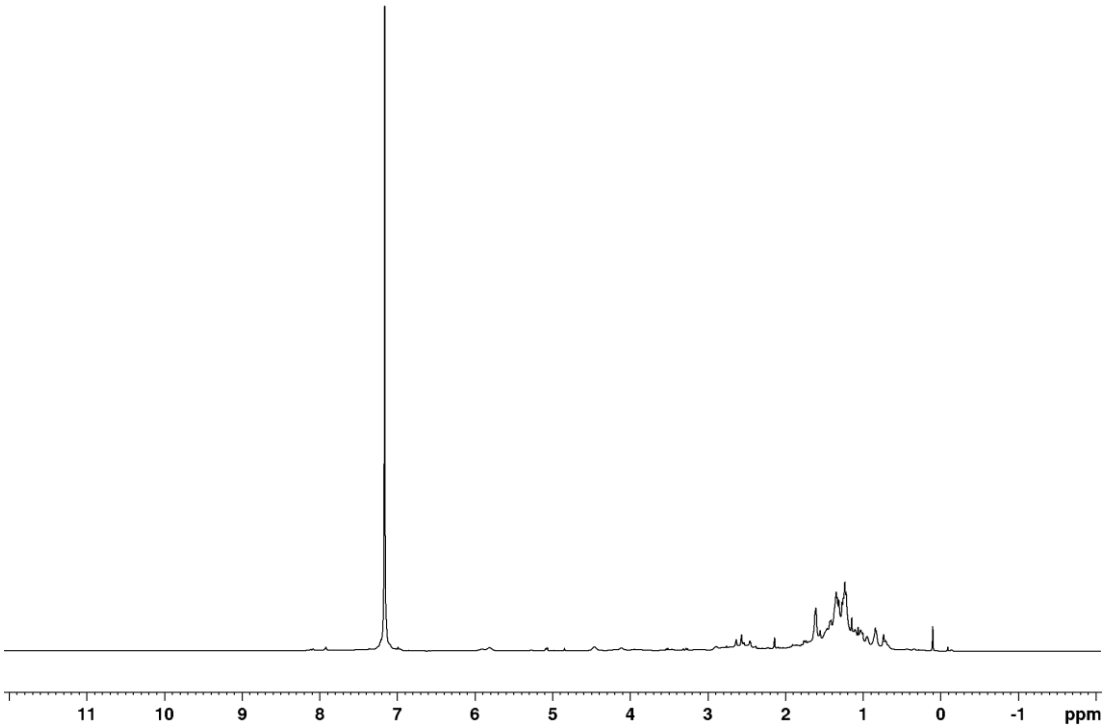


Figure S15. ^{1}H NMR spectrum of the mother liquor of the reaction of NHC-bis(acylgermylene) **2a** with CAAC^{Me} towards germylene radical **3** in C_6D_6.

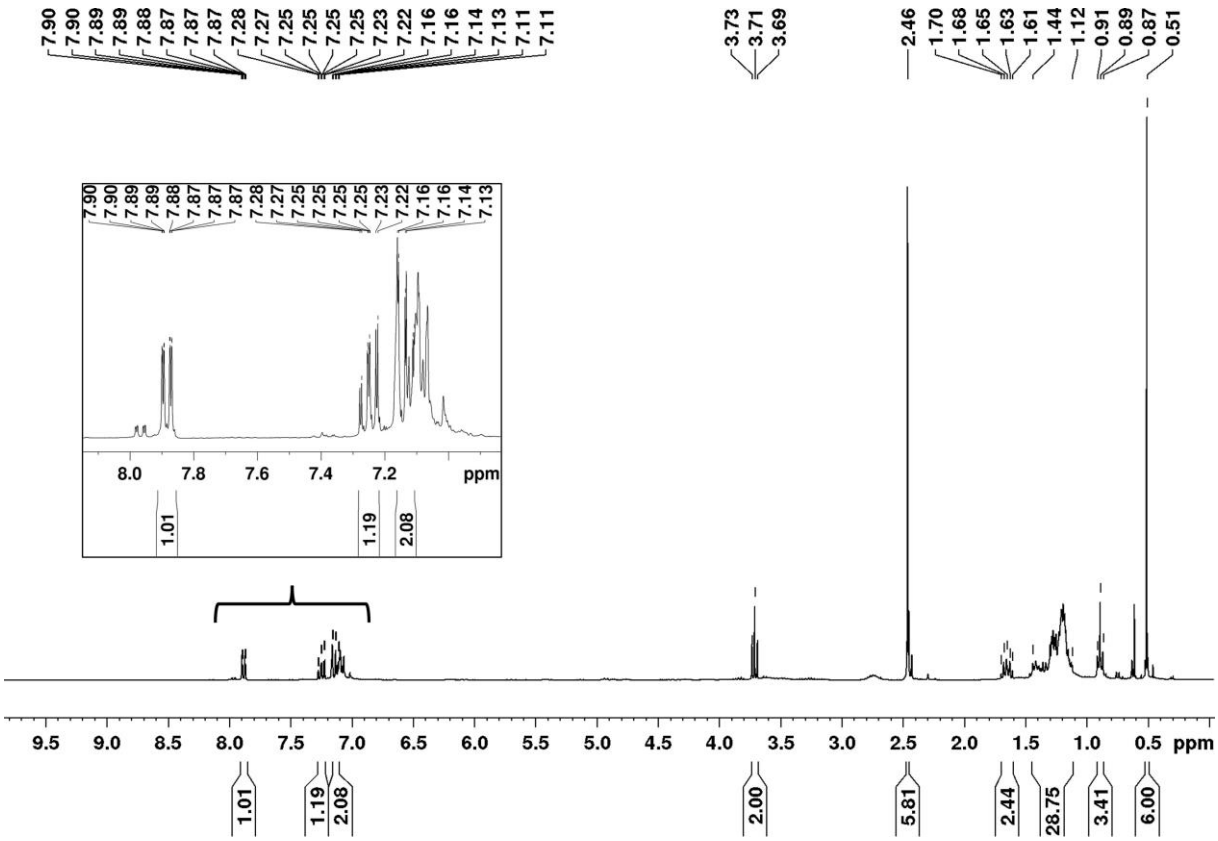


Figure S16. ^{1}H NMR spectrum of a mixture of siloxane **Si$_{OHex}$** and unidentified by-products. Only peaks assigned to **Si$_{OHex}$** are marked.

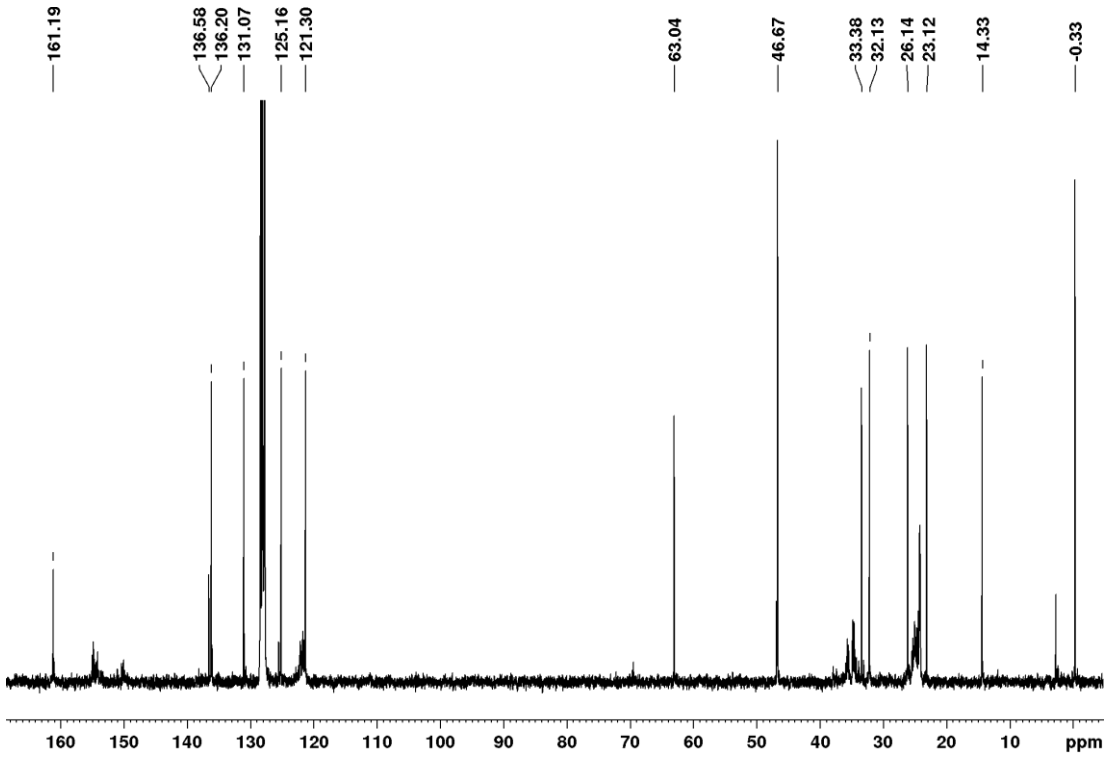


Figure S17. ^{13}C{^{1}H} NMR spectrum of siloxane **Si$_{OHex}$**.

