New Supramolecular Assemblies in Heterobimetallic Chemistry: Synthesis of a Homologous Series of Unsolvated Alkali-metal Zincates

David R. Armstrong, Helena S. Emerson, Alberto Hernán-Gómez,* Alan R. Kennedy and Eva Hevia*

WestCHEM, Department of Pure and Applied Chemistry,University of Strathclyde, Glasgow, UK, G11XL
eva.hevia@strath.ac.uk

EXPERIMENTAL SECTION

General Conditions

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. $Zn(CH_2SiMe_3)_2$, $NaCH_2SiMe_3$,[1] and KCH2SiMe$_3$[2] were synthesized as described in the literature. $LiCH_2SiMe_3$ was purchased from Sigma Aldrich Chemicals and used as received. TMEDA was distilled over CaH_2 prior to use All NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H, 155.50 MHz for ^{7}Li, and 100.62 MHz for ^{13}C. All ^{13}C NMR spectra were proton decoupled. Crystallographic data were collected at 123(2) K on an Oxford Diffraction diffractometer[3] with Mo Kα(λ= 0.71073 Å) and Cu Kα(λ= 1.5413 Å) radiation.

Crystallographic data were measured at 123(2) K on Oxford Diffraction diffractometers[3] with Mo Kα(λ= 0.71073 Å) or Cu Kα(λ= 1.5418 Å) radiation. Structures were refined to convergence on F^2 and against all independent reflections by the full-matrix least squares method using the SHELXL-97 program.[4] Selected crystallographic and refinement details are given in Table S1 (see the Supporting Information for details).

Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer; due to the extreme air-sensitivity of compounds **4** and **5** satisfactory analyses could not be obtained.

Synthesis of [LiZn(CH$_2$SiMe$_3$)$_3$] (1). To a solution of $LiCH_2SiMe_3$ (1 mL, 1M in pentane) in hexane (10 mL) was added $Zn(CH_2SiMe_3)_2$ (2.8 mL, 0.36 M in hexane). The resulting colourless solution was stirred for one hour at room temperature affording a white suspension. Hexane was removed under vacuum to yield a white solid which washed with hexane (3 mL) at -30°C (0.28 g, 84%). ^{1}H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) 0.19 (s, 27 H, Si(C*H*$_3$)$_3$), -1.11 (broad s, 6H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 3.4 (Si(*C*H$_3$)$_3$), 1.6 (broad, Si*C*H$_2$). ^{7}Li NMR (155.47 MHz, 298 K, C_6D_6): δ (ppm) -0.21 (broad, *Li*CH$_2$). ^{1}H NMR (400.03 MHz, 298 K, [D$_8$]THF): δ (ppm) -0.14 (s, 27 H, Si(C*H*$_3$)$_3$), -1.14 (broad s, 6H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, [D$_8$]THF): δ (ppm) 4.6 (Si(*C*H$_3$)$_3$), 2.7 (Si*C*H$_2$). ^{7}Li NMR (155.47 MHz, 298 K, [D$_8$]THF): δ (ppm) 1.38 (*Li*CH$_2$) Anal Calcd for $C_{12}H_{33}LiSi_3Zn$: C, 43.16; H, 9.96. Found: C, 43.13, H, 10.18.

Synthesis of [NaZn(CH$_2$SiMe$_3$)$_3$] (2). To a suspension of $NaCH_2SiMe_3$ (0.11 g, 1mmol) in hexane (10 mL) was added $Zn(CH_2SiMe_3)_2$ (2.8 mL, 0.36 M in hexane). The resulting white suspension was stirred for one hour. Compound **1** was isolated as a white solid by evaporation of the solvent *in vacuo* and washing with hexane (3 mL) at -30°C (0.24g, 70%). ^{1}H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) 0.28 (s, 27 H, Si(C*H*$_3$)$_3$), -1.14 (s, 6H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 3.9 (Si(*C*H$_3$)$_3$), 2.9 (Si*C*H$_2$). ^{1}H NMR (400.03 MHz, 298 K, [D$_8$]THF): δ (ppm) -0.14 (s, 27 H, Si(C*H*$_3$)$_3$), -1.14 (broad s, 6H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K,

[D_8]THF): δ (ppm) 4.6 (Si(*C*H_3)$_3$), 2.6 (Si*C*H_2).Anal Calcd for $C_{12}H_{33}NaSi_3Zn$: C, 41.18; H, 9.50. Found: C, 40.64 , H, 9.23.

Synthesis of [KZn(CH_2SiMe_3)$_3$] (3). Following the same procedure above for the synthesis of **1** and **2**, to a suspension of KCH_2SiMe_3 (0.11 g, 1mmol) in hexane (10 mL) was added $Zn(CH_2SiMe_3)_2$ (2.8 mL, 0.36 M in hexane), and the resulting thin suspension was stirred for one hour. Afterwards solvent was removed under vacuum affording a white solid which was washed with hexane (2 x 5 mL) at -30°C (0.16 g, 43%). ^{1}H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) 0.39 (s, 18 H, Si(C*H*$_3$)$_3$), 0.28 (s, 9 H, Si(C*H*$_3$)$_3$) -1.16 (s, 4H, SiC*H*$_2$), -1.27 (s, 2H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 4.4 (Si(*C*H_3)$_3$), 5.5, 4.1 (Si*C*H_2). ^{1}H NMR (400.03 MHz, 298 K, [D_8]THF): δ (ppm) -0.13 (s, 27 H, Si(C*H*$_3$)$_3$), -1.13 (broad s, 6H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, [D_8]THF): δ (ppm) 4.6 (Si(*C*H_3)$_3$), 2.7 (Si*C*H_2). Anal Calcd for $C_{12}H_{33}KSi_3Zn$: C, 39.37; H, 9.08. Found: C, 38.61, H, 8.68.

Synthesis of [(PMDETA)LiZn(CH_2SiMe_3)$_3$] (4). To a solution of $LiCH_2SiMe_3$ (1 mL, 1M in pentane) in hexane (20 mL) was added $Zn(CH_2SiMe_3)_2$ (2.8 mL, 0.36 M in hexane). After one hour stirring at room temperature all the volatiles were removed under vacuum and to the resulting white solid was added hexane (20 mL) and PMDETA (0.14 mL, 1 mmol). The suspension was stirred at room temperature for another hour and after gently heating the colorless solution was transferred to the freezer at -30°C. Crop of crystals of compound **4** were deposited overnight (0.45 g, 88%). ^{1}H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) 1.84 (s, 12H, N(C*H*$_3$)$_2$, PMDETA), 1.81 (s, 3H, N(C*H*$_3$), PMDETA), 1.64 – 1.48 (8H, m, NC*H*$_2$, PMDETA), 0.44 (s, 27 H, Si(C*H*$_3$)$_3$), -0.92 (s, 6H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 56.8, 53.0 (N*C*H$_2$, PMDETA), 45.7 (N(*C*H_3)$_2$, PMDETA), 45.3 (N(*C*H_3), PMDETA), 4.5 (Si(*C*H_3)$_3$), 2.4 (Si*C*H_2). ^{7}Li NMR (155.47 MHz, 298 K, C_6D_6): δ (ppm) -0.07 (*Li*CH_2).

Synthesis of [(TMEDA)$_2$NaZn(CH_2SiMe_3)$_3$] (5). To a suspension of $NaCH_2SiMe_3$ (0.11 g, 1mmol) in hexane (15 mL) was added $Zn(CH_2SiMe_3)_2$ (2.8 mL, 0.36 M in hexane). The resulting white suspension was stirred for one hour and all the volatiles were removed under vacuum. Then TMEDA (0.3 mL, 2 mmol) was introduced and the mixture was stirred for another hour. Compound **5** was isolated as a white solid by evaporation of the solvent *in vacuo* and washing with hexane (3 mL) at -30°C (0.26g, 45%). ^{1}H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) 1.86 (s, 24H, N(C*H*$_3$)$_2$, TMEDA), 1.81 (s, 8H, NC*H*$_2$, TMEDA), 0.39 (s, 27 H, Si(C*H*$_3$)$_3$), -0.85 (s, 4H, SiC*H*$_2$), -1.04 (s, 2H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 57.1 (N*C*H$_2$, TMEDA), 46.1 (N(*C*H_3)$_2$, TMEDA), 4.3 (Si(*C*H_3)$_3$), 2.7 (Si*C*H_2), -5.4 (Si*C*H_2).

