Dalton Transactions

Electronic Supplementary Information for:

Synthesis and structure of cationic guanidinate-bridged bimetallic {Li_7M} cubes with inverse crown counter anions

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General considerations

Synthesis. All reactions were carried out using conventional Schlenk techniques. Reagents were obtained from commerical sources and used as supplied. Toluene was either dried using an Innovative Technologies Solvent Purification System, or by refluxing over sodium-potassium alloy. Solvents for NMR spectroscopy were distilled under nitrogen off sodium-potassium alloy or molten potassium, and were stored over activated 4 Å molecular sieves.

X-ray crystallography. Data on **1** were collected using an Oxford Diffraction Xcalibur2 diffractometer using an enhance molybdenum X-ray source with graphite monochromator (λ = 0.71073 Å) and a CCD detector. Data on [**2**][**3**] were collected using an Oxford Diffraction SuperNova diffractometer using a copper microfocus X-ray source with mirror optics (λ = 1.54178 Å) and a CCD area detector.

NMR spectroscopy. NMR spectra were acquired using a Bruker Avance III spectrometer operating at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C) and 155.51 MHz (^{7}Li).

EPR spectroscopy. The X-band EPR spectrum of [**2**][**3**] was recorded on a Bruker EMX spectrometer using a dielectric X-band resonator. The Q-band EPR spectrum of [**2**][**3**] was recorded on a Bruker Elexsys spectrometer using a dielectric Q-band resonator. An Oxford Instruments continuous flow He-cryostat was used with both resonators. Field corrections were carried out using a Bruker E0361200 teslameter. This is only sensitive to fields between 1500-15000 G, so for the X-band measurement, a calibration plot of these fields *vs*. the Hall probe was made, and extrapolated to 0 G so as to obtain a correction for the peak at 1065 G. Samples were prepared and sealed in a glove box, ensuring the exclusion of atmospheric oxygen.

Elemental analysis. Elemental analyses on **1** and [**2**][**3**] were carried out at the Elemental Analysis Service of London Metropolitan University.

[Li_3(μ-hmds)$_2$(μ-hpp)] (1)

X-ray crystallography. A semi-empirical absorption correction from equivalents was applied.[1] The structure was solved by charge-flipping methods using Superflip,[2] and full-matrix least-square refinements on F^2 in SHELXL-97 were performed with anisotropic displacements for all non-hydrogen atoms.[3] Data were erroneously collected in the centric crystal class, resulting in lowered data completeness. During the least-square-refinement three ISOR restraints were applied to model reasonable displacement parameters for atoms at special positions (Li2, C13 and C17).

Table S1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{19}H_{48}Li_3N_5Si_4$
Formula weight	479.80
Temperature	100(2) K
Crystal system	tetragonal
Space group	$P4_2bc$
Unit cell dimensions	a = 16.4053(3) Å α = 90°
	b = 16.4053(3) Å β = 90°
	c = 21.4837(10) Å γ = 90°
Volume	5781.99(31) Å^3
Z	8
Density (calculated)	1.102 Mg/m^3
Absorption coefficient	0.220 mm^{-1}
F(000)	2096
Crystal size	0.18 × 0.23 × 0.24 mm^3
Theta range for data collection	3.12 to 28.66°.
Index ranges	$-18 < h < 21$, $-16 < k < 21$, $-28 < l < 10$
Reflections collected	12200
Independent reflections	4177 [R(int) = 0.0397]
Completeness to full theta	0.896
Max. and min. transmission	1.000, 0.892
Data / restraints / parameters	4177 / 19 / 297
Goodness-of-fit on F^2	0.995
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0393, wR_2 = 0.0989
R indices (all data)	R_1 = 0.0551, wR_2 = 0.1060
Flack parameter	0.3(3)
Largest diff. hole and peak	–0.221, 0.539 eÅ^{-3}

1. SCALE3 ABSPACK, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.52, 2009

2. L. Palatinus and G. Chapuis, *J. Appl. Cryst*., 2007, **40**, 786.

3. G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

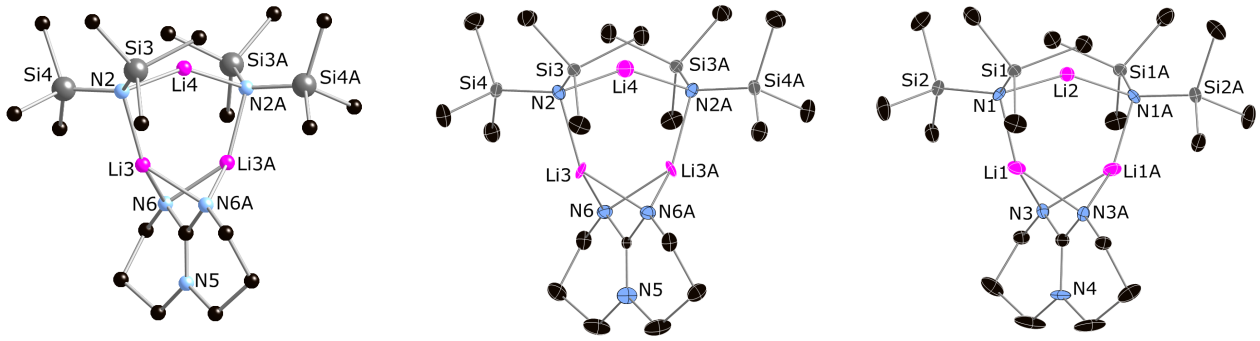

Figure S1. Molecular structure of **1b** (left), thermal ellipsoid plot of **1b** (50% probability, centre) and thermal ellipsoid plot of **1a** (50% probability, right), Selected bond lengths [Å] and angles [°] for **1b**: N(2)–Li(3) 2.060(17), N(2)–Li(4) 1.987(9), N(6)–Li(3) 2.051(13), N(2)-Li(3)-N(6) 132.4(6), N(2)-Li(4)-N(2A) 146.7(14).

