

Supporting Information

for

**Metal ion driven formation of 2*H*-silolides and -germolides**

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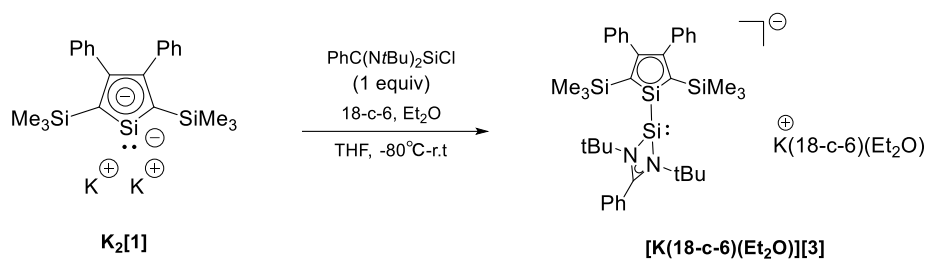
## Experimental Part

**General.** All manipulations of air- and moisture-sensitive compounds were carried out under an argon 5.0 or nitrogen 5.0 atmosphere using Schlenk techniques or a standard glove box (Braun Unilab). Glassware was dried in an oven at  $T = 120\text{ }^{\circ}\text{C}$  and evacuated prior to use. The solvents THF, diethylether and *n*-hexane were dried over sodium and distilled under a nitrogen atmosphere. Benzene- $d_6$  and THF- $d_8$  were stored over molecular sieves (4 Å) after drying over potassium. All used standard chemicals were obtained from commercial suppliers and used as delivered if not mentioned otherwise. Dipotassiumsilacyclopentadienediide  $\text{K}_2[\mathbf{1}]^{[S1]}$ , Dipotassiumgermacyclopentadienediide  $\text{K}_2[\mathbf{9}]^{[S1]}$ , and  $\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}$  ( $\mathbf{2}$ )<sup>[S2]</sup> were prepared according to modified literature procedures.

**NMR spectroscopy.** NMR spectra were recorded on Bruker Avance DRX 500 and Bruker Avance III 500 spectrometers.  $^1\text{H}$  NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (Benzene- $d_6$ :  $\delta\ ^1\text{H}(\text{C}_6\text{D}_5\text{H}) = 7.16$ ; THF- $d_8$ :  $\delta\ ^1\text{H}(\text{OC}_4\text{D}_7\text{H}) = 1.72, 3.58$ ; and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra by using the central line of the solvent signal (Benzene- $d_6$ :  $\delta\ ^{13}\text{C}(\text{C}_6\text{D}_6) = 128.06$ ; THF- $d_8$ :  $\delta\ ^{13}\text{C}(\text{OC}_4\text{D}_8) = 25.31, 67.21$ .  $^{29}\text{Si}$  and  $^{125}\text{Te}$  NMR spectra were calibrated against an external standard ( $\delta\ ^{29}\text{Si}(\text{Me}_2\text{SiHCl}) = 11.1$  versus tetramethylsilane (TMS) and  $\delta\ ^{125}\text{Te}(\text{Ph}_2\text{Te}_2) = 422.0$  versus dimethyltelluride ( $\text{Me}_2\text{Te}$ )). The  $^{29}\text{Si}\{^1\text{H}\}$  NMR inverse gated spectra were recorded with a relaxation delay  $D1 = 10\text{ s}$ .

**Mass spectrometry:** Mass spectra were recorded on a Waters Q-ToF Premier (ESI-MS) and Thermo Scientific DFS (CI-/EI-MS). The used method for each compound is given in the experimental part.

## Synthesis of [K][3]:



**[K(18-c-6)(Et<sub>2</sub>O)][3].** A solution of PhC(NtBu)<sub>2</sub>SiCl (0.3 mmol, 0.089 g) and 18-c-6 (0.3 mmol, 0.079 g) in THF (6 mL) was slowly added to a solution of K<sub>2</sub>[1] (0.3 mmol) in THF (10 mL) at -80 °C. The reaction mixture was stirred for 0.5 h at -80 °C and was allowed to warm to room temperature over 3 hours. The solvent was removed under vacuum. The residue was re-dissolved in Et<sub>2</sub>O (4 mL) and the filtrate was kept at +5 °C for one night to afford yellow crystals of [K(18-c-6)(Et<sub>2</sub>O)][3]. Yield: 164 mg (0.17 mmol, 57%).

NMR spectra recorded in C<sub>6</sub>D<sub>6</sub> at 305 K.

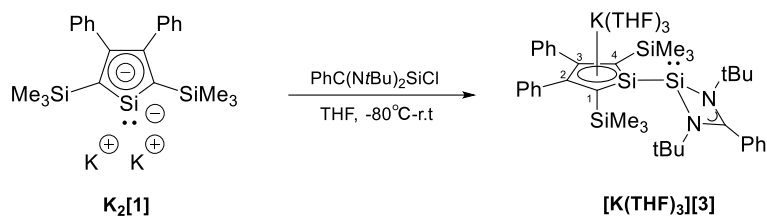
<sup>1</sup>H NMR (499.9 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = 0.52(s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.75 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.11 (t, 6 H, Et<sub>2</sub>O), 1.47 (s, 9 H, tBu), 3.16 (s, 24H, 18-c-6), 3.28 (q, 4 H, Et<sub>2</sub>O), 6.98-7.09 (m, 5 H, Ph), 7.28 (d, 1 H, Ph), 7.45-7.49 (m, 4 H, Ph), 7.85 (m, 1 H, Ph). (some protons of phenyl are overlapped by residual proton signals of the solvent C<sub>6</sub>D<sub>6</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = 4.9, 6.4 (Si(CH<sub>3</sub>)<sub>3</sub>), 15.6 (Et<sub>2</sub>O), 32.5 (CMe<sub>3</sub>), 53.9 (CMe<sub>3</sub>), 65.9 (Et<sub>2</sub>O), 70.1 (18-c-6), 123.1, 123.1, 126.3, 127.4, 128.9, 130.0, 131.3, 132.3, 132.4 (CH of Ph), 135.4 (C<sup>1/4</sup>), 137.1 (C<sup>1/4</sup>), 143.9 (C of amidinate-phenyl), 145.7 (C<sup>2/3</sup>), 146.6 (C<sup>2/3</sup>), 149.2 (PhC(NtBu)<sub>2</sub>), 150.2, 150.4 (C of silole-phenyl).

<sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = -15.1, -12.7, (SiMe<sub>3</sub>), 48.3 (SiN<sub>2</sub>), 58.9 (SiC<sub>2</sub>).

EA: C/H/N [%] calculated for C<sub>53</sub>H<sub>85</sub>KN<sub>2</sub>O<sub>7</sub>Si<sub>4</sub>: 62.80/8.45/2.76; found: 62.74/8.63/2.68.

MS (70 eV, EI): m/z (%) = 1012.24



[K(THF)<sub>3</sub>][**3**]. A solution of PhC(N*t*Bu)<sub>2</sub>SiCl (**2**) (0.3 mmol, 0.089 g) in THF (6 mL) was slowly added to a solution of K<sub>2</sub>[**1**] (0.3 mmol) in THF (10 mL) at -80 °C. The reaction mixture was stirred for 0.5 h at -80 °C and was allowed to warm to room temperature over 3 hours. The solvent was removed under vacuum. The residue was re-dissolved in mixed solution of THF and *n*-hexane (0.5:2 mL) and the filtrate was kept at +5 °C for one night to afford pale yellow crystals of [K(THF)<sub>3</sub>][**3**]. Yield: 133 mg (0.16 mmol, 53%).

NMR spectra for [K(THF)<sub>3</sub>][**3**] recorded in d<sub>8</sub>-THF at 305 K.

<sup>1</sup>H NMR (499.9 MHz, 305.0 K, d<sub>8</sub>-THF): δ = 0.03 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.11 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.25 (s, 18 H, *t*Bu), 6.78-6.82 (m, 4H, Ph), 6.86-6.90 (m, 10H, Ph), 7.69 (m, 1H, Ph).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, 305.0 K, d<sub>8</sub>-THF): δ = 4.4, 6.0, (Si(CH<sub>3</sub>)<sub>3</sub>), 32.2 (CMe<sub>3</sub>), 54.3 (CMe<sub>3</sub>), 123.3, 123.4, 125.6, 125.8, 126.4, 128.0, 128.3, 128.7, 128.9, 129.5, 129.8, 130.3, 131.5 (CH of Ph), 131.9 (C<sup>1/4</sup>), 131.9 (C<sup>1/4</sup>), 136.6 (C<sup>q</sup> of amidinate-phenyl), 141.6 (C<sup>2/3</sup>), 143.1 (C<sup>2/3</sup>), 149.2 (PhC(N*t*Bu)<sub>2</sub>), 151.9 (C<sup>q</sup> of silole-phenyl).

<sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, 305.0 K, d<sub>8</sub>-THF): δ = -15.1, -12.7, (SiMe<sub>3</sub>), 35.6 (SiN<sub>2</sub>), 70.5 (SiC<sub>2</sub>).

EA: C/H/N [%] calculated for C<sub>49</sub>H<sub>75</sub>KN<sub>2</sub>O<sub>3</sub>Si<sub>4</sub>: 66.01/8.48/3.14; found: 65.88/8.73/3.35.

HR-MS (ESI): *m/z* calculated for C<sub>49</sub>H<sub>75</sub>KN<sub>2</sub>O<sub>3</sub>Si<sub>4</sub>: 890.4492; found: 890.4489

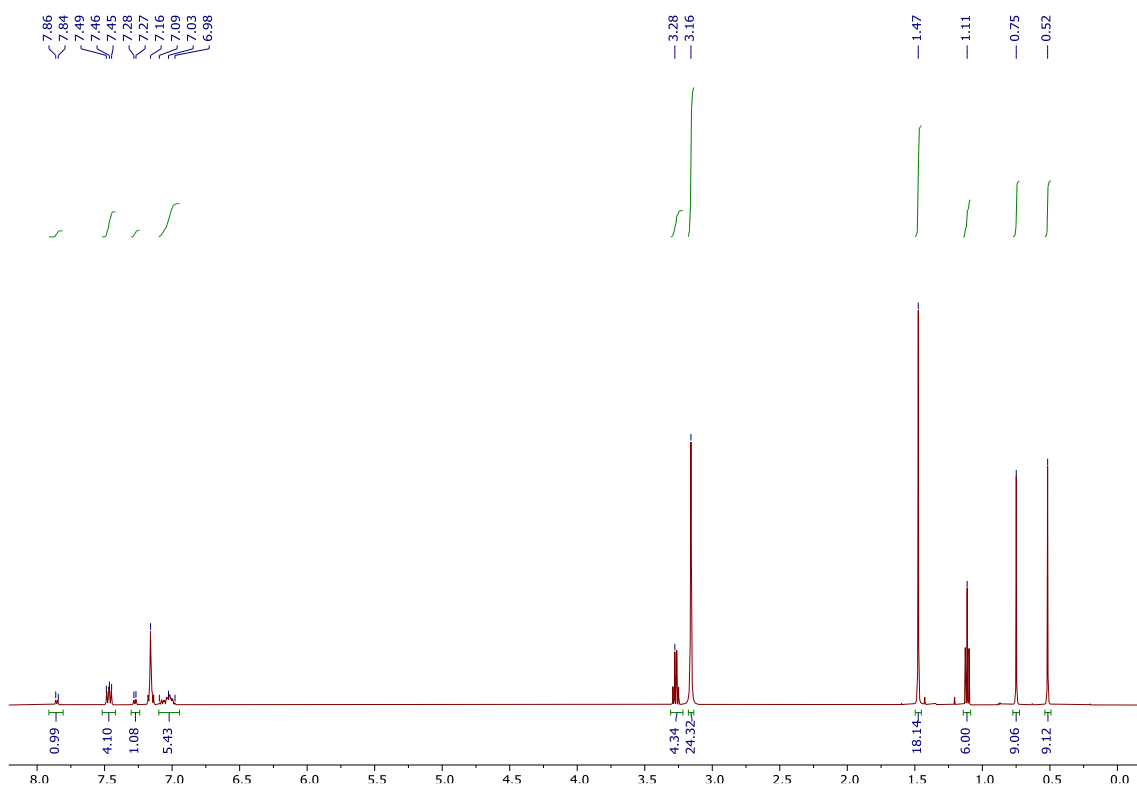


Figure S1a.  $^1\text{H}$  NMR (499.9 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{K}(18\text{-c-}6)(\text{Et}_2\text{O})][\mathbf{3}]$ .

