Supporting Information

for

Trialkylsilyl Substituted Silole and Germole Dianions

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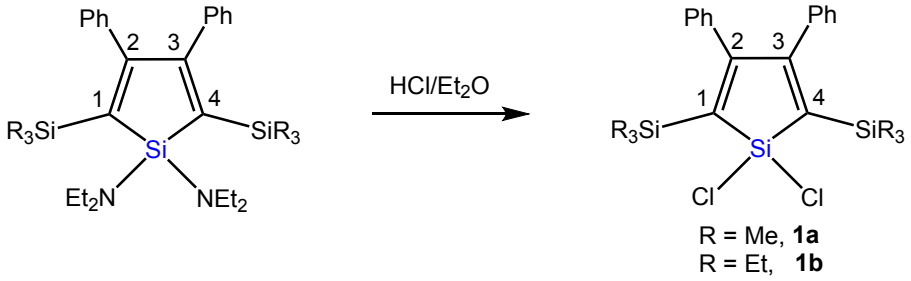
Experimental part

General. All reactions were performed under a controlled dry argon or nitrogen atmosphere using a high-vacuum line, standard Schlenk techniques, and a MBraun glovebox. The used glassware was dried in an oven at 140 °C and evacuated prior to use. Tetrahydrofuran (THF) was pre-dried over potassium hydroxide (KOH) and distilled. The solvents THF, diethylether (Et_2O), benzene and *n*-pentane were dried over sodium/potassium alloy and distilled under nitrogen prior to use. Toluene was dried over sodium and distilled under nitrogen prior to use. Deuterated benzene-d_6 was dried over sodium/potassium alloy, distilled and stored over molecular sieve (4 Å). All used standard chemicals were obtained from commercial suppliers and used as delivered if not mentioned otherwise. Dichloroheteroles **1**[1-2] and **2**[1],[3] were synthesized according to literature procedures. For new compounds, all available NMR spectra are provided. No satisfying combustion analysis was obtained for the bulk material of compounds K_2[**3**] and K_2[**4**], due to the sensitivity of the samples against moisture and air and due to contamination of the samples with variable amounts of THF and KCl. All the NMR data of silole dianions K_2[**3**] and germole dianions K_2[**4**] were recorded in THF in the presence of a sealed capillary containing D_2O.

NMR spectroscopy. NMR spectra were recorded on Bruker Avance DRX 500 and Bruker Avance III 500 spectrometers. ^{1}H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (benzene-d_6: δ ^{1}H(C_6D_5H) = 7.20; D_2O: δ ^{1}H(HDO) = 4.79 and ^{13}C{^{1}H} NMR spectra by using the central line of the solvent signal (benzene-d_6: δ ^{13}C (C_6D_6) = 128.0). The ^{29}Si{^{1}H} NMR inverse gated spectra were recorded with a relaxation delay D1 = 10 s. The ^{29}Si{^{1}H} INEPT spectra were recorded with the combination of D3 = 0.0068 s and D4 = 0.0313 s.

Synthesis of dichlorosiloles 1[1-2]



Scheme S1.

Procedure for 1a

To 6.85 g (13.1 mmol) of 1,1-bis(diethylamino)-3,4-diphenyl-2,5-bis(trimethylsilyl)silole dissolved in 100 mL diethyl ether at -80 °C, was slowly added a solution of 13.80 mL of HCl (55.2 mmol, 4 M in dioxane) dissolved in 30 mL diethyl ether. The reaction mixture was stirred for 18 h while warming to room temperature and a colorless solid precipitated. After removal of the solvents under vacuum, hexane was added and the resulting suspension filtered. The solvents were removed and the residue purified by vacuum transfer ($1 \cdot 10^{-3}$ mbar, 150 °C) to yield 3.91 g (8.7 mmol, 66.4%) of dichlorosilole **1a** as a colorless solid.

Procedure for 1b

To 5.13 g (8.5 mmol) of 1,1- bis(diethylamino)-3,4-diphenyl-2,5-bis(triethylsilyl)silole dissolved in 250 mL diethyl ether at -80 °C, was slowly added a solution of 8.48 mL of HCl (33.9 mmol, 4 M in dioxane). The reaction mixture was stirred for 20 min before the cooling was removed. After stirring for 10 min at room temperature, the solvents were removed under vacuum. Subsequently, hexane was added and the resulting suspension filtered. The filtrate was concentrated under vacuum and 2.04 g (3.8 mmol, 45.3%) of dichlorosilole **1b** crystallized at -24 °C as a colorless solid.

NMR data for **1a**: [1]

^{1}H NMR (499.9 MHz, T = 305.1 K, C_6D_6): δ = 0.16 (s, 18H, Si($C\underline{H}_3$)$_3$), 6.74 – 6.77 (m, 4H, $C_6\underline{H}_5$), 6.81 – 6.85 (m, 6H, $C_6\underline{H}_5$).

^{13}C{^{1}H} NMR (125.7 MHz, T = 305.0 K, C_6D_6): δ = 0.4 (Si$\underline{C}H_3$), 127.3 ($\underline{C}_6H_5$), 127.5 ($\underline{C}_6H_5$), 128.4 ($\underline{C}_6H_5$), 136.5 ($\underline{C}SiMe_3$), 140.5 (*i*-$\underline{C}_6H_5$), 170.2 ($\underline{C}C_6H_5$).

^{29}Si{^{1}H} NMR (99.3 MHz, T = 305.0 K, C_6D_6): δ = -8.0 ($\underline{Si}Me_3$), 19.2 ($\underline{Si}Cl_2$).

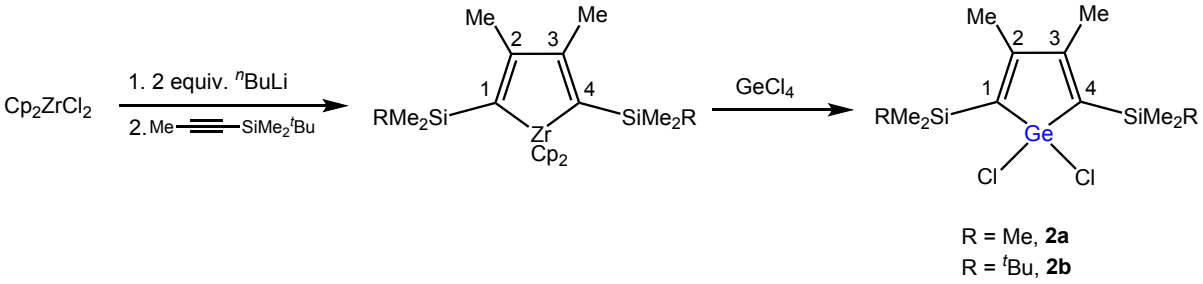
NMR data for **1b**: [1]

^{1}H NMR (499.9 MHz, T = 305.1 K, C_6D_6): δ = 0.68 (q, $^{3}J_{H,H}$ = 7.9 Hz, 12H, SiC$\underline{H}_2$CH$_3$), 1.02 (t, $^{3}J_{H,H}$ = 7.9 Hz, 18H, SiCH$_2$C$\underline{H}_3$), 6.79 – 6.88 (m, 10H, $C_6\underline{H}_5$).

$^{13}C\{^1H\}$ NMR (125.7 MHz, T = 305.0 K, C_6D_6): δ = 4.5 (Si<u>C</u>H_2CH_3), 7.8 ($SiCH_2$<u>C</u>H_3), 127.3 (<u>C</u>$_6H_5$), 127.4 (<u>C</u>$_6H_5$), 128.3 (<u>C</u>$_6H_5$), 134.9 (<u>C</u>$SiEt_3$), 140.7 (*i*-<u>C</u>$_6H_5$), 170.7 (<u>C</u>C_6H_5).

$^{29}Si\{^1H\}$ NMR (99.3 MHz, T = 305.0 K, C_6D_6): δ = 0.3 (<u>Si</u>Et_3), 19.0 (<u>Si</u>Cl_2).

Synthesis of dichlorogermoles 2[1],[3]



R = Me, **2a**
R = ^{t}Bu, **2b**

Scheme S2.

General procedure:

To 3.00 g (10.3 mmol) Cp_2ZrCl_2 suspended in 80 mL pentane at -90 °C, were slowly added 13.47 mL of ^{n}BuLi (21.6 mmol, 1.6 M in hexanes). After 1 h of stirring at that temperature, a solution of 3.19 mL (21.55 mmol) trimethylsilylpropyne or 4.32 mL (20.5 mmol) tert-butyldimethylsilylpropyne in 10 mL pentane was added dropwise and the reaction mixture was stirred for 16 h while warming to room temperature. The color of the solution changed from pale yellow to red brown during this time. Subsequently, 10 mL of THF were added to the flask, which was cooled to -10 °C before a solution of 2.20 g (10.3 mmol) of freshly condensed $GeCl_4$ in 5 mL pentane was added. The mixture was stirred and the solution was allowed to warm to room temperature. The color of the solution changed from red brown to green, turquoise, blue and finally back to a pale yellow and a colorless solid precipitated (approx. 18 h). After filtration, 20 mL of water were added to the solution and stirred for 10 min. The phases were separated and the organic layer dried over $MgSO_4$, filtered and the solvent evaporated. The pale yellow residue was washed with ice cold EtOH. 2.99 g (8.1 mmol, 79.2%) of the dichlorogermole **2a** and 0.85 g (1.9 mmol, 18.3 %) of the dichlorogermole **2b** were obtained as colorless crystals by recrystallization from hexane at -24 °C.

NMR data for **2a**: [1]

^1H NMR (499.9 MHz, 305.9 K, C_6D_6): δ = 0.35 (s, 18H, Si(CH_3)$_3$), 1.68 (s, 6H, CH_3).

$^{13}C\{^1H\}$ NMR (125.7 MHz, 305.0 K, C_6D_6): δ = 0.1 (Si(<u>C</u>H_3)$_3$), 19.4 (C(<u>C</u>H_3)), 132.8 (<u>C</u>Si(CH_3)$_3$), 160.9 (<u>C</u>CH_3).

$^{29}Si\{^1H\}$ NMR (99.3 MHz, 305.0 K, C_6D_6): δ = -7.7 (<u>Si</u>(CH_3)$_3$).

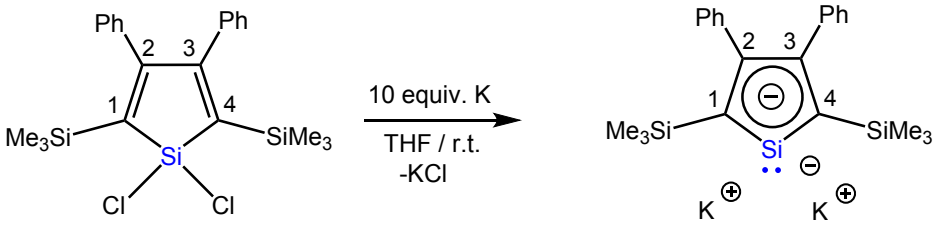
NMR data for **2b**: [1]

^1H NMR (499.9 MHz, 298.7 K, C_6D_6): δ = 0.40 (s, 12H, Si(CH_3)$_2$), 1.00 (s, 18H, SiC(CH_3)$_3$), 1.85 (s, 6H, CH_3).

$^{13}C\{^1H\}$ NMR (125.7 MHz, 299.1 K, C_6D_6): δ = -3.3 (Si(<u>C</u>H_3)$_2$), 19.0 (C(<u>C</u>H_3)), 21.3 (Si<u>C</u>(CH_3)$_3$), 27.5 (SiC(<u>C</u>H_3)$_3$), 132.0 (<u>C</u>Si^{t}BuMe$_2$), 161.7 (<u>C</u>Me).