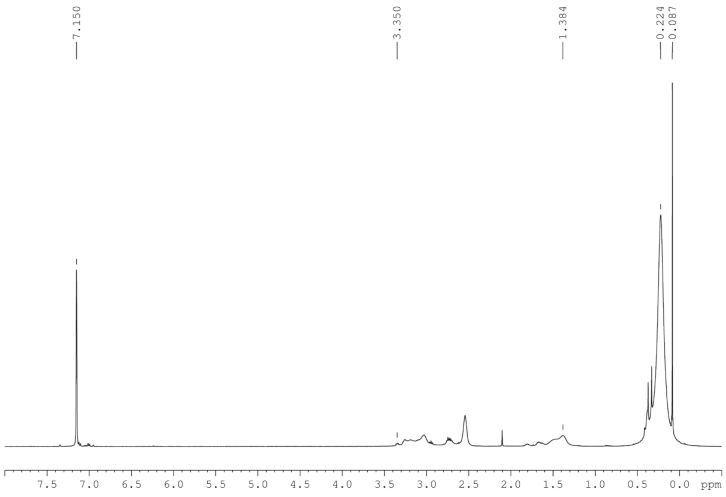

Figure S2. ^{1}H NMR spectrum of **1** recorded in benzene-d_6 at 298 K. The broad resonances in the region $\delta(^{1}H)$ = 1.38-3.35 ppm correspond to the [hpp] proton environments, and the broad resonance at $\delta(^{1}H)$ = 0.22 ppm is due to the $SiMe_3$ substituents. The sharp resonance at $\delta(^{1}H)$ = 0.09 ppm is due to small amount of hydrolysis, which was found to be unavoidable even if the solvent was distilled from sodium-potassium alloy and stored over activated 4 Å molecular sieves.

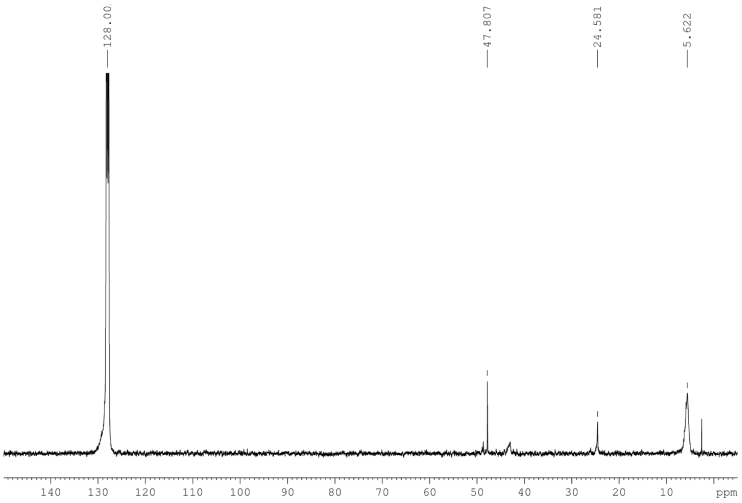

Figure S3. ^{13}C NMR spectrum of **1** recorded in benzene-d_6 at 298 K. The resonances at $\delta(^{13}C)$ = 47.81 and 24.58 ppm correspond to hpp ^{13}C NMR environments, and the resonance at $\delta(^{13}C)$ = 5.62 ppm ($\omega_{1/2}$ = 69.8 Hz) is due to the trimethylsilyl substituents. The low intensity of the signals is due to the fluxional behaviour of the compound.

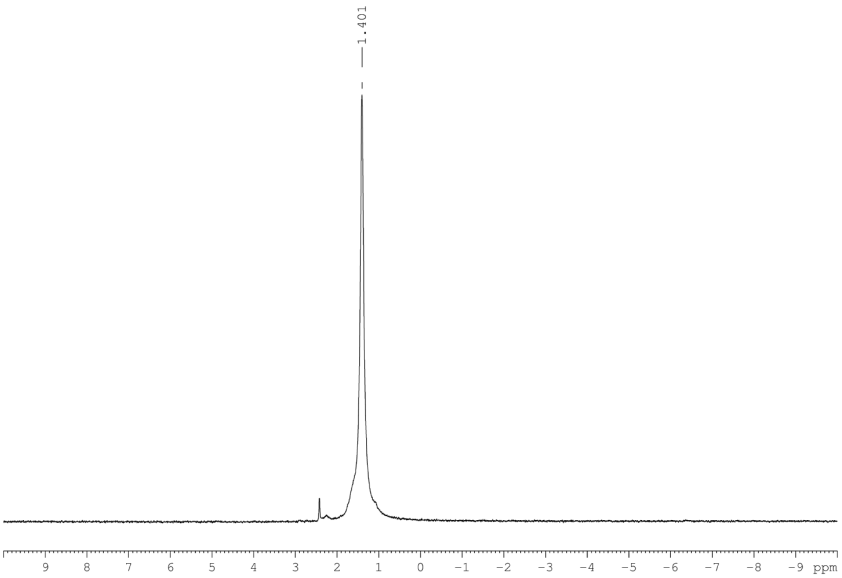

Figure S4. ^{7}Li NMR spectrum of **1** recorded in benzene-d_6 at 298 K.