Table S1. Selected crystallographic and refinement parameters.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{12}H_{33}Li1Si_3Zn1$	$C_{12}H_{33}Na_1Si_3Zn_1$	$C_{12}H_{33}K_1Si_3Zn_1$	$C_{21}H_{56}Li_1N_3Si_3Zn_1$	$C_{24}H_{65}N_4Na_1Si_3Zn_1$
Molecular Weight	333.96	350.01	366.12	507.27	582.45
Temperature (K)	123(2)	123(2)	123(2)	123(2)	123(2)
Wavelenght (Å)	1.54180	0.71073	0.71073	0.71073	1.54180
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/n	P 2_1/c	P 2_1/c	P 2_1/c
a (Å)	6.6086(1)	9.9657(2)	11.0083(11)	16.1037(4)	16.9890(6)
b (Å)	19.8732(4)	24.5335(4)	18.6159(10)	10.6433(2)	11.2669(3)
c (Å)	15.9308(4)	16.5399(3)	11.2426(10)	18.4366(4)	19.2447(6)
β (°)	99.070(2)	90.708(2)	115.011(11)	91.390(2)	90.577(3)
Cell volume (Å^3)	2066.10(7)	4043.59(13)	2087.9(3)	3159.04(12)	3683.5(2)
Z	4	8	4	4	4
ρcalc (g.cm-3)	1.074	1.15	1.165	1.067	1.05
μ (mm^{-1})	3.157	1.398	1.532	0.902	2.088
F (000)	720.0	1504	784	1112	1280
2θ max(°)	146.38	60.36	59.84	58.0	146.28
Index ranges	-5≤*h*≤8 -24≤*k*≤24 -19≤*l*≤19	-13≤*h*≤13 -34≤*k*≤32 -21≤*l*≤22	-15≤*h*≤14 -25≤*k*≤24 -15≤*l*≤15	-21≤*h*≤21 -14≤*k*≤13 -25≤*l*≤24	-21≤*h*≤20 -13≤*k*≤9 -23≤*l*≤21
Reflections collected	19027	43450	21930	31044	19805
Reflections unique	4119	11018	5515	8256	7314
Reflections obs.	3464	8753	3182	6171	5267
R_{int}	0.0369	0.0403	0.0664	0.0449	0.0489
No. Parameters	187	406	196	300	368
Goodnes-of-fit-on F^2 (*GOF*)	1.02	1.076	0.998	1.033	1.02
Final *R* indices [I>2σ(I)]	0.0306	0.0378	0.0512	0.0402	0.0429
R indices (all data)	0.0781	0.0803	0.1287	0.0849	0.1066
Largest diff. peak and hole (e Å^{-3})	0.380 and -0.297	0.682 and -0.362	1.244 and -0.363	0.424 and -0.327	0.304 and -0.232

Table S2. Selected bond distances (Å) and angles (deg) for alkali-metal zincate **1**

	M = Li (**1**)
Zn1-C1	2.056(2)
Zn1-C5	2.051(2)
Zn1-C9’	2.021(2)
Li-C1	2.257(4)
Li1-C5	2.226(4)
Li1-C9	2.241(4)
Li1-C11	2.515(4)

	M = Li (**1**)
C1-Zn1-C5	112.7(1)
C1-Zn1-C9	124.1(1)
C5-Zn1-C9	123.2(1)
C1-Li1-C5	99.4(1)
C1-Li1-C9	125.8(2)
C5-Li1-C9	126.7(2)
C11-Li1-C1	108.6(1)
C11-Li1-C5	111.9(1)
C11-Li1-C9	81.5(1)

Table S3. Selected bond distances (Å) and angles (deg) for alkali-metal zincate **2**

	M = Na (**2**)[a]
Zn1-C1	2.051(2)
Zn1-C5	2.056(2)
Zn1-C9	2.074(2)
Zn2-C17	2.065(2)
Zn2-C21	2.052(2)
Zn2-C13	2.047(2)
Na1-C1	2.700(2)
Na1-C13’	2.684(2)
Na1-C9	2.670(2)
Na1-C11’	3.215(2)
Na1-C14’	2.975(3)
Na1-C20’	2.984(3)
Na2-C5	2.697(2)
Na2-C17	2.655(2)
Na2-C21	2.658(2)
Na2-C7	2.816(3)
Na2-C4’	3.216(3)

	M = Na (**2**)
C1-Zn1-C5	128.57(9)
C1-Zn1-C9	122.97(8)
C5-Zn1-C9	108.46(9)
C13-Zn2-C17	121.28(9)
C13-Zn2-C21	119.60(9)
C17-Zn2-C21	119.12(9)
C1-Na1-C9	84.91(7)
C13’-Na1-C14’	66.58(7)
C1-Na1-C13’	108.14(7)
C9-Na1-C14’	98.76(7)
C11-Na1-C20’	164.17(6)
C5-Na2-C7	69.67(7)
C17-Na2-C21	83.85(7)
C5-Na2-C21	102.19(8)
C7-Na2-C17	98.44(7)
C4’-Na2-C5	102.09(7)
C4’-Na2-C7	89.04(8)
C4’-Na2-C21	97.26(8)
C4’-Na2-C17	123.22(7)

Table S4. Selected bond distances (Å) and angles (deg) for alkali-metal zincate **3**.

	M = K (**3**)
Zn1-C1	2.044(3)
Zn1-C5	2.042(4)
Zn1-C9	2.057(3)
K1-C1	3.119(3)
K1-C5’	3.141(4)
K1-C9’	3.093(3)
K1-C3	3.331(4)
K1-C11’	3.209(5)
K1-C12’	3.530(4)
K1-C2’	3.417(5)

	M = K (**3**)
C1-Zn1-C5	121.3(1)
C1-Zn1-C9	123.9(1)
C5-Zn1-C9	114.4(1)
C2’-K1-C12’	172.8(1)
C1-K1-C3	58.00(9)
C5’-K1-C9’	93.80(9)
C3-K1-C9’	123.28(9)
C1-K1-C5’	84.88(9)
C11’-K1-C12’	74.5(1)
C11’-K1-C3	76.0(1)
C11’-K1-C9’	60.4(1)

Table S5. Selected bond distances (Å) and angles (deg) for alkali-metal zincate **4**

	M = Li (**4**)
Zn1-C1	2.041(2)
Zn1-C5	2.061(2)
Zn1-C9'	2.049(2)
Li1-C5	2.388(4)
Li1-N1	2.133(3)
Li1-N2	2.196(3)
Li1-N3	2.166(4)

	M = Li (**4**)
C1-Zn1-C5	123.01(8)
C1-Zn1-C9	120.61(8)
C5-Zn1-C9	116.37(8)
N1-Li1-C5	122.1(2)
N1-Li1-N2	83.6(1)
N1-Li1-N3	119.3(1)
N2-Li1-C5	101.4(1)
N2-Li1-N3	85.3(1)
N3-Li1-C5	118.6(1)

Table S6. Selected bond distances (Å) and angles (deg) for alkali-metal zincate **5**

	M = Na (**5**)
Zn1-C1	2.053(3)
Zn1-C5	2.035(3)
Zn1-C9	2.055(3)
Na1-C1	3.022(3)
Na1-C9	3.029(3)
Na1-N1	2.565(3)
Na1-N2	2.519(2)
Na1-N3	2.64(1)
Na1-N4	2.62(1)

	M = Na (**5**)
C1-Zn1-C5	122.1(1)
C1-Zn1-C9	117.2(1)
C5-Zn1-C9	120.7(1)
C1-Na1-C9	70.82(8)
C1-Na1-N1	90.79(8)
C9-Na1-N4	91.6(3)
N1-Na1-N4	111.5(3)
N2-Na1-N3	172.0(2)

NMR Spectra

Table S7. Chemical shifts (ppm) in the ^{1}H and ^{13}C NMR spectra of the alkali-metal zincates **1**–**5** in C_6D_6.[a]

Compound	$\delta^{1}H$ (CH_2)	$\delta^{1}H$ (CH_3)	$\delta^{13}C$ (CH_2)	$\delta^{13}C$ (CH_3)
$Li(CH_2SiMe_3)$	-2.03	0.16	-4.4	3.3
$Li(CH_2SiMe_3)$[b]	-2.44	0.15		
$Na(CH_2SiMe_3)$ [b]	-2.60	0.18		
$Zn(CH_2SiMe_3)_2$	-0.63	0.05	3.2	3.1
$[LiZn(CH_2SiMe_3)_3]$ (**1**)	-1.11 (-1.14)	0.19 (-0.14)	1.6 (2.7)	3.4 (4.6)
$[NaZn(CH_2SiMe_3)_3]$ (**2**)	-1.14 (-1.14)	0.28 (-0.14)	2.9 (2.6)	3.9 (4.6)
$[KZn(CH_2SiMe_3)_3]$ (**3**)	-1.16, -1.27 (-1.13)	0.39, 0.28 (-0.13)	5.5, 4.1 (2.7)	4.4 (4.6)
$[(PMDETA)LiZn(CH_2SiMe_3)_3]$ (**4**)	-0.92	0.44	2.4	4.5
$[(TMEDA)_2NaZn(CH_2SiMe_3)_3]$ (**5**)	-0.84	0.41	2.7	4.3

[a] Chemical shifts (ppm) of the alkali-metal zincates **1**–**3** in $[D_8]$-THF denoted in parenthesis. [b] Low solubility and poor stability of $M(CH_2SiMe_3)$ (M = Na, K) precluded the acquisition of meaningful ^{13}C NMR spectra

$[LiZn(CH_2SiMe_3)_3]$ (1)

It is noticeable that the signal assigned to the methylene (Zn-CH_2) fragments in the $^{13}C\{^{1}H\}$ NMR spectrum is broad as well as the peak observed in the ^{7}Li NMR spectrum. According to the retention of the contacted ion-pair solid state structure in solution, the broadening of the signals is possibly due to a ^{7}Li-^{13}C coupling.[5] Indeed, the solvent separated version of **1,** characterized by NMR spectroscopy in $[D_8]$THF solution, shows sharp signals.