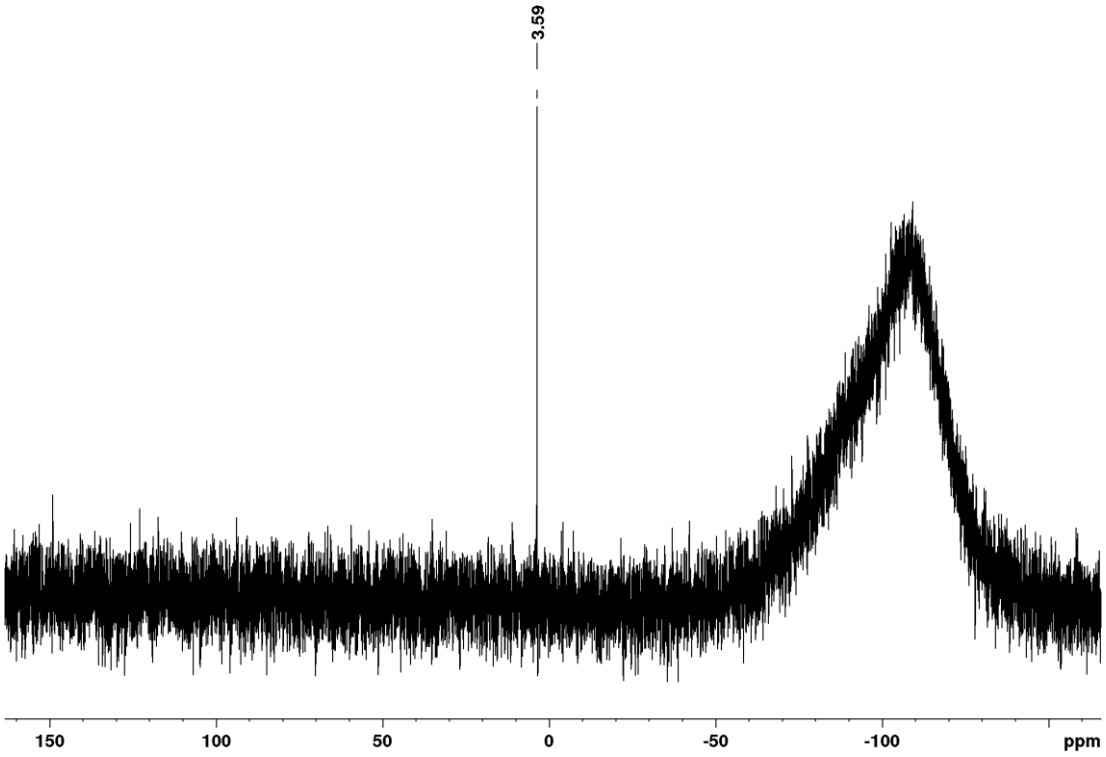


Figure S18. $^{29}Si\{^{1}H\}$ NMR spectrum of siloxane $\mathbf{Si_{OHex}}$.

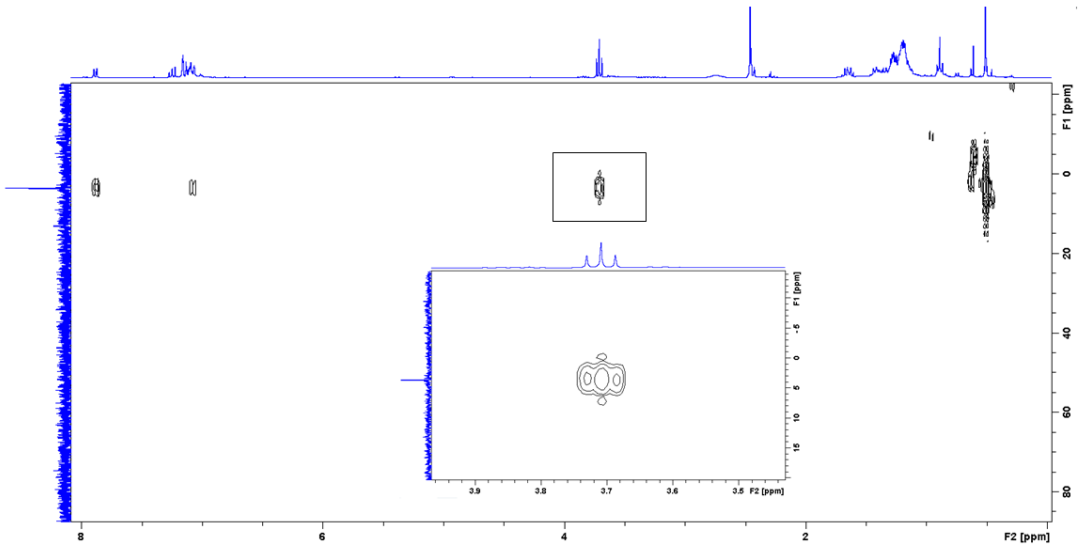


Figure S19. ^{29}Si-^{1}H-HMBC NMR spectrum of siloxane $\mathbf{Si_{OHex}}$.

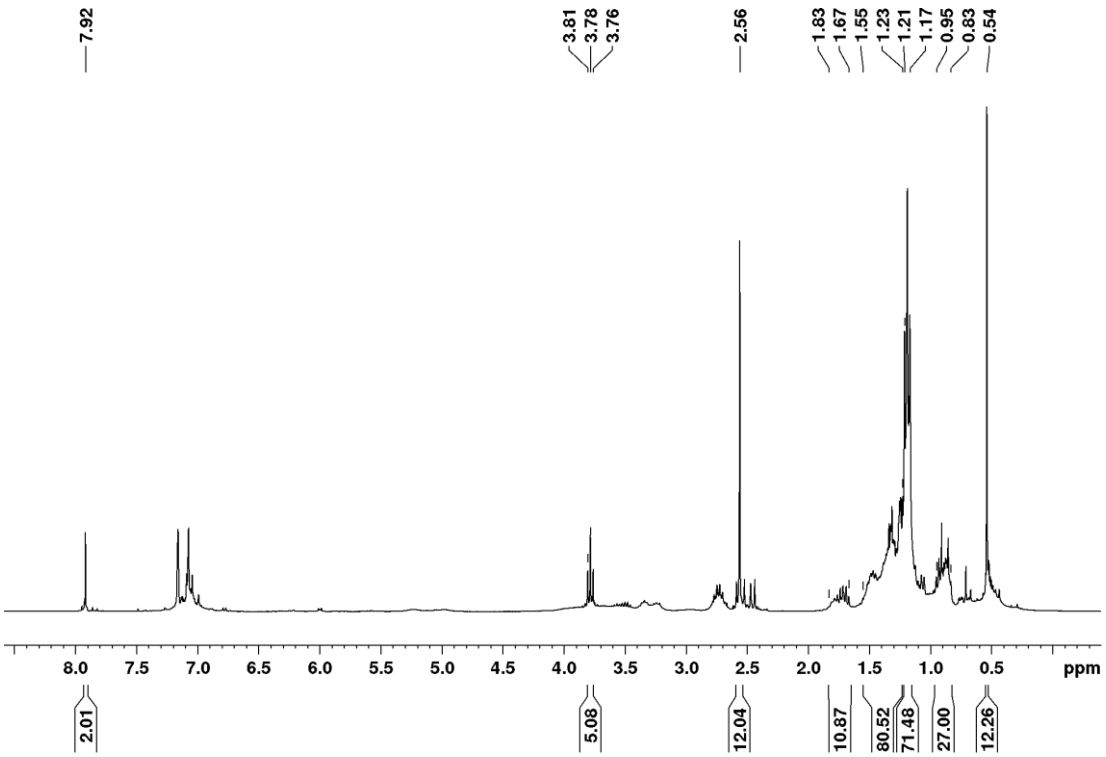


Figure S20. ^{1}H NMR spectrum of a mixture of bis(siloxane) **Bis-Si$_{OHex}$** and unidentified by-products. Only peaks assigned to **Bis-Si$_{OHex}$** are marked.

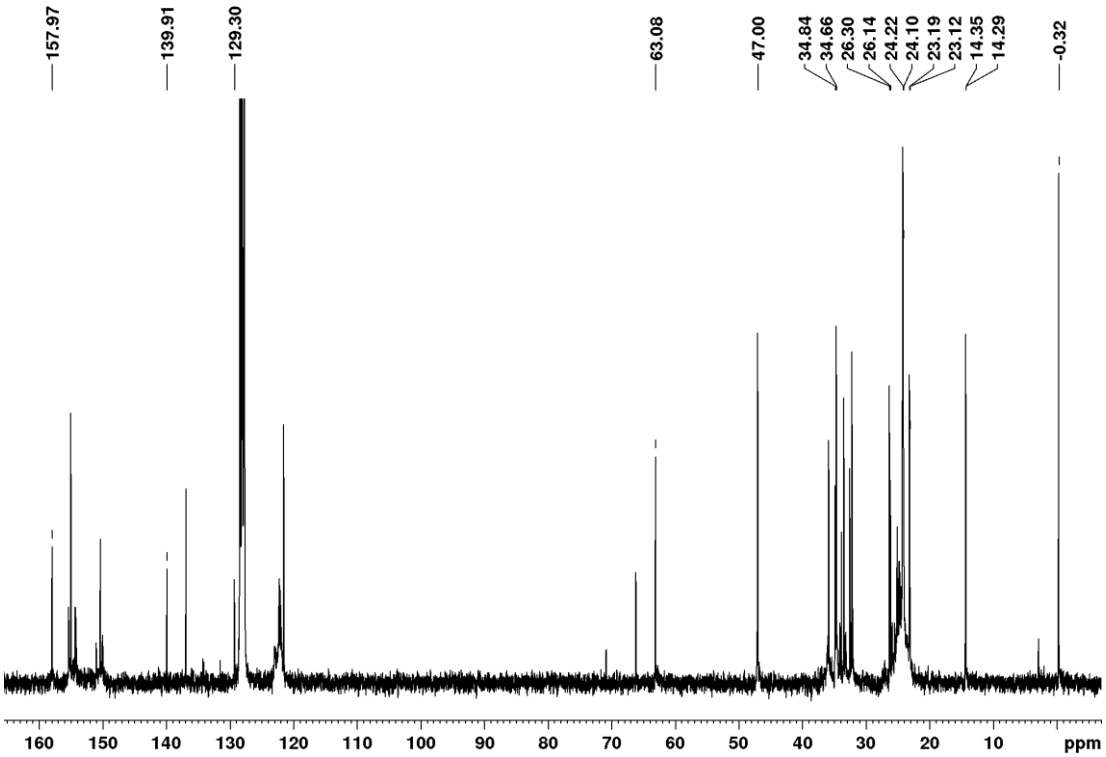


Figure S21. ^{13}C{^{1}H} NMR spectrum of a mixture of bis(siloxane) **Bis-Si$_{OHex}$** and unidentified by-products. Only peaks assigned to **Bis-Si$_{OHex}$** are marked.