$^{29}Si\{^1H\}$ NMR (99.3 MHz, 299.0 K, C_6D_6): δ = 0.4 (<u>Si</u>^{t}BuMe$_2$).

Synthesis of silole dianion K_2[3a]



1a K_2[**3a**]

Scheme S3.

At room temperature, THF (25 mL) was added to a mixture of 1 equivalent of dichlorosilole **1a** (400 mg, 0.894 mmol) and 10 equivalents of K (349.4 mg, 8.94 mmol), then the reaction mixture was kept stirring overnight. The resulting deep red-brown solution was filtered by using a PTFE syringe filter to remove the KCl. The filtrate was used for NMR spectroscopy without any further purification. Based on the analysis of the NMR spectra, the yield of compound K_2[**3a**] is almost quantitative. Suitable yellow crystals of K_2[**3a**] were obtained by recrystallization from THF/hexane (1:2) at -30 °C.

NMR data for K_2[**3a**]:

^{1}H NMR (499.87 MHz, 305.0 K, THF): δ = 7.22-7.25 (m, 8H, Ph), 7.07-7.09 (m, 2H, Ph), 0.39 (s, 18H, $Si(CH_3)_3$).

$^{13}C\{^{1}H\}$ NMR (125.71 MHz, 305.0 K, THF): δ = 149.9 (C_{ipso}-Ph), 145.8 (2xCSi), 140.5 (2xCPh), 130.4 (Ph), 126.1 (Ph), 121.1 (Ph), 5.6 ($Si(CH_3)_3$).

$^{29}Si\{^{1}H\}$ NMR (99.31 MHz, 305.0 K, THF): δ = 148.5 (SiC_4), -15.8 ($Si(CH_3)_3$).

CP MAS ^{29}Si NMR: 130.7 (SiC_4), -14.8 ($Si(CH_3)_3$).

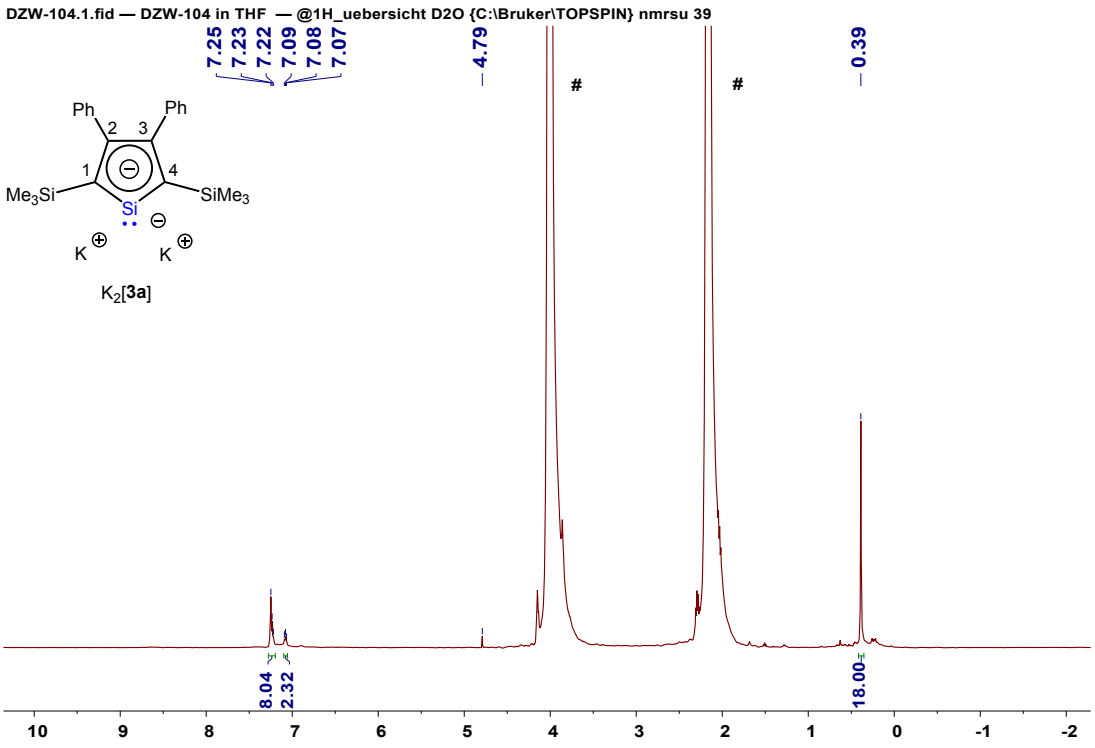


Figure S1a. ^{1}H NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**3a**] (#: THF).

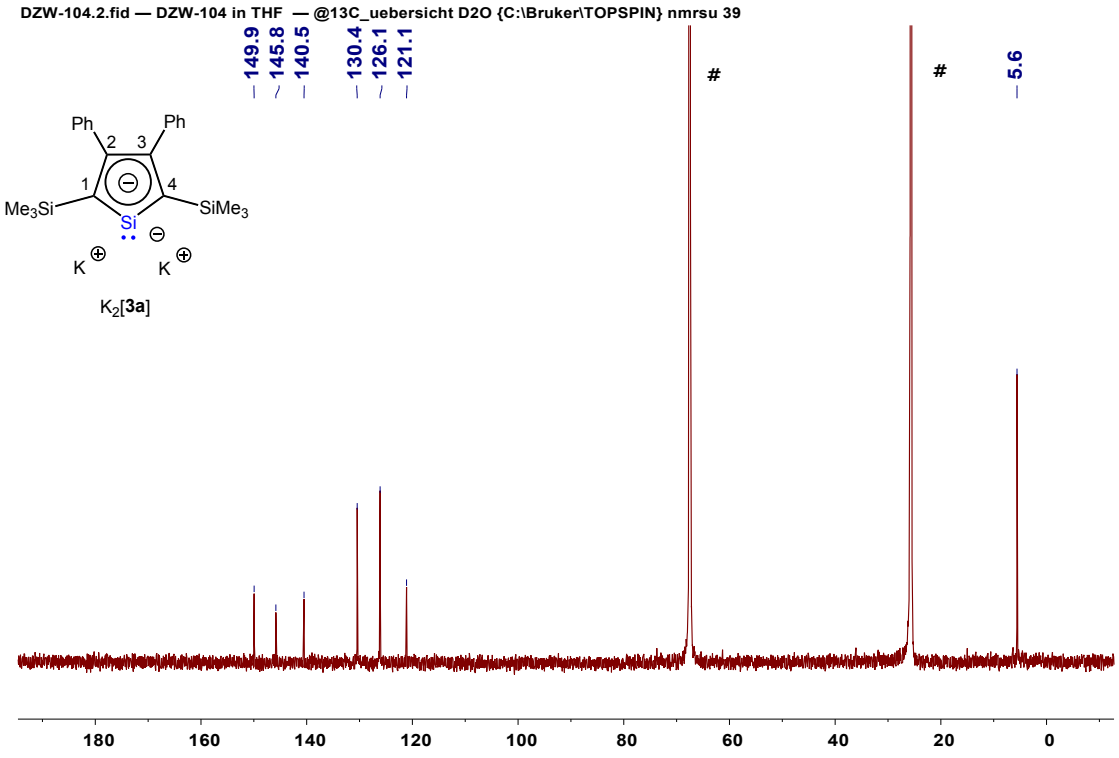


Figure S1b. ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, THF) spectrum of K_2[**3a**] (#: THF).

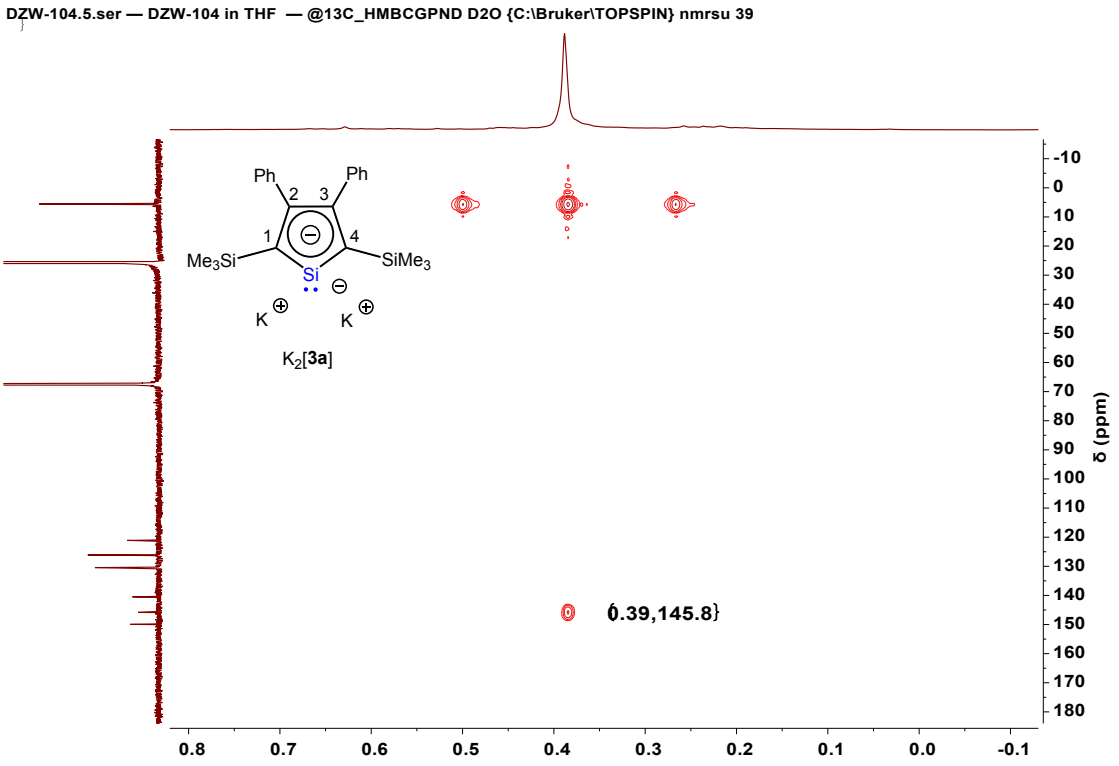


Figure S1c. $^{1}H^{13}C$ HMBC NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**3a**].