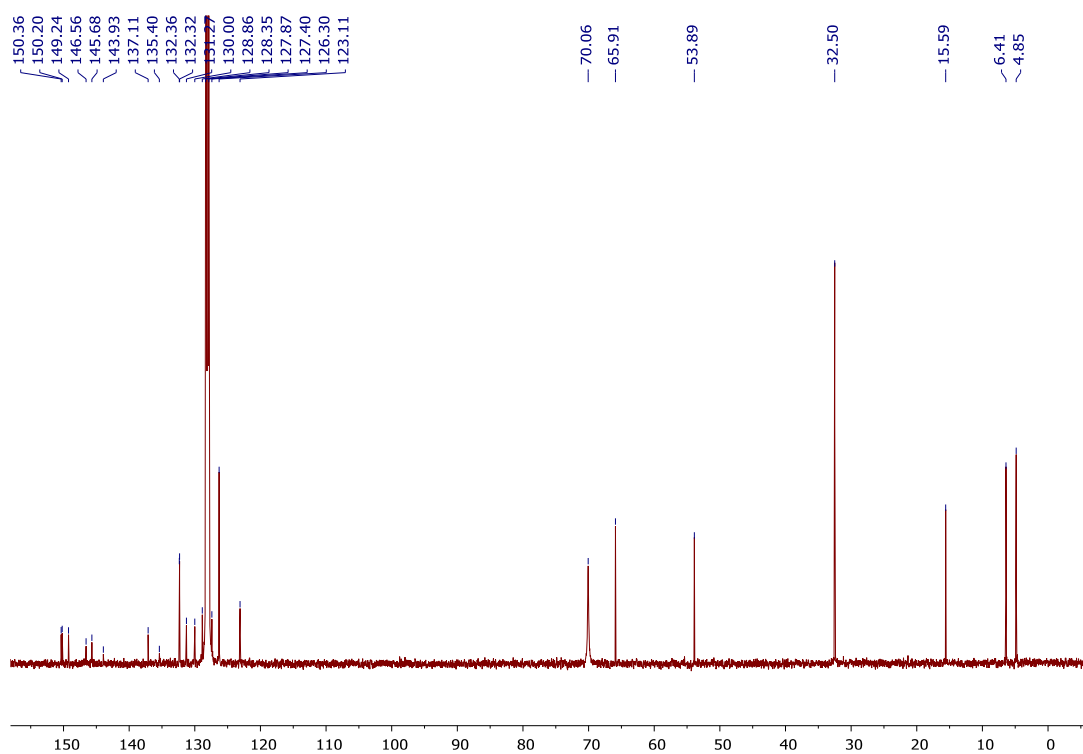


Figure S1b.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{K}(18\text{-c-}6)(\text{Et}_2\text{O})][\mathbf{3}]$ .

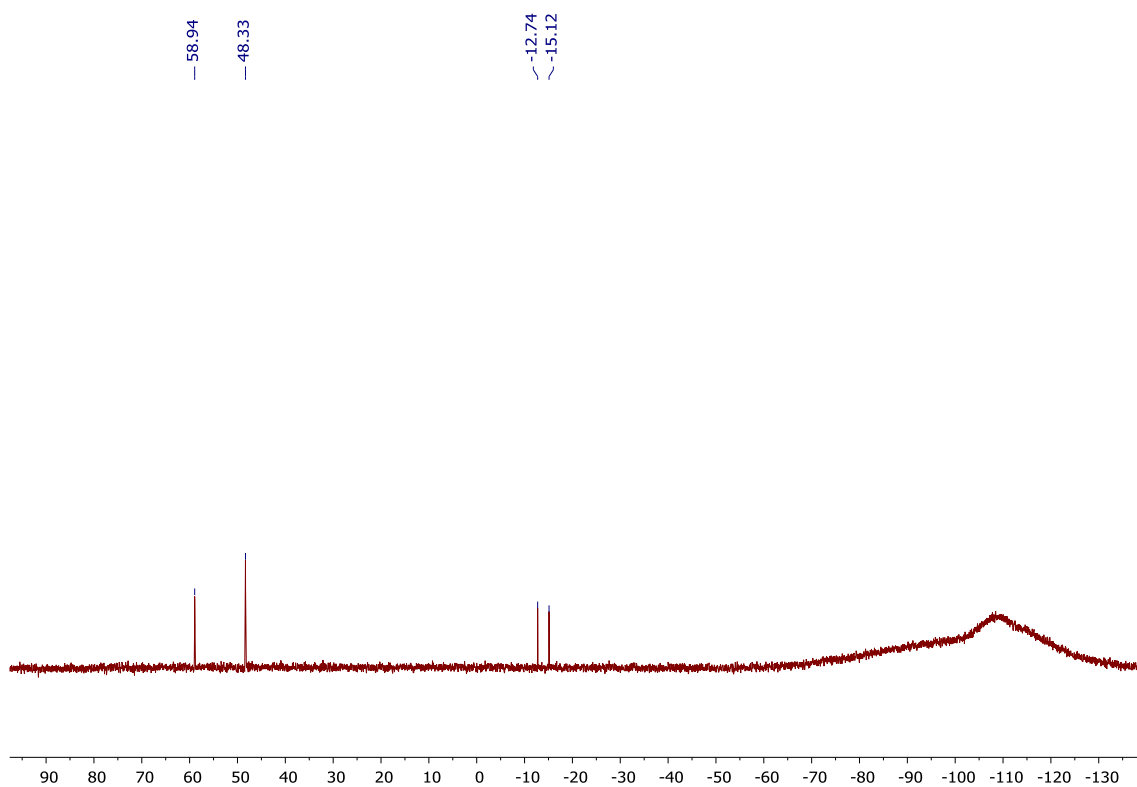


Figure S1c.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{K}(18\text{-c-}6)(\text{Et}_2\text{O})][\mathbf{3}]$ .

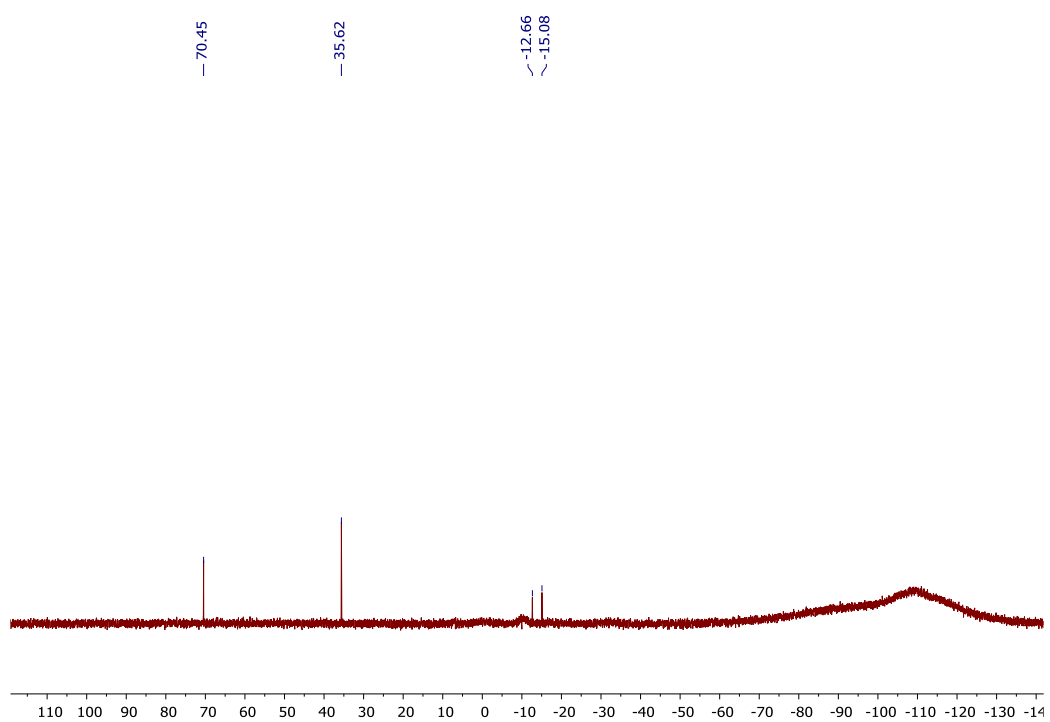
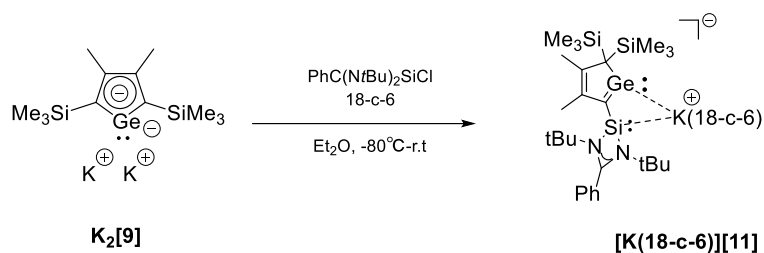


Figure S1d.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz, 305.0 K,  $d_8\text{-THF}$ ) spectrum of  $[\text{K}(\text{THF})_3][\mathbf{3}]$ .

## Synthesis of [K(18-c-6)][11]:



**[K(18-c-6)][11].** A solution of PhC(NtBu)<sub>2</sub>SiCl (0.3 mmol, 0.089 g) and 18-c-6 (0.3 mmol, 0.079 g) in Et<sub>2</sub>O (6 mL) was slowly added to a solution of K<sub>2</sub>[9] (0.3 mmol) in Et<sub>2</sub>O (10 mL) at -80 °C. The reaction mixture was stirred for 0.5 h at -80 °C and was allowed to warm to room temperature over 3 hours. The solvent was removed under vacuum. The residue was re-dissolved in n-hexane (2 mL) and was kept at room temperature for one night to afford yellow crystals of [K(18-c-6)][11]. Yield: 18 mg (0.1 mmol, 33%)

NMR spectra recorded in C<sub>6</sub>D<sub>6</sub> at 305 K.

<sup>1</sup>H NMR (499.9 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = 0.50 (s, 18H, SiMe<sub>3</sub>), 1.36 (s, 18H, tBu), 2.56 (s, 3H, Me), 2.62 (s, 3H, Me), 7.20-7.21 (m, 2H, Ph), 7.48-7.49 (m, 2H, Ph). (one phenyl proton is overlapped by residual proton signals of the solvent C<sub>6</sub>D<sub>6</sub>, protons of 18-c-6 are overlapping with those of Et<sub>2</sub>O).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = 4.6 (SiMe<sub>3</sub>), 18.8 (Me), 23.6 (Me), 32.6 (CMe<sub>3</sub>), 53.5 (CMe<sub>3</sub>), 69.5 (SiCSi), 70.0 (18-c-6), 131.0, 133.9, 137.4 (CH of Ph), 148.4 (GeC-C), 153.1 (C of amidinate-phenyl), 154.5 (Ph-C), 163.6 (Ge=C-C), 210.2 (Ge=C-Si).

<sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = -12.0 (SiMe<sub>3</sub>), 29.2 (SiN<sub>2</sub>).

EA: C/H/N [%] calculated for C<sub>39</sub>H<sub>71</sub>GeKN<sub>2</sub>O<sub>6</sub>Si<sub>3</sub>: 54.47/8.32/3.26;

found: 54.42/8.25/3.35.

HR-MS (EI): m/z calculated for C<sub>39</sub>H<sub>71</sub>GeKN<sub>2</sub>O<sub>6</sub>Si<sub>3</sub>: 860.3469; found: 860.3473.