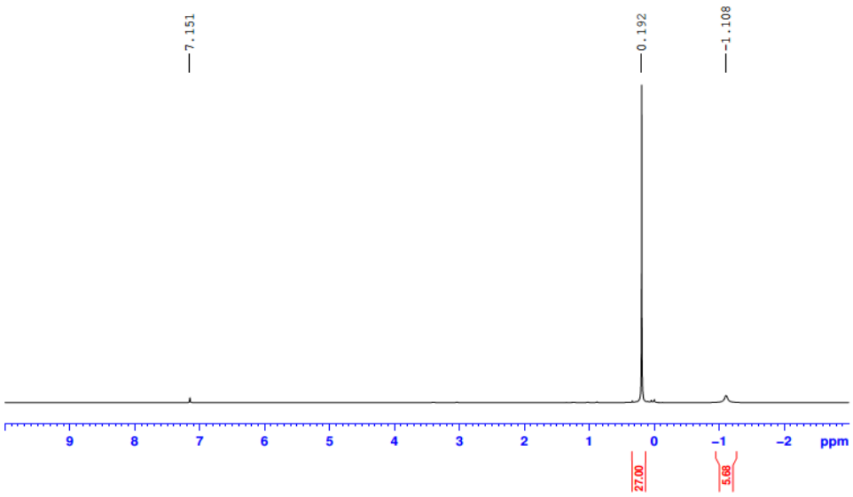


Figure S1. ^{1}H NMR of **1** in C_6D_6 solution at 298K

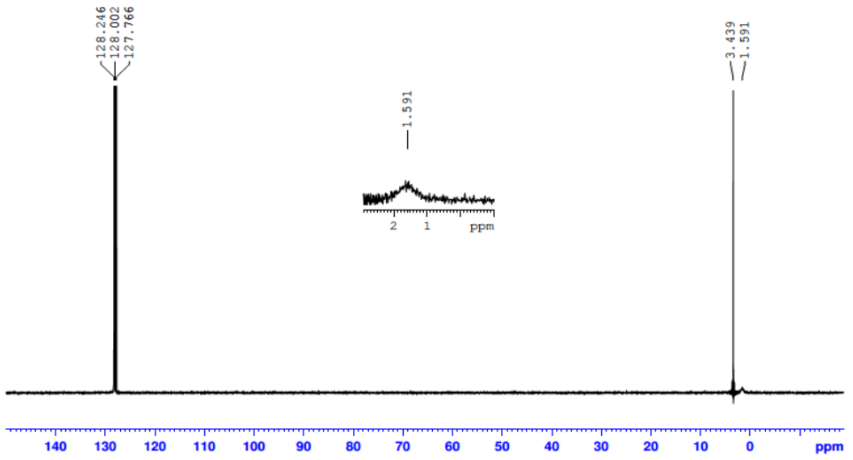


Figure S2. $^{13}C\{^{1}H\}$ NMR of **1** in C_6D_6 solution at 298K

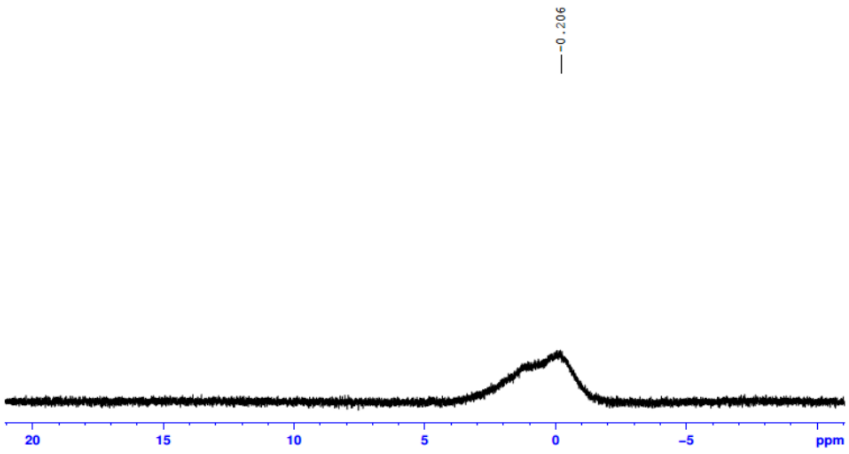


Figure S3. ^{7}Li NMR of **1** in C_6D_6 solution at 298K

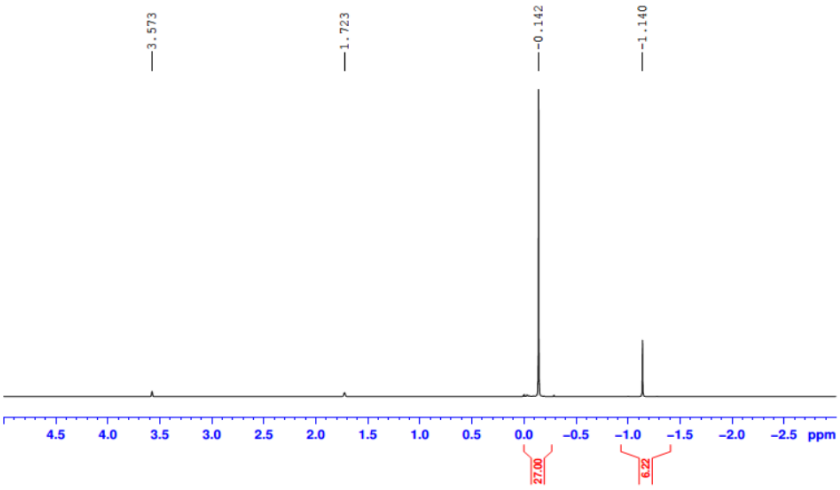


Figure S4. ^{1}H NMR of **1** in [D_8]THF solution at 298K

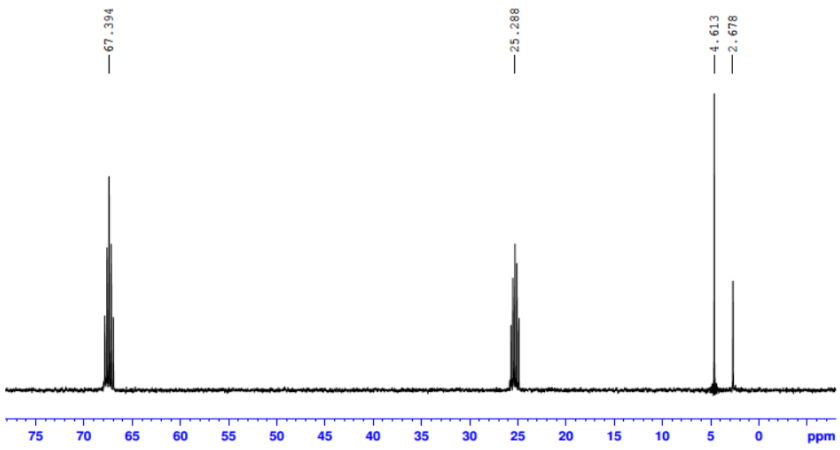


Figure S5. ^{13}C{^{1}H} NMR of **1** in [D_8]THF solution at 298K

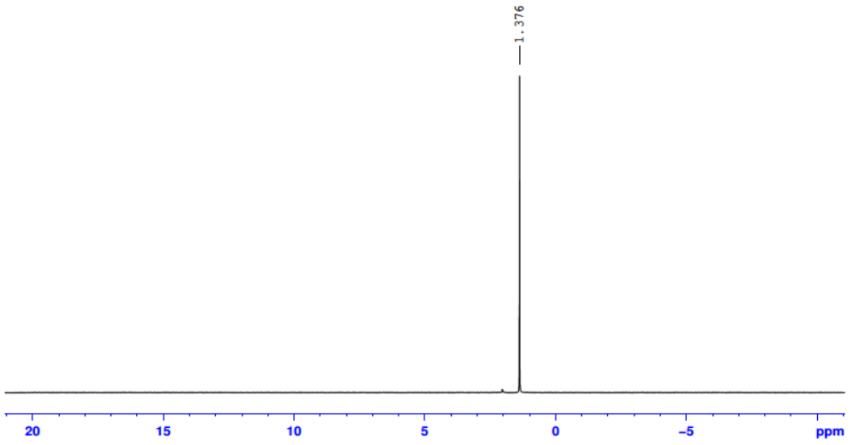


Figure S6. ^{7}Li NMR of **1** in [D_8]THF solution at 298K

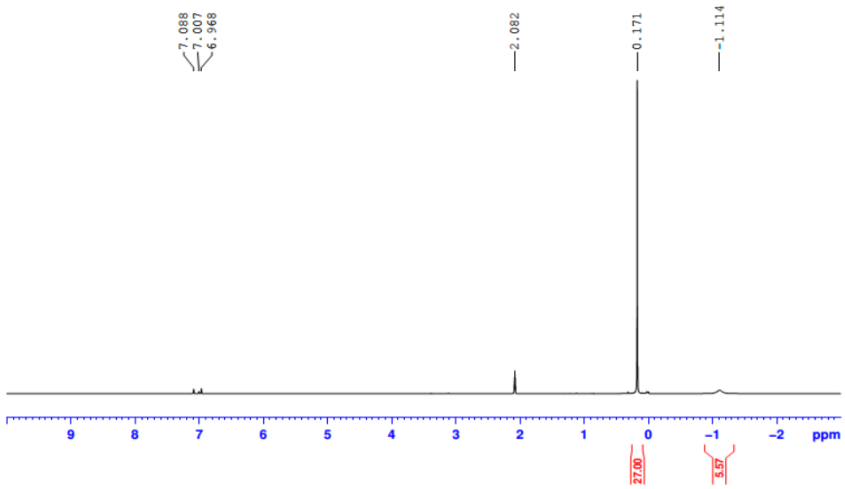


Figure S7. ^{1}H NMR of **1** in C_7D_7 solution at 298K

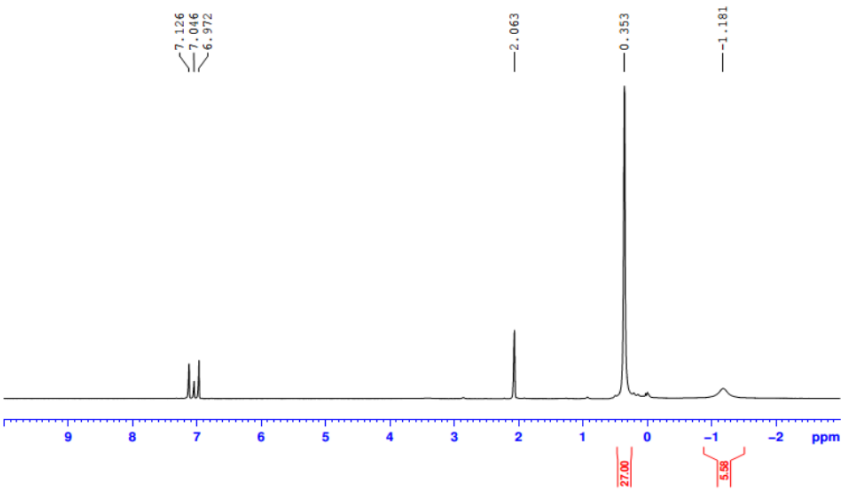