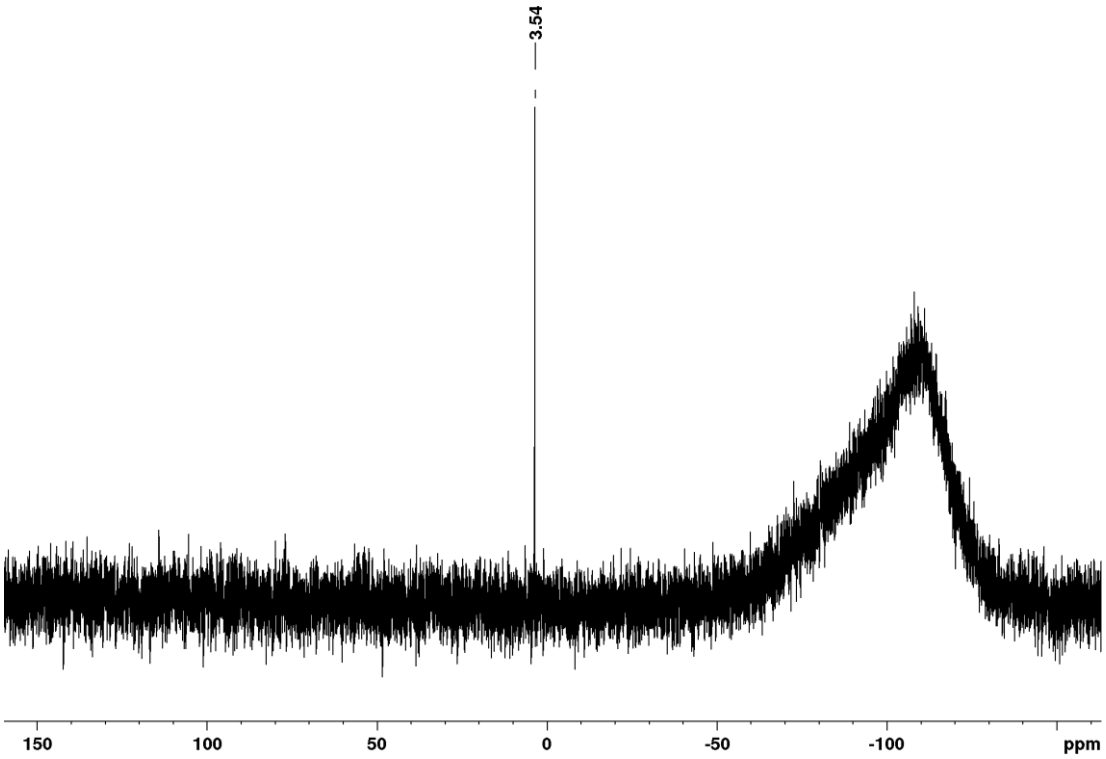


Figure S22. $^{29}Si\{^{1}H\}$ NMR spectrum of bis(siloxane) **Bis-Si$_{OHex}$**.

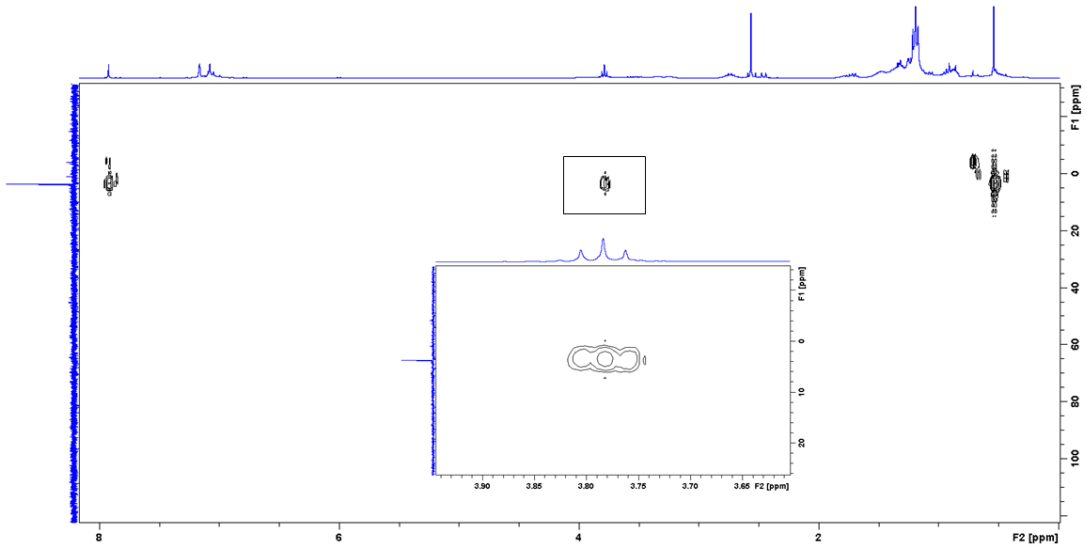


Figure S23. ^{29}Si-^{1}H-HMBC NMR spectrum of bis(siloxane) **Bis-Si$_{OHex}$**.

3.3 IR spectroscopic data

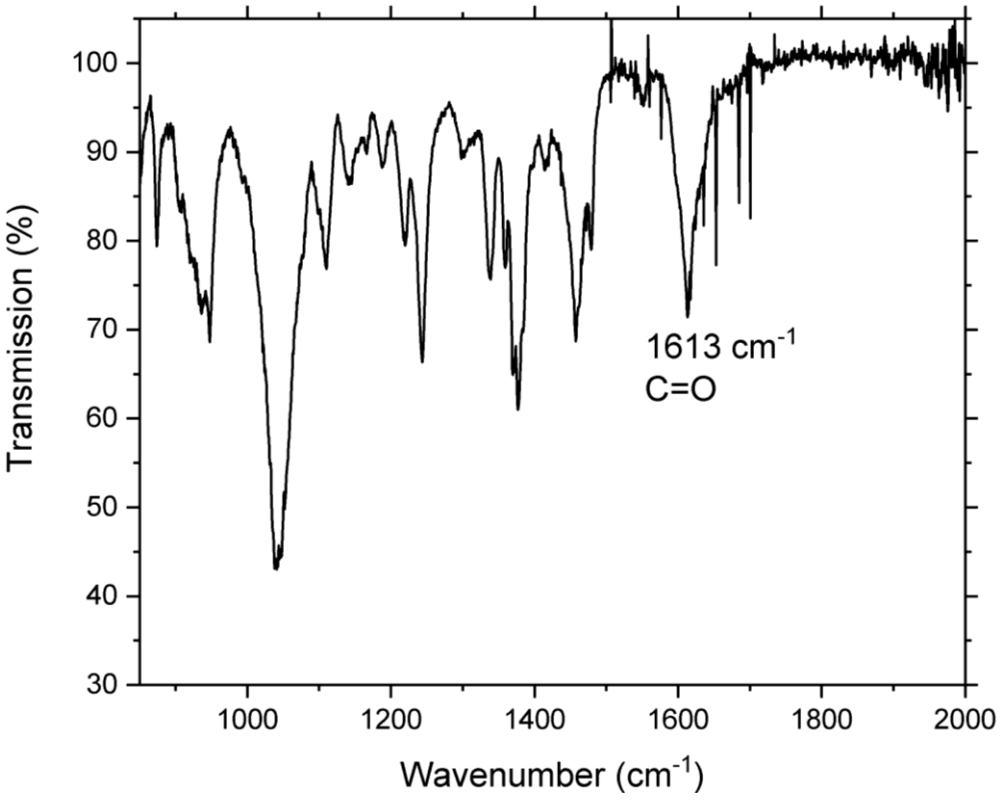


Figure S24. IR spectrum of NHC-bis(germylene) **2a**.

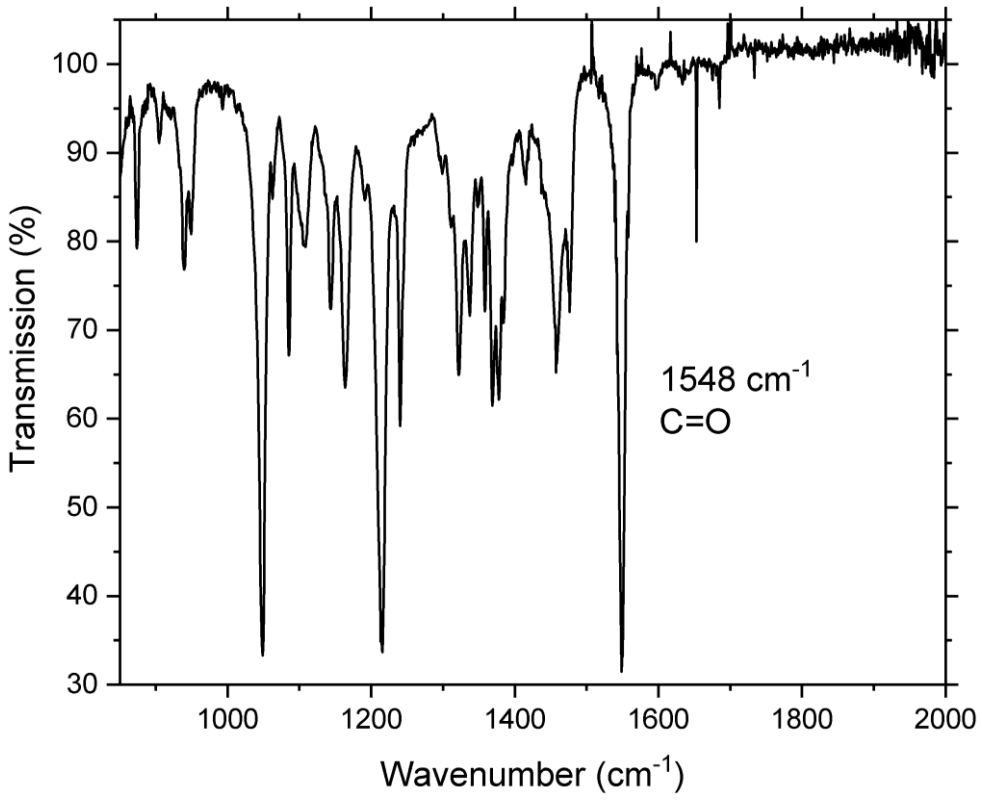


Figure S25. IR spectrum of NHC-bis(germylene) **2b**.

3.4 DFT calculations

NHC-Bis(carboxylgermylene) 2a

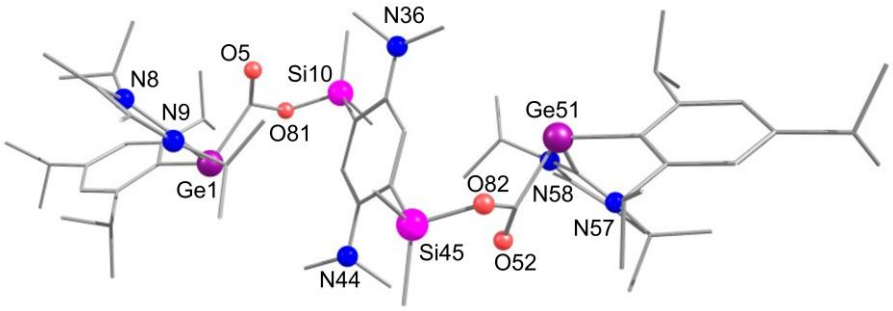


Figure S26. Optimized structure of NHC-bis(germylene) **2a** (Gibbs free energy = −5033900.3832 kcal mol^{-1}). Hydrogen atoms omitted for clarity.