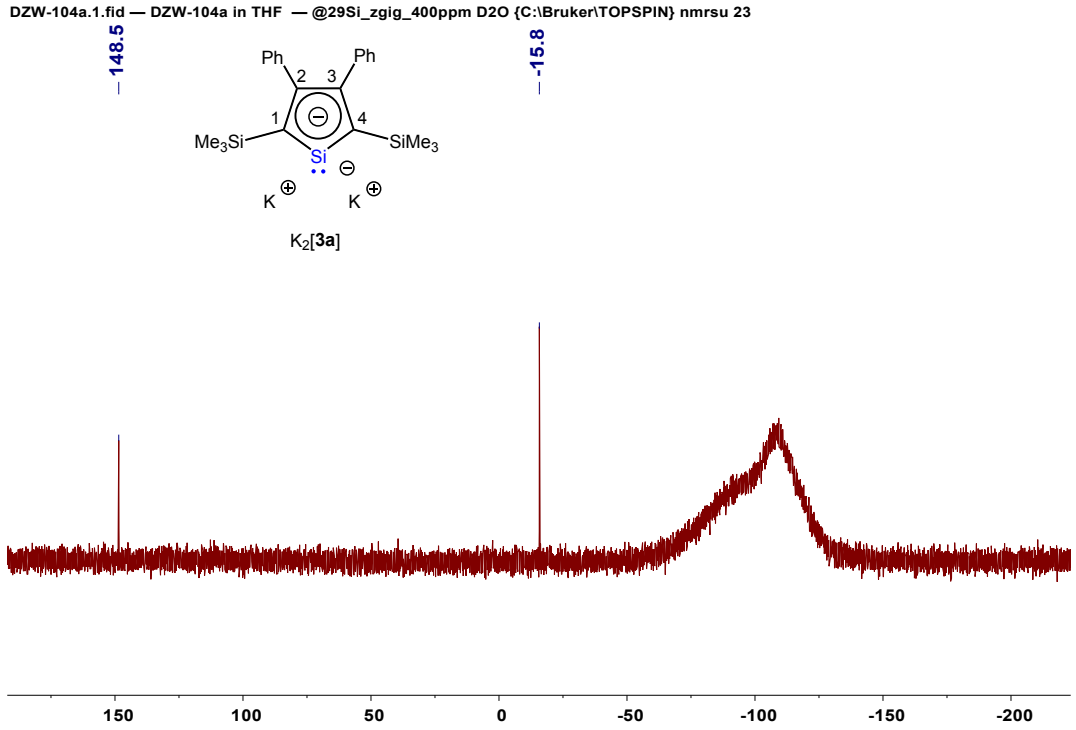


Figure S1d. $^{29}Si\{^{1}H\}$ NMR (99.31 MHz, 305.0 K, THF) spectrum of K_2[**3a**].

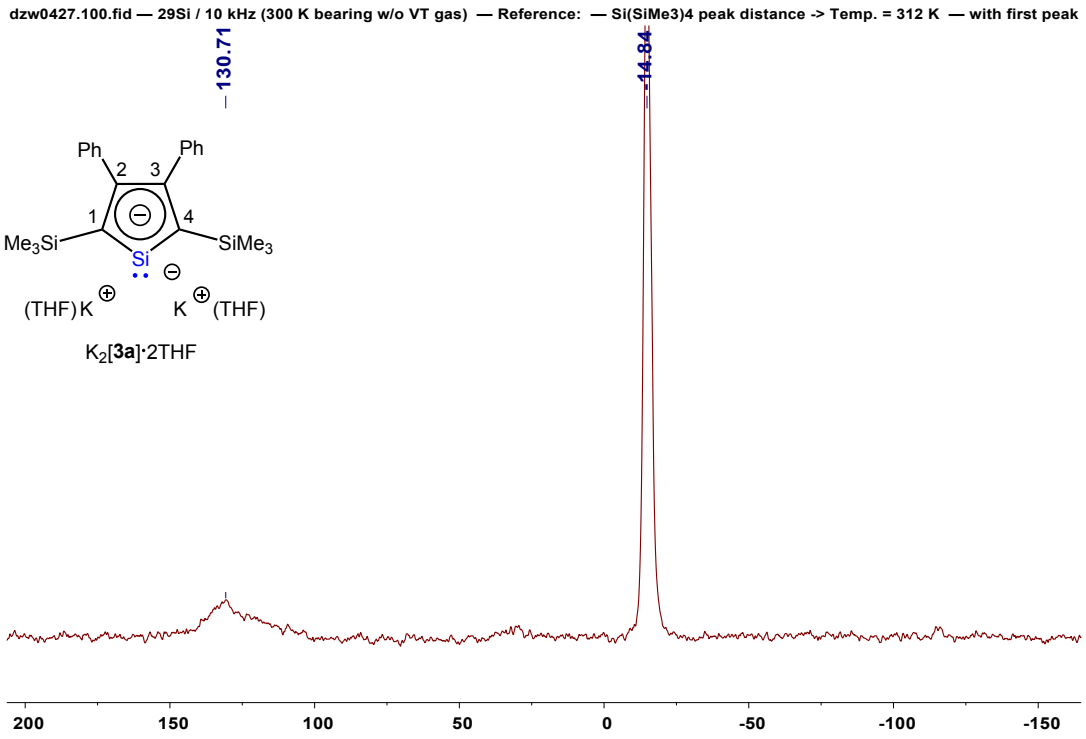
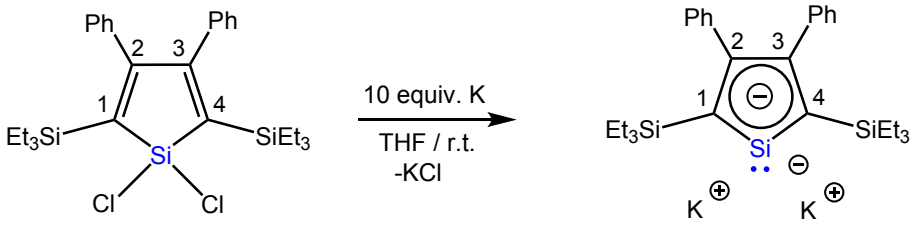


Figure S1e. CP MAS ^{29}Si NMR (99.31 MHz, 305.0 K) spectrum of K_2[**3a**]•2THF.

Synthesis of silole dianion K_2[3b]



1b K_2[**3b**]

Scheme S4.

At room temperature, THF (5 mL) was added to a mixture of 1 equivalent of dichlorosilole **1b** (237.7 mg, 0.447 mmol) and 10 equivalents of K (174.7 mg, 4.47 mmol), then the reaction mixture was kept stirring overnight. The resulting deep red-brown solution was filtered by using a PTFE syringe filter to remove the KCl. The filtrate was used for NMR spectroscopy without any further purification. Based on the analysis of the NMR spectra, compound K_2[**3b**] is contaminated with unknown by-products (less than 18% from ^{1}H NMR spectroscopy).

NMR data for K_2[**3b**]:

^{1}H NMR (499.87 MHz, 305.0 K, THF): δ = 7.20-6.85 (m, 10H, Ph), 1.24-1.27 (t, $^3J_{H,H}$ = 7.9 Hz, 18H, $Si(CH_2C\underline{H}_3)_3$), 0.90-0.95 (q, $^3J_{H,H}$ = 7.9 Hz, 12H, $Si(C\underline{H}_2CH_3)_3$).

^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, THF): δ = 150.1 ($\underline{C}_{ipso}$-Ph), 140.3 (2x$\underline{C}$Ph), 140.1 (2x$\underline{C}$Si), 130.3 (Ph), 126.0 (Ph), 121.1 (Ph), 9.0 ($Si(CH_2\underline{C}H_3)_3$), 8.6 ($Si(\underline{C}H_2CH_3)_3$).

^{29}Si{^{1}H} NMR (99.31 MHz, 305.0 K, THF): δ = 161.4 (SiC_4), -6.3 ($Si(CH_2CH_3)_3$).

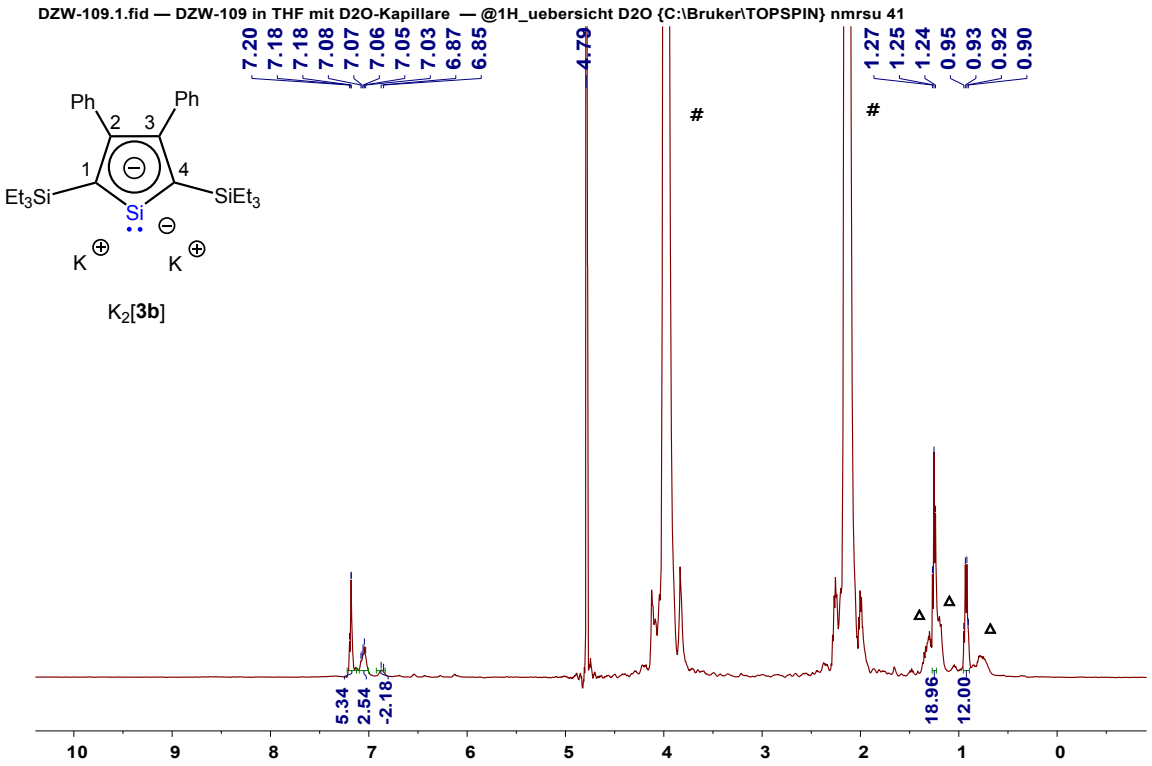


Figure S2a. ^{1}H NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**3b**] (#: THF; **Δ:** impurities).

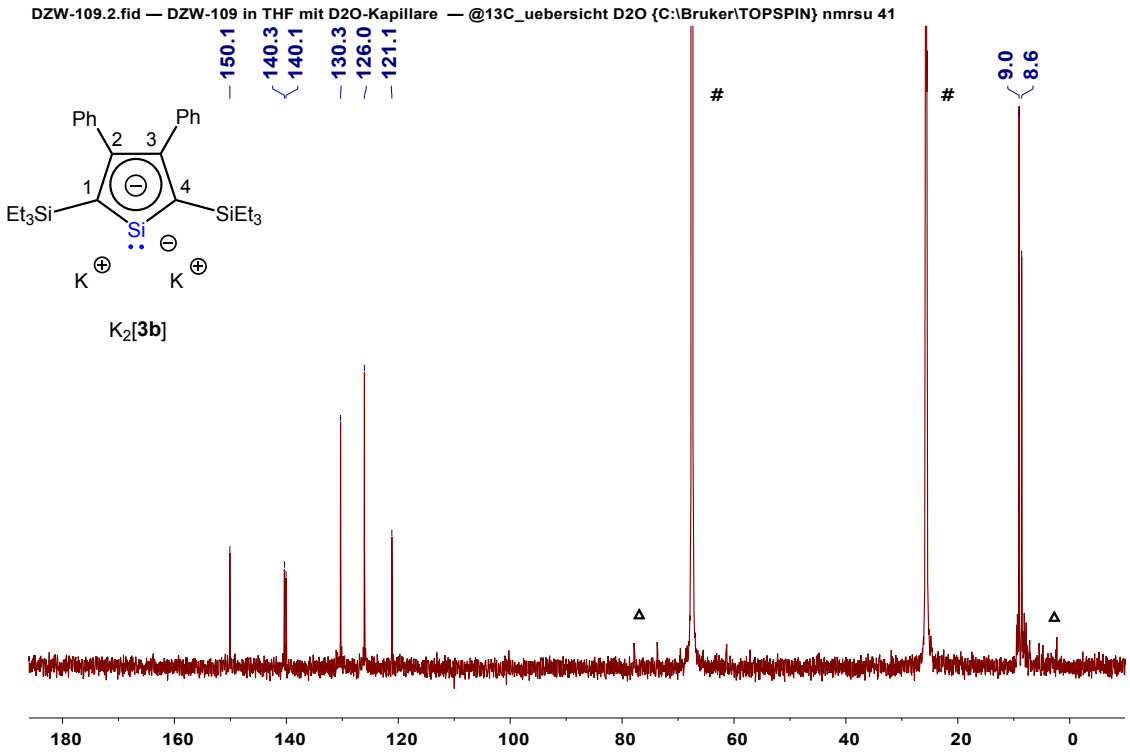


Figure S2b. ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, THF) spectrum of K_2[**3b**] (#: THF; **Δ:** impurities).