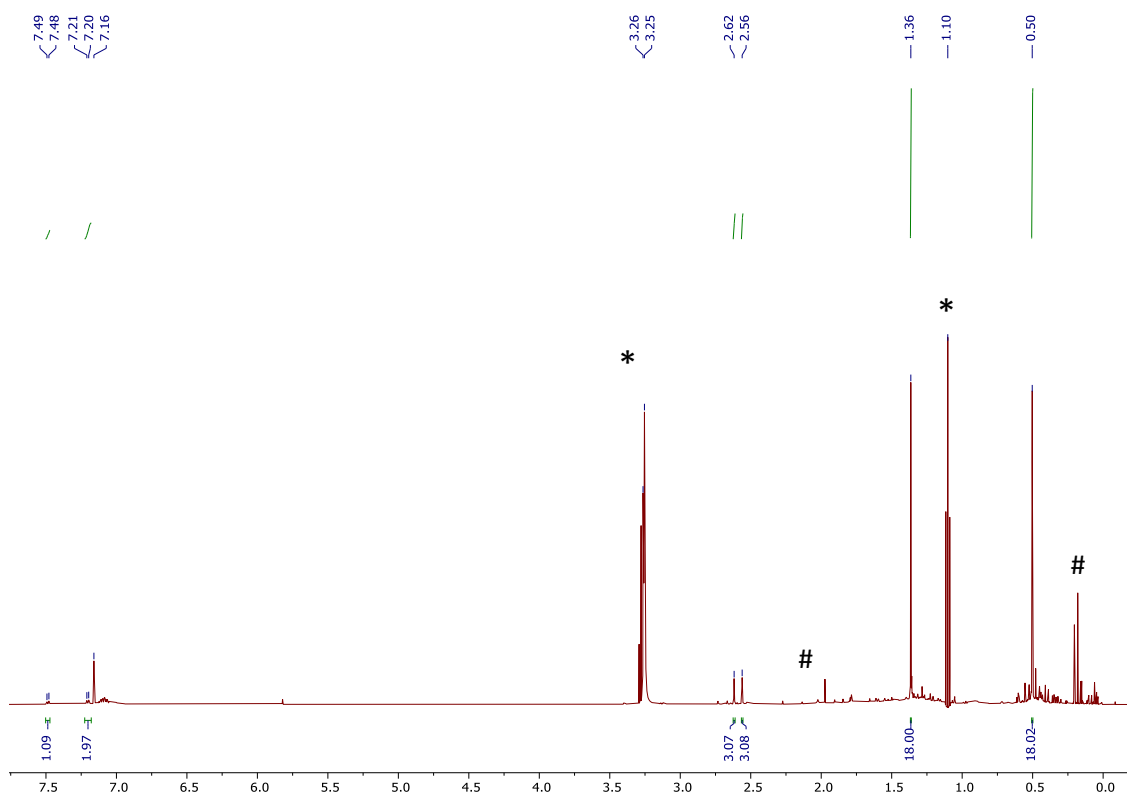


Figure S2a.  $^1\text{H}$  NMR (499.9 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{K}(18\text{-c-}6)][\mathbf{11}]$  ( $^*\text{Et}_2\text{O}$ ), ( $\#$  unknown impurities).

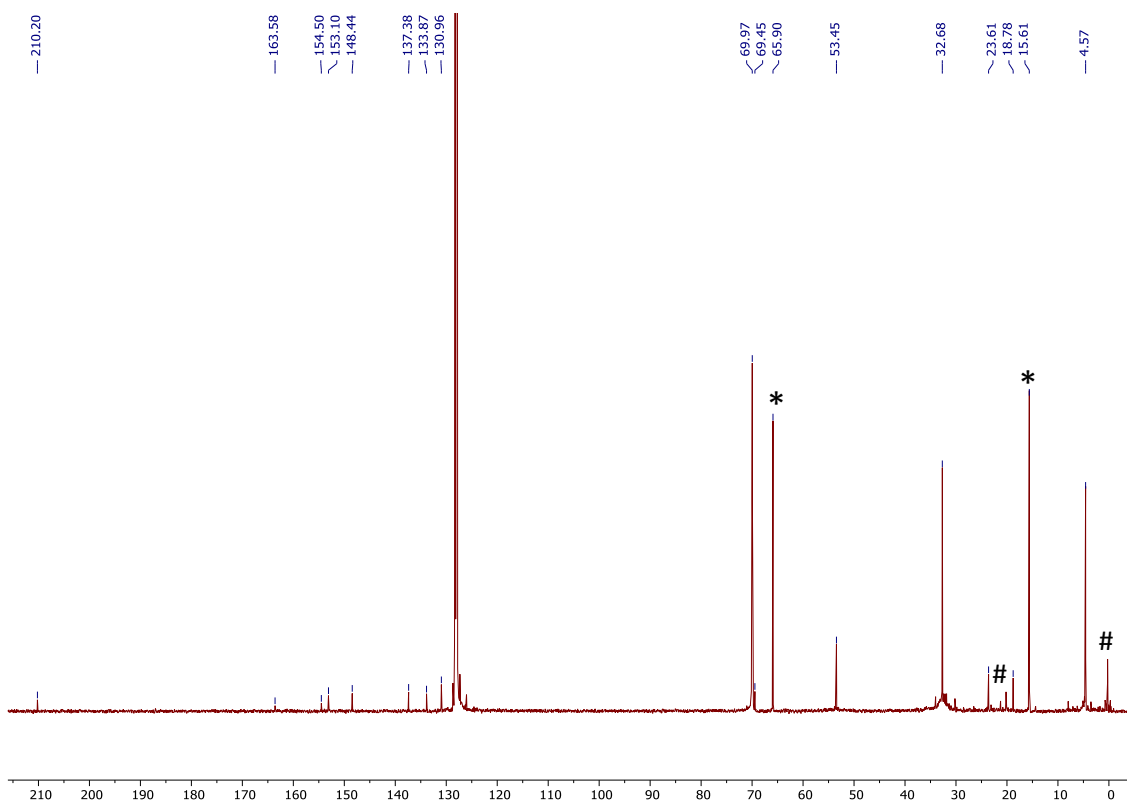


Figure S2b.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{K}(18\text{-c-}6)][\mathbf{11}]$  ( $^*\text{Et}_2\text{O}$ ), ( $\#$  unknown impurities).



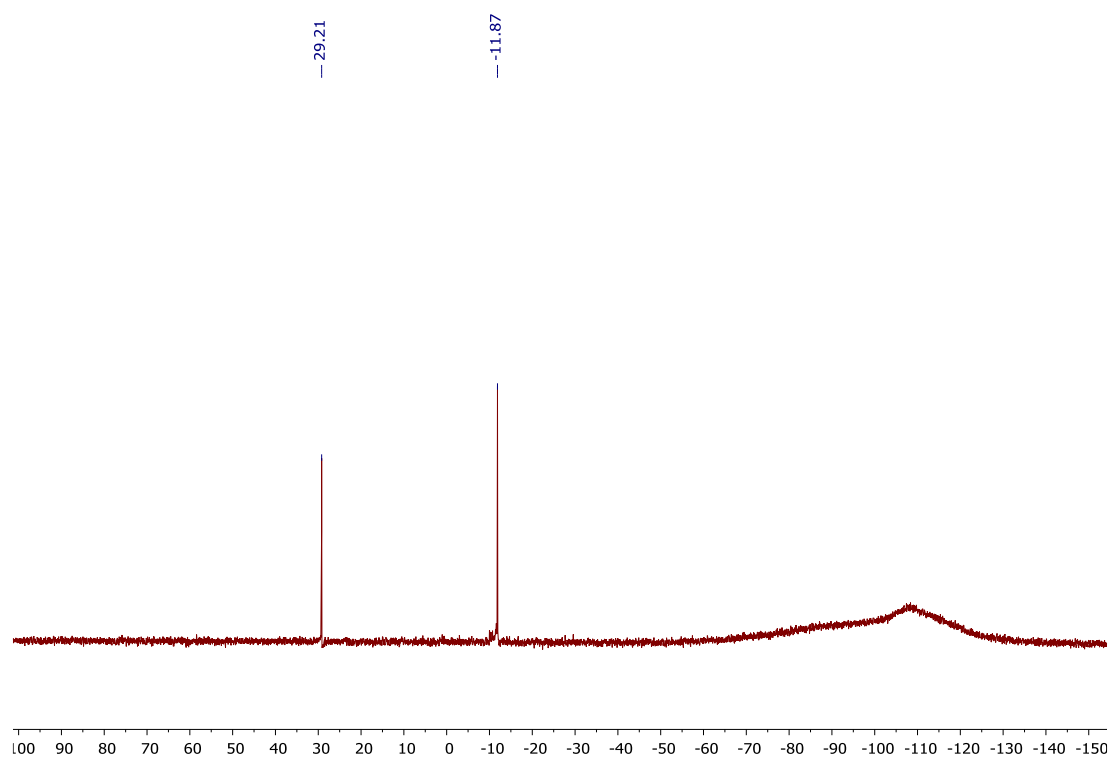
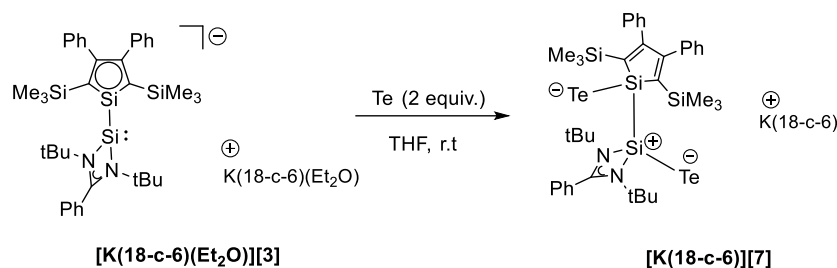


Figure S2c.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{K}(18\text{-c-}6)]\mathbf{[11]}$ .

### Synthesis of *bissilicontelluride* [K(18-c-6)][7]:



**[K(18-c-6)][7]**: THF (5 mL) was added to the mixture of [K(18-c-6)(Et<sub>2</sub>O)][**3**] (122 mg, 0.12 mmol) and Te powder (32 mg, 0.24 mmol) at room temperature. The reaction was kept stirring for overnight. After that, the solvent was removed and the residue was extract by Et<sub>2</sub>O (8 mL). The solvent was removed, and the residue was washed with *n*-hexane (3 x 4 mL) to afford a dark powder. Dark single crystals suitable for XRD investigations were obtained by recrystallization from Et<sub>2</sub>O solution at room temperature. Yield: 100 mg (0.08 mmol, 70%)

NMR spectra recorded in d<sub>8</sub>-THF at 305 K.

<sup>1</sup>H NMR (499.9 MHz, 305.0 K, d<sub>8</sub>-THF): δ = 0.17 (s, 18H, SiMe<sub>3</sub>), 1.42 (s, 18H, tBu), 3.68 (s, 24H, 18-c-6), 6.82-6.85 (m, 2H, Ph), 6.88-6.91 (m, 8H, Ph), 7.39-7.43 (m, 1H, Ph), 7.47-7.49 (m, 2H, Ph), 7.52-7.55 (m, 1H, Ph), 7.59 (d, 1H, Ph).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, 305.0 K, d<sub>8</sub>-THF): δ = 4.5 (C of SiMe<sub>3</sub>), 33.1, 56.1 (C of tBu), 71.2 (18-c-6), 125.5, 126.9, 128.3, 128.5, 129.5, 130.3, 130.6, 130.7, 130.9 (CH of Ph), 133.9 (C<sup>1/4</sup>), 145.8 (C<sup>2/3</sup>), 153.7 (C of amidinate), 164.0 (C of amidinate-phenyl), 170.4 (C of silole-phenyl).

<sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, 305.0 K, d<sub>8</sub>-THF): δ = -0.7 (SiC<sub>2</sub>), -9.9, -10.0 (SiMe<sub>3</sub>), -32.2 (SiN<sub>2</sub>).

<sup>125</sup>Te{<sup>1</sup>H} NMR (157.8 MHz, 305.0 K, d<sub>8</sub>-THF): δ = -802.00 (TeSi (silole)), -1233.96 (TeSi (silylene)).

EA: C/H/N [%] calculated for C<sub>49</sub>H<sub>75</sub>KN<sub>2</sub>O<sub>6</sub>Si<sub>4</sub>Te<sub>2</sub>: 49.26/6.33/2.34;

found: 48.98/6.52/2.13.

HR-MS (ESI): m/z calculated for C<sub>49</sub>H<sub>75</sub>KN<sub>2</sub>O<sub>6</sub>Si<sub>4</sub>Te<sub>2</sub>+Na: 1221.2362; found:

1221.2349.