Figure S8. ^{1}H NMR of **1** in C_7D_7 solution at 213K

[NaZn(CH$_2$SiMe$_3$)$_3$] (2)

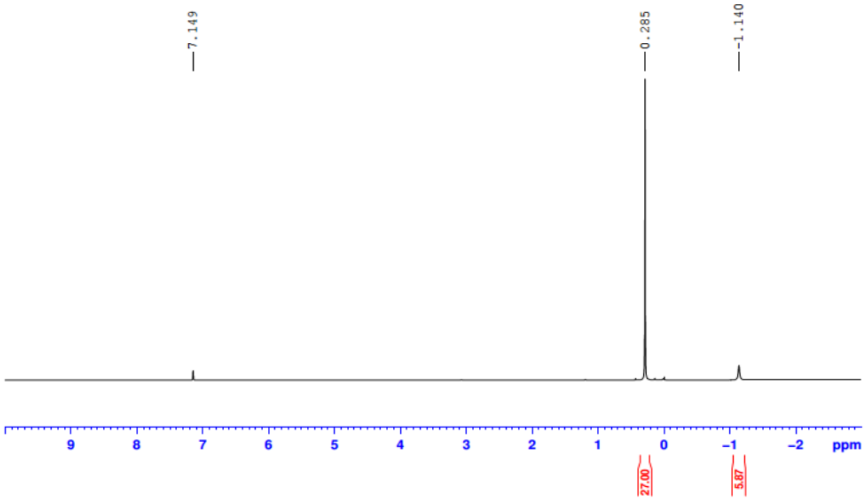


Figure S9. ^{1}H NMR of **2** in C_6D_6 solution at 298K

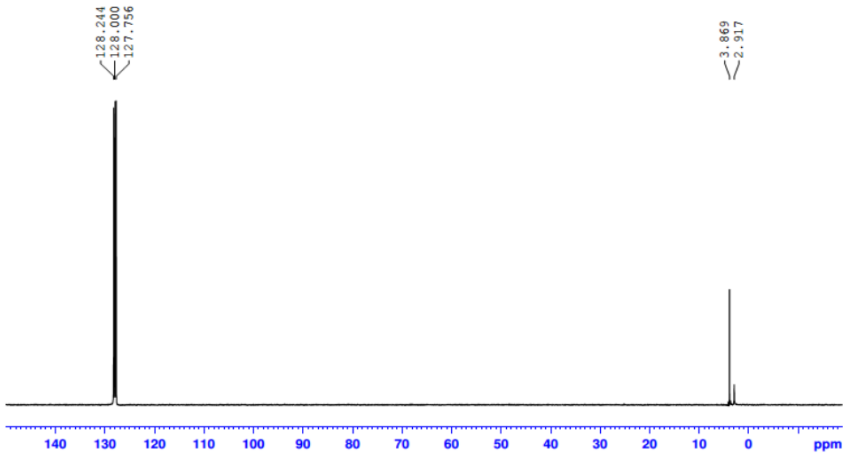


Figure S10. $^{13}C\{^1H\}$ NMR of **2** in C_6D_6 solution at 298K

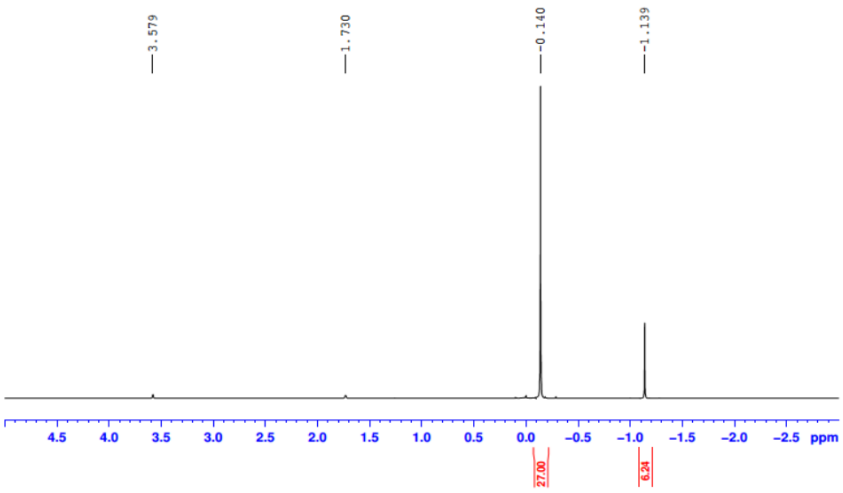


Figure S11. ^{1}H NMR of **2** in [D_8]THF solution at 298K

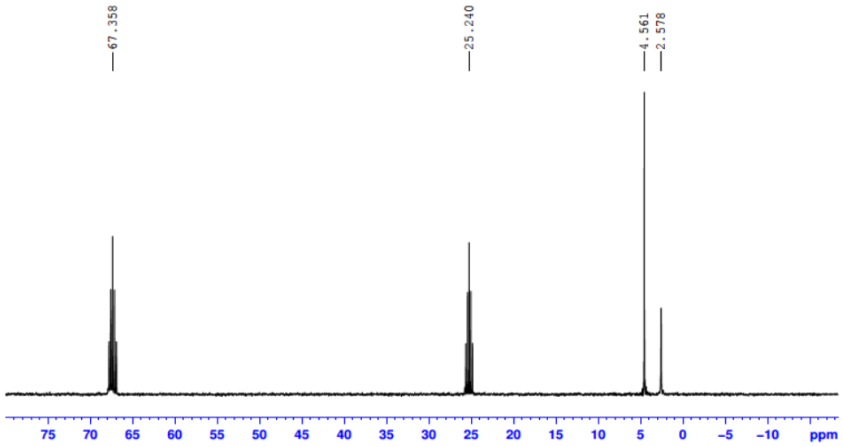


Figure S12. $^{13}C\{^{1}H\}$ NMR of **2** in [D_8]THF solution at 298K

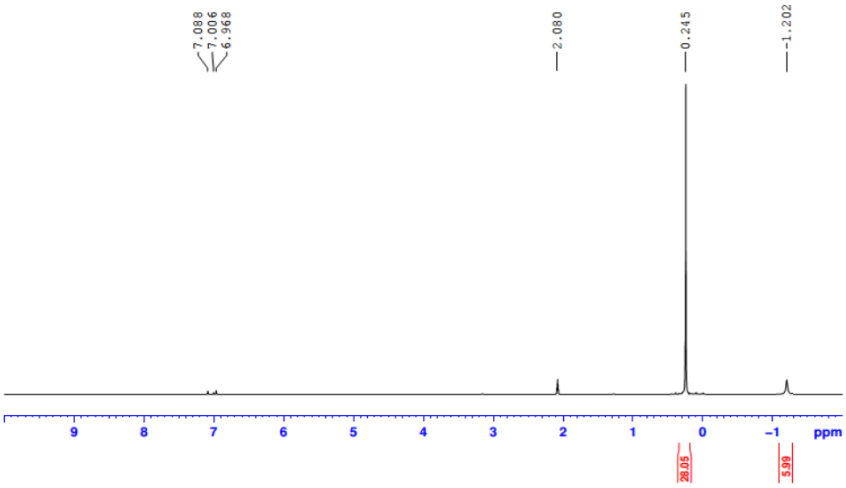


Figure S13. ^{1}H NMR of **2** in C_7D_7 solution at 298K

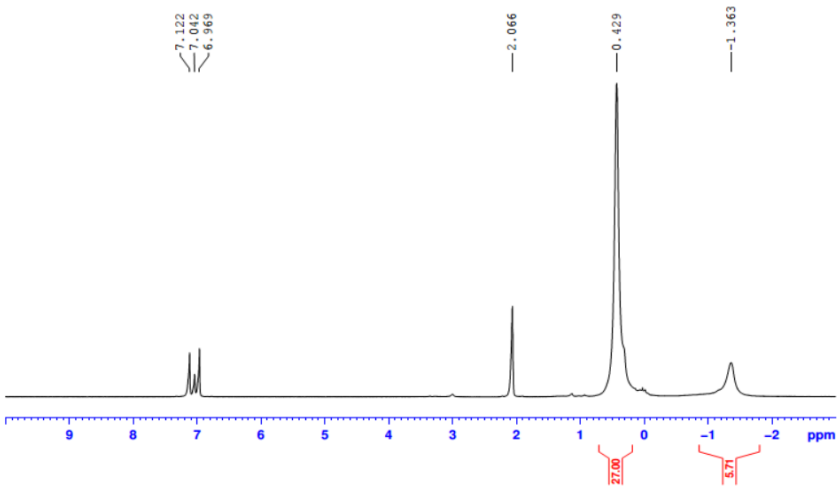


Figure S14. ^{1}H NMR of **2** in C_7D_7 solution at 213K

[KZn(CH$_2$SiMe$_3$)$_3$] (3)