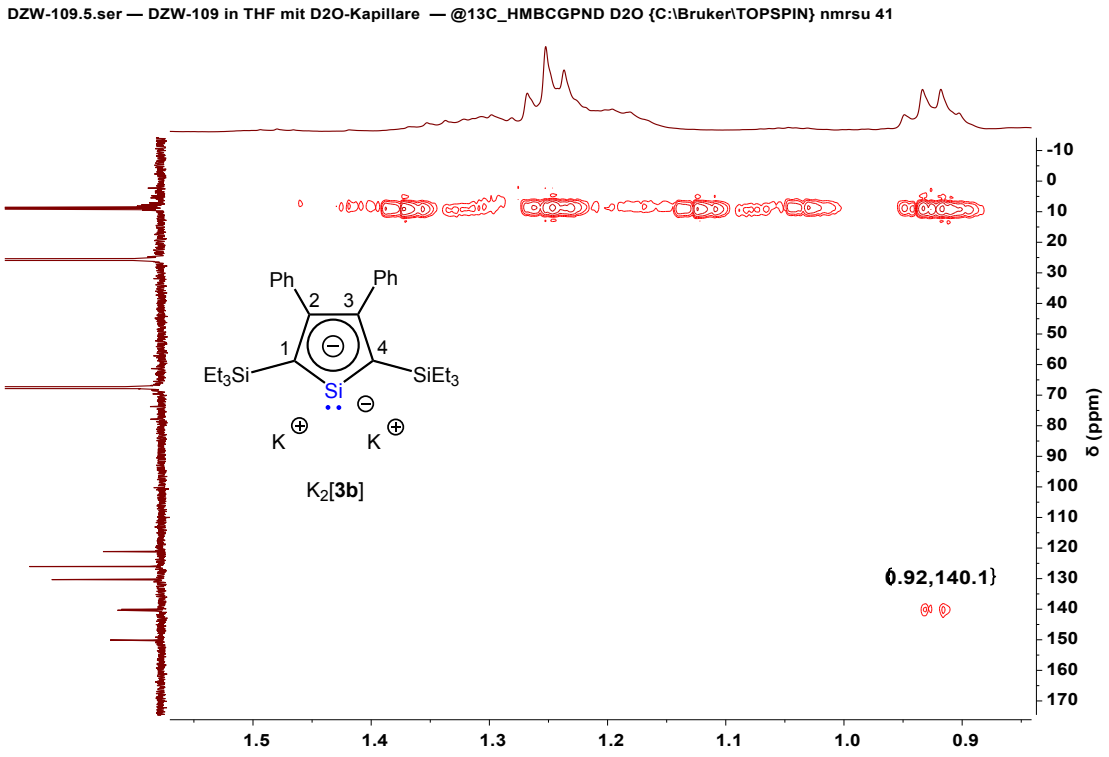


Figure S2c. $^{1}H^{13}C$ HMBC NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**3b**].

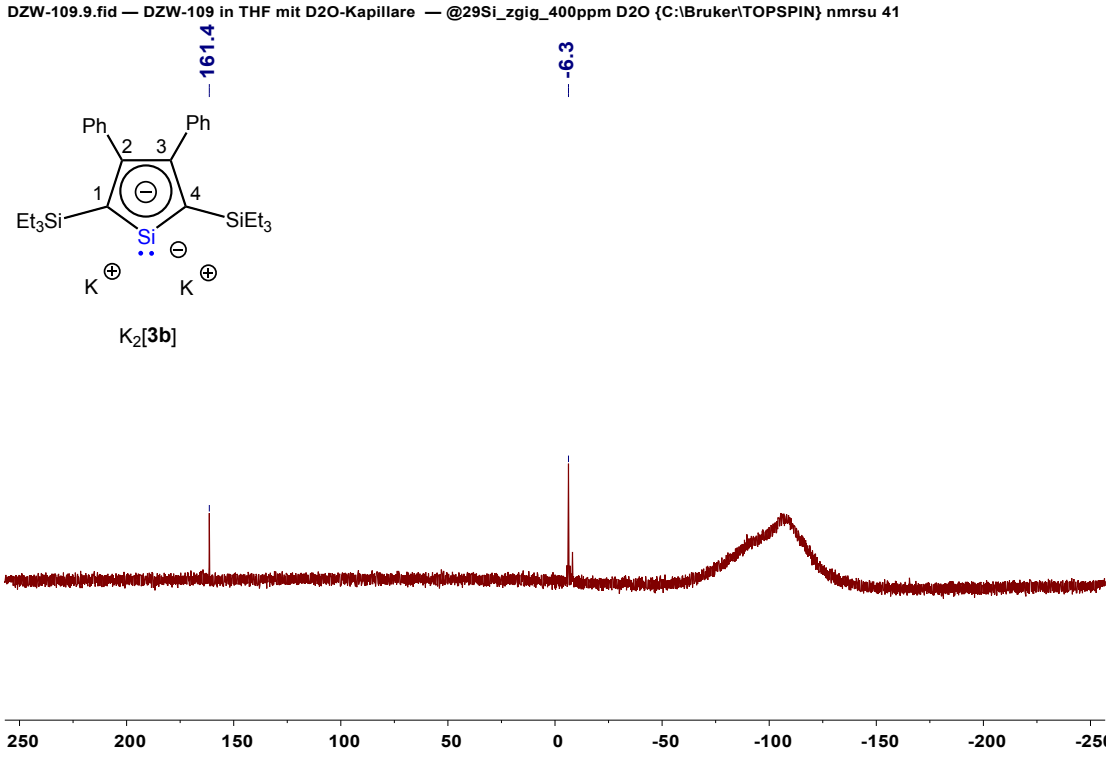
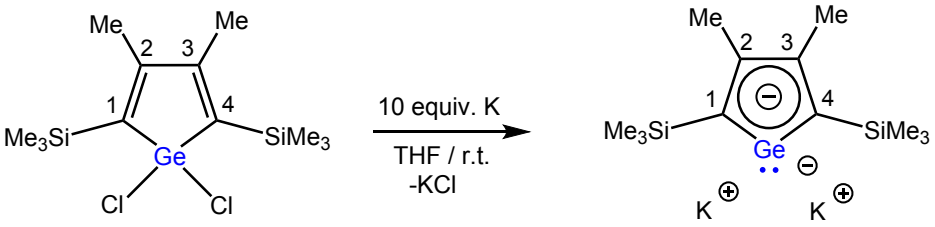


Figure S2d. $^{29}Si\{^{1}H\}$ NMR (99.31 MHz, 305.0 K, THF) spectrum of K_2[**3b**].

Synthesis of germole dianion K_2[4a]



2a K_2[**4a**]

Scheme S5.

At room temperature, THF (25 mL) was added to a mixture of 1 equivalent of dichlorogermole **2a** (1.500 g, 4.08 mmol) and 10 equivalents of K (1.590 g, 40.80 mmol), then the reaction mixture was kept stirring overnight. The red-brown solution was filtered by using a PTFE syringe filter to remove the KCl. The filtrate was used for NMR spectroscopy without any purification. ^{1}H NMR spectroscopy indicated almost quantitative formation of compound K_2[**4a**]. Recrystallization of the residue from THF/hexane (1:2) at -30 °C afforded K_2[**4a**] as air- and moisture sensitive yellow crystals.

NMR data for K_2[**4a**]:

^{1}H NMR (499.9 MHz, 305.0 K, THF): δ = 0.35 (s, 18H, Si(C$\underline{H}_3$)$_3$), 2.47 (s, 6H, C$\underline{H}_3$).

^{13}C{^{1}H} NMR (125.7 MHz, 305.0 K, THF): δ = 4.9 (Si(C$\underline{H}_3$)$_3$), 20.9 (C$\underline{H}_3$), 130.8 (2xC$\underline{C}$CH$_3$), 156.2 (2xC$\underline{C}$Si).

^{29}Si{^{1}H} NMR (99.3 MHz, 305.0 K, THF): δ = -15.9 ($\underline{Si}$(CH$_3$)$_3$).

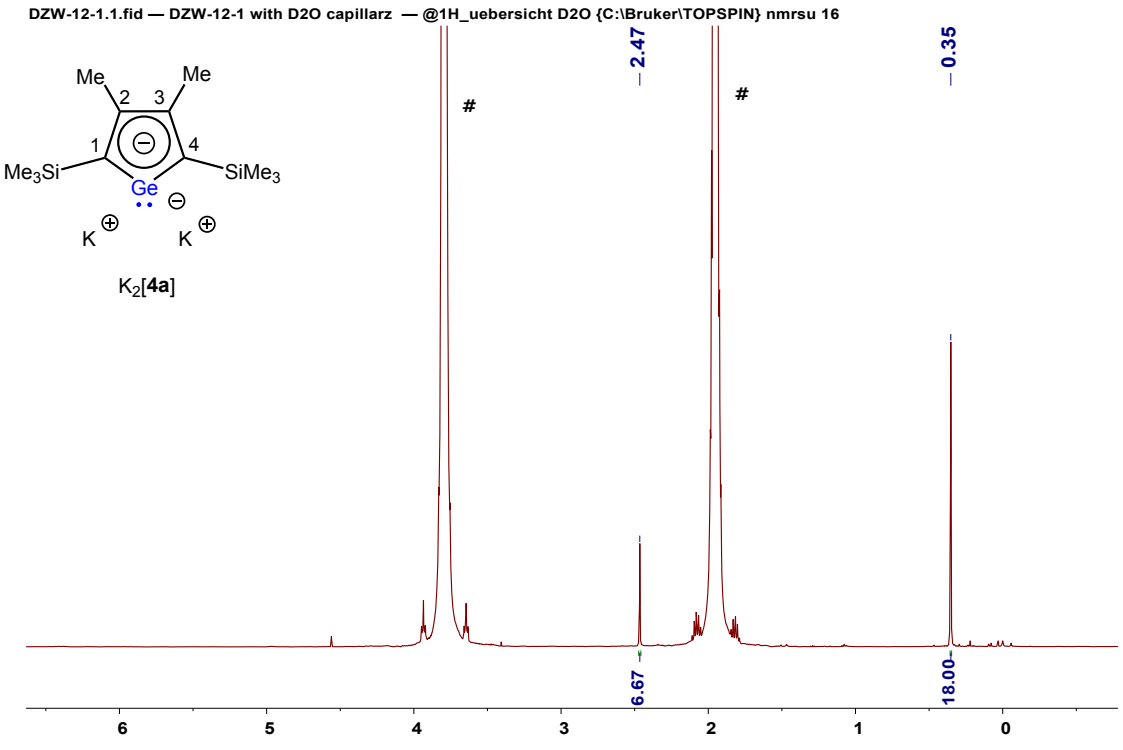


Figure S3a. ^{1}H NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**4a**] (#: THF).