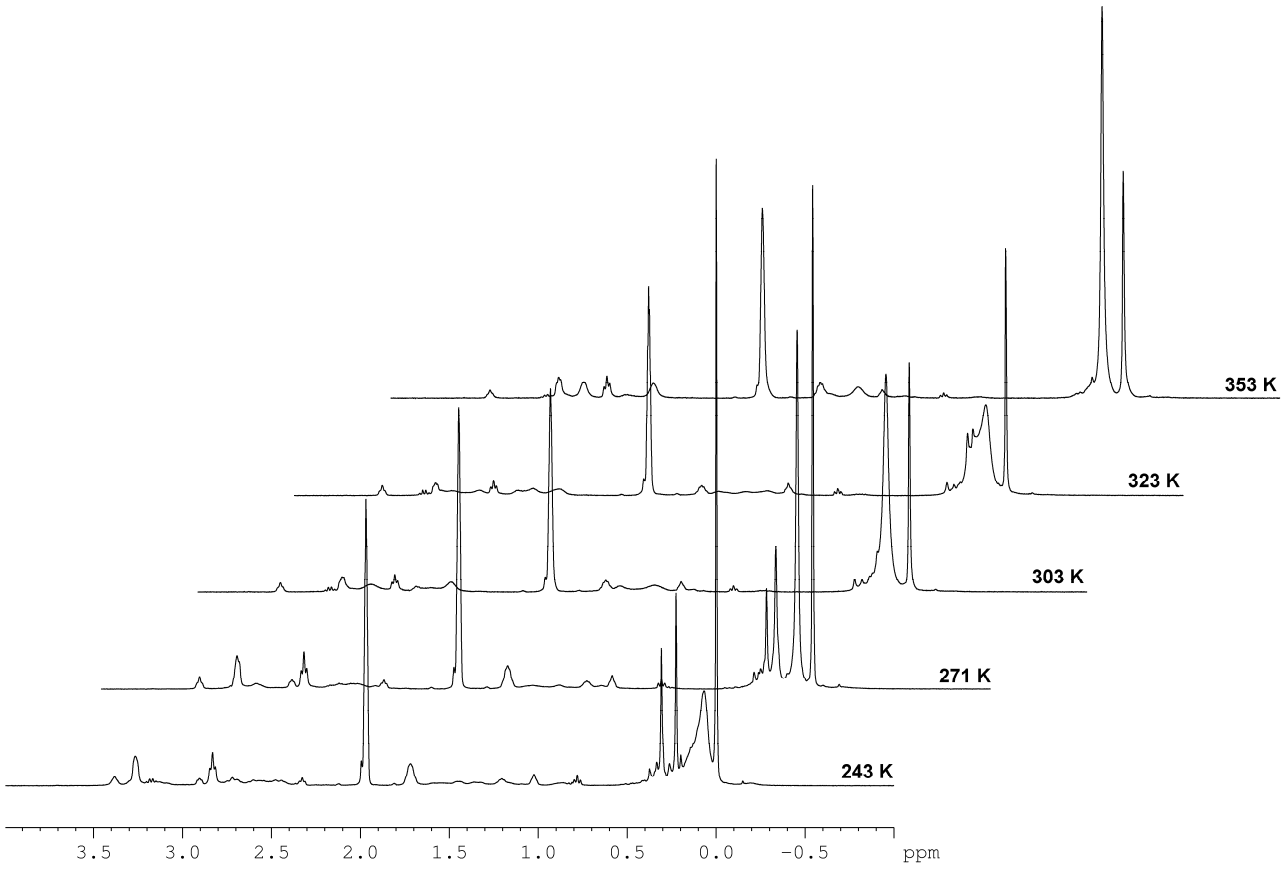

Figure S5. Variable-temperature ^{1}H NMR spectrum of **1** recorded in toluene-d_8. The temperature-non-dependent singlet at 0.08 ppm is due to hydrolysis.

$[MnLi_7(\mu_8\text{-}O)(\mu,\mu'\text{-}hpp)_6][\{Li(\mu\text{-}hmds)\}_5(\mu_5\text{-}Cl)]$ [2][3]

X-ray crystallography. A semi-empirical absorption correction from equivalents was applied.[1] The crystal was only poorly diffracting and no better crystal could be found. Repeated experiments also resulted only weakly scattering crystals. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix anisotropic least squares (SHELXL97).[2] The H-atoms were calculated geometrically and a riding model was used during refinement process.

Table S2. Crystal data and structure refinement for [**2**][**3**]

Empirical formula	$C_{86}H_{178}ClLi_{12}MnN_{23}OSi_{10}$	
Formula weight	1988.96	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 20.1096(12) Å	α = 90°.
	b = 24.4769(15) Å	β = 105.769(6)°.
	c = 24.9736(17) Å	γ = 90°.
Volume	11829.9(13) Å^3	
Z	4	
Density (calculated)	1.117 Mg/m^3	
Absorption coefficient	0.284 mm^{-1}	
F(000)	4260	
Crystal size	0.200 × 0.100 × 0.100 mm^3	
Theta range for data collection	2.92 to 24.04°.	
Index ranges	-22<=*h*<=21, -26<=*k*<=27, -25<=*l*<=18	
Reflections collected	21119	
Independent reflections	7584 [*R*(int) = 0.0906]	
Completeness to theta = 21.00°	99.7%	
Max. and min. transmission	1.00000 and 0.66492	
Data / restraints / parameters	7584 / 0 / 617	
Goodness-of-fit on F^2	1.040	
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0857, *wR*2 = 0.1979	
R indices (all data)	*R*1 = 0.1783, *wR*2 = 0.2215	
Largest diff. peak and hole	0.491 and -0.273 e.Å^3	

1. SCALE3 ABSPACK, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.52, 2009

2. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

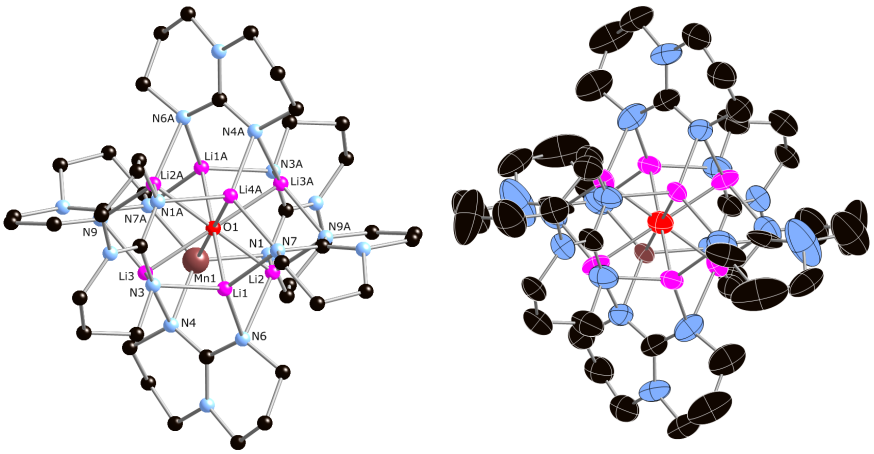

Figure S6. Molecular structure of the cation **2** in [**2**][**3**]: ball and stick model (left) and thermal ellipsoid plot (50% probability, right).