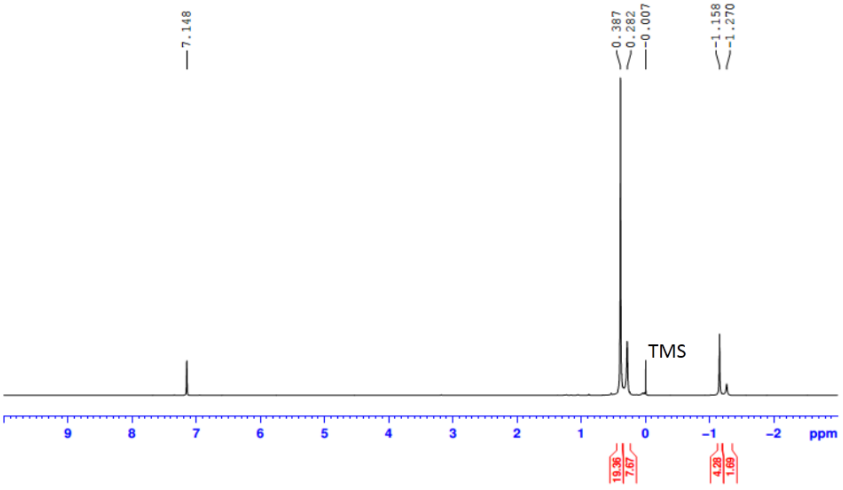


Figure S15. ^{1}H NMR of **3** in C_6D_6 solution at 298K

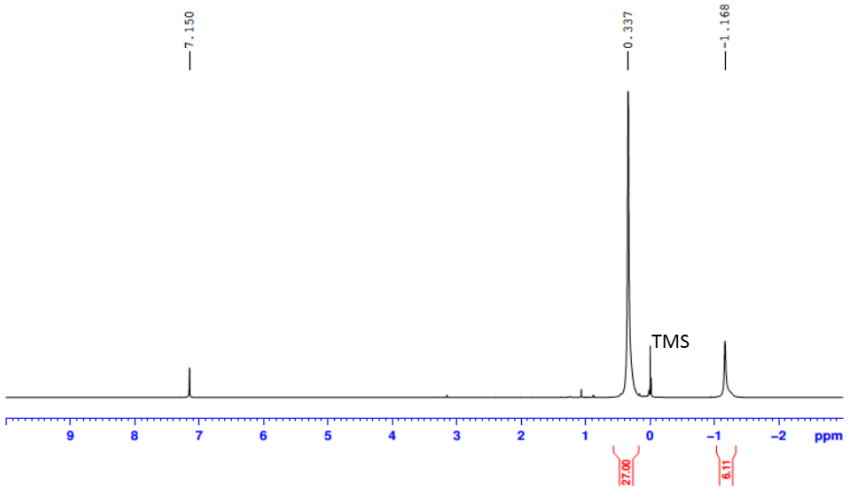


Figure S16. ^{1}H NMR of **2** in C_6D_6 solution at 313K

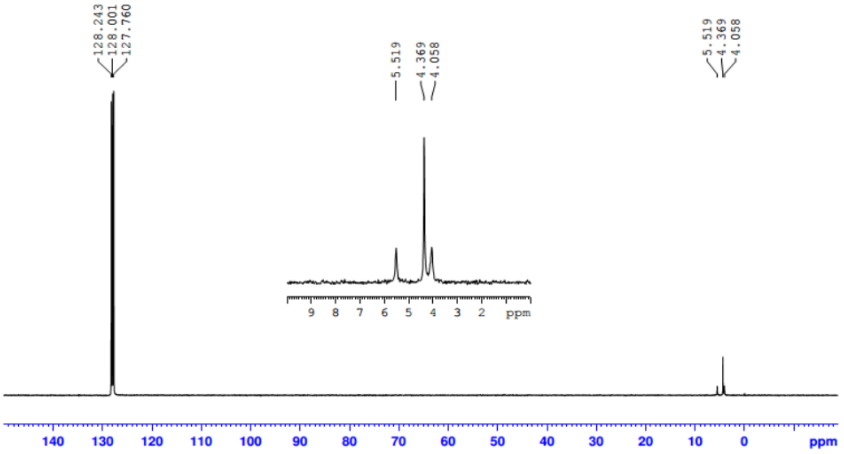


Figure S17. $^{13}C\{^{1}H\}$ NMR of **3** in C_6D_6 solution at 298K

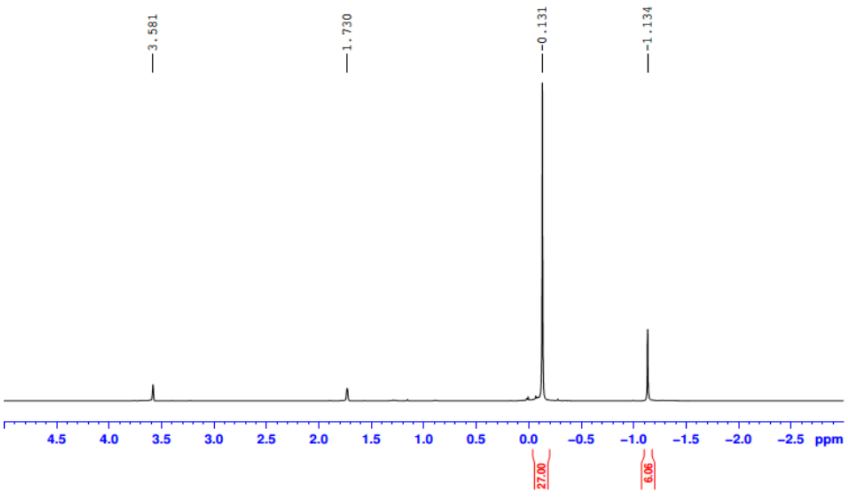


Figure S18. ^{1}H NMR of **3** in $[D_8]$THF solution at 298K

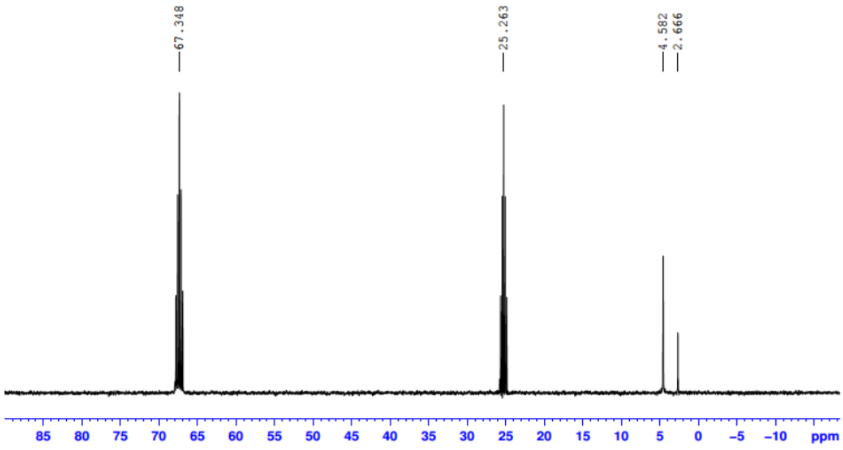


Figure S19. $^{13}C\{^{1}H\}$ NMR of **3** in $[D_8]$THF solution at 298K

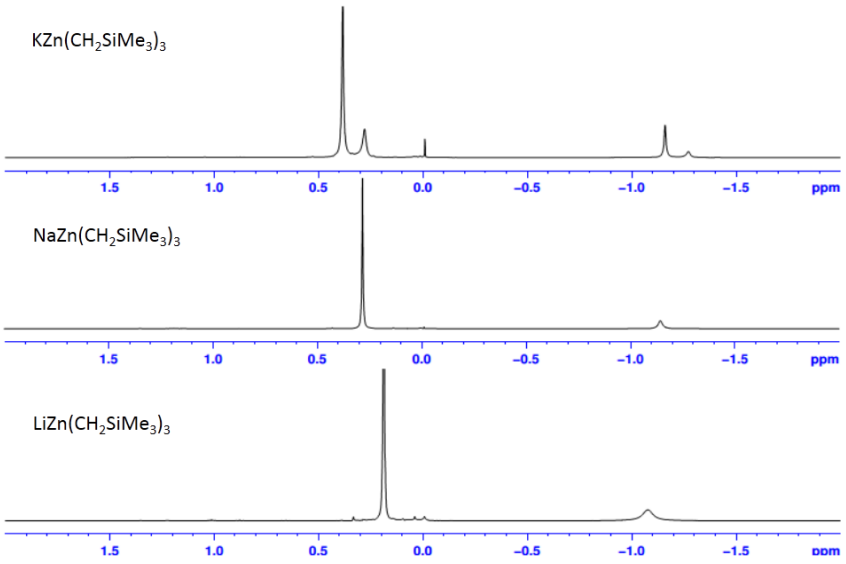


Figure S20. Comparison of ^{1}H NMR spectra for **1**-**3** in C_6D_6 solution at 298K