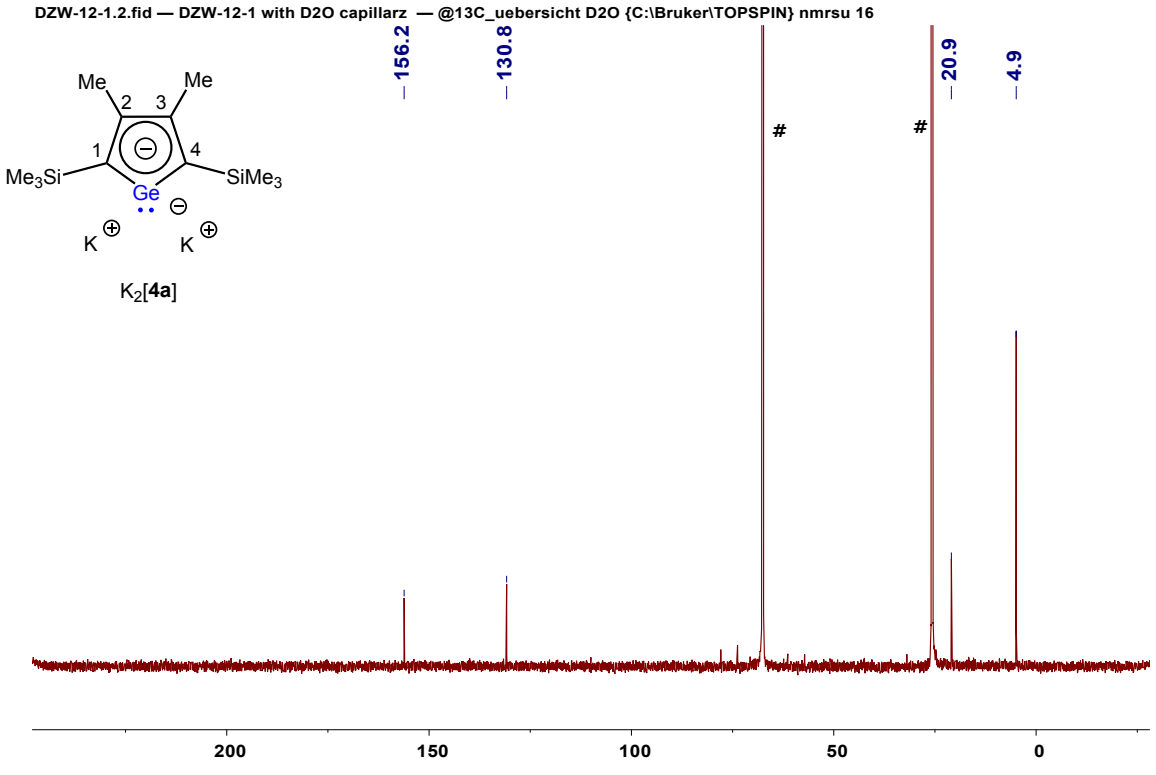


Figure S3b. ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, THF) spectrum of K_2[**4a**] (#: THF).

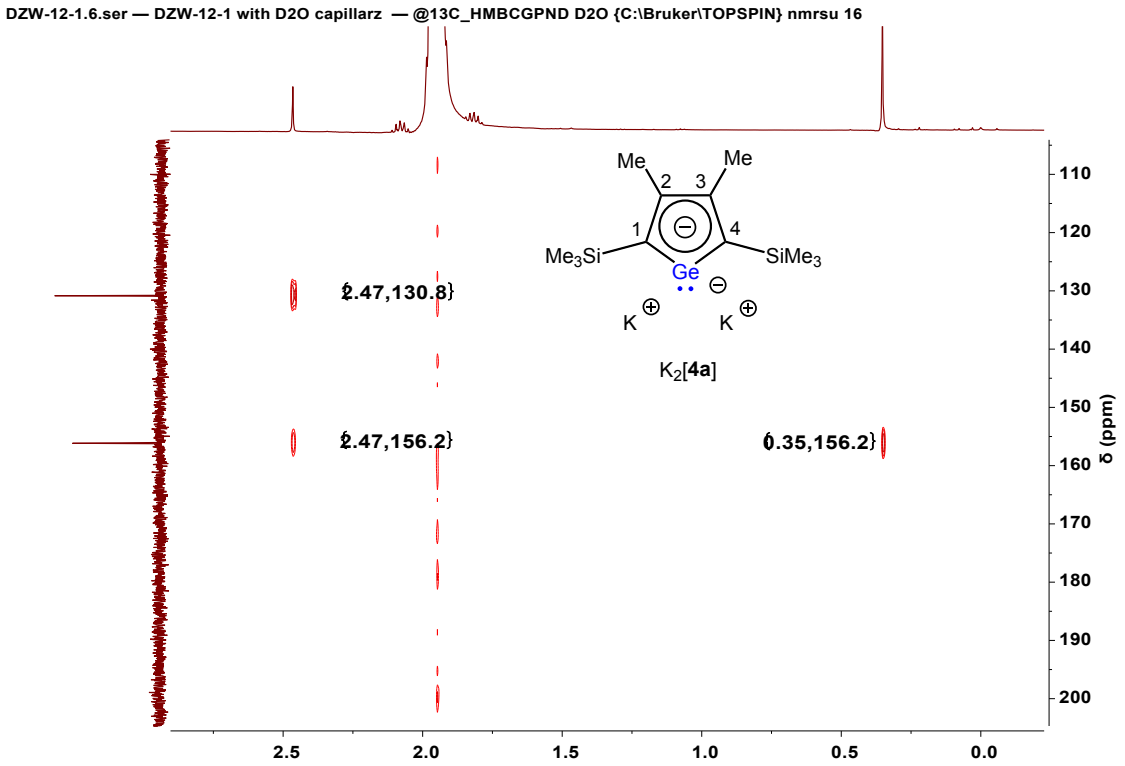


Figure S3c. $^{1}H^{13}C$ HMBC NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**4a**].

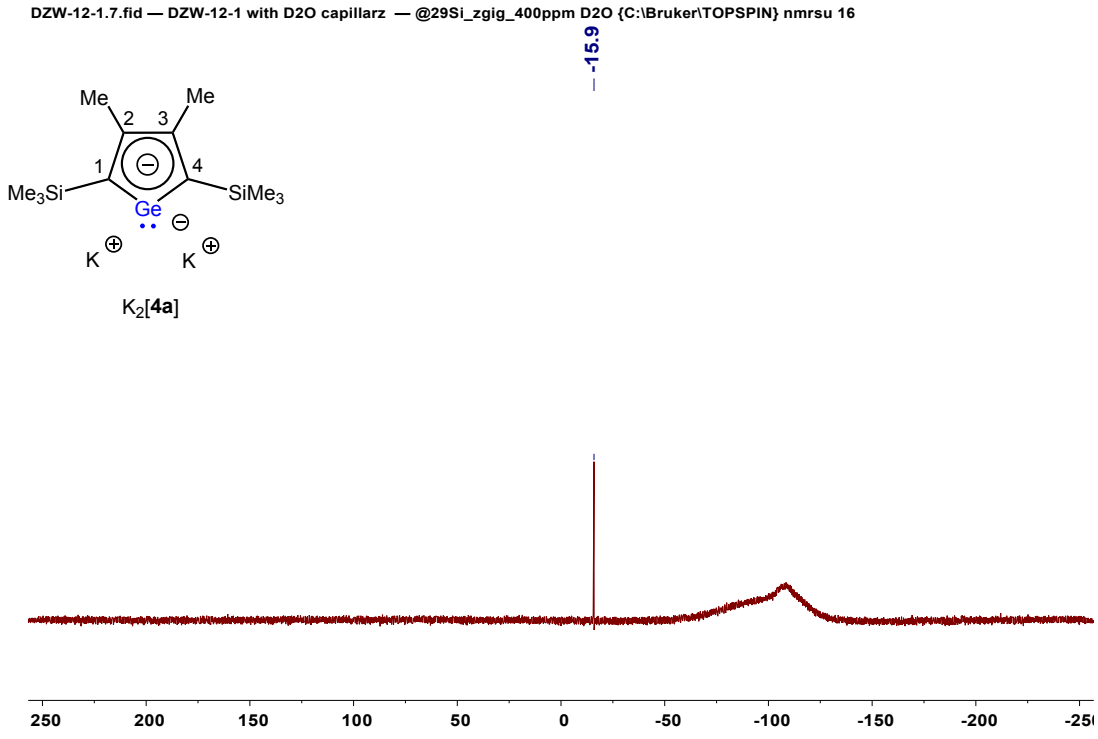
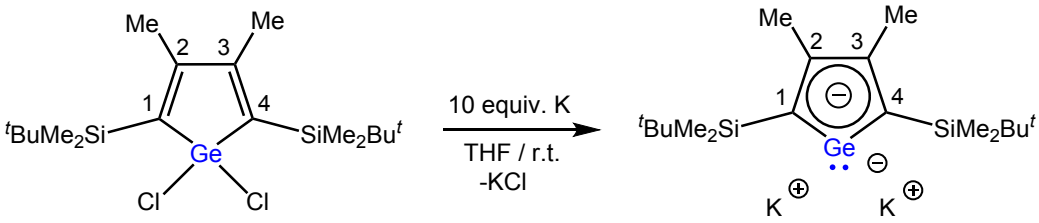


Figure S3d. $^{29}Si\{^{1}H\}$ NMR (99.31 MHz, 305.0 K, THF) spectrum of K_2[**4a**].

Synthesis of germole dianion K_2[4b]



2b K_2[**4b**]

Scheme S6.

At room temperature, THF (5 mL) was added to a mixture of 1 equivalent of dichlorogermole **2b** (246 mg, 0.543 mmol) and 10 equivalents of K (212 mg, 5.43 mmol), then the reaction mixture was kept stirring overnight. The red-brown solution was filtered by using a PTFE syringe filter to remove the KCl. The filtrate was used for NMR spectroscopy without any purification. ^{1}H NMR spectroscopy indicated almost quantitative formation of compound K_2[**4b**].

NMR data for K_2[**4b**]:

^{1}H NMR (499.9 MHz, 305.0 K, THF): δ = 0.50 (s, 12H, Si(C$\underline{H}_3$)$_2$), 1.29(s, 18H, SiC(C$\underline{H}_3$)$_3$), 2.56 (s, 6H, C$\underline{H}_3$).

^{13}C{^{1}H} NMR (125.7 MHz, 305.0 K, THF): δ = 0.0 (Si(C$\underline{H}_3$)$_2$), 17.5 (Si$\underline{C}$(CH$_3$)$_3$), 21.6 ($\underline{C}$H$_3$), 28.3 (SiC($\underline{C}$H$_3$)$_3$), 129.6 (2x$\underline{C}$CH$_3$), 150.8 (2x$\underline{C}$Si).

^{29}Si{^{1}H} NMR (99.3 MHz, 305.0 K, THF): δ = -5.9 ($\underline{Si}$(CH$_3$)$_3$).