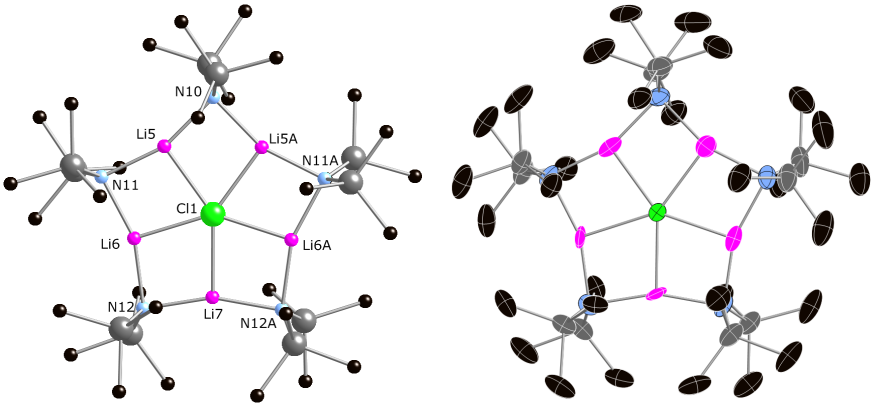

Figure S7. Molecular structure of the anion **3** in [**2**][**3**]: ball and stick model (left) and thermal ellipsoid plot (50% probability, right).

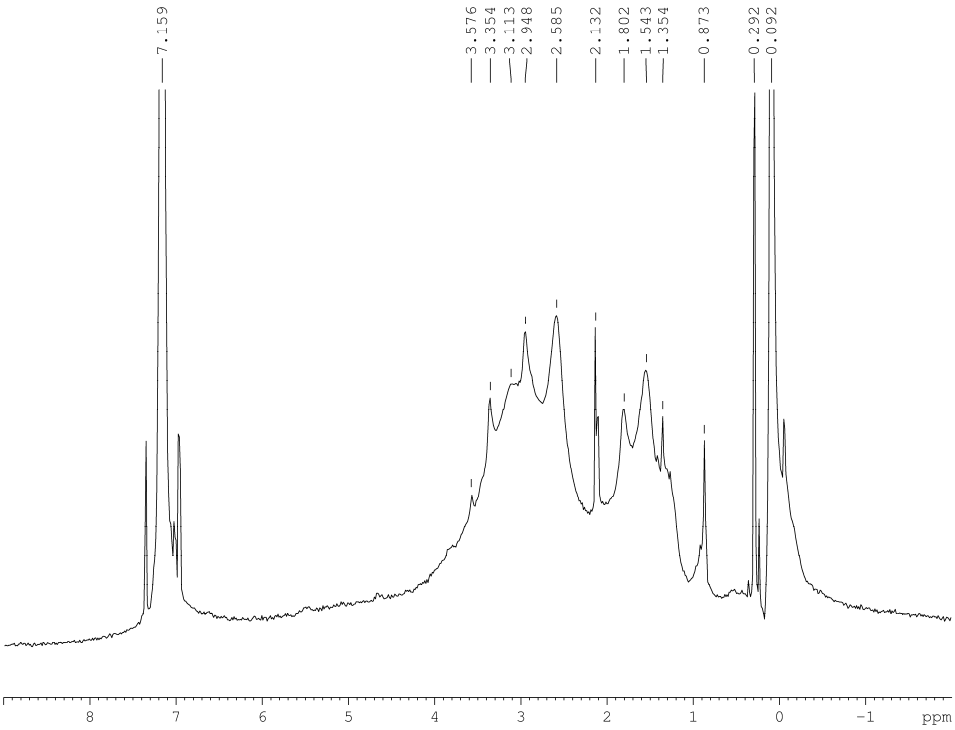

Figure S8. ^{1}H NMR spectrum of [**2**][**3**] recorded in benzene-d_6 at 298 K. The resonances of the $[hpp]^-$ ^{1}H environments are in the region $\delta(^{1}H)$ = 0.87-3.58 ppm, and the $SiMe_3$ substituents have $\delta(^{1}H)$ = 0.29, 0.09 ppm.

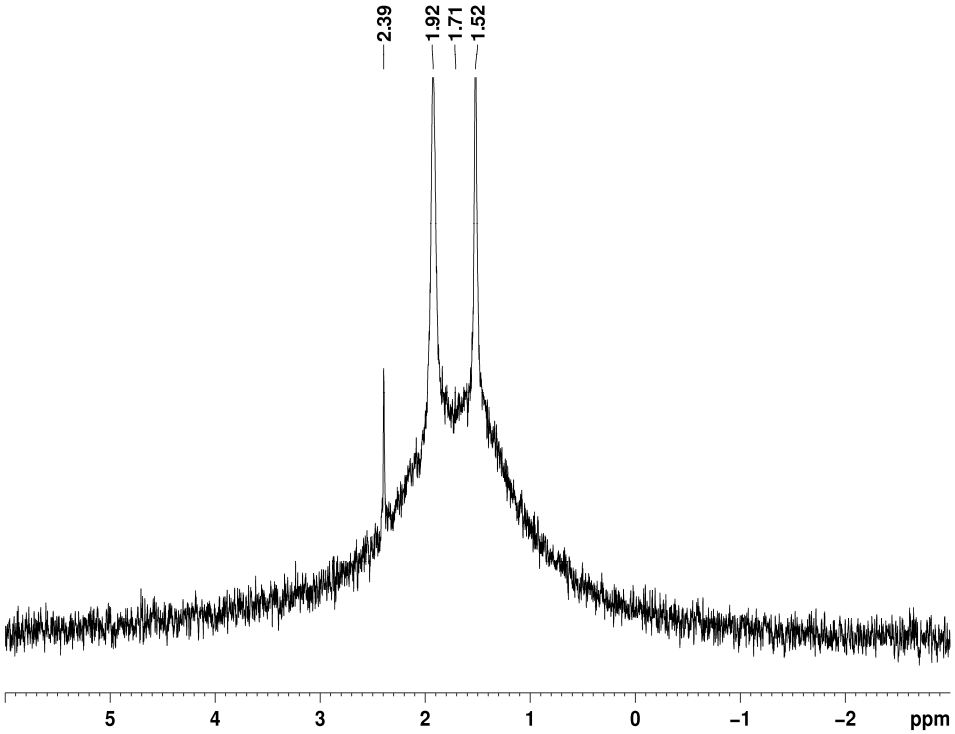

Figure S9. ^{7}Li NMR spectrum of [**2**][**3**] recorded in benzene-d_6 at 298 K.