Table S3. Atomic coordinates of the optimized structure of NHC-bis(germylene) **2a**.

32	4.833945000	-0.217993000	-0.517951000
6	3.911781000	-1.077225000	1.100097000
6	6.785158000	-0.783294000	-0.689186000
6	5.205785000	1.483319000	0.625679000
8	3.539722000	-0.451258000	2.100210000
6	7.325420000	-2.016924000	-0.233348000
6	7.648575000	0.132051000	-1.362361000
7	6.225585000	1.831993000	1.462198000
7	4.419923000	2.593001000	0.510904000
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6	8.713413000	-2.247341000	-0.332947000
6	6.433512000	-3.090858000	0.386212000
6	9.026859000	-0.140491000	-1.451206000
6	7.113719000	1.381512000	-2.070369000
6	6.097229000	3.170321000	1.860925000
6	7.120458000	0.811274000	2.063339000
6	4.949891000	3.652895000	1.254383000
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6	-6.439710000	3.005585000	-1.926297000
6	-6.781426000	4.511927000	0.087244000
1	-9.684409000	-0.584919000	1.959296000
1	-6.024152000	-1.443297000	1.858518000
6	-7.250525000	-1.224079000	3.596691000
6	-7.751526000	-2.692206000	1.578754000
6	-7.064984000	-3.900825000	-2.731966000
1	-6.947537000	0.073832000	-1.426993000
6	-6.637335000	-0.477548000	-3.480352000
6	-8.607587000	-1.152600000	-1.960707000
6	-4.370013000	-5.030174000	-1.296769000
1	-3.051397000	-1.494493000	0.539499000
6	-2.784431000	-3.514993000	1.181677000
6	-2.015231000	-2.478432000	-1.055134000
6	-11.090175000	1.567898000	0.965904000
1	-7.457185000	3.197496000	-2.330590000
1	-5.743301000	3.749034000	-2.367591000
1	-6.114403000	2.005446000	-2.273071000
1	-6.813520000	4.570163000	1.194692000
1	-6.018763000	5.233320000	-0.273872000
1	-7.764613000	4.857075000	-0.298054000
1	-6.799867000	-2.089596000	4.127777000
1	-6.741814000	-0.301460000	3.942861000

1	-8.316311000	-1.156014000	3.902127000
1	-8.846669000	-2.710758000	1.764828000
1	-7.590147000	-2.838024000	0.492474000
1	-7.312151000	-3.564729000	2.107039000
1	-8.044297000	-4.050666000	-2.231129000
1	-7.256708000	-3.367497000	-3.684715000
1	-6.663082000	-4.900472000	-2.984961000
1	-7.214599000	0.383882000	-3.872443000
1	-5.564119000	-0.201760000	-3.453764000
1	-6.774682000	-1.323708000	-4.185621000
1	-8.874674000	-1.450040000	-0.928723000
1	-9.189277000	-0.238728000	-2.194069000
1	-8.928235000	-1.943548000	-2.667093000
1	-4.908859000	-5.642965000	-2.044200000
1	-3.297970000	-5.024842000	-1.577699000
1	-4.455105000	-5.546364000	-0.317326000
1	-3.607355000	-3.515140000	1.924816000
1	-2.641514000	-4.548790000	0.808107000
1	-1.855811000	-3.213068000	1.707762000
1	-1.912580000	-3.459432000	-1.563567000
1	-2.293218000	-1.707288000	-1.798409000
1	-1.028503000	-2.205190000	-0.638367000
1	-11.265207000	2.564520000	0.501868000
6	-11.867252000	0.525098000	0.138539000
6	-11.607266000	1.631498000	2.415914000
1	-12.956688000	0.741525000	0.139581000
1	-11.519197000	0.509448000	-0.914650000
1	-11.726802000	-0.496389000	0.551975000
1	-11.473597000	0.657387000	2.932571000
1	-11.061059000	2.398360000	3.002145000
1	-12.689744000	1.878580000	2.443694000
8	3.323472000	-2.277574000	0.798113000
8	-3.323824000	2.278128000	-0.797880000

NHC-Bis(amidylgermylene) 2b

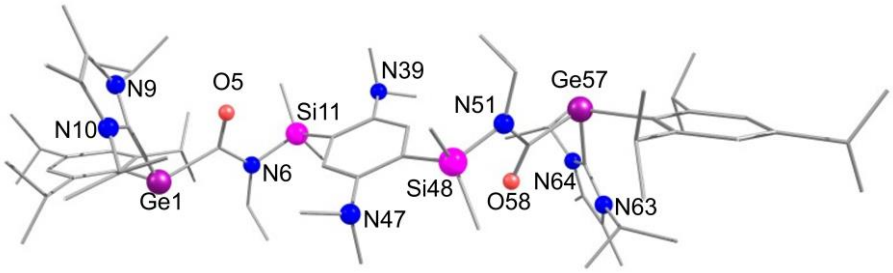


Figure S27. Optimized structure of NHC-bis(germylene) **2b** (Gibbs free energy = −5107565.0053 kcal mol^{-1}). Hydrogen atoms omitted for clarity.

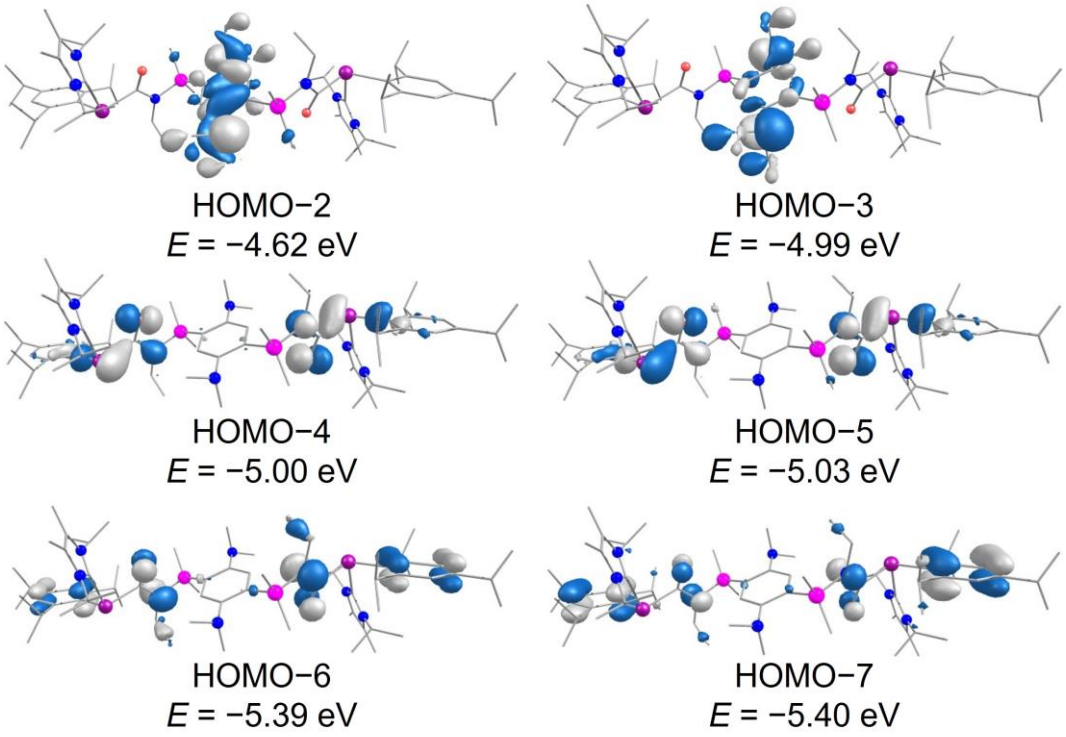


Figure S28. Selected occupied frontier orbitals of NHC-bis(germylene) **2b** (contour value 0.036). Hydrogen atoms omitted for clarity.

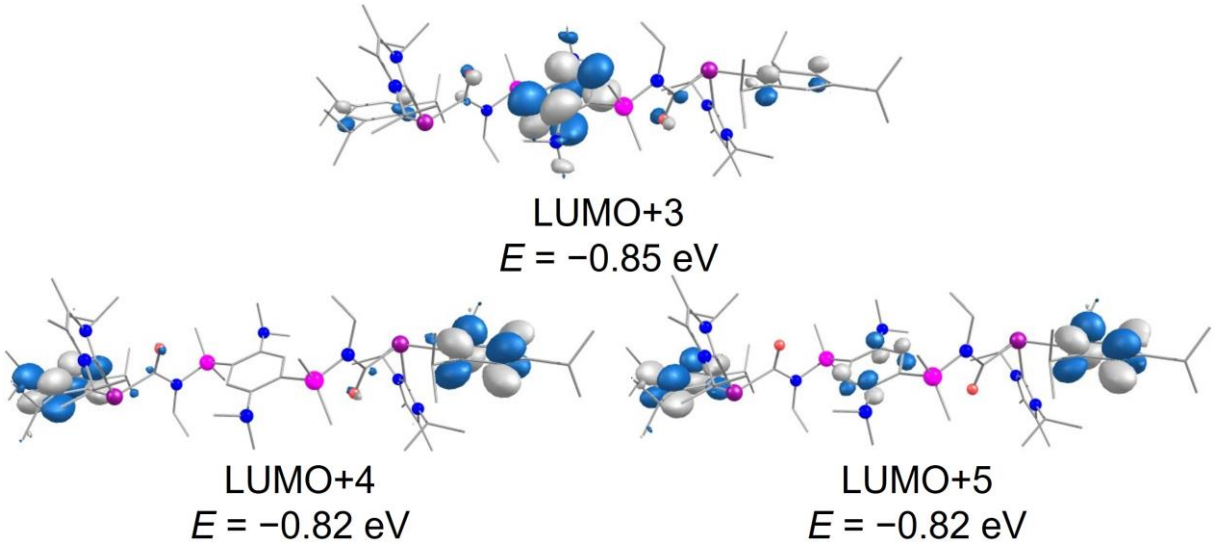


Figure S29. Selected unoccupied frontier orbitals of NHC-bis(germylene) **2b** (contour value 0.036). Hydrogen atoms omitted for clarity.

Table S4. Atomic coordinates of the optimized structure of NHC-bis(germylene) **2b**.