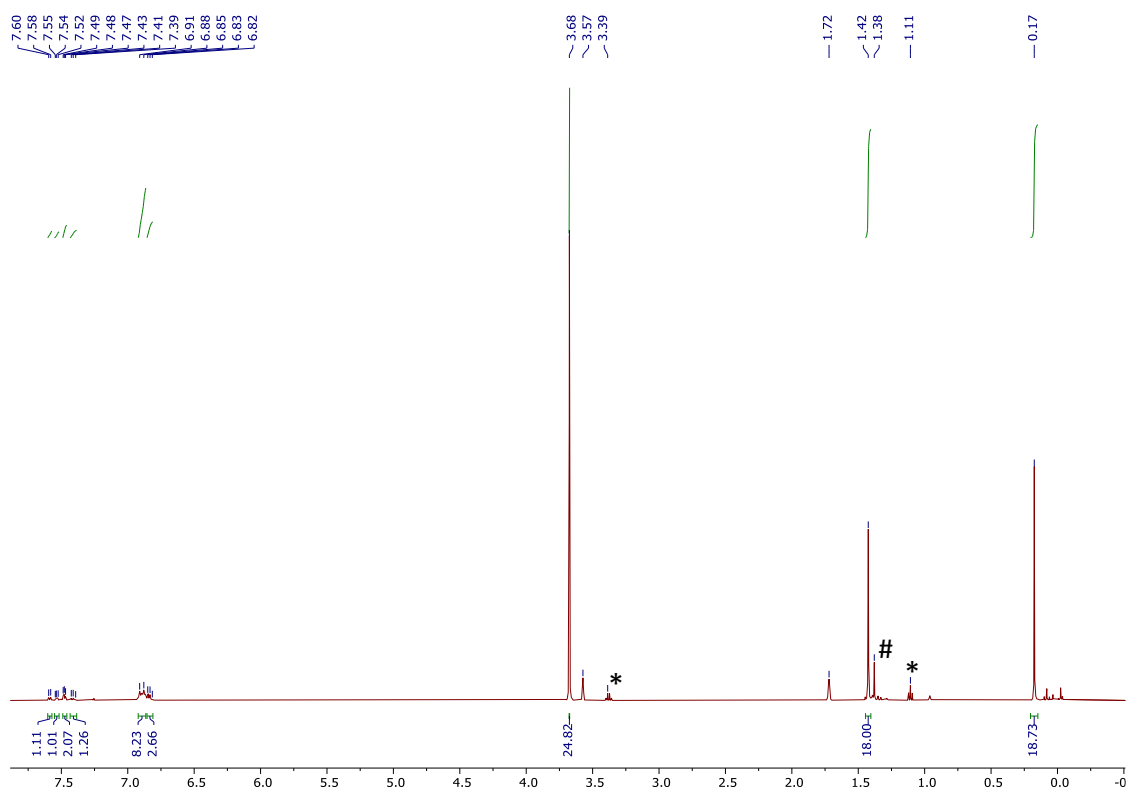


Figure S3a.  $^1\text{H}$  NMR (499.9 MHz, 305.0 K,  $d_8$ -THF) spectrum of  $[\text{K}(18\text{-c-6})][\text{7}]$  (\* $\text{Et}_2\text{O}$ ), (#unknown impurities).

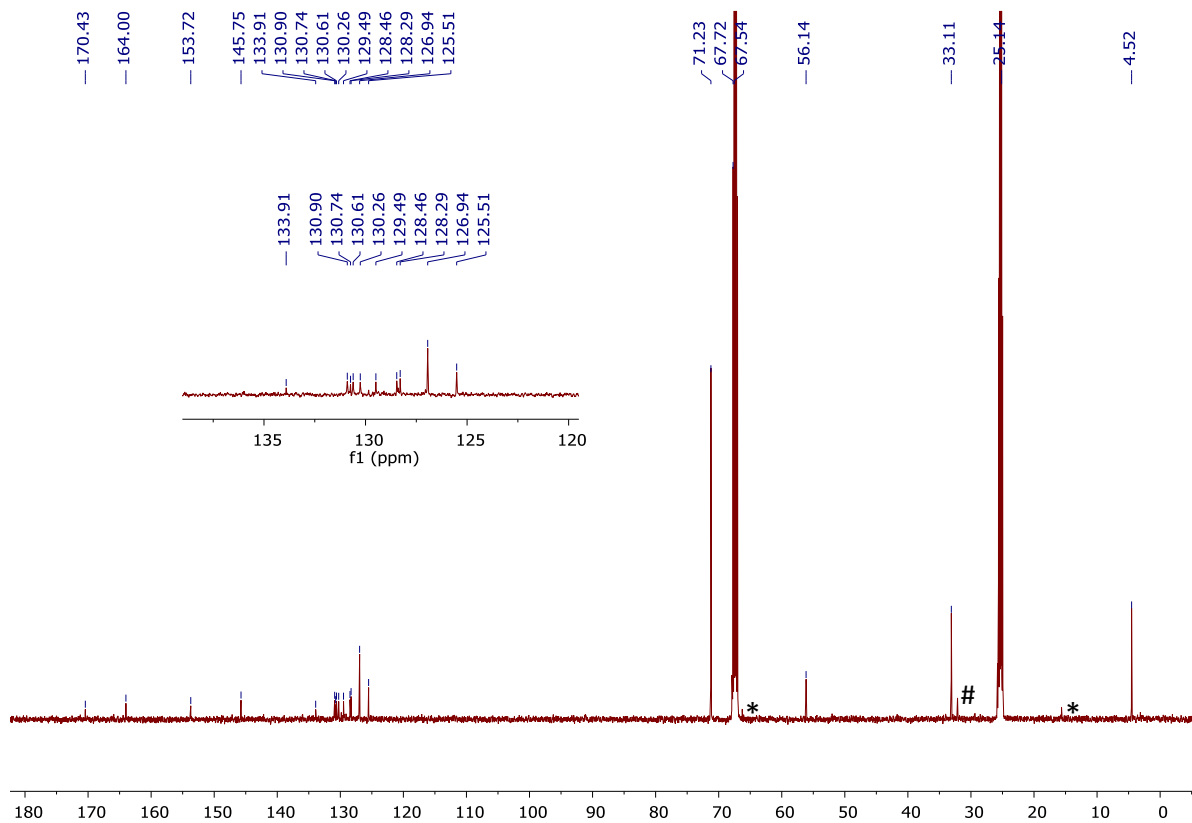


Figure S3b.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, 305.0 K,  $d_8$ -THF) spectrum of  $[\text{K}(18\text{-c-6})][\text{7}]$  (\* $\text{Et}_2\text{O}$ ), (#unknown impurities).

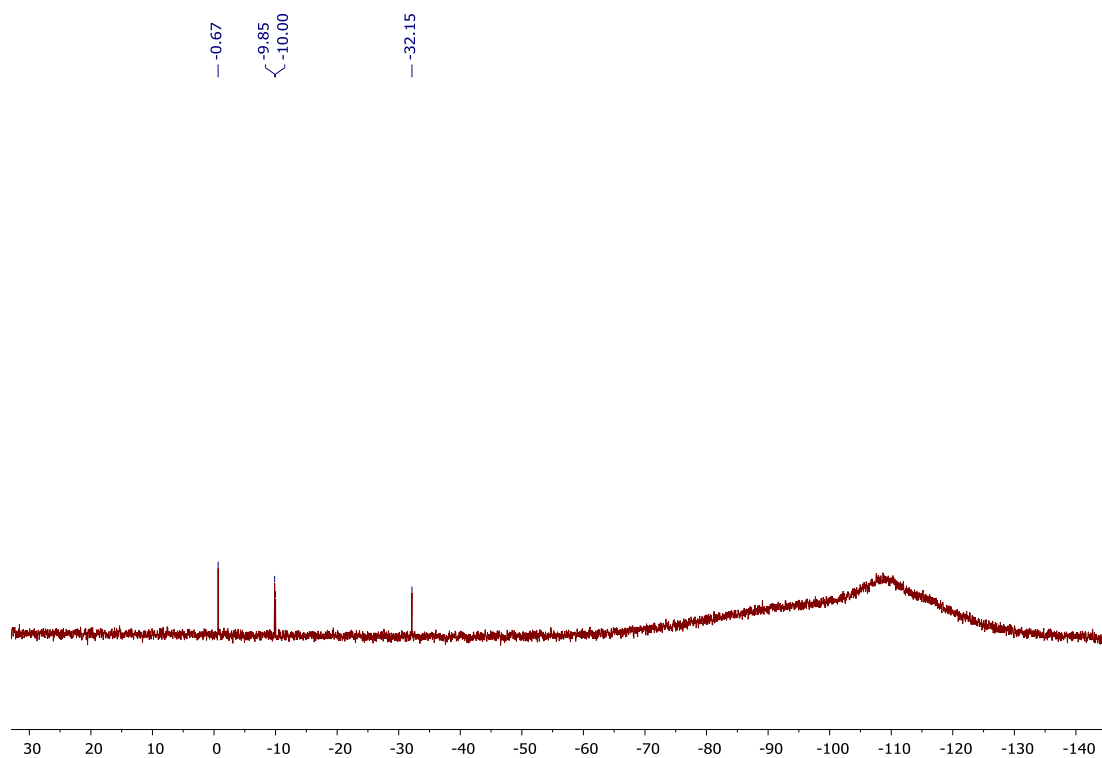


Figure S3c.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz, 305.0 K,  $d_8$ -THF) spectrum of  $[\text{K}(18\text{-c-}6)][\text{7}]$

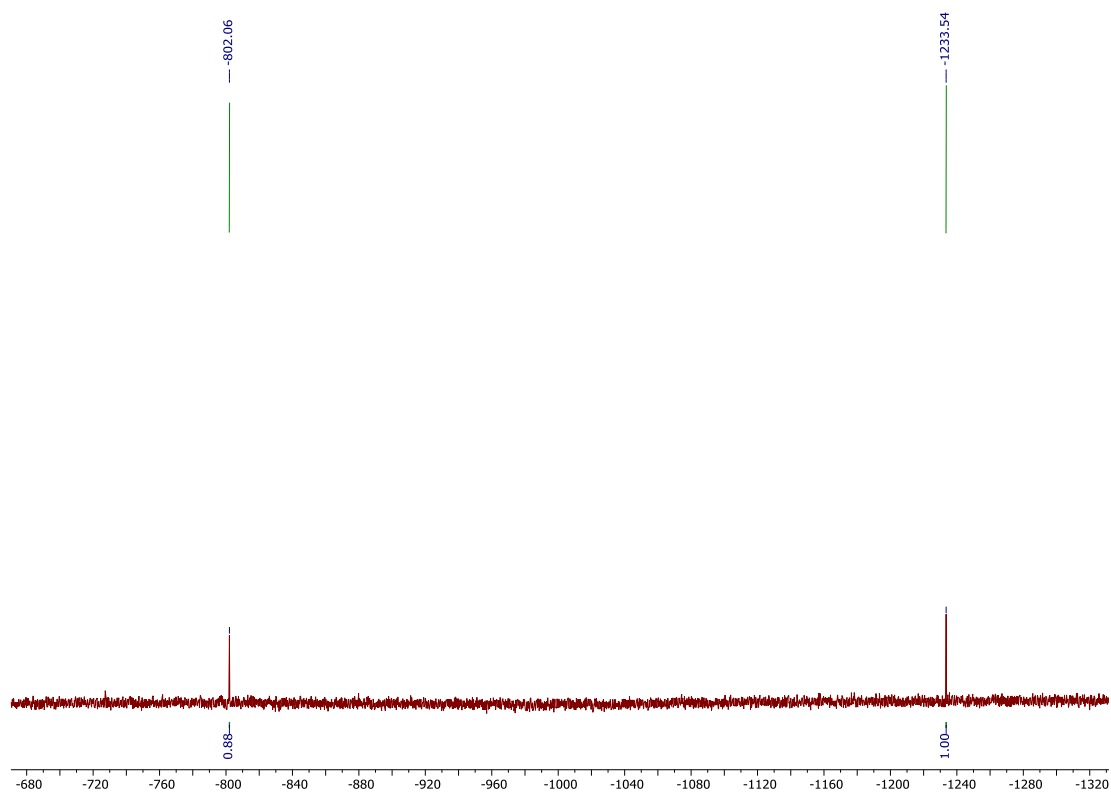
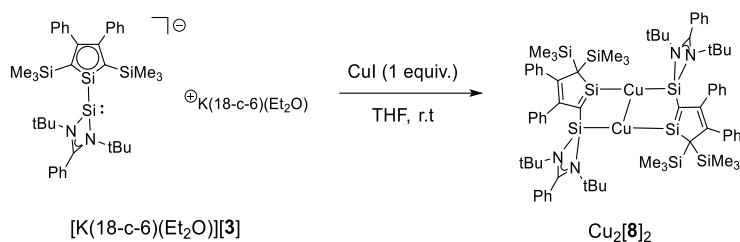


Figure S3d.  $^{125}\text{Te}\{^1\text{H}\}$  NMR (157.8 MHz, 305.0 K,  $d_8$ -THF) spectrum of  $[\text{K}(18\text{-c-}6)][\text{7}]$ .