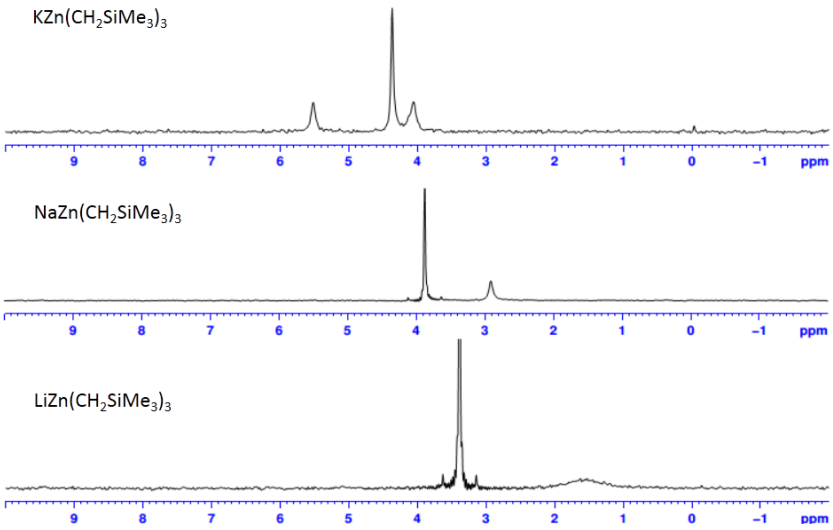


Figure S21. Comparison of ^{1}H NMR spectra for **1**-**3** in C_6D_6 solution at 298K

[(PMDETA)LiZn(CH$_2$SiMe$_3$)$_3$] (4).

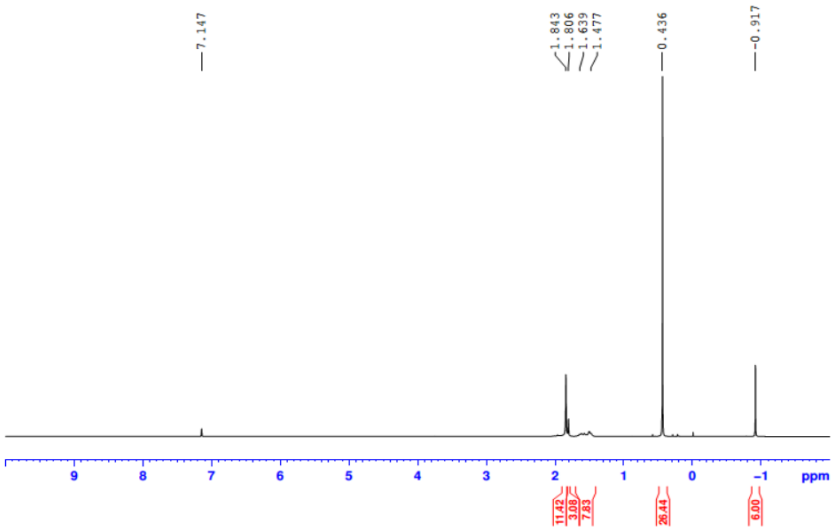


Figure S22. ^{1}H NMR of **4** in C_6D_6 solution at 298K

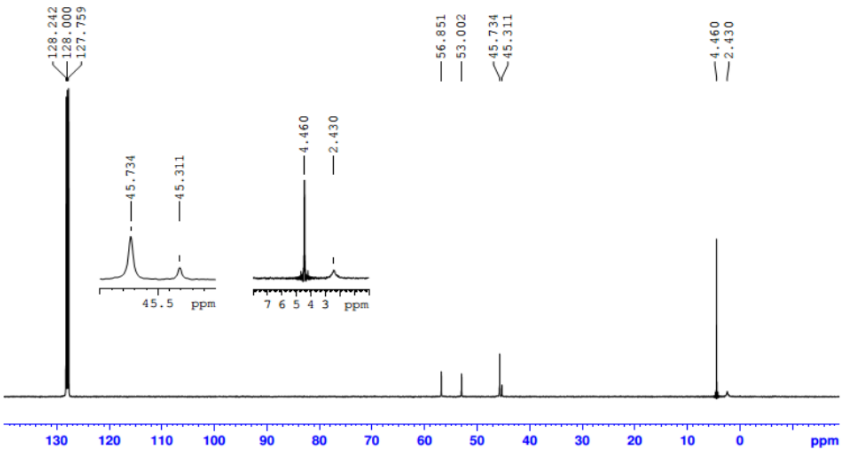


Figure S23. $^{13}C\{^{1}H\}$ NMR of **4** in C_6D_6 solution at 298K

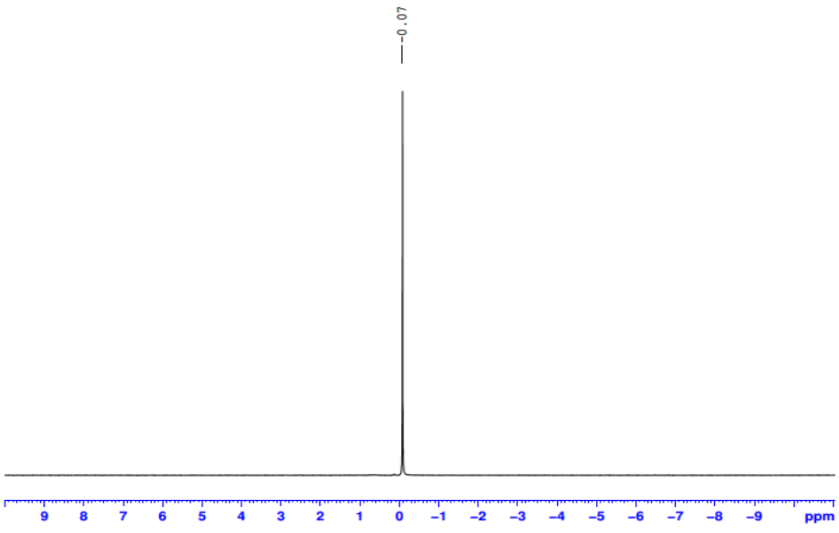


Figure S24. ^{7}Li NMR of **4** in $[D_8]THF$ solution at 298K

[(TMEDA)$_2$NaZn(CH$_2$SiMe$_3$)$_3$] (5).

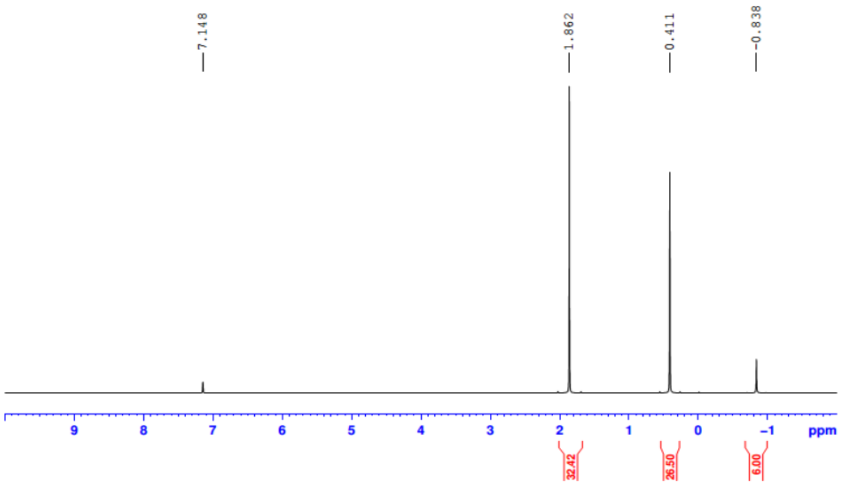


Figure S25. ^{1}H NMR of **5** in C_6D_6 solution at 298K

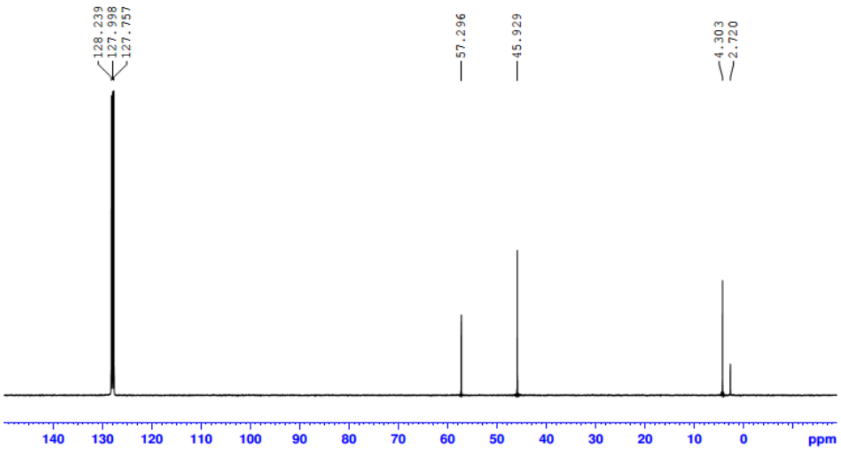


Figure S26. ^{13}C{^{1}H} NMR of **5** in C_6D_6 solution at 298K

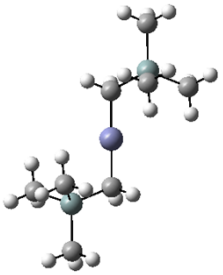
DFT calculations

Density Functional Theory calculations[6] were performed using the Gaussian computational package G03.[7] In this series of calculations the B3LYP density functionals[8] and the 6-31G(d) basis set[9] were used. For the Monomers and Dimers of MZn(CH$_2$SiMe$_3$)$_3$ a frequency analysis was performed after each geometry optimisation. The energy values quoted include the zero point energy contribution. For the Trimers of MZn(CH$_2$SiMe$_3$)$_3$, the energy value quoted is the total energy value only.