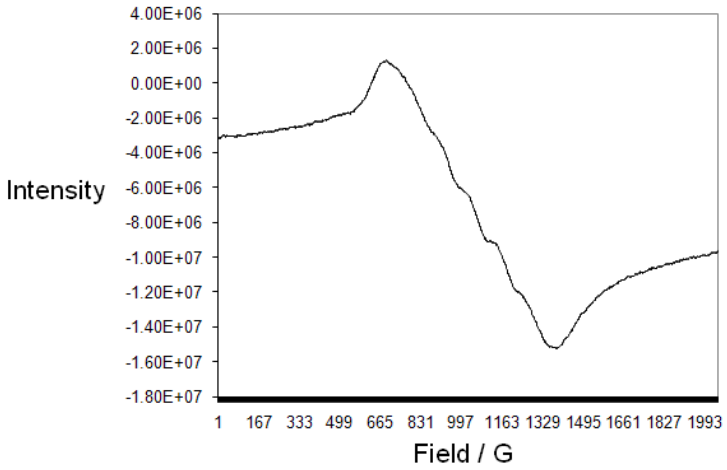

Figure S10. Q-band EPR spectrum of a polycrystalline sample of [**2**][**3**] recorded at $T = 5$ K.

$[CoLi_7(\mu_8\text{-}O)(\mu\text{-}hpp)_6][\{Li(\mu\text{-}hmds)\}_5(\mu_5\text{-}Cl)]$ [4][3]

X-ray crystallography. An analytical absorption correction from crystal faces was carried out.[4] EXYZ and EADP constraints were applied to the Co/Li mixed positions. The SQUEEZE function of PLATON was applied to two independent toluene molecules, which could not be refined due to severe disorder at special positions.[5]

Table S3. Crystal data and structure refinement for [**4**][**3**]

Empirical formula	$C_{86}H_{178}ClCoLi_{12}N_{23}OSi_{10}$
Formula weight	1824.81
Temperature	123(1) K
Crystal system	monolinic
Space group	*C*2/*c*
Unit cell dimensions	a = 20.1006(4) Å α = 90°
	b = 24.5598(4) Å β = 105.786(2)°
	c = 24.9957(5) Å γ = 90°
Volume	11874.2(4) Å^3
Z	2
Density (calculated)	1.021 Mg/m^3
Absorption coefficient	2.679 mm^{-1}
F(000)	3932
Crystal size	0.44 x 0.22 x 0.14 mm^3
Theta range for data collection	3.09 to 76.56 °.
Index ranges	$-24 < h < 24$, $-30 < k < 29$, $-31 < l < 29$
Reflections collected	43649
Independent reflections	12325 [R(int) = 0.0293]
Completeness to full theta	0.988
Max. and min. transmission	0.414, 0.783
Data / restraints / parameters	12325 / 0 / 604
Goodness-of-fit on F^2	1.091
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0629, wR_2 = 0.1746
R indices (all data)	R_1 = 0.0653, wR_2 = 0.1763
Largest diff hole and peak	–0.481, 0.639 eÅ^{-3}

4. R. C. Clark and J. S. Reid, *Acta Cryst*., 1995, **A51**, 887.

5. P. Sluis and A. L. Spek, *Acta Cryst*., 1990, **A46**, 194.

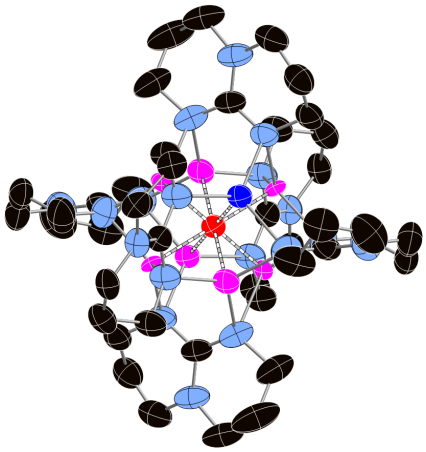

Figure S11. Molecular structure of the cation **4** in [**4**][**3**]: thermal ellipsoid plot (50% probability). Nitrogen = light blue, oxygen = red, lithium = pink, cobalt = dark blue.

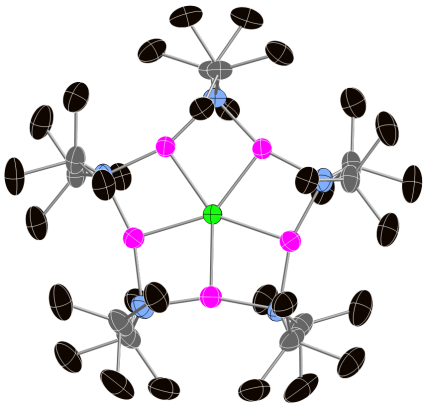

Figure S12. Molecular structure of the cation **3** in [**4**][**3**]: thermal ellipsoid plot (50% probability, right). Silicon = grey, chlorine = green.

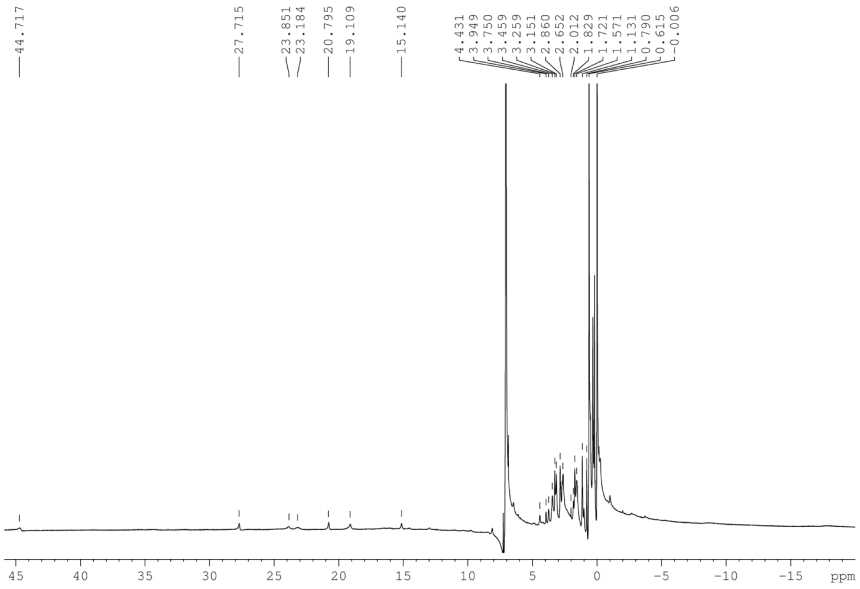

Figure S13. ^{1}H NMR spectrum of [**4**][**3**] recorded in benzene-d_6 at 298 K.