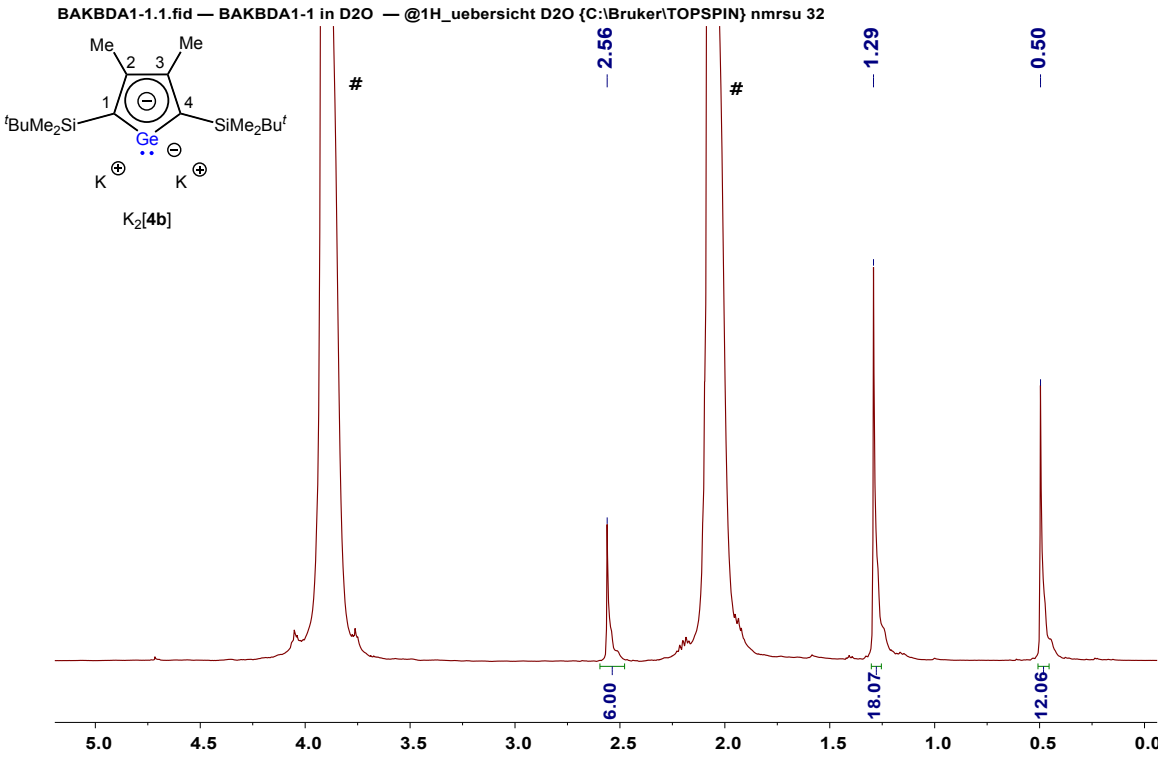


Figure S4a. ^{1}H NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**4b**] (#: THF).

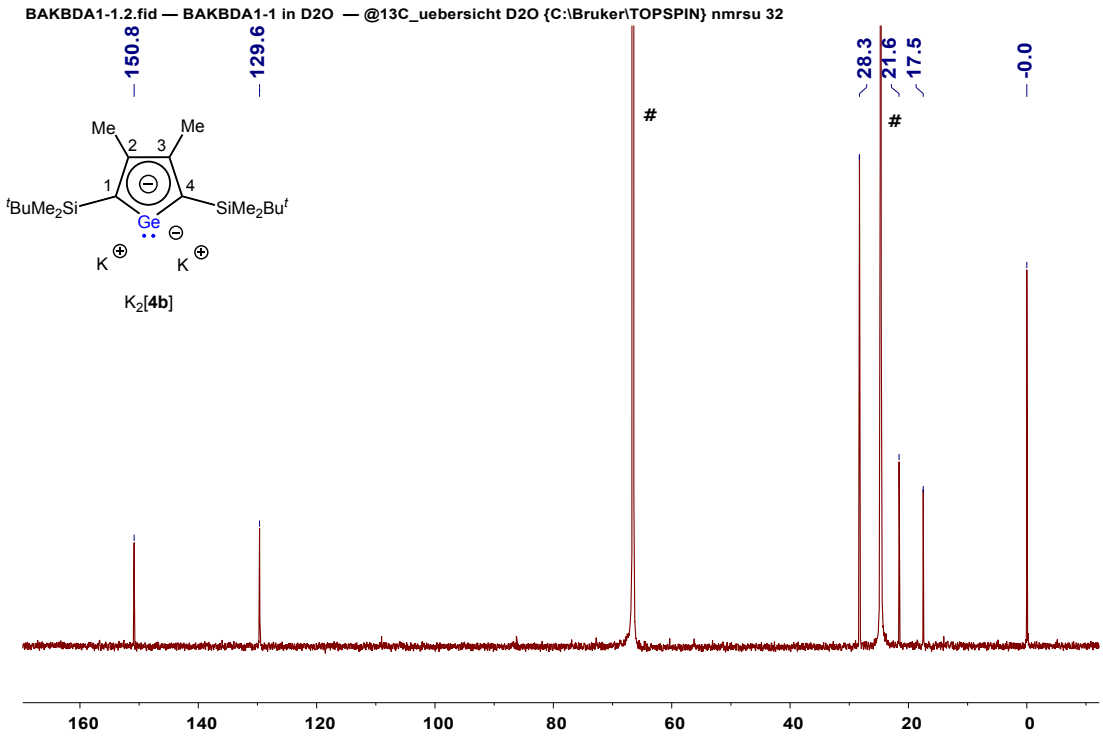


Figure S4b. ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, THF) spectrum of K_2[**4b**] (#: THF).

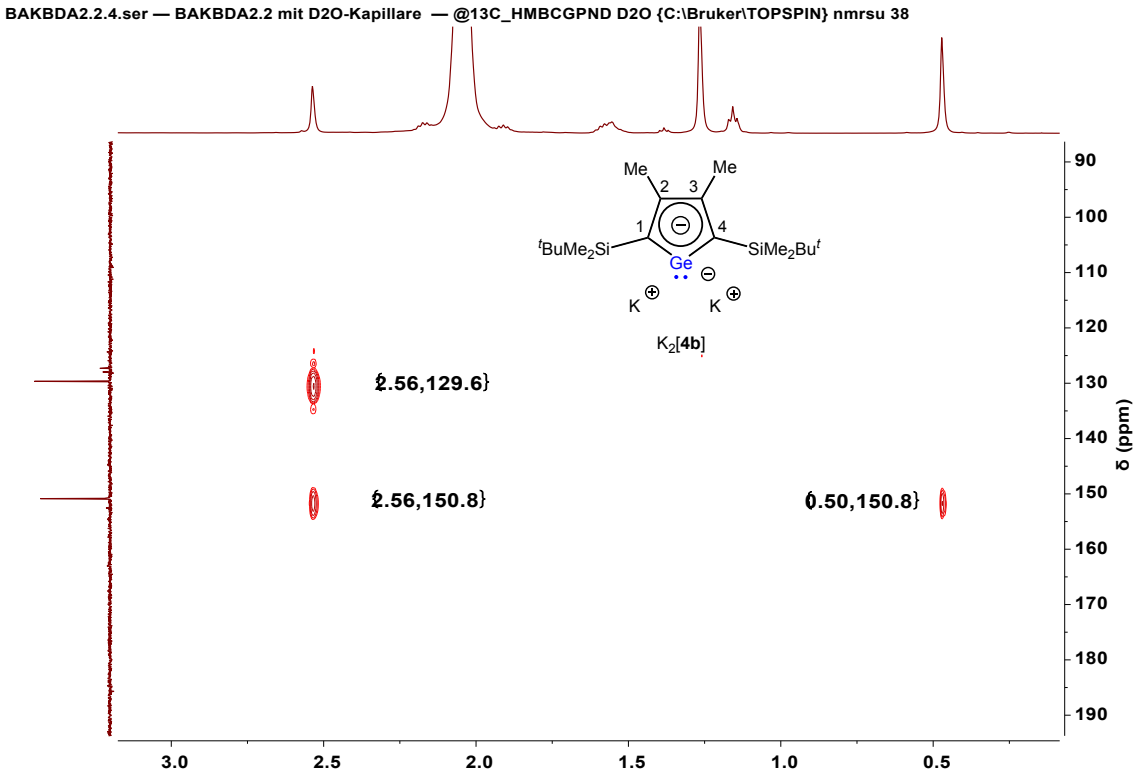


Figure S4c. $^{1}H^{13}C$ HMBC NMR (499.87 MHz, 305.0 K, THF) spectrum of K_2[**4b**].

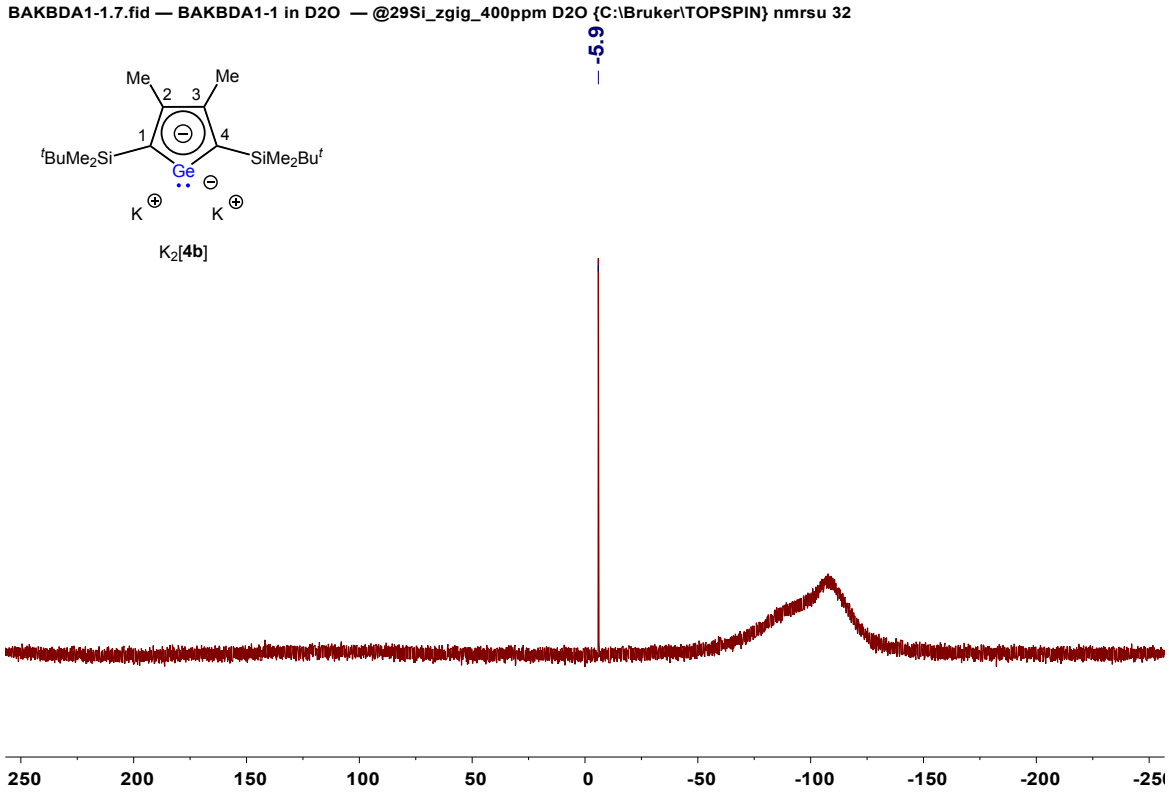


Figure S4d. $^{29}Si\{^{1}H\}$ NMR (99.31 MHz, 305.0 K, THF) spectrum of K_2[**4b**].