## Synthesis of the dimeric Cu-silylene silolide Cu<sub>2</sub>[**8**]<sub>2</sub>:



Cu<sub>2</sub>[**8**]<sub>2</sub>: THF (5 mL) was added to the mixture of [K(18-c-6)(Et<sub>2</sub>O)][**3**] (152 mg, 0.12 mmol) and CuI (29 mg, 0.15 mmol) at room temperature. The reaction was kept stirring for overnight. After that, the solvent was removed and the residue was extract by Et<sub>2</sub>O (8 mL). The solvent was removed, and the residue was washed with *n*-hexane (3 x 2 mL) to afford the pale brown solid. The solid was re-dissolved in mixed solution of THF and *n*-hex (0.5:2 mL) and the filtrate was kept at +5 °C for overnight to afford yellow crystals Cu<sub>2</sub>[**8**]<sub>2</sub> (Yield: 112 mg (53%)).

NMR spectra recorded in C<sub>6</sub>D<sub>6</sub> at 305 K.

<sup>1</sup>H NMR (499.9 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = 0.50 (s, 36H, SiMe<sub>3</sub>), 1.25 (s, 36H, tBu), 7.42 (m, 5H, Ph), 7.51 (m, 7H, Ph) (one phenyl proton is overlapped by residual proton signals of the solvent C<sub>6</sub>D<sub>6</sub>, protons of 18-c-6 are overlapping with those of Et<sub>2</sub>O).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = 4.7 (SiMe<sub>3</sub>), 32.0 (CMe<sub>3</sub>), 54.3 (CMe<sub>3</sub>), 124.8, 125.4, 129.9, 130.1, 130.6, 132.1, 133.5 (CH of Ph), 141.0 (C of amidinate-phenyl), 145.6 (SiC-C), 146.3 (C of amidinate), 153.0 (Si=C-C), 165.3 (Si=C-Si). C of Si-C-Si and some of C of phenyl could not be assigned due to the bad signal to noise ratio.

<sup>29</sup>Si{<sup>1</sup>H} NMR (99.4 MHz, 305.0 K, C<sub>6</sub>D<sub>6</sub>): δ = -5.8 (SiMe<sub>3</sub>), 15.1 (SiC<sub>2</sub>), 238.9(SiN<sub>2</sub>).

An accurate combusting analysis of Cu<sub>2</sub>[**8**]<sub>2</sub> could not be obtained as a small amount of a by-product of unknown structure co-crystallized and could not be separated.

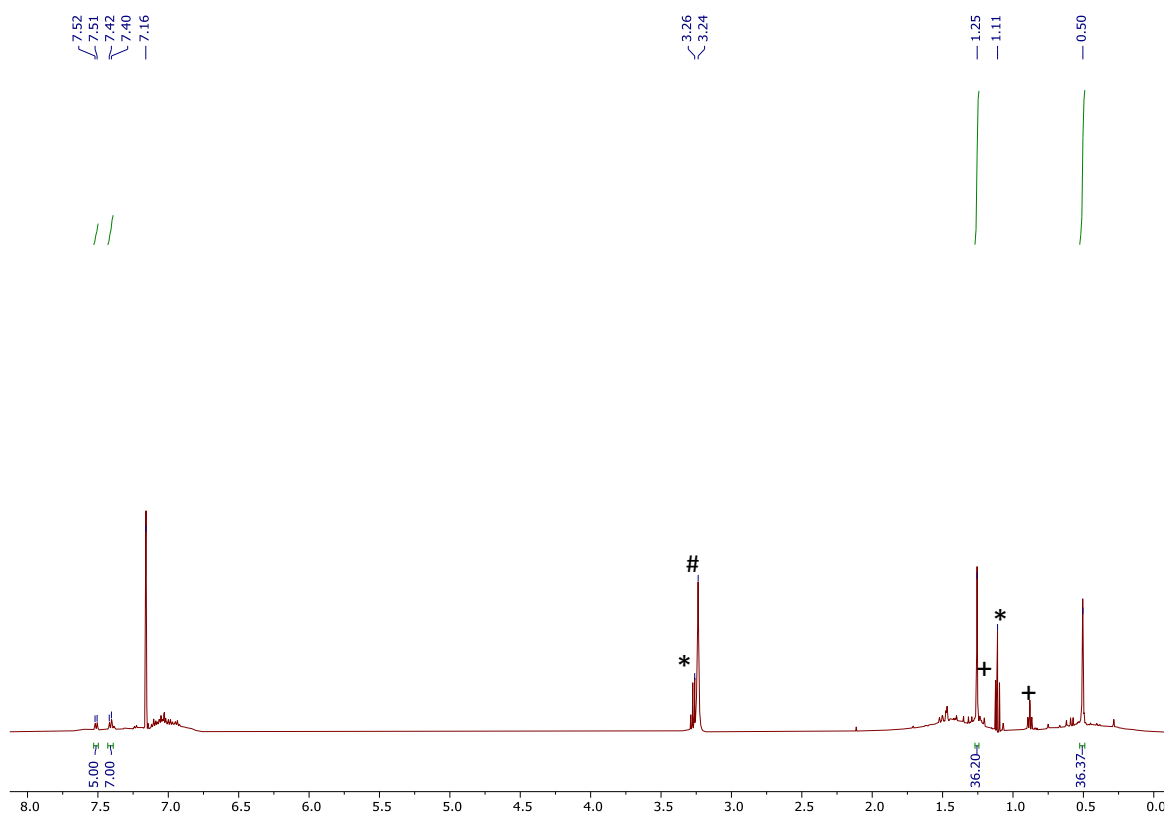


Figure S4a.  $^1\text{H}$  NMR (499.9 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $\text{Cu}_2[\mathbf{8}]_2$  (\* $\text{Et}_2\text{O}$ , #18-C-6, +n-hexane).

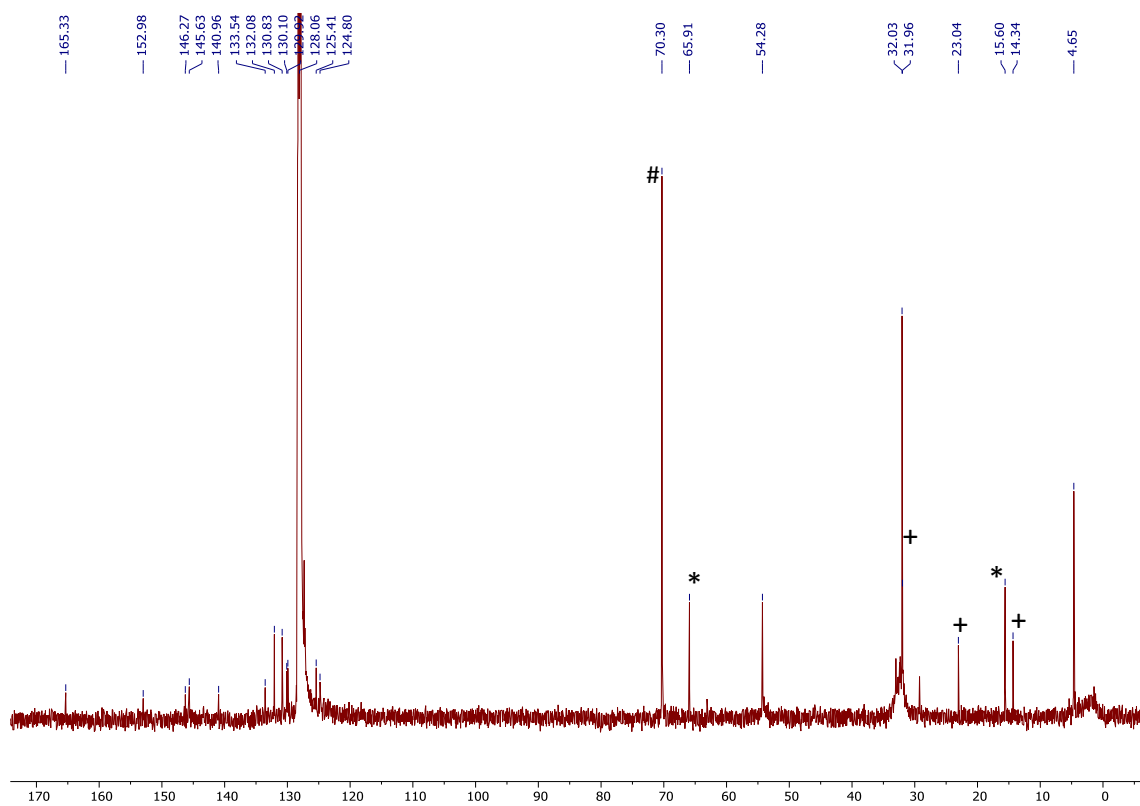


Figure S4b.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, 305.0 K,  $d_8\text{-THF}$ ) spectrum of  $\text{Cu}_2[\mathbf{8}]_2$  (\* $\text{Et}_2\text{O}$ , #18-c-6, +n-hexane).

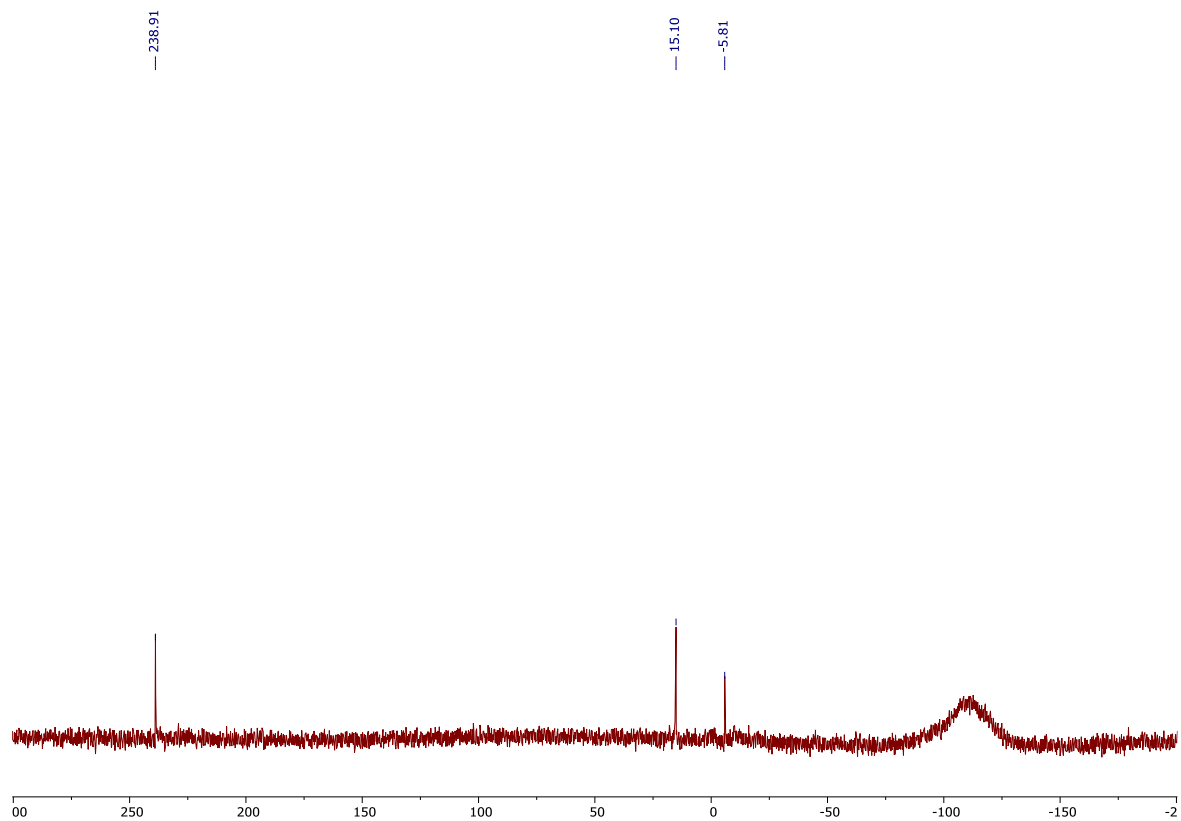
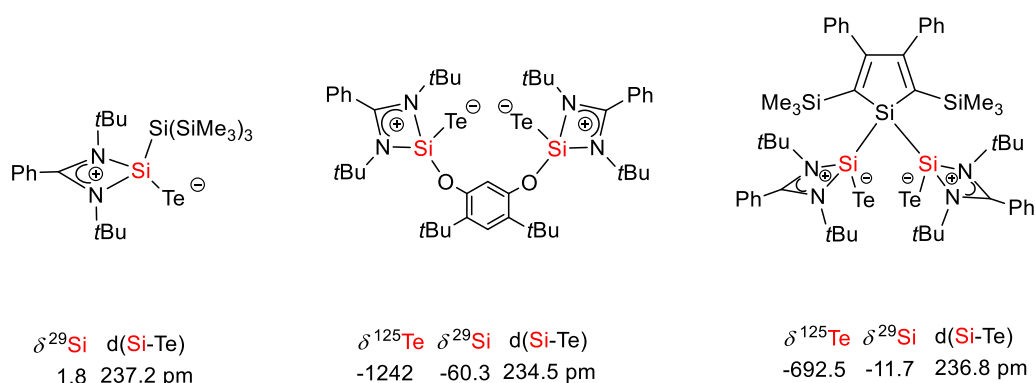
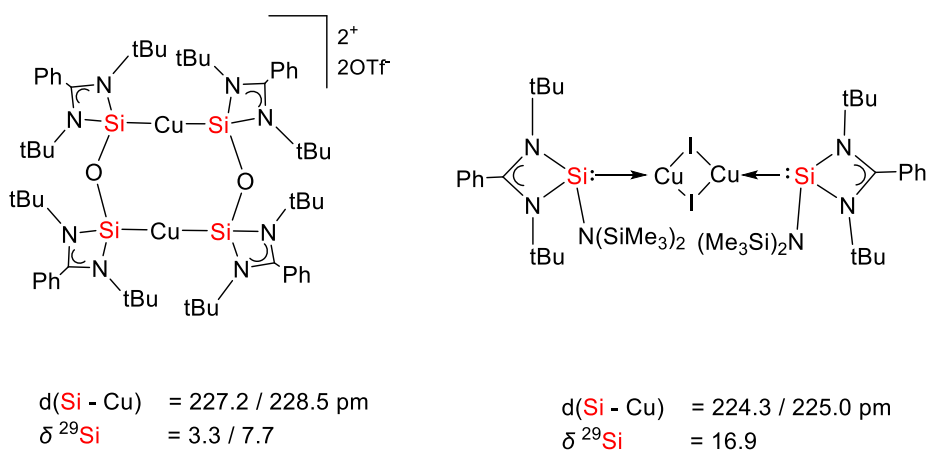