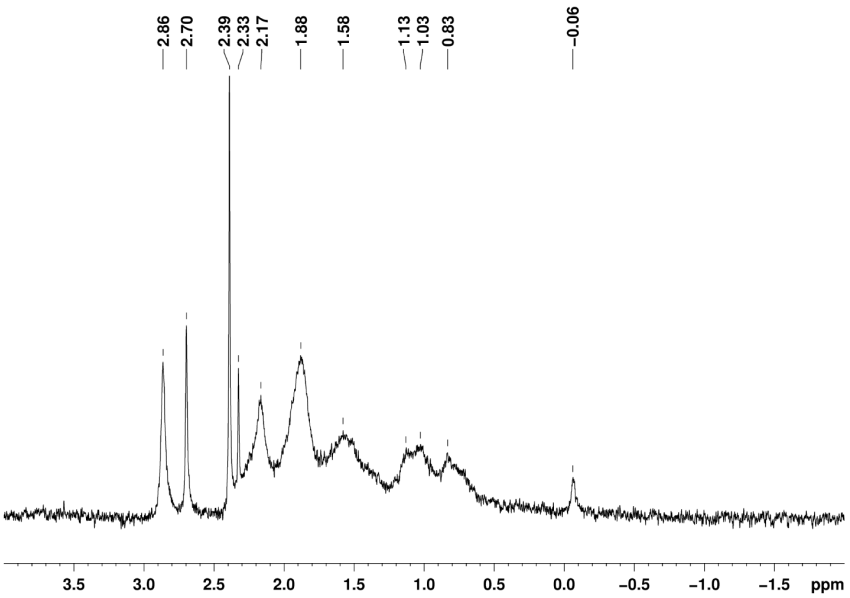

Figure S14. ^{7}Li NMR spectrum of [**4**][**3**] recorded in benzene-d_6 at 298 K.

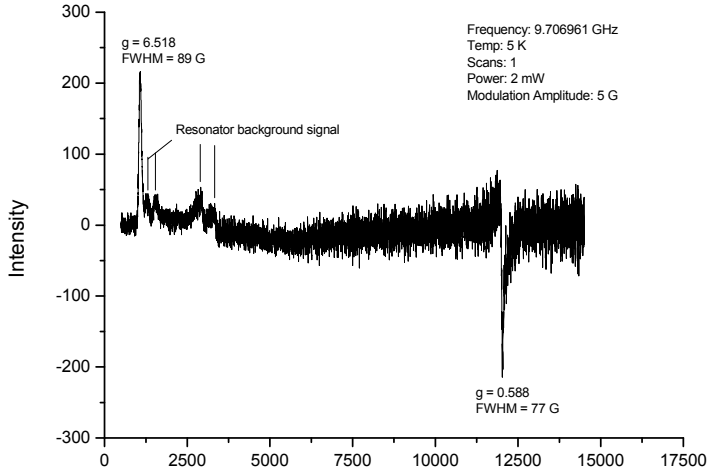

Figure S15. X-band EPR spectrum of a polycrystalline sample of [**4**][**3**]. The resonance at 1062 G has full width at half-maximum = 89 ± 1.5 G.

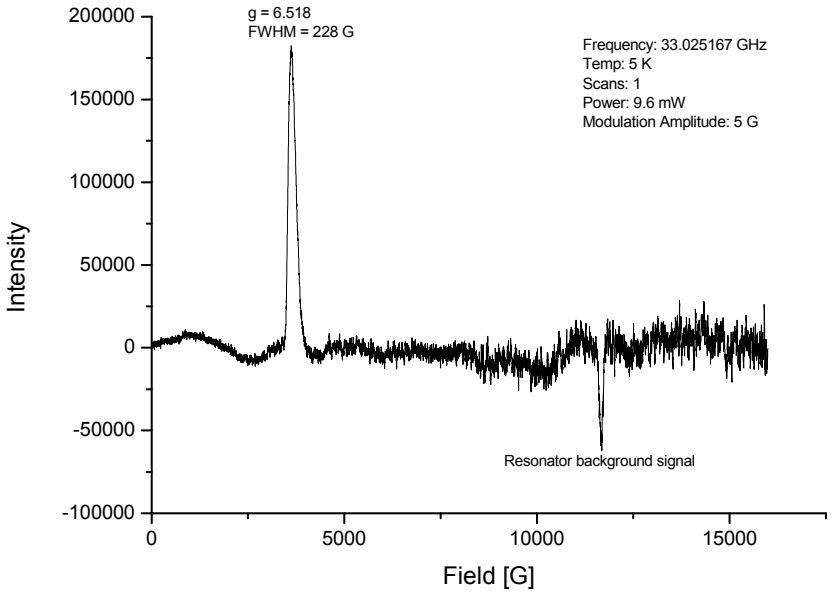

Figure S16. Q-band EPR spectrum of a polycrystalline sample of [**4**][**3**]. The resonance at 3650 G has full width at half-maximum = 228 ± 4 G.

$[ZnLi_7(\mu_8\text{-}O)(\mu\text{-}hpp)_6][Zn(hmds)_3]$ [5][$Zn(hmds)_3$]

A semi-empirical absorption correction from equivalents was applied.1 The crystals were only weakly diffracting. EXYZ and EADP constraints were applied to the Zn/Li mixed positions. Several restraints (DFIX, SIMU, DELU, ISOR) were used to refine the disordered hmds ligands.