32	-6.273820000	-0.348762000	-1.161343000
6	-4.687336000	0.449637000	-0.072057000
6	-8.015865000	0.724223000	-0.821219000
6	-6.662360000	-1.639973000	0.432719000
8	-4.281762000	-0.105973000	0.973021000
7	-3.918239000	1.467258000	-0.608255000
6	-8.146852000	2.076430000	-0.389051000
6	-9.220220000	-0.002669000	-1.082994000
7	-7.190580000	-1.410055000	1.668469000
7	-6.552782000	-2.996983000	0.326172000
14	-2.558165000	2.044620000	0.449723000
6	-4.176530000	1.973208000	-1.959295000
6	-9.426883000	2.639311000	-0.196673000
6	-6.945637000	2.983101000	-0.133330000
6	-10.477718000	0.593901000	-0.869220000
6	-9.220520000	-1.443506000	-1.602834000
6	-7.427348000	-2.616189000	2.338345000
6	-7.336565000	-0.044477000	2.228357000
6	-7.012972000	-3.626862000	1.487391000
6	-5.879191000	-3.628606000	-0.830786000
6	-1.147531000	0.795483000	0.296023000
6	-3.232057000	2.447426000	2.165412000
6	-1.979248000	3.660608000	-0.352608000
6	-3.288316000	1.328727000	-3.026797000
1	-4.056826000	3.075916000	-1.969030000
1	-5.242800000	1.779306000	-2.208250000
1	-9.508642000	3.685184000	0.146355000
6	-10.609018000	1.917219000	-0.414225000
1	-6.042062000	2.349748000	-0.183352000
6	-6.954544000	3.631428000	1.262770000
6	-6.831885000	4.059370000	-1.230852000
1	-11.387434000	0.000887000	-1.063615000
1	-8.159012000	-1.743936000	-1.742524000
6	-9.879329000	-1.541661000	-2.990702000
6	-9.859598000	-2.419686000	-0.599133000
6	-8.073244000	-2.745177000	3.679886000

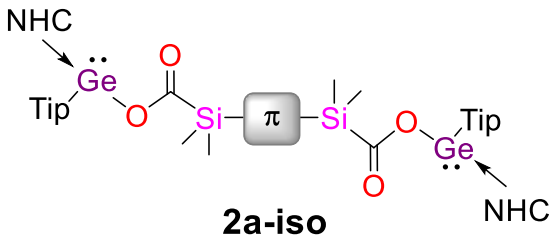
1	-7.027118000	0.595810000	1.383274000
6	-6.341582000	0.192873000	3.368877000
6	-8.792102000	0.297619000	2.554193000
6	-7.067398000	-5.104655000	1.702122000
1	-5.805546000	-2.784775000	-1.557193000
6	-6.709364000	-4.734798000	-1.486332000
6	-4.453651000	-4.037400000	-0.448607000
6	0.098565000	1.067394000	0.909842000
6	-1.230124000	-0.287697000	-0.601019000
1	-4.257874000	2.856738000	2.060565000
1	-2.595143000	3.211227000	2.655255000
1	-3.292494000	1.548548000	2.805582000
1	-1.610924000	3.513288000	-1.388078000
1	-1.142599000	4.063333000	0.253233000
1	-2.790145000	4.419406000	-0.370364000
1	-3.476463000	0.235592000	-3.070444000
1	-2.212008000	1.483878000	-2.807615000
1	-3.505049000	1.755135000	-4.028560000
6	-11.974827000	2.535353000	-0.146525000
1	-7.823972000	4.307242000	1.405662000
1	-6.037703000	4.239302000	1.414369000
1	-6.986799000	2.868106000	2.066047000
1	-6.813521000	3.603117000	-2.241037000
1	-5.906768000	4.661421000	-1.104869000
1	-7.696596000	4.756447000	-1.197072000
1	-9.817668000	-2.578151000	-3.386255000
1	-9.375664000	-0.866935000	-3.712467000
1	-10.952948000	-1.258907000	-2.956299000
1	-10.936002000	-2.193331000	-0.443700000
1	-9.362801000	-2.368294000	0.390364000
1	-9.793077000	-3.468034000	-0.962033000
1	-9.154743000	-2.496443000	3.642855000
1	-7.606922000	-2.087332000	4.438544000
1	-7.985321000	-3.787812000	4.040699000
1	-6.345606000	1.270215000	3.632081000
1	-5.325234000	-0.073204000	3.020810000
1	-6.590700000	-0.372151000	4.290047000
1	-9.447335000	0.087601000	1.685992000
1	-8.866357000	1.382802000	2.765119000
1	-9.173604000	-0.243601000	3.443225000
1	-7.288416000	-5.320444000	2.764906000
1	-6.106880000	-5.599963000	1.456039000
1	-7.859731000	-5.588972000	1.093300000
1	-7.751994000	-4.398574000	-1.653767000
1	-6.730492000	-5.673773000	-0.898938000
1	-6.269528000	-4.974736000	-2.475373000
1	-4.434898000	-4.853523000	0.303482000
1	-3.911566000	-3.164814000	-0.032808000
1	-3.911482000	-4.394622000	-1.346866000
7	0.146888000	2.139623000	1.872804000
6	1.229876000	0.287952000	0.601096000
6	-0.098823000	-1.067158000	-0.909737000
1	-2.192303000	-0.501599000	-1.089898000
1	-11.797865000	3.595892000	0.142430000
6	-12.674469000	1.840024000	1.038478000
6	-12.866041000	2.535788000	-1.402816000
6	-0.115754000	1.677649000	3.235665000
6	1.331515000	2.981606000	1.799530000
6	1.147276000	-0.795219000	-0.295959000
1	2.192065000	0.501869000	1.089945000
7	-0.147164000	-2.139424000	-1.872684000

1	-13.646005000	2.324669000	1.273483000
1	-12.042087000	1.870693000	1.949451000
1	-12.877284000	0.772270000	0.808385000
1	-13.093701000	1.500419000	-1.734310000
1	-12.368086000	3.054877000	-2.247062000
1	-13.834204000	3.042942000	-1.205435000
1	-1.019228000	1.039536000	3.248894000
1	-0.292726000	2.546852000	3.904629000
1	0.735314000	1.081089000	3.657150000
1	1.495266000	3.303328000	0.752455000
1	2.269224000	2.483338000	2.159839000
1	1.178692000	3.887702000	2.424419000
14	2.558000000	-2.044207000	-0.449999000
6	0.114866000	-1.677362000	-3.235635000
6	-1.331583000	-2.981673000	-1.798999000
7	3.918086000	-1.467001000	0.608056000
6	3.231753000	-2.446371000	-2.165894000
6	1.979420000	-3.660521000	0.351912000
1	1.018249000	-1.039126000	-3.249199000
1	0.291700000	-2.546525000	-3.904687000
1	-0.736448000	-1.080912000	-3.656779000
1	-1.494898000	-3.303445000	-0.751868000
1	-2.269523000	-2.483596000	-2.158965000
1	-1.178787000	-3.887728000	-2.423952000
6	4.176296000	-1.973113000	1.959052000
6	4.687257000	-0.449340000	0.072046000
1	4.257744000	-2.855334000	-2.061382000
1	2.595002000	-3.210281000	-2.655780000
1	3.291712000	-1.547316000	-2.805857000
1	1.610817000	-3.513512000	1.387329000
1	1.143047000	-4.063431000	-0.254182000
1	2.790584000	-4.419032000	0.369723000
6	3.288018000	-1.328769000	3.026579000
1	4.056597000	-3.075824000	1.968655000
1	5.242550000	-1.779228000	2.208102000
32	6.273922000	0.348653000	1.161382000
8	4.281658000	0.106609000	-0.972842000
1	3.476178000	-0.235644000	3.070415000
1	2.211721000	-1.483859000	2.807309000
1	3.504680000	-1.755337000	4.028289000
6	8.015827000	-0.724510000	0.821077000
6	6.662643000	1.640097000	-0.432450000
6	8.146622000	-2.076676000	0.388699000
6	9.220292000	0.002167000	1.082948000
7	7.190802000	1.410334000	-1.668258000
7	6.553115000	2.997092000	-0.325713000
6	9.426577000	-2.639702000	0.196224000
6	6.945297000	-2.983142000	0.132781000
6	10.477703000	-0.594545000	0.869075000
6	9.220793000	1.442925000	1.603002000
6	7.427853000	2.616567000	-2.337859000
6	7.336650000	0.044840000	-2.228380000
6	7.013517000	3.627133000	-1.486758000
6	5.879513000	3.628607000	0.831302000
1	9.508190000	-3.685534000	-0.146967000
6	10.608814000	-1.917809000	0.413874000
1	6.041804000	-2.349683000	0.182848000
6	6.954202000	-3.631219000	-1.263441000
6	6.831334000	-4.059589000	1.230101000
1	11.387504000	-0.001691000	1.063562000
1	8.159327000	1.743464000	1.742784000

6	9.879686000	1.540820000	2.990842000
6	9.859962000	2.419152000	0.599398000
6	8.074002000	2.745736000	-3.679260000
1	7.027212000	-0.595556000	-1.383381000
6	6.341583000	-0.192271000	-3.368883000
6	8.792138000	-0.297348000	-2.554352000
6	7.068222000	5.104961000	-1.701179000
1	5.805842000	2.784700000	1.557620000
6	6.709703000	4.734721000	1.486948000
6	4.453979000	4.037458000	0.449153000
6	11.974536000	-2.536101000	0.146089000
1	7.823557000	-4.307113000	-1.406401000
1	6.037288000	-4.238942000	-1.415215000
1	6.986612000	-2.867750000	-2.066572000
1	6.812915000	-3.603510000	2.240366000
1	5.906166000	-4.661521000	1.103922000
1	7.695970000	-4.756756000	1.196289000
1	9.818208000	2.577278000	3.386505000
1	9.375954000	0.866099000	3.712565000
1	10.953262000	1.257909000	2.956360000
1	10.936327000	2.192652000	0.443892000
1	9.363110000	2.367965000	-0.390082000
1	9.793612000	3.467466000	0.962430000
1	9.155487000	2.496958000	-3.642057000
1	7.607805000	2.088022000	-4.438110000
1	7.986189000	3.788430000	-4.039929000
1	6.345596000	-1.269549000	-3.632352000
1	5.325262000	0.073742000	-3.020688000
1	6.590623000	0.372970000	-4.289938000
1	9.447485000	-0.087304000	-1.686241000
1	8.866309000	-1.382556000	-2.765171000
1	9.173558000	0.243774000	-3.443482000
1	7.289349000	5.320930000	-2.763904000
1	6.107783000	5.600397000	-1.455054000
1	7.860604000	5.589009000	-1.092204000
1	7.752309000	4.398442000	1.654421000
1	6.730906000	5.673725000	0.899599000
1	6.269826000	4.974627000	2.475978000
1	4.435234000	4.853693000	-0.302813000
1	3.911921000	3.164931000	0.033199000
1	3.911779000	4.394543000	1.347448000
1	11.797413000	-3.596536000	-0.143148000
6	12.674375000	-1.840587000	-1.038688000
6	12.865669000	-2.537008000	1.402439000
1	13.645837000	-2.325345000	-1.273761000
1	12.042043000	-1.870903000	-1.949710000
1	12.877370000	-0.772930000	-0.808306000
1	13.093462000	-1.501761000	1.734223000
1	12.367575000	-3.056243000	2.246514000
1	13.833766000	-3.044260000	1.204989000

Table S5. Reaction enthalpies determined with DFT calculations at the BP86-D3(BJ)/def2-TZVPP//BP86-D3(BJ)/def2-SVP level of theory.