Figure S4c.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz, 305.0 K,  $\text{C}_6\text{D}_6$ ) spectrum of  $\text{Cu}_2[\mathbf{8}]_2$ .

**Reference compounds pertinent to the discussion:**



**Figure S5:** NMR spectroscopic and structural data of silicon tellurides pertinent to the discussion. [S3-S5]

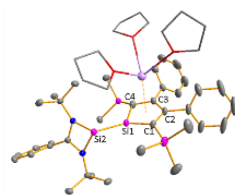
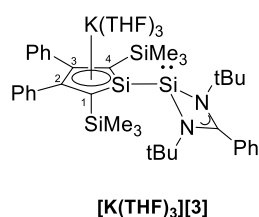


**Figure S6:** Selected NMR spectroscopic and structural data of Cu(I) complexes of amidinate stabilized silylenes. [S6, S7]

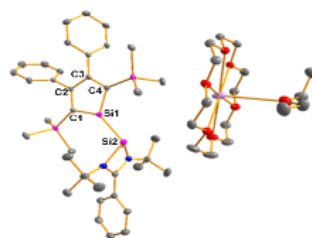
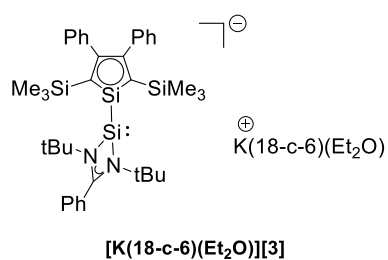


## Details of single crystal X-ray diffraction analysis

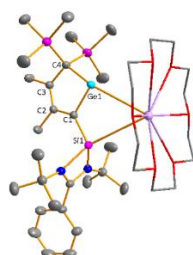
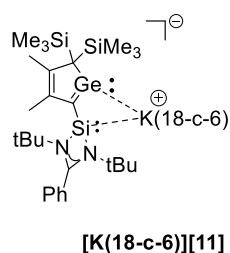
Single crystal X-ray data were measured on a Bruker AXS Apex II diffractometer (Mo-K $\alpha$  radiation,  $\lambda = 0.71073\text{\AA}$ , Kappa 4 circle goniometer, Bruker Apex II detector). The crystal was kept at 100.0 K during data collection. Absorption corrections based on symmetry-related measurements (multi-scan) were performed with the program SADABS.<sup>[S8]</sup> The structures were solved with the program SHELXS and refined with SHELXL.<sup>[S9]</sup> Pertinent data are summarized in Tables S1-S5. CCDC-2368314 (S1), CCDC-2368318 (S2), CCDC-2368313(S3), CCDC-2368316 (S4), CCDC-2368315 (S5), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]. The crystallographic data can be obtained free of charge from <https://www.ccdc.cam.ac.uk/structures/> quoting the CCDC numbers 2368313-2368316 and 2368318.

**Table S1.**

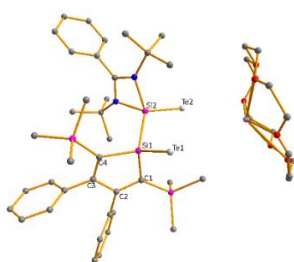
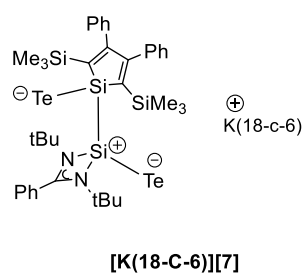
Name	[K(THF) <sub>3</sub> ] <sub>3</sub> ·THF·hexane
CCDC	2368314
Empirical formula	C <sub>57.67</sub> H <sub>93</sub> KN <sub>2</sub> O <sub>4.66</sub> Si <sub>4</sub>
Formula weight	1040.42
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.2492(5)
b (Å)	13.0948(7)
c (Å)	23.2301(13)
α (deg)	103.325(2)
β (deg)	91.573(2)
γ (deg)	93.515(2)
V (Å <sup>3</sup> )	3025.3(3)
Z	2
D (calc) (Mg/m <sup>3</sup> )	1.142
μ (mm <sup>-1</sup> )	0.212
F(000)	1131
θ range (°)	1.602, 30.034
Index ranges	-14,14; -18,18; -32,32
Ref.collected	193642
Independent reflections	17724 (R(int) = 0.0534)
Completeness to θ (°)	(30.03)100%
Goodness-of-fit on F <sup>2</sup>	1.122
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0641 wR <sub>2</sub> = 0.1607
R indices (alldata)	R <sub>1</sub> = 0.0737 wR <sub>2</sub> = 0.1672
Δρ <sub>max, min</sub> (e.Å <sup>-3</sup> )	0.991, -0.477

**Table S2.**

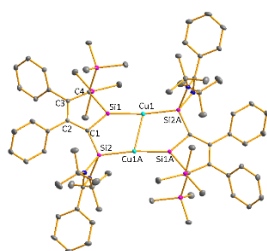
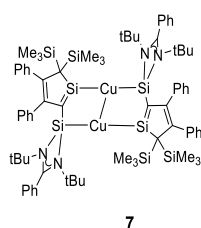
Name	[K(18-C-6)(Et <sub>2</sub> O)] <sub>3</sub> Et <sub>2</sub> O
CCDC	2368318
Empirical formula	C <sub>54</sub> H <sub>87.50</sub> KN <sub>2</sub> O <sub>7.25</sub> Si <sub>4</sub>
Formula weight	1032.21
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	14.3502(6)
b (Å)	29.6584(12)
c (Å)	31.1403(12)
α (deg)	64.5446(16)
β (deg)	87.8632(17)
γ (deg)	80.4353(17)
V (Å <sup>3</sup> )	11791.8(8)
Z	8
D (calc) (Mg/m <sup>3</sup> )	1.163
μ (mm <sup>-1</sup> )	0.22
F(000)	4468
θ range (°)	1.265, 34.971
Index ranges	-23,23; -47,47; -50,50
Ref.collected	664021
Independent reflections	103614 (R(int) = 0.0476)
Completeness to θ (°)	(34.97)100.00%
Goodness-of-fit on F <sup>2</sup>	1.098
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0618    wR <sub>2</sub> = 0.1443
R indices (alldata)	R <sub>1</sub> = 0.0781    wR <sub>2</sub> = 0.1524
Δρ <sub>max, min</sub> (e.Å <sup>-3</sup> )	1.979, -1.122

**Table S3.**

Name	[K(18-C-6)][11]
CCDC	2368313
Empirical formula	C <sub>39</sub> H <sub>71</sub> GeKN <sub>2</sub> O <sub>6</sub> Si <sub>3</sub>
Formula weight	859.93
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	12.4586(4)
b (Å)	13.0885(4)
c (Å)	17.1275(6)
α (deg)	95.5876(14)
β (deg)	95.5032(14)
γ (deg)	115.7735(12)
V (Å <sup>3</sup> )	2473.14(14)
Z	2
D (calc) (Mg/m <sup>3</sup> )	1.155
μ (mm <sup>-1</sup> )	0.816
F(000)	920
θ range (°)	1.749 ,30.034
Index ranges	-17,17; -18,18; -24,24
Ref.collected	137762
Independent reflections	14466 (R(int) = 0.0359)
Completeness to θ (°)	(30.03)100.00%
Goodness-of-fit on F <sup>2</sup>	1.069
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0376 wR <sub>2</sub> = 0.0984
R indices (alldata)	R <sub>1</sub> = 0.0494 wR <sub>2</sub> = 0.1075
Δρ <sub>max, min</sub> (e.Å <sup>-3</sup> )	0.577, -0.305

**Table S4.**

Name	[K(18-C-6)]7
CCDC	2368316
Empirical formula	C <sub>49</sub> H <sub>75</sub> KN <sub>2</sub> O <sub>6</sub> Si <sub>4</sub> Te <sub>2</sub>
Formula weight	1194.798
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	21.6369(8)
b (Å)	11.8608(4)
c (Å)	22.6135(9)
α (deg)	90
β (deg)	103.4752(1)
γ (deg)	90
V (Å <sup>3</sup> )	5643.6(4)
Z	4
D (calc) (Mg/m <sup>3</sup> )	1.406
μ (mm <sup>-1</sup> )	1.237
F(000)	2440.083
θ range (°)	1.85, 34.97
Index ranges	-34,34; -19,19; -36,36
Ref.collected	387403
Independent reflections	24788 (R(int) = 0.0381)
Completeness to θ (°)	(34.97)100.00%
Goodness-of-fit on F <sup>2</sup>	1.048
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0287 wR <sub>2</sub> = 0.0620
R indices (alldata)	R <sub>1</sub> = 0.0334 wR <sub>2</sub> = 0.0643
Δρ <sub>max, min</sub> (e.Å <sup>-3</sup> )	1.103, -0.854

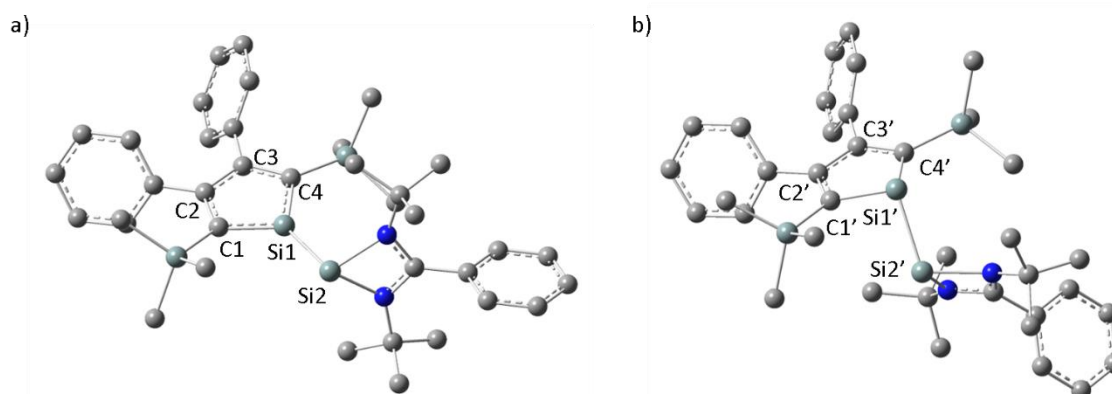
**Table S5.**

Name	$\text{Cu}_2[\mathbf{8}]_2$
CCDC	2368315
Empirical formula	$\text{C}_{74}\text{H}_{102}\text{Cu}_2\text{N}_4\text{Si}_8$
Formula weight	1399.39
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	14.1025(13)
b (Å)	17.5632(17)
c (Å)	15.1034(15)
$\alpha$ (deg)	90
$\beta$ (deg)	101.596(3)
$\gamma$ (deg)	90
V (Å <sup>3</sup> )	3664.5(6)
Z	2
D (calc) (Mg/m <sup>3</sup> )	1.268
$\mu$ (mm <sup>-1</sup> )	0.755
F(000)	1488
$\theta$ range (°)	1.800, 40.249
Index ranges	-25,25; -31,31; -27,27
Ref.collected	264268
Independent reflections	23058 (R(int) = 0.0439)
Completeness to $\theta$ (°)	(40.25)100.00%
Goodness-of-fit on $F^2$	1.003
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0253$ $wR_2 = 0.0680$
R indices (alldata)	$R_1 = 0.0309$ $wR_2 = 0.0710$
$\Delta\rho_{\text{max, min}}$ (e.Å <sup>-3</sup> )	0.595, -0.519