Details of X-ray Analysis of K_2[3a]•2THF and K_2[4a]•2THF.

Single crystal X-ray data were measured on a Bruker AXS Apex II diffractometer (Mo-Kα radiation, λ = 0.71073Å, Kappa 4 circle goniometer, Bruker Apex II detector). The crystals were kept at 100.0 K for K_2[**3a**]•2THF and 180.0 K for K_2[**4a**]•2THF individually during data collection. Absorption corrections based on symmetry-related measurements (multi-scan) were performed with the program SADABS.[4] The structures were solved with the program SHELXS and refined with SHELXL.[5]Pertinent data are summarized in Table S1 and S2. CCDC-1815293 (K_2[**3a**]•2THF), CCDC-1500976 (K_2[**4a**]•2THF) 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].

Table S1. Crystal data and structure refinement for K_2[**3a**]•2THF.

Identification code	crd195y_5	
Empirical formula	C30 H44 K2 O2 Si3	
Formula weight	599.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3874(4) Å	α = 68.719(2)°.
	b = 11.8915(5) Å	β = 70.7867(19)°.
	c = 15.1500(6) Å	γ = 79.654(2)°.
Volume	1642.77(12) $Å^3$	
Z	2	
Density (calculated)	1.211 Mg/m^3	
Absorption coefficient	0.422 mm^{-1}	
F(000)	640	
Crystal size	0.440 x 0.160 x 0.120 mm^3	
Theta range for data collection	1.506 to 34.971°	
Index ranges	-16<=h<=16, -19<=k<=19, -24<=l<=24	
Reflections collected	49374	
Independent reflections	49374 (R(int) = ?)	
Observed reflections (I > 2(I))	56670	
Completeness to theta = 25.026°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	1.0000and 0.9136	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	49374 / 0 / 341	
Goodness-of-fit on F^2	1.068	
Final R indices (I>2sigma(I))	R1 = 0.0414, wR2 = 0.0899	
R indices (all data)	R1 = 0.0675, wR2 = 0.1003	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.518 and -0.496 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for K_2[**4a**]•2THF.

Identification code	dzw12_180k	
Empirical formula	C20 H40 Ge K2 O2 Si2	
Formula weight	519.49	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/C$	
Unit cell dimensions	a = 10.5394(4) Å	α = 90°.
	b = 21.2764(9) Å	β = 110.2654(13)°.
	c = 13.4435(6) Å	γ = 90°.
Volume	11477.8(5) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	1.474 mm^{-1}	
F(000)	1096	
Crystal size	0.600 x 0.200 x 0.200 mm^3	
Theta range for data collection	1.877 to 27.102°	
Index ranges	-13<=h<=13, -27<=k<=27, -17<=l<=17	
Reflections collected	87886	
Independent reflections	6255 (R(int) = 0.0256)	
Observed reflections (I > 2(I))	5251	
Completeness to theta = 25.026°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8127 and 0.5436	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6255 / 0 / 297	
Goodness-of-fit on F^2	1.125	
Final R indices (I>2sigma(I))	R1 = 0.0376, wR2 = 0.0920	
R indices (all data)	R1 = 0.0495, wR2 = 0.1012	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.518 and -0.488 e.$Å^{-3}$	

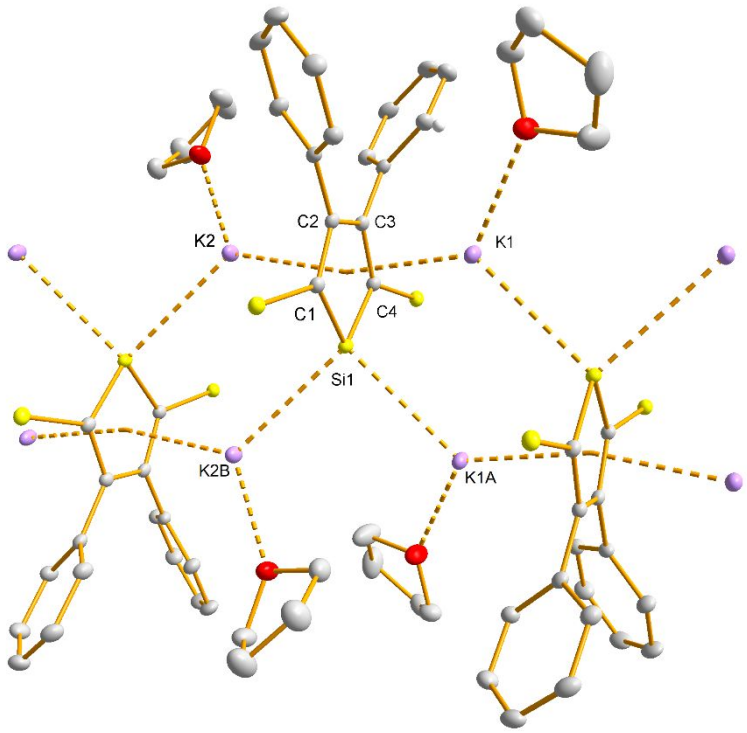


Figure S5. Polymeric structure of K_2[**3a**] • 2 THF in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms and methyl groups of $SiMe_3$ are omitted for clarity).

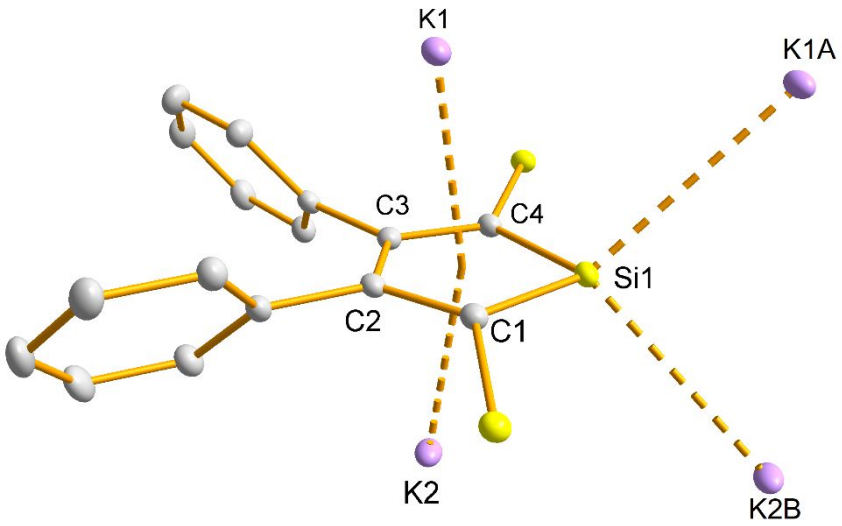


Figure S6. Repeating unit of K_2[**3a**] in the crystal (thermal ellipsoids at 50% probability, all hydrogen atoms, THF molecules and methyl groups of $SiMe_3$ are omitted for clarity). Selected bond lengths (pm) and angles (°): C1–C2 143.8(17), C2–C3 142.3(16), C3–C4 143.8(16), Si1–C1 186.0(12), Si1–C4 186.1(12), Si1–K1 340.7(4), Si1–K2 338.9(4), Si1–K1B 344.9(4), Si1–K1A 343.3(4), K1–silole centroid 281.4(3), K2–silole centroid 281.0(3), $\sum_{\text{silole ring}}$ 540.0 (sum of internal bond angles of the silole ring).

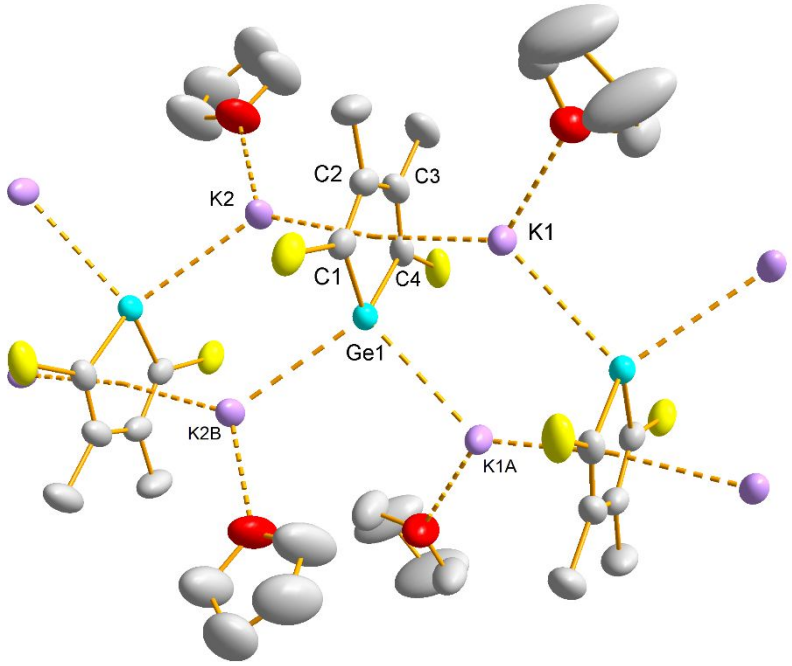


Figure S7. Polymeric structure of K_2[**4a**] • 2 THF in the crystal (thermal ellipsoids at 30% probability, all hydrogen atoms and methyl groups of $SiMe_3$ are omitted for clarity).

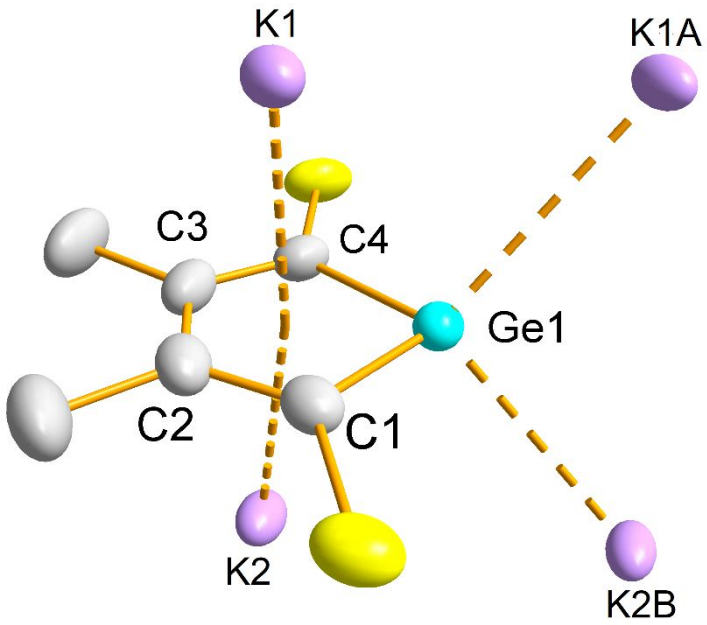
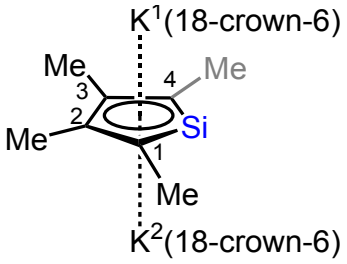
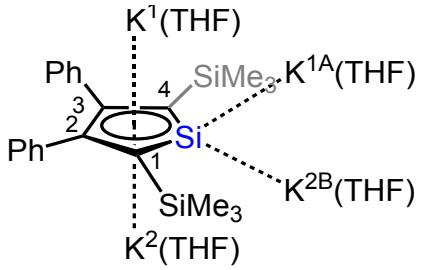


Figure S8. Repeating unit of K_2[**4a**] in the crystal (thermal ellipsoids at 30% probability, all hydrogen atoms, THF molecules and methyl groups of $SiMe_3$ are omitted for clarity). Selected bond lengths (pm) and angles (°): C1–C2 141.5(4), C2–C3 139.5(4), C3–C4 142.0(4), Ge1–C1 194.9(3), Ge1–C4 194.2(2), Ge1–K1 333.2(7), Ge1–K2 332.2(7), Ge1–K2B 345.5(8), Ge1–K1A 342.9(7), K1–germole centroid 277.5(8), K2–germole centroid 277.7(8), $\sum_{\text{germole ring}}$ 540.0 (sum of internal bond angles of germole ring).