Table S4. Crystal data and structure refinement for [**5**][$Zn(hmds)_3$]

Empirical formula	$C_{60}H_{126}Li_7N_{21}OSi_6Zn_2$	
Formula weight	1505.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	*Pba*2	
Unit cell dimensions	a = 27.7860(13) Å	α = 90°.
	b = 24.4230(11) Å	β = 90°.
	c = 12.1310(7) Å	γ = 90°.
Volume	8232.3(7) Å^3	
Z	4	
Density (calculated)	1.155 Mg/m^3	
Absorption coefficient	0.720 mm^{-1}	
F(000)	3224	
Crystal size	0.1 × 0.1 × 0.05 mm^3	
Theta range for data collection	2.89 to 23.25°.	
Index ranges	-30<=h<=22, -25<=k<=25, -12<=l<=13	
Reflections collected	33772	
Independent reflections	10107 [R(int) = 0.1008]	
Completeness to theta = 23.25°	94.5 %	
Max. and min. transmission	1.000 and 0.785	
Data / restraints / parameters	10107 / 199 / 937	
Goodness-of-fit on F^2	0.876	
Final R indices [I>2σ(I)]	R1 = 0.0481, wR2 = 0.1150	
R indices (all data)	R1 = 0.1317, wR2 = 0.1268	
Absolute structure parameter	0.013(19)	
Largest diff. peak and hole	0.380 and -0.232 e.Å^{-3}	

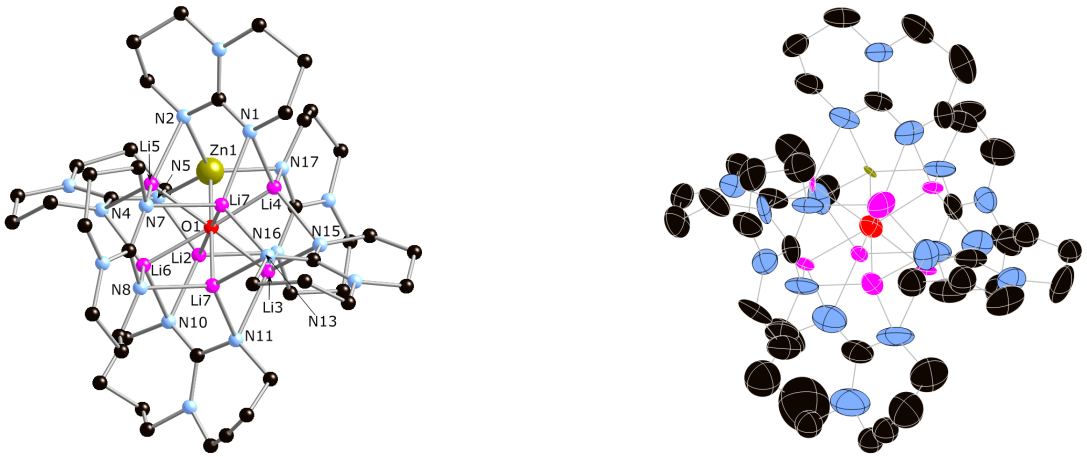

Figure S17. Molecular structure of the cation **5** in [**5**][Zn(hmds)$_3$]: ball and stick model (left) and thermal ellipsoid plot (50% probability, right).

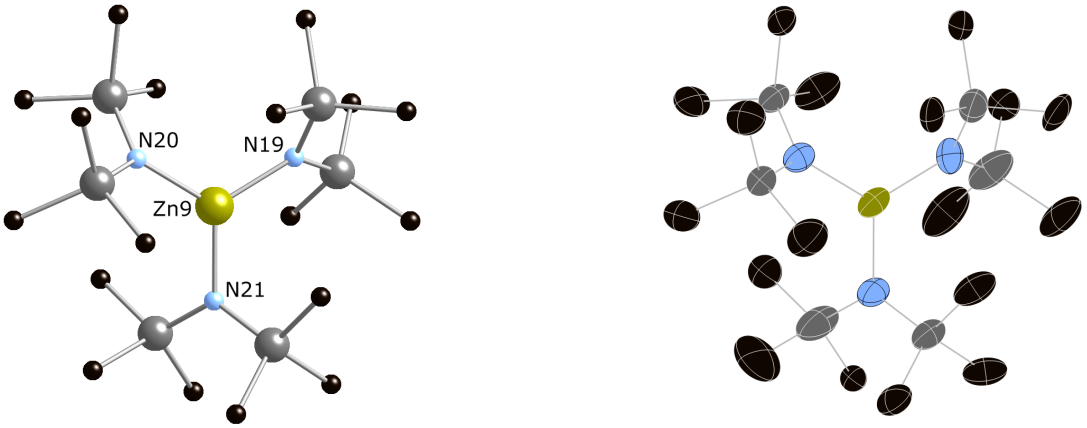

Figure S18. Molecular structure of the [Zn(hmds)$_3$]$^-$ in [**5**][Zn(hmds)$_3$]: ball and stick model (left) and thermal ellipsoid plot (50% probability, right).