## Computational Details

All quantum chemical calculations were carried out using the Gaussian16 package.<sup>[S10]</sup> The natural bond orbital (NBO)<sup>[S11]</sup> analysis was done with the program NBO 7.0.<sup>[S12]</sup> The molecular structure optimization were performed using the M06-2X functional<sup>[S13]</sup> along with the 6-311+G(d,p) basis set. The effect of the solvent benzene (dielectric constant = 2.274)<sup>[S14]</sup> on the energies has been considered using the SCIPCM model.<sup>[S15]</sup> Every stationary point was identified by a subsequent frequency calculation either as minimum (Number of imaginary frequencies (NIMAG): 0) or transition state (TS) (NIMAG: 1). The 1*H*-tetrolide/2*H*-tetrolide rearrangement has been computed first using a set of model compounds (Table S7). In this case, intrinsic reaction coordinate (IRC)-type of calculations<sup>[S16]</sup> verified the connections between transition states and corresponding minima. The stationary points were then optimized for the real molecules (Tables S8 – S11). The optimized molecular structures of all compounds are given in cartesian coordinates in a separate file, readable by the Mercury program distributed by CCDC. Silicon NMR chemical shift calculations were performed using the GIAO method as implemented in the Gaussian 16 program, the M06L functional and a 6-311G(2d,p) basis set for molecular structures optimized at the M06-2X/6-311+G(d,p) level of theory.<sup>[S17, S18]</sup> The calculated isotropic Si chemical shieldings were transferred to the tetramethylsilane (TMS) scale by using the calculated Si shielding for TMS (PG: Td) obtained for the same model chemistry ( $\sigma(\text{Si}) = 362.17$ , see Table S11).

Interestingly, the optimization of the structure of the isolated anion  $[3]^-$  leads to pyramidalization of the silicon centre and localisation of the silole ring, in contrast to the experimental finding (see structure of  $[K(18-C-6)Et_2O][3]$ ). The delocalized structure of  $[3]^-$  with silicon in a trigonal planar coordination environment was obtained only with inclusion of solvent effects during the structure optimization (see Figure S7 and Table S6)).



**Figure S7.** Optimized molecular structure of  $[3]^-$  (a) applying the PCM model for the solvent benzene (at SCIPCM/M062X/6-311+G(d,p)) and (b) as isolated molecule (at M062X/6-311+G(d,p)).

**Table S6.** Selected atom distances and angles of optimized structures of  $[3]^-$  applying the PCM model for the solvent benzene and as isolated molecule. For comparison data of the sc-XRD analysis of  $[K(18-c-6)Et_2O][3]$  is given as well.

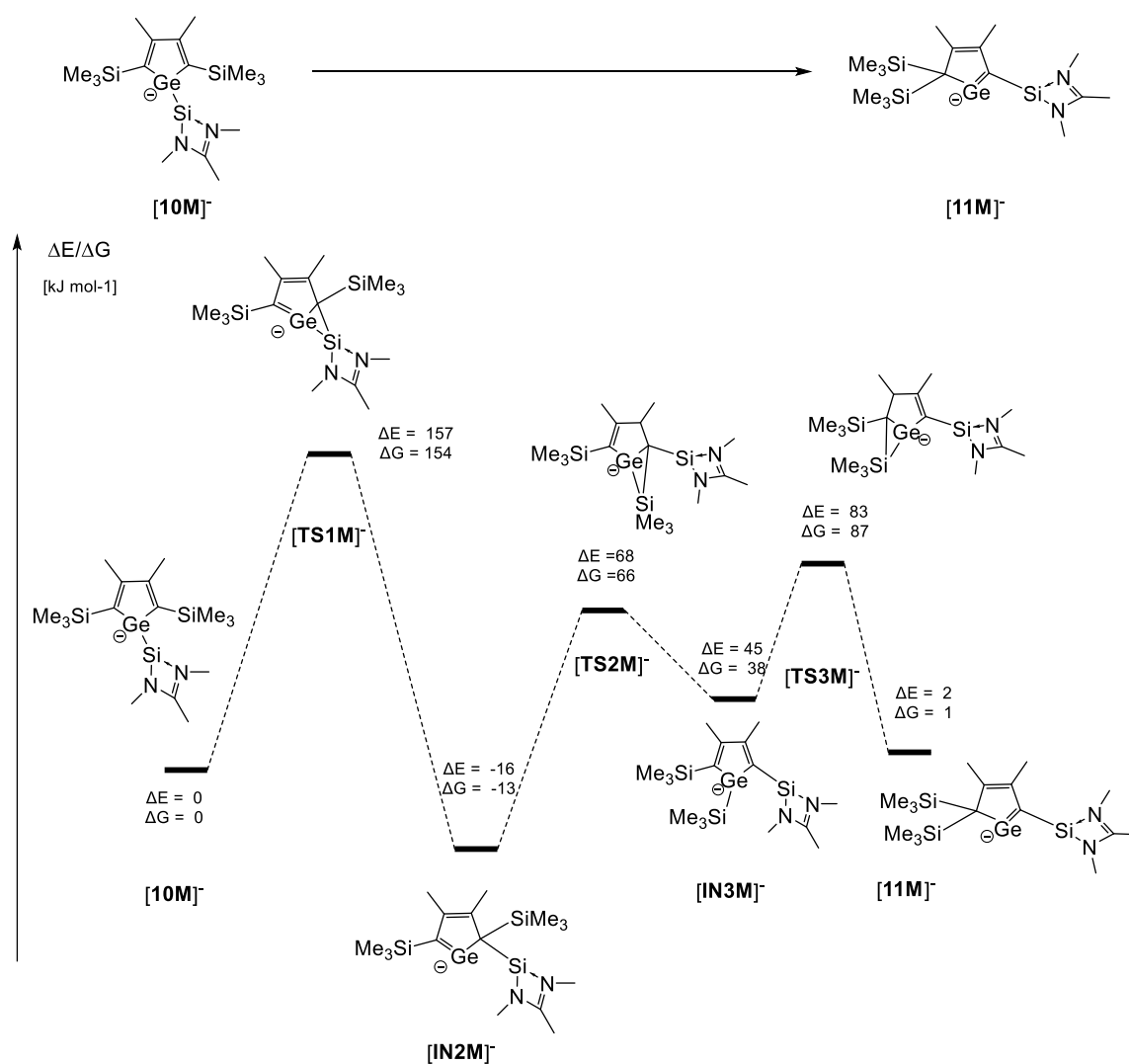
	SCIPCM/M062X/6-311+G(d,p)		M062X/6-311+G(d,p)	sc-XRD [K(18-C-6)Et <sub>2</sub> O] [3]
	Bond length (pm)		Bond length (pm)	Bond length (pm)
C1-C2	142.39	C1'-C2'	139.53	143.32
C2-C3	141.94	C2'-C3'	144.25	142.00
C3-C4	142.13	C3'-C4'	139.47	143.25
Si1-C1	181.51	Si1'-C1'	185.94	181.69
Si1-C4	181.66	Si1'-C4'	186.00	181.19
Si1- Si2	234.16	Si1'- Si2'	236.80	233.37
	Angle (°)		Angle (°)	Angle (°)
$\Sigma\alpha$ (Si1)	359.6	$\Sigma\alpha$ (Si1')	313.4	359.8



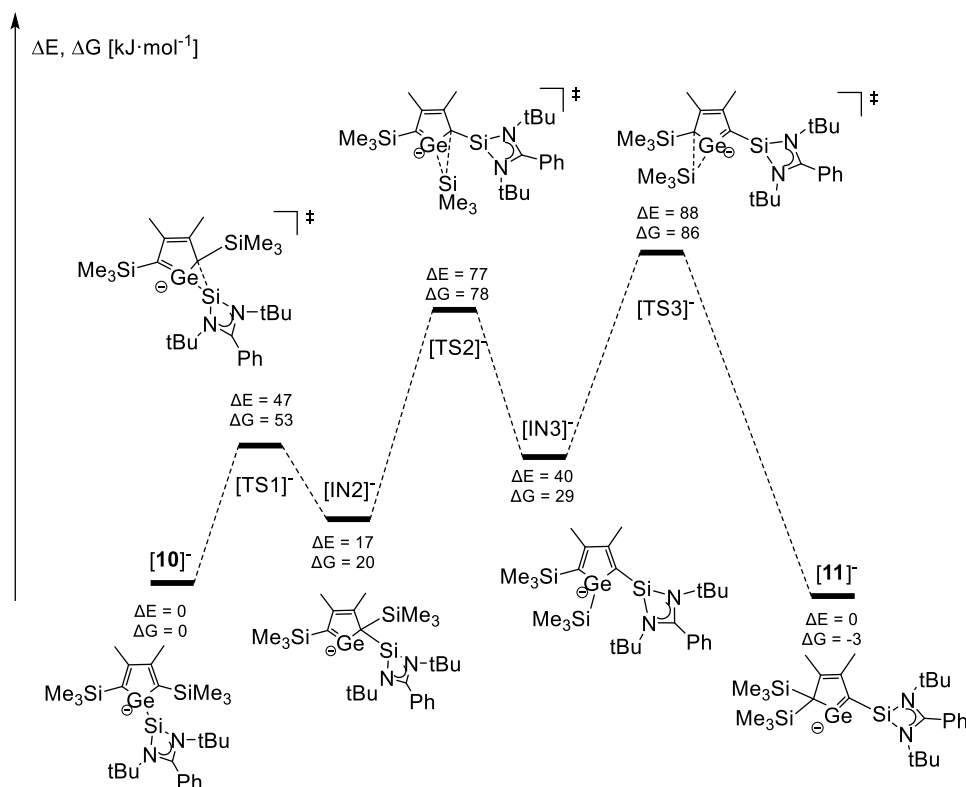
**Table S7.** Calculation of the reaction coordinate of the rearrangement  $[10\mathbf{M}]^- \rightarrow [11\mathbf{M}]^-$  (M062X/6-311+G(d,p)).

Cpd	E [a.u]	G [a.u]	$\Delta E$ (kJ·mol <sup>-1</sup> )	$\Delta G$ (kJ·mol <sup>-1</sup> )
$[10\mathbf{M}]^-$	-3684.45948	-3684.06779	0	0
$[\mathbf{TS1M}]^-$	-3684.39980	-3684.00900	157	154
$[\mathbf{IN2M}]^-$	-3684.46562	-3684.07289	-16	-13
$[\mathbf{TS2M}]^-$	-3684.43363	-3684.04265	68	66
$[\mathbf{IN3M}]^-$	-3684.44244	-3684.05343	45	38
$[\mathbf{TS3M}]^-$	-3684.42797	-3684.03452	83	87
$[11\mathbf{M}]^-$	-3684.458616	-3684.067543	2	1

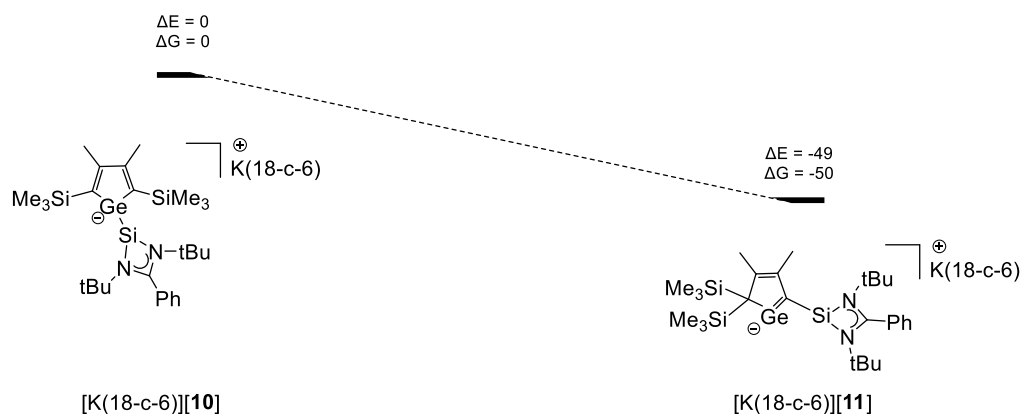
**Figure S8.** Reaction coordinate of the rearrangement  $[10\mathbf{M}]^- \rightarrow [11\mathbf{M}]^-$  (M062X/6-311+G(d,p)).