Geometry optimization for $Zn(CH_2SiMe_3)_2$

Zn-C	1.925 Å
C-Zn-C	178.1 °

E = -2676.024427 a.u.



Geometry optimization for $[LiCH_2SiMe_3]_6$ –C1 symmetry

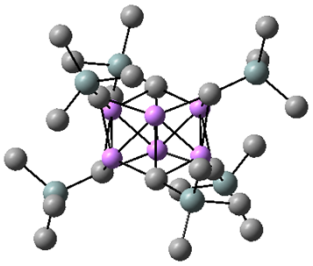
Each C of a CH_2 is bonded to 3 neighbouring Li atoms.The range of these bonds is:

2.174 – 2.183 Å

2.186 – 2.195 Å

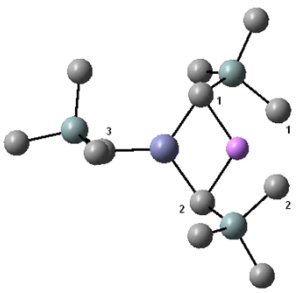
2.262 – 2.279 Å

E = -2735.988528 a.u.



Geometry optimization for $LiZn(CH_2SiMe_3)_2$

$Li-C_1$	2.093 Å
$Li-C_2$	2.090 Å
$Li...C_{Me1}$	2.407 Å
$Li...C_{Me2}$	2.374 Å
$Zn-C_1$	2.110 Å
$Zn-C_2$	2.126 Å
$Zn-C_3$	1.982 Å
C_1-Li-C_2	113.1 °
C_1-Zn-C_2	110.9 °
$Li-C_1-Zn$	68.1 °
$Li-C_2-Zn$	67.9 °
C_1-Zn-C_3	126.8 °
C_2-Zn-C_3	122.3 °



E = -3132.024283 a.u.

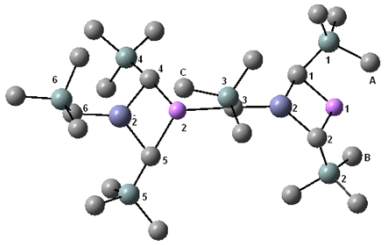
Geometry optimization for $[LiZn(CH_2SiMe_3)_2]_2$

Li_1-C_1	2.113 Å	Li_1-C_B	2.390 Å
Li_1-C_2	2.118 Å	C_1-Si_1	1.878 Å
Li_1-C_A	2.342 Å	C_2-Si_2	1.877 Å

C_3-Si_3	1.879 Å
Si_1-C_A	1.934 Å
Si_2-C_B	1.930 Å
Si_3-C_C	1.909 Å
Zn_1-C_1	2.103 Å
Zn_1-C_2	2.086 Å
Zn_1-C_3	2.013 Å
Li_2-C_3	2.309 Å
Li_2-C_4	2.147 Å
Li_2-C_5	2.168 Å
Li_2-C_C	2.720 Å
C_4-Si_4	1.880 Å
C_5-Si_5	1.881 Å
C_6-Si_6	1.870 Å
Zn_2-C_4	2.103 Å
Zn_2-C_5	2.105 Å
Zn_2-C_6	1.995 Å

C_1-Li_1-C_2	110.1 °
C_1-Zn_1-C_2	112.8 °
Li_1-C_1-Zn_1	67.9 °
Li_1-C_2-Zn_1	68.2 °
Zn_1-C_1-Si_1	125.5 °
Zn_1-C_2-Si_2	118.4 °
Zn_1-C_3-Si_3	111.3 °
Zn_1-C_3-Li_2	158.0 °
C_4-Li_2-C_5	103.6 °
C_4-Zn_2-C_5	107.4 °
Li_2-C_4-Zn_2	68.9 °
Li_2-C_5-Zn_2	68.4 °
Zn_2-C_4-Si_4	108.9 °
Zn_2-C_5-Si_5	107.9 °
Zn_2-C_6-Si_6	115.4 °

E = -3132.024283 a.u.



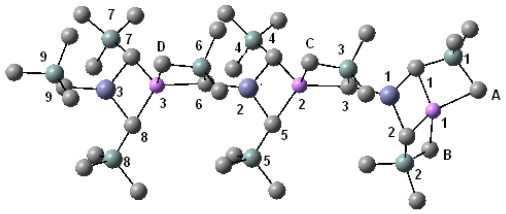
Geometry optimization for $[LiZn(CH_2SiMe_3)_2]_3$

Li_1-C_1	2.139 Å
Li_1-C_2	2.125 Å
Li_1-C_A	2.325 Å
Li_1-C_B	2.388 Å
C_1-Si_1	1.879 Å
C_2-Si_2	1.877 Å
C_3-Si_3	1.877 Å
Si_1-C_A	1.933 Å
Si_2-C_B	1.929 Å
Si_3-C_C	1.913 Å
Zn_1-C_1	2.091 Å
Zn_1-C_2	2.086 Å
Zn_1-C_3	2.018 Å
Li_2-C_3	2.290 Å
Li_2-C_4	2.191 Å
Li_2-C_5	2.202 Å
Li_2-C_C	2.645 Å
C_4-Si_4	1.884 Å
C_5-Si_5	1.884 Å
C_6-Si_6	1.879 Å
Si_6-C_D	1.912 Å
Zn_2-C_4	2.080 Å
Zn_2-C_5	2.079 Å
Zn_2-C_6	2.031 Å
Li_3-$C_{\wedge}$	2.307 Å
Li_3-C_7	2.168 Å
Li_3-C_8	2.164 Å
Li_3-C_D	2.704 Å
C_7-Si_7	1.879 Å
C_8-Si_8	1.879 Å
C_9-Si_9	1.869 Å
Zn_3-C_7	2.101 Å
Zn_3-C_8	2.101 Å
Zn_3-C_9	1.997 Å

C_1-Li_1-C_2	110.2 °

C_1-Zn_1-C_2	113.7 °	Zn_3-C_7-Si_7	108.3 °
Li_1-C_1-Zn_1	67.7 °	Zn_3-C_8-Si_8	108.9 °
Li_1-C_2-Zn_1	68.1 °	Zn_3-C_9-Si_9	115.9 °
Zn_1-C_1-Si_1	125.9 °		
Zn_1-C_2-Si_2	118.7 °		
Zn_1-C_3-Si_3	110.8°		
Zn_1-C_3-Li_2	159.6 °		
C_4-Li_2-C_5	110.7 °		
C_4-Zn_2-C_5	110.0 °		
Li_2-C_4-Zn_2	68.9 °		
Li_2-C_5-Zn_2	68.7 °		
Zn_2-C_4-Si_4	109.6 °		
Zn_2-C_5-Si_5	110.1 °		
Zn_2-C_6-Si_6	111.1 °		
Zn_2-C_6-Li_3	158.4 °		
C_7-Li_3-C_8	102.9 °		
C_7-Zn_3-C_8	107.5 °		
Li_3-C_7-Zn_3	68.8 °		
Li_3-C_8-Zn_3	68.9 °		

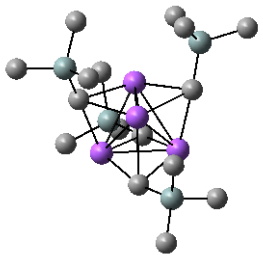
E = -9397.3491391 a.u.



Geometry optimization for $[NaCH_2SiMe_3]_4$ –C_2 symmetry

Each C of a CH_2 is bonded to 3 neighbouring Na atoms.The range of these bonds is from 2.552 Å to 2.677 Å.

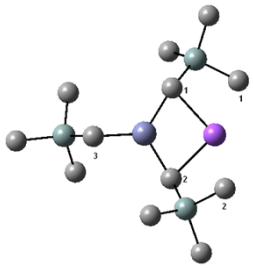
E = -2443.002271 a.u.



Geometry optimization for $NaZn(CH_2SiMe_3)_2$

Na-C_1	2.471 Å
Na-C_2	2.458 Å
Na…C_{Me1}	2.647 Å
Na…C_{Me2}	2.667 Å
Zn-C_1	2.105 Å
Zn-C_2	2.098 Å
Zn-C_3	1.996 Å
C_1-Na-C_2	95.3 °
C_1-Zn-C_2	120.2 °
Na-C_1-Zn	71.9 °
Na-C_2-Zn	72.3 °
C_1-Zn-C_3	120.2 °
C_2-Zn-C_3	119.1 °

E =-3286.778482 a.u.