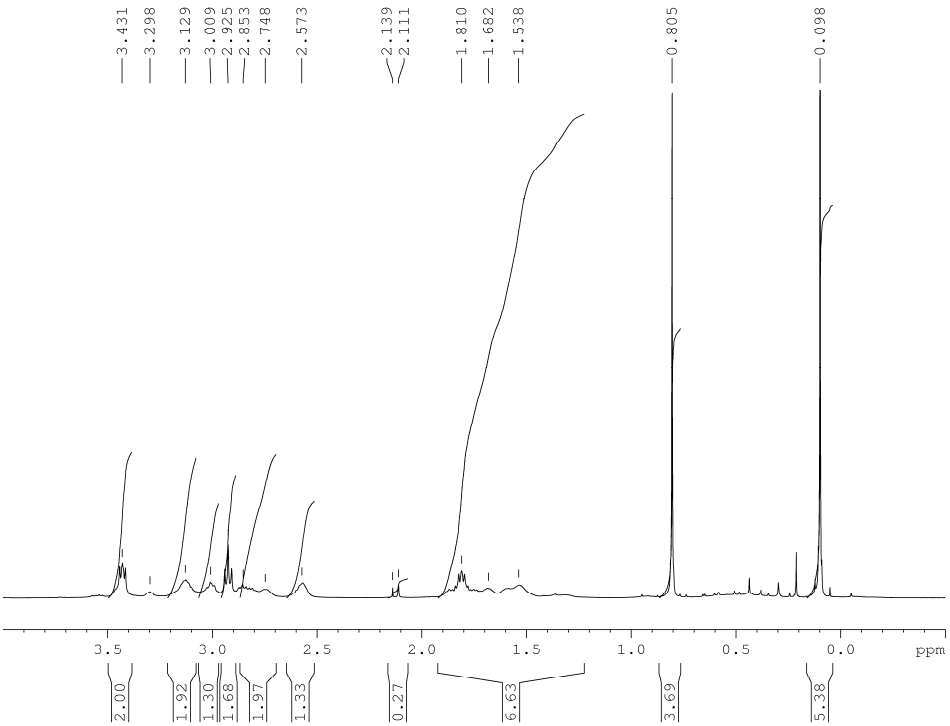

Figure S19. ^{1}H NMR spectrum of [**5**][Zn(hmds)$_3$] in the region 4.0 to -1.0 ppm, recorded in benzene-d$_6$ at 298 K. No resonances observed at lower field (except solvent).

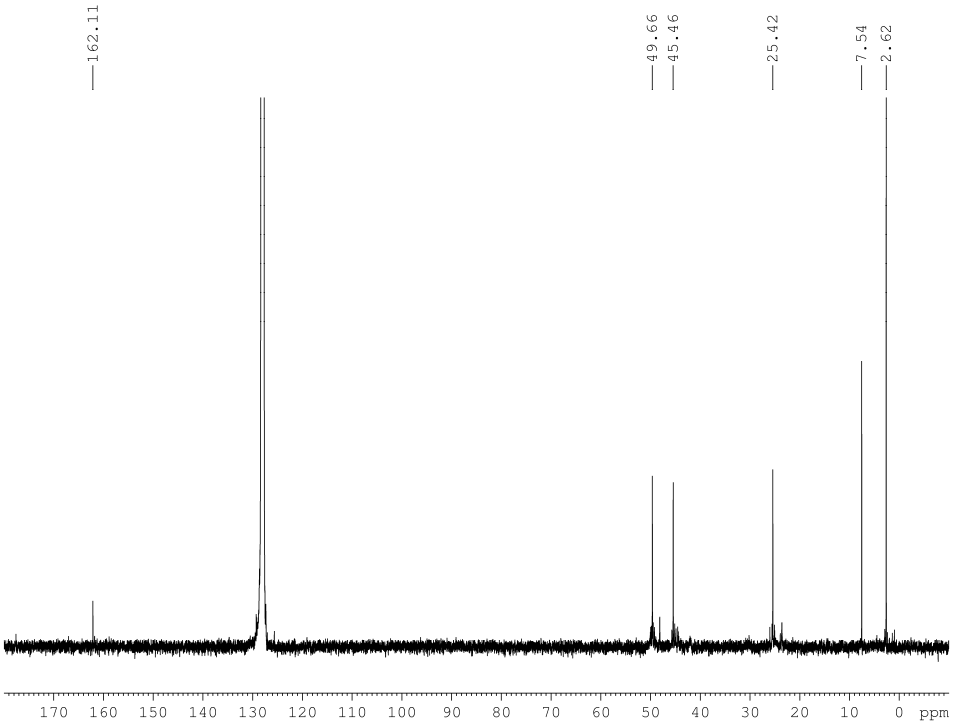

Figure S20. ^{13}C NMR spectrum of [**5**][Zn(hmds)$_3$] recorded in benzene-d$_6$ at 298 K.

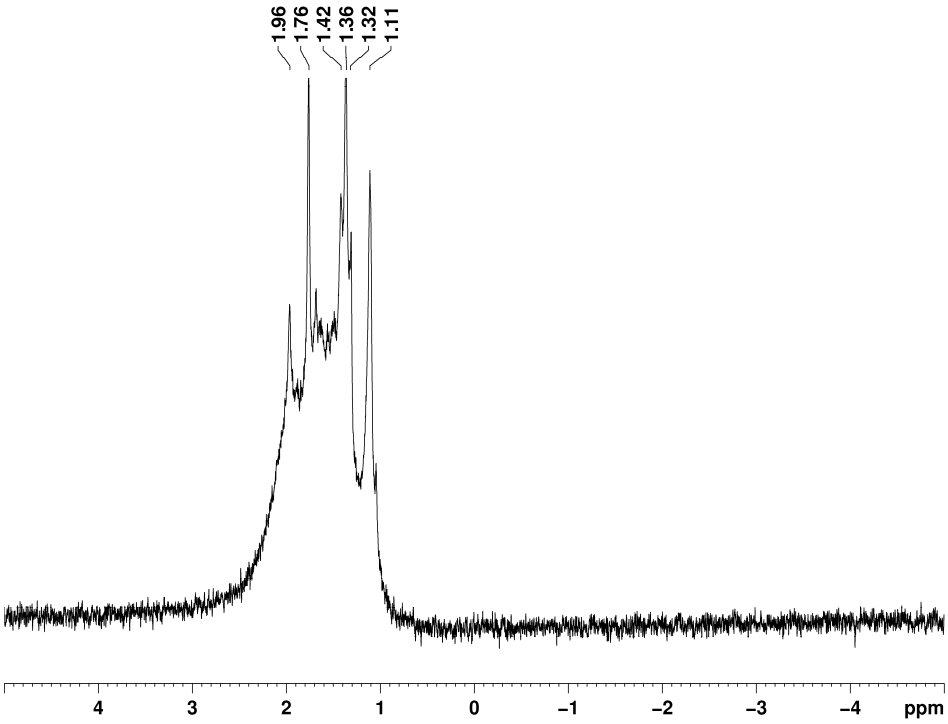

Figure S21. ^{7}Li NMR spectrum of [**5**][Zn(hmds)$_3$] recorded in benzene-d$_6$ at 298 K.