**Figure S9.** Reaction coordinate of the rearrangement  $[10]^- \rightarrow [11]^-$  (SCIPCM/M062X/6-311+G(d,p)//M062X/6-311+G(d,p)).



**Figure S10.** Energy difference of the ion pairs  $[K(18-c-6)][10]$  and  $[K(18-c-6)][11]$  (SCIPCM/M062X/6-311+G(d,p)//M062X/6-311+G(d,p)).



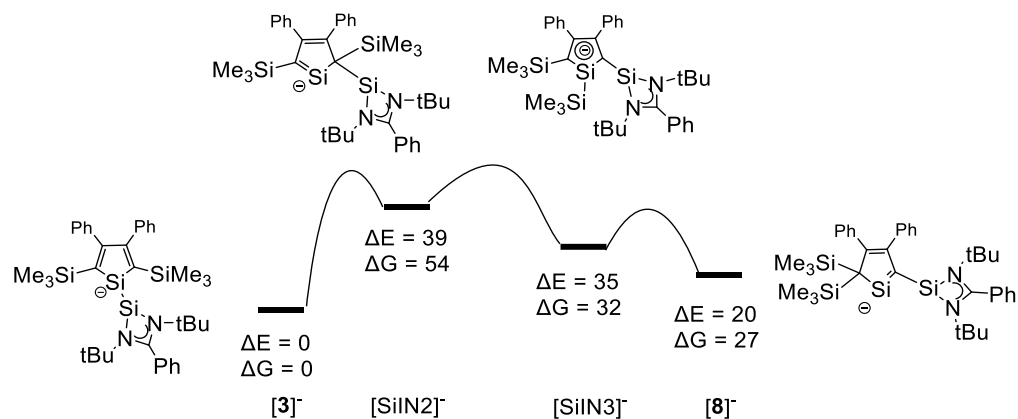
**Table S8.** Calculation of the reaction coordinate of the rearrangement [10]<sup>-</sup> → [11]<sup>-</sup> (see also Figure S9)

Cpd	Model	E [a.u]	G [a.u]	ΔE (kJ·mol <sup>-1</sup> )	ΔG (kJ·mol <sup>-1</sup> )	E <sup>sol</sup> [a.u] (single point)	ΔE <sup>sol</sup> (kJ·mol <sup>-1</sup> ) (single point)	ΔG <sup>sol</sup> (kJ·mol <sup>-1</sup> ) (single point)
[10] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4112.00933	-4111.40419	0	0			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.04522	0	0
[TS1] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4111.99194	-4111.38420	46	52			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.02739	47	53
[IN2] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4112.00297	-4111.39666	17	20			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.03859	17	20
[TS2] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4111.98035	-4111.37496	76	77			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.01591	77	78
[IN3] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4111.99266	-4111.39164	44	33			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.03010	40	29
[TS3] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4111.97516	-4111.37070	90	88			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.01170	88	86
[11] <sup>-</sup>	M06-2X/6-311+G(d,p)	-4112.00897	-4111.40498	1	-2			
	M06-2X(SCIPCM)/6-311+G(d,p)					-4112.04518	0	-3

**Table S9.** Energy difference of the ion pairs [K(18-c-6)][**10**] and [K(18-c-6)][**11**] (see also Figure S10)

Cpd	Method	E [a.u]	G [a.u]	$\Delta E$ (kJ·mol <sup>-1</sup> )	$\Delta G$ (kJ·mol <sup>-1</sup> )	$E^{\text{sol}}$ [a.u] (single point)	$\Delta E^{\text{sol}}$ (kJ·mol <sup>-1</sup> ) (single point)	$\Delta G^{\text{sol}}$ (kJ·mol <sup>-1</sup> ) (single point)
[K(18-c-6)] <b>[10]</b>	M06-2X/6-311+G(d,p) M06-2X(SCIPCM)/6-311+G(d,p)	-5634.84234	-5633.88629	0	0	-5634.85838	0	0
[K(18-c-6)] <b>[11]</b>	M06-2X/6-311+G(d,p) M06-2X(SCIPCM)/6-311+G(d,p)	-5634.86781	-5633.91211	-67	-68	-5634.87687	-49	-50

**Table S10.** Reaction coordinate of the rearrangement [3]<sup>-</sup> → [8]<sup>-</sup> (SCIPCM/M062X/6-311+G(d,p)//M062X/6-311+G(d,p)).



Cpd	method	E [a.u.]	G [a.u.]	ΔE (kJ·mol <sup>-1</sup> )	ΔG (kJ·mol <sup>-1</sup> )	E <sup>sol</sup> [a.u.] (single point)	ΔE <sup>sol</sup> (kJ·mol <sup>-1</sup> ) (single point)	ΔG <sup>sol</sup> (kJ·mol <sup>-1</sup> ) (single point)
[3] <sup>-</sup>	M06-2X/6-311+G(d,p) M06-2X(SCIPCM)/6-311+G(d,p)	-2707.94339	-2707.23932	0	0	-2707.97903	0	0
[SiIN2] <sup>-</sup>	M06-2X/6-311+G(d,p) M06-2X(SCIPCM)/6-311+G(d,p)	-2707.92944	-2707.21989	37	51	-2707.96435	39	54
[SiIN3] <sup>-</sup>	M06-2X/6-311+G(d,p) M06-2X(SCIPCM)/6-311+G(d,p)	-2707.9311	-2707.22839	32	29	-2707.96576	35	32
[8] <sup>-</sup>	M06-2X/6-311+G(d,p) M06-2X(SCIPCM)/6-311+G(d,p)	-2707.93541	-2707.22858	21	28	-2707.97129	20	27

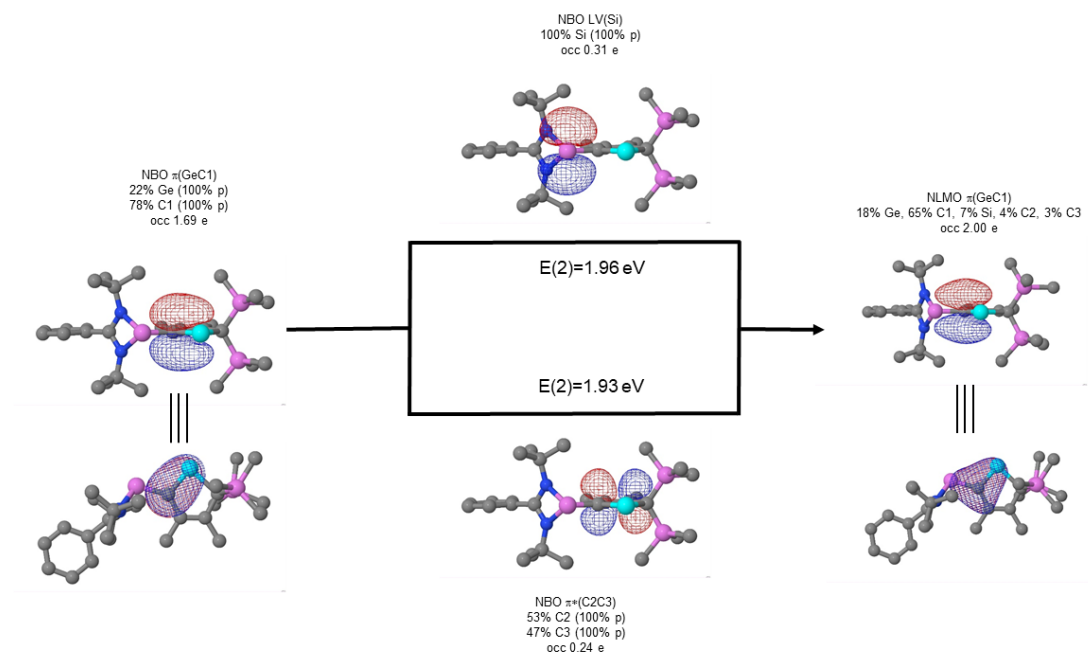
## 2<sup>nd</sup> order perturbation analysis of the conjugation in 2H-germolide [11]

Figure S11 summarises the results of the 2<sup>nd</sup> order perturbation analysis of 2H-germolide [11]. At the top, the delocalization of electron density from the  $\pi(\text{GeC1})$  NBO (occupation 1.69 e) into the  $3p(\text{Si})$  NBO (occupation 0.31 e) is shown.

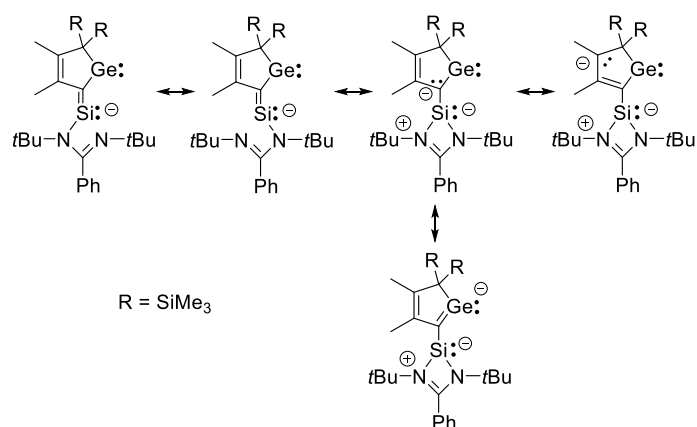
At the bottom, the delocalization of electron density from the  $\pi(\text{GeC1})$  NBO (occupation 1.69 e) into the  $\pi^*(\text{C2C3})$  NBO (occupation 0.24 e) is shown.

Both delocalizations are connected with substantial 2<sup>nd</sup> order perturbation energies ( $E(2) = 1.96$  eV and  $E(2) = 1.93$  eV) and lead to the  $\pi(\text{GeC1})$  NLMO with contribution mainly from C1(65%), but also significant contributions from orbitals of Ge (18%), Si (7%), C2 (4%), C3 (3%).

In summary, the strongly polarized GeC1  $\pi$ -bond (78% C) is delocalized to the exocyclic SiN2 unit and to the endocyclic C=C  $\pi$ -bond, suggesting contributions from the resonance structures shown in Scheme S1.



**Figure S11:** Results of the 2<sup>nd</sup> order perturbation analysis of 2H-germolide [11] indicating the  $\pi$ -delocalization between  $\pi(\text{Ge-C1})$  and  $\pi^*(\text{C2C3})$  (bottom) and the  $\sigma^*/\pi$  hyperconjugation between  $\pi(\text{Ge-C1})$  and  $\sigma^*(\text{SiN2})$  (top) (at M06-2X/6-311+G(d,p), isodensity value 0.04).



**Scheme S1:** Possible resonance structures for the 2*H*-germolide [11].

**Table S11.** Calculated Si NMR chemical shifts for silolides and germolides.

	Model	$\delta^{29}\text{Si}$ (Si1)	$\delta^{29}\text{Si}$ (Si2)	$\delta^{29}\text{Si}$ (SiMe <sub>3</sub> )
<p style="text-align: center;"><b>[K][3]</b></p>	M06L/6-311G(2d,p) M06-2X/6-311+G(d,p)	66.04	44.55	-13.85 -13.65
<p style="text-align: center;"><b>[3]<sup>-a</sup></b></p>	M06L/6-311G(2d,p) M06-2X(SCIPCM)/6-311+G(d,p)	75.43	32.81	-11.48 -16.13
<p style="text-align: center;"><b>[3]<sup>-a</sup></b></p>	M06L/6-311G(2d,p) M06-2X/6-311+G(d,p)	47.00	72.40	-12.83 -14.99
<p style="text-align: center;"><b>[11]<sup>-</sup></b></p>	M06L/6-311G(2d,p) M06-2X/6-311+G(d,p)		38.03	-10.78 -14.61

(a) For the difference between the molecule structure of [3]<sup>-</sup> in dependence of the solvent see Table S6.

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