Reaction	ΔG (kcal mol^{-1})
1 + CO_2 → **2a**	−5.996
1 + CO_2 → **2a-iso**	5.391
1 + ^{Et}NCO → **2b**	−18.87



2a-iso

Scheme S1. Structure of the constitutional isomer **2a-iso** with Ge–O and Si–C bonds, which is not formed in the reaction of NHC-bis(germylene) **1** with CO_2 (π = 2,5-(*N*,*N*,*N'*,*N'*-tetramethyldiamino)-*p*-phenylene, Tip = 2,4,6-triisopropylphenyl, NHC = 1,3-diisopropylimidazol-4,5-dimethyl-2-ylidene).

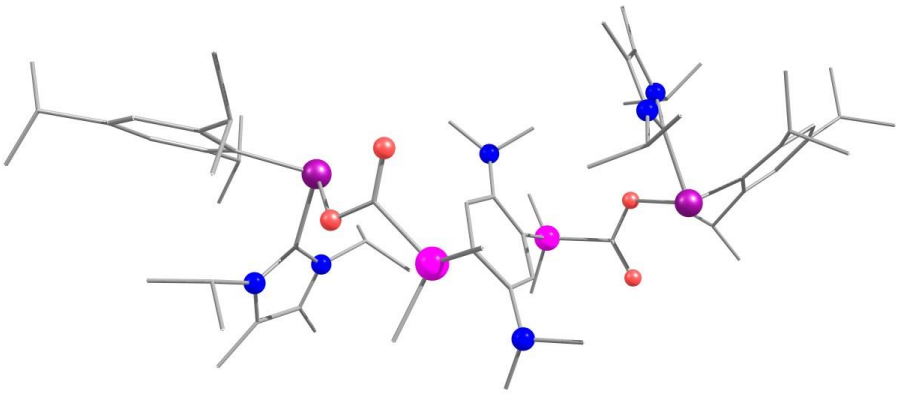


Figure S30. Optimized structure of germylenyl ester **2a-iso** (Gibbs free energy = −5033888.9967 kcal mol^{-1}). Hydrogen atoms omitted for clarity.

Table S6. Atomic coordinates of the optimized structure of the germylenyl ester **2a-iso**.

32	4.457169000	-0.579419000	-0.590818000
6	6.357476000	-1.319876000	-0.870392000
6	5.184676000	1.358504000	-0.129430000
6	6.908592000	-2.415555000	-0.152824000
6	7.144487000	-0.707428000	-1.886947000
7	6.251637000	1.760851000	0.618635000
7	4.609008000	2.502949000	-0.599544000
14	2.086071000	-0.506696000	3.114783000
6	8.260005000	-2.767810000	-0.359517000
6	6.075532000	-3.234461000	0.832132000

6	8.481364000	-1.102299000	-2.082520000
6	6.550750000	0.340807000	-2.832859000
6	6.364010000	3.156630000	0.608154000
6	7.075056000	0.808943000	1.405445000
6	5.320863000	3.629848000	-0.170872000
6	3.330938000	2.485489000	-1.354858000
6	0.892982000	0.340497000	1.899216000
6	3.114476000	0.697723000	4.144609000
6	1.196406000	-1.782820000	4.185690000
1	8.697484000	-3.595268000	0.224994000
6	9.072622000	-2.110779000	-1.298740000
1	5.009343000	-2.970647000	0.678684000
6	6.416599000	-2.898086000	2.295585000
6	6.191480000	-4.747062000	0.567608000
1	9.080114000	-0.608718000	-2.866981000
1	5.502175000	0.529457000	-2.508794000
6	6.460575000	-0.208579000	-4.269538000
6	7.294396000	1.686719000	-2.788425000
6	7.451357000	3.936769000	1.273494000
1	6.702286000	-0.175118000	1.072415000
6	6.772726000	0.932742000	2.900428000
6	8.561589000	0.866879000	1.046082000
6	5.019959000	5.041142000	-0.559964000
1	3.128272000	1.397342000	-1.468458000
6	3.470892000	3.084191000	-2.756725000
6	2.186621000	3.075298000	-0.527882000
6	0.013707000	1.338001000	2.371500000
6	0.805952000	-0.046225000	0.544267000
1	3.979492000	0.169444000	4.597457000
1	2.505096000	1.144851000	4.953672000
1	3.507980000	1.513112000	3.504897000
1	0.805171000	-2.592998000	3.537663000
1	0.356055000	-1.325011000	4.745690000
1	1.895843000	-2.238177000	4.917881000
6	10.537939000	-2.489559000	-1.473369000
1	7.485133000	-3.106360000	2.521533000
1	5.795171000	-3.501577000	2.990481000
1	6.211093000	-1.831977000	2.510972000
1	5.967294000	-4.986583000	-0.492249000
1	5.470734000	-5.301803000	1.204057000
1	7.205909000	-5.139303000	0.795483000
1	5.961597000	0.519176000	-4.944789000
1	5.884972000	-1.155965000	-4.293043000
1	7.469535000	-0.417497000	-4.683602000
1	8.344531000	1.576672000	-3.132313000
1	7.320225000	2.104121000	-1.762366000
1	6.808008000	2.434764000	-3.450258000
1	8.422987000	3.826188000	0.747856000
1	7.605973000	3.627360000	2.325577000
1	7.195028000	5.013466000	1.275728000
1	7.308478000	0.130166000	3.445931000
1	5.688761000	0.798454000	3.071914000
1	7.095435000	1.902849000	3.331111000
1	8.702279000	0.820525000	-0.051192000
1	9.057789000	-0.027065000	1.473377000
1	9.076417000	1.762264000	1.447665000
1	5.625801000	5.736214000	0.051999000
1	3.954984000	5.304892000	-0.408674000
1	5.264932000	5.239169000	-1.624940000
1	4.330686000	2.638031000	-3.295371000
1	3.596638000	4.185150000	-2.743039000

1	2.552053000	2.862735000	-3.335910000
1	2.295856000	4.164942000	-0.354630000
1	2.100970000	2.561615000	0.449933000
1	1.231138000	2.912264000	-1.061172000
7	0.018217000	1.652544000	3.783372000
6	-0.851947000	1.987240000	1.471479000
6	-0.119225000	0.547830000	-0.345243000
1	1.434801000	-0.874170000	0.186801000
1	10.741621000	-3.324078000	-0.765461000
6	11.465784000	-1.318652000	-1.093652000
6	10.834529000	-3.001923000	-2.895700000
6	0.443733000	3.018223000	4.071769000
6	-1.237560000	1.304379000	4.446037000
6	-0.912569000	1.647033000	0.103252000
1	-1.507604000	2.788627000	1.853136000
7	-0.275635000	0.061973000	-1.667856000
1	12.534503000	-1.611675000	-1.169003000
1	11.273756000	-0.975556000	-0.056352000
1	11.307017000	-0.449994000	-1.767794000
1	10.664020000	-2.207030000	-3.652617000
1	10.179968000	-3.858299000	-3.156934000
1	11.891168000	-3.330907000	-2.989520000
1	1.415523000	3.216789000	3.577159000
1	0.581393000	3.143952000	5.167259000
1	-0.284781000	3.799986000	3.730875000
1	-1.494195000	0.249559000	4.223687000
1	-2.107145000	1.936273000	4.130232000
1	-1.119033000	1.408573000	5.545751000
14	-1.993372000	2.820966000	-0.933962000
6	-1.599052000	-0.484886000	-1.962630000
6	0.779987000	-0.783760000	-2.203036000
6	-1.910957000	2.614640000	-2.812653000
6	-1.510926000	4.598493000	-0.500307000
1	-2.395660000	0.095672000	-1.460165000
1	-1.788885000	-0.476391000	-3.056273000
1	-1.686998000	-1.544607000	-1.612276000
1	1.782155000	-0.358089000	-1.997851000
1	0.774565000	-1.821209000	-1.779243000
1	0.649784000	-0.871400000	-3.302092000
1	-2.226313000	3.561042000	-3.298957000
1	-0.875800000	2.373603000	-3.128312000
1	-2.571246000	1.807298000	-3.180480000
1	-1.606020000	4.779462000	0.588303000
1	-0.469762000	4.826307000	-0.809767000
1	-2.191134000	5.307747000	-1.017095000
32	-5.213369000	0.365922000	1.042988000
6	-7.152392000	0.280008000	0.343464000
6	-4.650793000	-1.340159000	-0.093368000
6	-7.809405000	1.341009000	-0.335439000
6	-7.875194000	-0.923646000	0.583643000
7	-4.882207000	-1.684221000	-1.393800000
7	-3.825179000	-2.305935000	0.403209000
6	-9.092782000	1.124404000	-0.882732000
6	-7.168915000	2.719871000	-0.482370000
6	-9.161937000	-1.096850000	0.040583000
6	-7.314115000	-2.025170000	1.488491000
6	-4.200123000	-2.863314000	-1.720253000
6	-5.738186000	-0.871852000	-2.295241000
6	-3.521852000	-3.255822000	-0.577344000
6	-3.298951000	-2.246610000	1.791132000
1	-9.586579000	1.938725000	-1.440453000