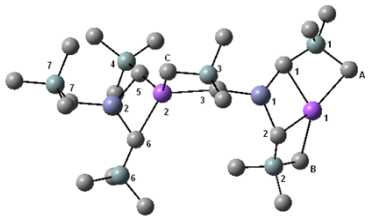
Geometry optimization for $[NaZn(CH_2SiMe_3)_2]_2$

Na_1-C_1	2.505 Å
Na_1-C_2	2.489 Å
Na_1-C_A	2.628 Å
Na_1-C_B	2.656 Å
C_1-Si_1	1.875 Å
C_2-Si_2	1.876 Å
C_3-Si_3	1.870 Å
Si_1-C_A	1.932 Å
Si_2-C_B	1.931 Å
Si_3-C_C	1.919 Å
Zn_1-C_1	2.079 Å
Zn_1-C_2	2.075 Å
Zn_1-C_3	2.033 Å
Na_2-C_3	2.656 Å
Na_2-C_4	2.499 Å
Na_2-C_5	2.507 Å
Na_2-C_C	2.796 Å
C_4-Si_4	1.877 Å
C_5-Si_5	1.876 Å
C_6-Si_6	1.865 Å
Zn_2-C_4	2.091 Å
Zn_2-C_5	2.090 Å
Zn_2-C_6	2.007 Å

C_1-Na_1-C_2	93.6 °
C_1-Zn_1-C_2	122.5 °

Na_1-C_1-Zn_1	71.5 °
Na_1-C_2-Zn_1	71.9 °
Zn_1-C_1-Si_1	125.8 °
Zn_1-C_2-Si_2	118.3 °
Zn_1-C_3-Si_3	113.9 °
Zn_1-C_3-Na_2	155.5 °
C_4-Na_2-C_5	87.9 °
C_4-Zn_2-C_5	112.4 °
Na_2-C_4-Zn_2	71.9 °
Na_2-C_5-Zn_2	71.7 °
Zn_2-C_4-Si_4	110.0 °
Zn_2-C_5-Si_5	110.5 °
Zn_2-C_6-Si_6	114.0 °

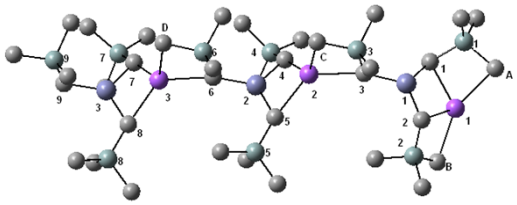
E = -6573.574848 a.u.



Geometry optimization for $[NaZn(CH_2SiMe_3)_2]_3$

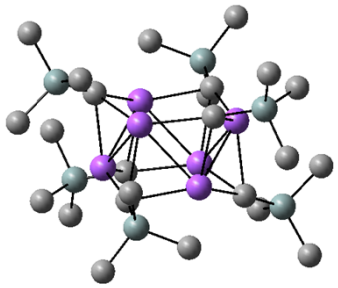
Na_1-C_1	2.515 Å
Na_1-C_2	2.497 Å
Na_1-C_A	2.633 Å
Na_1-C_B	2.653 Å
C_1-Si_1	1.876 Å
C_2-Si_2	1.876 Å
C_3-Si_3	1.871 Å
Si_1-C_A	1.931 Å
Si_2-C_B	1.930 Å
Si_3-C_C	1.922 Å
Zn_1-C_1	2.075 Å
Zn_1-C_2	2.070 Å
Zn_1-C_3	2.038 Å
Na_2-C_3	2.629 Å
Na_2-C_4	2,531 Å
Na_2-C_5	2.540 Å
Na_2-C_C	2.780 Å
C_4-Si_4	1.881 Å
C_5-Si_5	1.881 Å
C_6-Si_6	1.872 Å
Si_6-C_D	1.918 Å
Zn_2-C_4	2.069 Å
Zn_2-C_5	2.069 Å
Zn_2-C_6	2.045 Å
Na_3-C_6	2.642 Å
Na_3-C_7	2.512 Å
Na_3-C_8	2.508 Å
Na_3-C_D	2.830 Å
C_7-Si_7	1.876 Å
C_8-Si_8	1.876 Å
C_9-Si_9	1.864 Å
Zn_3-C_7	2.088 Å
Zn_3-C_8	2.089 Å
Zn_3-C_9	2.009 Å

E = -9861.617922 a.u.



Geometry optimization for $[KCH_2SiMe_3]_6$ –C_i symmetry

Each C of a CH_2 is bonded to 3 neighbouring K atoms.The range of these bonds is:



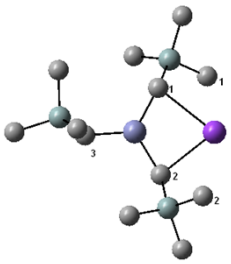
(a) 2.987 – 2.995 Å
(b) 3.013 – 3.018 Å
(c) 3.021 – 3.026 Å

E = -6290.117682 a.u.

Geometry optimization for $KZn(CH_2SiMe_3)_2$

K-C_1	2.894 Å
K-C_2	2.872 Å
K…C_{Me1}	3.099 Å
K…C_{Me2}	3.093 Å
Zn-C_1	2.080 Å
Zn-C_2	2.096 Å
Zn-C_3	2.005 Å
C_1-K-C_2	79.2 °
C_1-Zn-C_2	123.4 °
K-C_1-Zn	78.4 °
K-C_2-Zn	78.7 °
C_1-Zn-C_3	104.8 °
C_2-Zn-C_3	114.5 °

E = -3724.381870 a.u.

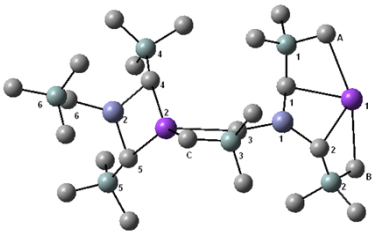


Geometry optimization for $[KZn(CH_2SiMe_3)_2]_2$

K_1-C_1	2.909 Å	Si_3-C_C	1.921 Å
K_1-C_2	2.950 Å	Zn_1-C_1	2.072 Å
K_1-C_A	3.100 Å	Zn_1-C_2	2.059 Å
K_1-C_B	3.123 Å	Zn_1-C_3	2.036 Å
C_1-Si_1	1.873 Å	K_2-C_3	3,146 Å
C_2-Si_2	1.873 Å	K_2-C_4	2.946 Å
C_3-Si_3	1.865 Å	K_2-C_5	2.935 Å
Si_1-C_A	1.927 Å	K_2-C_C	3.295 Å
Si_2-C_B	1.923 Å	C_4-Si_4	1.872 Å

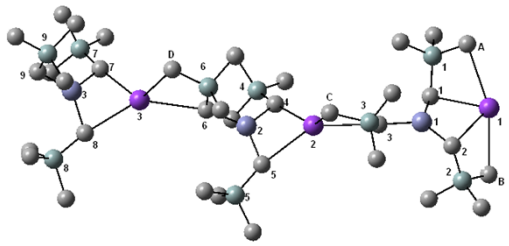
C_5-Si_5	1.872 Å	Zn_2-C_4-Si_4	111.8 °
C_6-Si_6	1.859 Å	Zn_2-C_5-Si_5	112.1 °
Zn_2-C_4	2.073 Å	Zn_2-C_6-Si_6	111.9 °
Zn_2-C_5	2.072 Å		
Zn_2-C_6	2.011 Å	E = -7448.783134 a.u.	

C_1-K_1-C_2	77.8 °
C_1-Zn_1-C_2	126.0 °
K_1-C_1-Zn_1	78.2 °
K_1-C_2-Zn_1	77.4 °
Zn_1-C_1-Si_1	118.2 °
Zn_1-C_2-Si_2	114.3 °
Zn_1-C_3-Si_3	115.9 °
Zn_1-C_3-K_2	147.7 °
C_4-K_2-C_5	71.6 °
C_4-Zn_2-C_5	112.2 °
K_2-C_4-Zn_2	75.3 °
K_2-C_5-Zn_2	75.6 °



Geometry optimization for $[KZn(CH_2SiMe_3)_2]_3$

K_1-C_1	2.925 Å	K_3-C_6	3.145 Å
K_1-C_2	2.950 Å	K_3-C_7	2.938 Å
K_1-C_A	3.107 Å	K_3-C_9	2.933 Å
K_1-C_B	3.117 Å	K_3-C_D	3.305 Å
C_1-Si_1	1.872 Å	C_7-Si_7	1.872 Å
C_2-Si_2	1.874 Å	C_8-Si_8	1.872 Å
C_3-Si_3	1.869 Å	C_9-Si_9	1.860 Å
Si_1-C_A	1.925 Å	Zn_3-C_7	2.073 Å
Si_2-C_B	1.923 Å	Zn_3-C_8	2.075 Å
Si_3-C_C	1.920 Å	Zn_3-C_9	2.012 Å
Zn_1-C_1	2.072 Å		
Zn_1-C_2	2.056 Å	E = -11174.4271974 a.u.	
Zn_1-C_3	2.038 Å		
K_2-C_3	3.132 Å		
K_2-C_4	2,967 Å		
K_2-C_5	2.965 Å		
K_2-C_C	3.264 Å		
C_4-Si_4	1.876 Å		
C_5-Si_5	1.876 Å		
C_6-Si_6	1.865 Å		
Si_6-C_D	1.917 Å		
Zn_2-C_4	2.061 Å		
Zn_2-C_5	2.059 Å		
Zn_2-C_6	2.037 Å		



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