Table S3. Comparison of experimental structures of dipotassium silole dianions K_2[**9**] and K_2[**3a**].



[K(18-crown-6)]$_2$[**9**]



K_2[**3a**]

Bond length [pm]	[K(18-crown-6)]$_2$[**9**]	K_2[**3a**]•2THF
Si^1–C^1	183.0 / 185.1	186.0 / 186.1
Si^1–K^1	338.7	340.7
Si^1–K^2	336.4	338.9
Si^1–K^{1A}	–	343.3
Si^1–K^{2B}	–	344.9
K^1–C^1	313.9 / 313.8	318.2 / 312.6
K^2–C^2	298.0 / 298.6	295.8 / 293.5
C^1–C^2	140	143.8
C^2–C^3	144	142.3
C^3–C^4	138	143.8

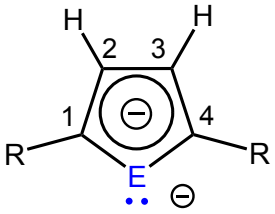
Computational Details

All quantum chemical calculations were carried out using the Gaussian09 package.[6] The molecular structure optimizations were performed using the M06-2X functional[7] along with the def2-tzvp basis set for all elements. [8] Every stationary point was identified by a subsequent frequency calculation as minimum (Number of imaginary frequencies (NIMAG): 0). The SCF energies (E(SCF)) are given in Table S4 for all optimized molecular structures obtained with this method. NMR chemical shift computations were performed using the GIAO method as implemented in Gaussian 09 and the M06-L functional along with the 6-311(2d,p) basis set for molecular structures obtained at the M06-2X/def2-tzvp level of theory. [9,10] Nucleus Independent Chemical Shifts (NICS) and NICS(zz) were calculated in order to evaluate the aromaticity of silole (**10**) and germole dianions (**11**). Tables S5, S6 collect these results and allow a comparison with typical aromatic compounds and anions such as cyclopentadienyl (Cp^-) and benzene (C_6H_6). NICS values were calculated according to the general formula NICS(zz)(r) = σ(zz) × (-1) (σ(zz) eigen value of the z-component of the chemical shielding tensor of the ghost atom).[11]

Table S4. Calculated absolute energies, E(SCF), and free enthalpies at 298 K, G^{298}, for compounds of interest.

Compound	Method/basis set	E(SCF) [a.u.]	NIMAG ZPVE [kJ mol^{-1}]	G^{298} [a.u.]
3a	M06-2X/def2-tzvp	-1723.60470	0, 1122	-1723.23783
3a [a]		-1723.80904	0, 1128	-1723.43737
K_2[3a] [b]		-2923.56481	0, 1136	-2923.19756
K_2[3a] [a][b]		-2923.60951	0, 1137	-2923.24012
10a		-1025.54547	0, 240	-1025.48993
10b		-522.72629	0, 303	-522.64215
10c		-444.10312	0, 160	-444.06897
11a		-2813.08145	0, 237	-2813.02798
11b		-2310.26134	0, 301	-2310.17931
11c		-2231.65330	0, 157	-2231.62138
12a		-1026.81694	0, 298	-1026.73915
12c		-445.45515	0, 217	-445.39984
13a		-2814.33667	0, 295	-2814.26005
13c		-2232.97366	0, 212	-2232.92111
Cp^-		-193.50697	0, 208	-193.45423
C_6H_6		-232.22469	0, 265	-232.15116
[a] calculated in THF solution [b] η^5, η^5-coordination of potassium ions to silole ring.				

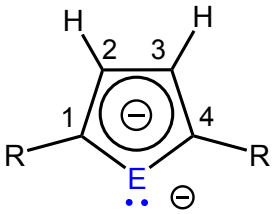
Table S5. NICS(total) values of model heterodianions **10** and **11,** cyclopentadienyl (Cp^-) and benzene (C_6H_6) (calculated at the M06-2X/def2-tzvp//M06-2X/def2-tzvp level of theory) at several distances d from the ring center.



10: E = Si;**11**: E = Ge

d (pm)	**10a** E = Si, R = SiH_3	**10b** E = Si, R = CH_3	**10c** E = Si, R = H	**11a** E = Ge, R = SiH_3	**11b** E = Ge, R = CH_3	**11c** E = Ge, R = H	Cp^-	C_6H_6
30	-2.2	-2.0	-2.2	-2.3	-2.1	-2.7	-1.9	-2.2
20	-4.9	-4.2	-5.1	-5.3	-4.6	-4.6	-4.7	-5.2
10	-8.1	-7.2	-9.7	-8.6	-7.8	-7.8	-10.5	-10.2
0	-7.0	-8.3	-11.5	-7.6	-9.1	-9.5	-13.2	-7.4
-10	-8.1	-7.2	-9.7	-8.6	-7.8	-7.8	-10.5	-10.2
-20	-4.9	-4.2	-5.1	-5.3	-4.6	-4.6	-4.7	-5.2
-30	-2.2	-2.0	-2.2	-2.3	-2.1	-2.7	-1.9	-2.2

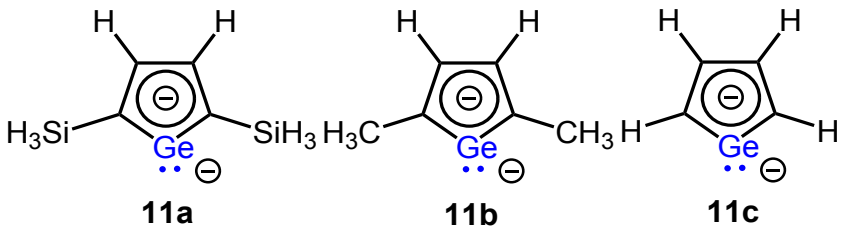
Table S6. NICS(zz) values of model heterodianions **10** and **11**, cyclopentadienyl (Cp^-) and benzene (C_6H_6) (calculated at the M06-2X/def2-tzvp//M06-2X/def2-tzvp level of theory) at several distances d from the ring center.



10: E = Si;**11**: E = Ge

d [pm]	**10a** E = Si, R = SiH_3	**10b** E = Si, R = CH_3	**10c** E = Si, R = H	**11a** E = Ge, R = SiH_3	**11b** E = Ge, R = CH_3	**11c** E = Ge, R = H	Cp^-	C_6H_6
30	-8.3	-7.9	-9.1	-9.0	-8.5	-9.8	-8.1	-8.3
20	-17.0	-16.2	-19.3	-18.0	-17.0	-19.9	-18.6	-18.1
10	-25.4	-23.9	-31.9	-25.7	-23.7	-31.1	-35.5	-31.0
0	-8.6	-6.3	-18.5	-7.3	-4.9	-18.0	-17.7	-16.6
-10	-25.4	-23.9	-31.9	-25.7	-23.7	-31.1	-35.5	-31.0
-20	-17.0	-16.2	-19.3	-18.0	-17.0	-19.9	-18.6	-18.1
-30	-8.3	-7.9	-9.1	-9.0	-8.5	-9.8	-8.1	-8.3

Table S7. Calculated energies of frontier orbitals for compounds **11a-11c**.



	11a	**11b**	**11c**
E(LP(Ge)) (eV)	1.86	3.08	3.05
E(π(4)) (eV)	8.83	10.30	—

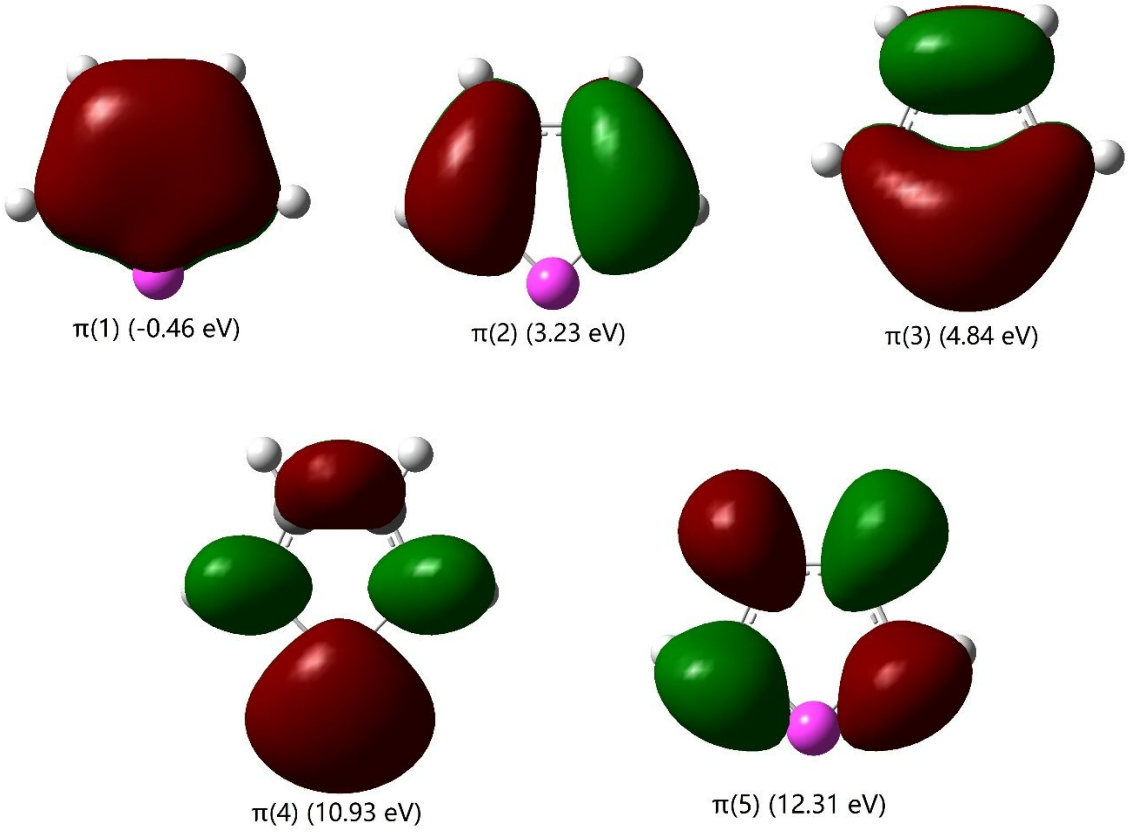


Figure S9. Frontier orbitals of the π system of the parent silole dianion **10c** (isodensity value 0.03).

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