6	-9.776969000	-0.093319000	-0.731633000
1	-6.284286000	2.754101000	0.185285000
6	-6.669801000	2.974928000	-1.916228000
6	-8.110466000	3.844070000	-0.011657000
1	-9.702326000	-2.041053000	0.225149000
1	-6.289345000	-1.717261000	1.795838000
6	-8.137134000	-2.130789000	2.787151000
6	-7.192869000	-3.388392000	0.786148000
6	-4.236733000	-3.543843000	-3.049984000
1	-6.151869000	-0.102927000	-1.619043000
6	-4.916784000	-0.148083000	-3.363757000
6	-6.925664000	-1.667050000	-2.845095000
6	-2.628562000	-4.438347000	-0.386042000
1	-3.909591000	-1.438660000	2.252329000
6	-3.554963000	-3.536165000	2.575450000
6	-1.848522000	-1.765021000	1.801655000
6	-11.146901000	-0.310562000	-1.362016000
1	-7.507151000	2.949841000	-2.647203000
1	-6.181411000	3.969810000	-1.990365000
1	-5.922273000	2.214645000	-2.212474000
1	-8.478499000	3.652662000	1.017204000
1	-7.574259000	4.816115000	-0.007999000
1	-8.996701000	3.955384000	-0.672713000
1	-7.690818000	-2.872700000	3.483300000
1	-8.182535000	-1.151413000	3.304891000
1	-9.180143000	-2.448300000	2.576201000
1	-8.185638000	-3.760991000	0.456542000
1	-6.541697000	-3.331347000	-0.108777000
1	-6.766521000	-4.152925000	1.470185000
1	-5.199522000	-4.067596000	-3.226755000
1	-4.084921000	-2.835182000	-3.887206000
1	-3.432573000	-4.302537000	-3.104198000
1	-5.590285000	0.504581000	-3.954185000
1	-4.161330000	0.494225000	-2.875542000
1	-4.413290000	-0.837659000	-4.071582000
1	-7.457678000	-2.192359000	-2.028867000
1	-7.645064000	-0.954527000	-3.295058000
1	-6.638936000	-2.397540000	-3.627761000
1	-2.370588000	-4.874850000	-1.369848000
1	-1.678770000	-4.163900000	0.114455000
1	-3.108079000	-5.238417000	0.215720000
1	-4.602635000	-3.877032000	2.452247000
1	-2.876841000	-4.361952000	2.284515000
1	-3.385582000	-3.338483000	3.652902000
1	-1.156508000	-2.451509000	1.273798000
1	-1.770393000	-0.767656000	1.328214000
1	-1.488028000	-1.672295000	2.844517000
1	-11.412337000	0.633110000	-1.889382000
6	-11.107022000	-1.437223000	-2.413091000
6	-12.232490000	-0.572326000	-0.300444000
1	-12.093729000	-1.560691000	-2.907914000
1	-10.351411000	-1.226835000	-3.197597000
1	-10.841387000	-2.409382000	-1.945650000
1	-12.032300000	-1.513333000	0.254769000
1	-12.273167000	0.251144000	0.441352000
1	-13.234903000	-0.667820000	-0.769089000
8	2.874656000	-2.489638000	1.304222000
6	3.209873000	-1.422070000	1.834080000
8	4.203903000	-0.656415000	1.395252000
8	-4.141778000	3.202048000	0.785604000
8	-4.255716000	1.319447000	-0.466818000

6	-3.718227000	2.482996000	-0.126614000

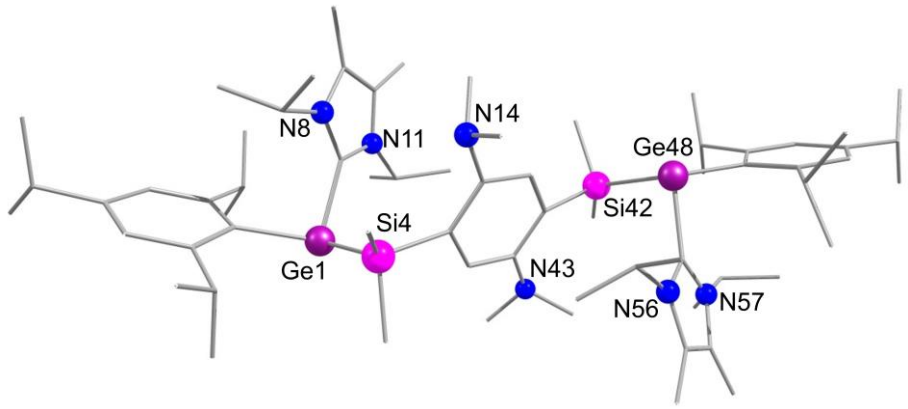


Figure S31. Optimized structure of NHC-bis(germylene) **1** (Gibbs free energy = −4797087.9210 kcal mol^{-1}). Hydrogen atoms omitted for clarity.

Table S7. Atomic coordinates of the optimized structure of NHC-bis(germylene) **1**.

32	4.509271000	0.464519000	-1.074076000
6	6.503024000	0.496047000	-0.552665000
6	4.053644000	-1.198573000	0.085880000
14	3.041977000	1.921093000	0.269773000
6	3.235208000	2.609209000	2.044878000
6	1.386951000	0.982612000	0.055536000
6	2.834987000	3.515944000	-0.776593000
7	4.475145000	-1.561991000	1.337717000
6	4.026631000	-2.849445000	1.655887000
6	5.228996000	-0.641716000	2.226952000
7	3.320868000	-2.259917000	-0.375138000
6	3.290522000	-3.290645000	0.569012000
6	2.672946000	-2.261390000	-1.712113000
7	1.147855000	0.094990000	2.383370000
6	0.536681000	1.042935000	3.312285000
6	0.658496000	0.255107000	1.027455000
6	1.049691000	-1.274529000	2.880709000
6	7.171560000	1.592441000	0.066443000
6	7.297048000	-0.628679000	-0.931277000
6	8.540957000	1.500072000	0.389192000
6	6.447083000	2.909299000	0.307140000
6	9.307099000	0.362567000	0.085187000
6	8.666567000	-0.680952000	-0.603959000
6	10.772317000	0.267031000	0.489755000
6	6.719962000	-1.804291000	-1.719442000
6	6.548496000	3.797005000	-0.949298000
6	6.885422000	3.667061000	1.567643000
6	6.751320000	-3.125188000	-0.930841000
6	7.405237000	-1.948922000	-3.090428000
6	4.275531000	-3.561407000	2.945779000
6	2.546521000	-4.578160000	0.420336000
6	6.673752000	-1.090764000	2.461363000
6	4.455533000	-0.360807000	3.518234000
6	3.396753000	-3.181635000	-2.700630000
6	1.171838000	-2.534962000	-1.621486000
6	0.832391000	1.033499000	-1.246160000
6	-0.397319000	0.435397000	-1.603875000
6	-1.137224000	-0.284245000	-0.619598000

6	-0.578791000	-0.323059000	0.676605000
6	11.696769000	0.069132000	-0.726434000
6	10.985409000	-0.839025000	1.542530000
1	9.038758000	2.346516000	0.890619000
1	9.248570000	-1.573230000	-0.890805000
1	5.375520000	2.645146000	0.430182000
1	6.220330000	4.537795000	1.747273000
1	7.918881000	4.065055000	1.480558000
1	6.849128000	3.016733000	2.466244000
1	5.984298000	4.745347000	-0.820201000
1	6.142117000	3.272449000	-1.837995000
1	7.608372000	4.053328000	-1.162892000
1	5.657457000	-1.552460000	-1.923729000
1	6.924174000	-2.750578000	-3.691589000
1	8.479660000	-2.210636000	-2.986097000
1	7.342379000	-1.001927000	-3.664079000
1	6.280011000	-3.947493000	-1.510093000
1	6.211463000	-3.038519000	0.032575000
1	7.793968000	-3.434795000	-0.704083000
1	5.259865000	0.294040000	1.634026000
1	7.219330000	-0.278283000	2.981377000
1	7.195080000	-1.274807000	1.504145000
1	6.741183000	-1.999194000	3.094551000
1	4.919375000	0.503509000	4.034061000
1	4.474786000	-1.214897000	4.223775000
1	3.404993000	-0.104033000	3.275510000
1	4.071547000	-4.642547000	2.822440000
1	3.618419000	-3.191971000	3.761484000
1	5.323420000	-3.455302000	3.285776000
1	2.877351000	-5.292484000	1.198508000
1	2.718998000	-5.053536000	-0.565084000
1	1.450817000	-4.441856000	0.538097000
1	2.820560000	-1.212189000	-2.051986000
1	2.910442000	-3.098704000	-3.693559000
1	3.353029000	-4.247317000	-2.395757000
1	4.457894000	-2.892760000	-2.817401000
1	0.674116000	-2.172285000	-2.542503000
1	0.719710000	-1.988934000	-0.774191000
1	0.939220000	-3.613880000	-1.522284000
1	1.892078000	4.040156000	-0.508963000
1	2.823718000	3.310069000	-1.866330000
1	3.677450000	4.211801000	-0.582961000
1	2.416653000	3.334357000	2.244051000
1	4.191474000	3.159991000	2.147936000
1	3.196404000	1.824242000	2.818278000
1	1.382937000	1.592974000	-2.015185000
1	-1.135475000	-0.860872000	1.461002000
1	1.493337000	-1.969206000	2.140711000
1	0.003431000	-1.611479000	3.098061000
1	1.623475000	-1.364364000	3.828211000
1	0.659249000	2.074753000	2.932000000
1	1.040092000	0.983546000	4.301442000
1	-0.558570000	0.854654000	3.468023000
1	11.040509000	1.238483000	0.962979000
1	12.764317000	0.061416000	-0.419959000
1	11.555491000	0.877614000	-1.472481000
1	10.341186000	-0.674591000	2.430600000
1	10.731176000	-1.837045000	1.126059000
1	12.042577000	-0.874371000	1.882016000
1	11.489229000	-0.895823000	-1.235802000
14	-2.699836000	-1.383933000	-0.815802000

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6	0.073841000	0.899067000	-3.972854000
1	0.990883000	0.284793000	-3.877973000
1	0.381243000	1.977682000	-3.957661000
1	-0.380222000	0.698917000	-4.966211000
1	-2.008907000	2.371681000	-3.022231000
1	-2.609109000	1.021679000	-4.057946000
1	-2.839797000	0.965246000	-2.275669000
6	-2.185374000	-3.061601000	-0.044369000
6	-3.049792000	-1.814818000	-2.650185000
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1	-2.105461000	-1.753999000	-3.229298000
1	-1.859080000	-2.949637000	1.009278000
1	-1.352104000	-3.514322000	-0.621893000
1	-3.035116000	-3.773391000	-0.057624000
32	-4.142927000	-0.286264000	0.838713000
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6	-6.749722000	-1.878316000	0.175515000
6	-8.361133000	-0.201959000	1.737899000
6	-8.134902000	-2.105414000	0.294711000
6	-8.967659000	-1.271191000	1.060838000
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1	-8.579924000	-2.966404000	-0.231802000
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7	-5.201216000	1.772719000	-1.312159000
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6	-5.084986000	3.129422000	-1.638254000
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1	-5.795441000	4.931142000	-2.547344000
1	-5.491700000	3.618968000	-3.719316000
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1	-5.722869000	-0.179313000	-1.544943000
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1	-1.304835000	4.320768000	0.399290000
1	-0.506710000	2.998868000	1.295201000
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1	-2.398014000	3.335473000	3.106081000
1	-4.080503000	2.900335000	2.669954000
6	-6.435091000	1.263447000	2.414719000
1	-5.325748000	1.215541000	2.328043000

6	-6.760364000	1.182994000	3.916247000
6	-6.896766000	2.600787000	1.806688000
1	-6.586878000	2.696133000	0.746927000
1	-8.003273000	2.697822000	1.841623000
1	-6.468536000	3.461839000	2.363055000
1	-7.851865000	1.253323000	4.110268000
1	-6.272163000	2.014170000	4.468694000
1	-6.401558000	0.225987000	4.346868000
6	-5.937761000	-2.876827000	-0.641558000
1	-4.935286000	-2.418273000	-0.776523000
6	-6.513474000	-3.137606000	-2.042910000
6	-5.746222000	-4.188625000	0.141555000
1	-5.275691000	-3.996361000	1.127061000
1	-6.722296000	-4.686081000	0.327773000
1	-5.103818000	-4.901910000	-0.417954000
1	-7.502294000	-3.641495000	-2.000934000
1	-5.835509000	-3.791327000	-2.630530000
1	-6.644151000	-2.192392000	-2.608938000
6	-10.470349000	-1.506380000	1.140703000
1	-10.878953000	-0.746350000	1.844153000
6	-10.808203000	-2.897777000	1.708788000
6	-11.140039000	-1.281122000	-0.229611000
1	-10.922555000	-0.264990000	-0.618230000
1	-10.767852000	-2.012495000	-0.978410000
1	-12.242619000	-1.398625000	-0.163281000
1	-10.440066000	-3.704843000	1.040371000
1	-11.905727000	-3.029017000	1.816844000
1	-10.341067000	-3.048453000	2.703389000

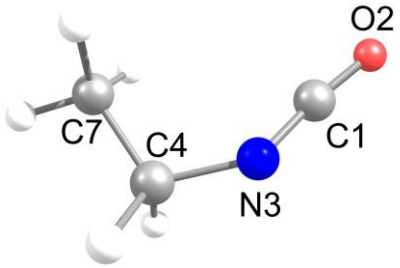

Figure S32. Optimized structure of ^{Et}NCO (Gibbs free energy = −155229.1075 kcal mol^{-1}).

Table S8. Atomic coordinates of the optimized structure of ^{Et}NCO.

6	-1.223249000	0.081888000	0.013500000
8	-2.296363000	-0.423519000	-0.046745000
7	-0.193252000	0.712526000	0.135146000
6	1.228266000	0.629727000	-0.087488000
1	1.458584000	1.056188000	-1.090406000
1	1.725987000	1.297177000	0.648406000
6	1.785809000	-0.792202000	0.025502000
1	1.327459000	-1.460226000	-0.732890000
1	1.583262000	-1.218411000	1.029259000
1	2.883412000	-0.790743000	-0.135512000

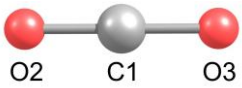

Figure S33. Optimized structure of CO_2 (Gibbs free energy = −118403.2332 kcal mol^{-1}).

Table S9. Atomic coordinates of the optimized structure of CO_2.

6	0.000000000	0.000000000	0.000000000
8	0.000000000	0.000000000	1.175202000
8	0.000000000	0.000000000	-1.175202000

Germylene radical 3

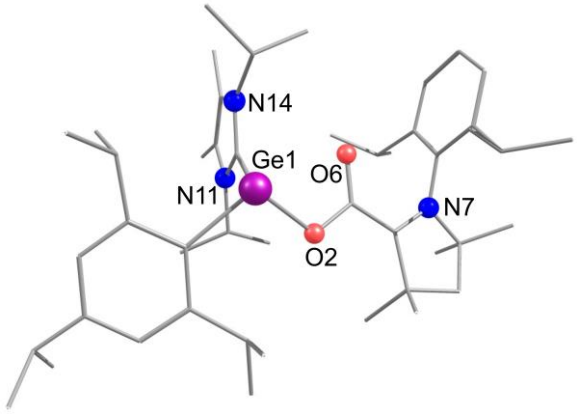

Figure S34. Optimized structure of germylene radical **3**. Hydrogen atoms omitted for clarity.

Table S10. Atomic coordinates of the optimized structure of germylene radical **3**.

32	1.146128000	0.111771000	-1.586309000
8	-0.020748000	-1.116680000	-0.557868000
6	3.008907000	-0.474674000	-0.863791000
6	0.919388000	1.571835000	-0.057362000
6	-1.258155000	-0.675912000	-0.368038000
8	-1.571850000	0.508928000	-0.588798000
7	-3.501253000	-1.307810000	0.441407000
6	-2.207016000	-1.649840000	0.110125000
6	-4.167051000	-0.103781000	0.035745000
6	-4.223192000	-2.437582000	1.101089000
7	1.186038000	1.485181000	1.267031000
6	0.967062000	2.717423000	1.889220000
6	1.533783000	0.206126000	1.924611000
7	0.515054000	2.844437000	-0.277958000
6	0.540421000	3.577287000	0.909884000
6	-0.022063000	3.281822000	-1.586687000
6	-1.968684000	-3.138755000	0.296576000
6	-1.449156000	-3.791425000	-0.998732000
6	-0.979125000	-3.432097000	1.441193000
6	-3.398511000	-3.649357000	0.617592000
6	-5.684126000	-2.523590000	0.657880000
6	-4.180188000	-2.303569000	2.633242000
6	-4.291762000	0.979213000	0.931192000
6	-4.695445000	-0.026459000	-1.274116000

6	-5.405050000	1.122859000	-1.641338000
6	-4.429162000	-1.102332000	-2.317048000
6	-5.583595000	2.176949000	-0.747614000
6	-5.018071000	2.105527000	0.522709000
6	-3.557150000	1.019496000	2.261782000
6	-4.489528000	1.286706000	3.450453000
6	-2.419914000	2.052370000	2.204563000
6	-3.344170000	-0.627347000	-3.300069000
6	-5.693286000	-1.544427000	-3.066318000
6	1.214825000	3.005705000	3.331503000
6	0.203546000	5.025235000	1.031227000
6	0.399845000	-0.288779000	2.822257000
6	2.898371000	0.246093000	2.606635000
6	-1.535231000	3.498914000	-1.532619000
6	0.754062000	4.461933000	-2.168803000
6	4.016214000	0.518428000	-0.895466000
6	3.378310000	-1.775200000	-0.424470000
6	4.671685000	-2.011361000	0.056462000
6	2.404301000	-2.943078000	-0.535854000
6	5.649657000	-1.010009000	0.091970000
6	5.306066000	0.241951000	-0.412861000
6	7.031932000	-1.275730000	0.663138000
6	3.775318000	1.913570000	-1.471738000
6	3.997574000	3.024335000	-0.435703000
6	4.619892000	2.147902000	-2.733170000
6	2.661871000	-4.095420000	0.439047000
6	2.374602000	-3.456707000	-1.985871000
6	7.762338000	-2.399539000	-0.086066000
6	6.963447000	-1.565382000	2.170714000
1	-3.856878000	-4.044716000	-0.301608000
1	-3.395431000	-4.463606000	1.356620000
1	-6.244885000	-1.623305000	0.948001000
1	-6.157030000	-3.392591000	1.140275000
1	-5.772387000	-2.647958000	-0.428499000
1	-3.152914000	-2.173852000	2.999122000
1	-4.597443000	-3.210672000	3.097343000
1	-4.777808000	-1.447636000	2.972123000
1	-2.126524000	-3.580605000	-1.840740000
1	-1.384788000	-4.885459000	-0.875198000
1	-0.457087000	-3.405927000	-1.259779000
1	-0.002373000	-2.983811000	1.221706000
1	-0.842579000	-4.519323000	1.560899000
1	-1.332610000	-3.026083000	2.399278000
1	-5.817421000	1.198162000	-2.649621000
1	-6.146638000	3.063549000	-1.049796000
1	-5.121911000	2.951678000	1.205798000
1	-3.087945000	0.038700000	2.406746000
1	-2.813857000	3.073694000	2.075523000
1	-1.754738000	1.833464000	1.360930000
1	-1.832249000	2.035443000	3.136501000
1	-4.929361000	2.295574000	3.397338000
1	-3.935982000	1.218799000	4.401146000
1	-5.322516000	0.567839000	3.488180000
1	-4.029485000	-1.980915000	-1.794283000
1	-3.716921000	0.210081000	-3.912926000
1	-3.053480000	-1.442323000	-3.982916000
1	-2.451712000	-0.275572000	-2.765868000
1	-6.104052000	-0.732516000	-3.687047000
1	-6.487381000	-1.867348000	-2.375255000
1	-5.463474000	-2.384590000	-3.741106000
1	0.815017000	3.995717000	3.586775000

1	2.289953000	3.009754000	3.571555000
1	0.730638000	2.274099000	3.992501000
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1	0.146439000	5.306511000	2.090829000
1	-0.765293000	5.264983000	0.572405000
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1	0.265564000	0.325965000	3.724083000
1	0.626940000	-1.313821000	3.149395000
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1	3.664780000	0.619035000	1.913352000
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1	2.902876000	0.858466000	3.520064000
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1	0.446540000	4.612004000	-3.214679000
1	1.836745000	4.270287000	-2.158591000
1	0.561356000	5.401994000	-1.632389000
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1	-1.906659000	3.670892000	-2.554697000
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1	6.066942000	1.027946000	-0.425822000
1	2.726374000	1.976084000	-1.796880000
1	3.754178000	4.013199000	-0.857488000
1	5.048463000	3.057356000	-0.107277000
1	3.373636000	2.872884000	0.456481000
1	4.388664000	3.127724000	-3.183433000
1	4.423117000	1.368763000	-3.485080000
1	5.697453000	2.129670000	-2.504525000
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1	1.835113000	-4.821286000	0.388134000
1	2.099305000	-2.654157000	-2.687410000
1	1.642633000	-4.272892000	-2.100641000
1	3.364708000	-3.838593000	-2.285770000
1	7.618864000	-0.350388000	0.528777000
1	7.971813000	-1.699868000	2.595725000
1	6.390021000	-2.485541000	2.369390000
1	6.468911000	-0.742273000	2.709830000
1	7.829264000	-2.179951000	-1.162749000
1	7.236002000	-3.361245000	0.026140000
1	8.784931000	-2.532791000	0.303499000

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