Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A Monomeric (Trimethylsilyl)methyl Lithium Complex: Synthesis, Structure, Decomposition and Preliminary Reactivity Studies

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NMR Spectra of complexes 1 and 2

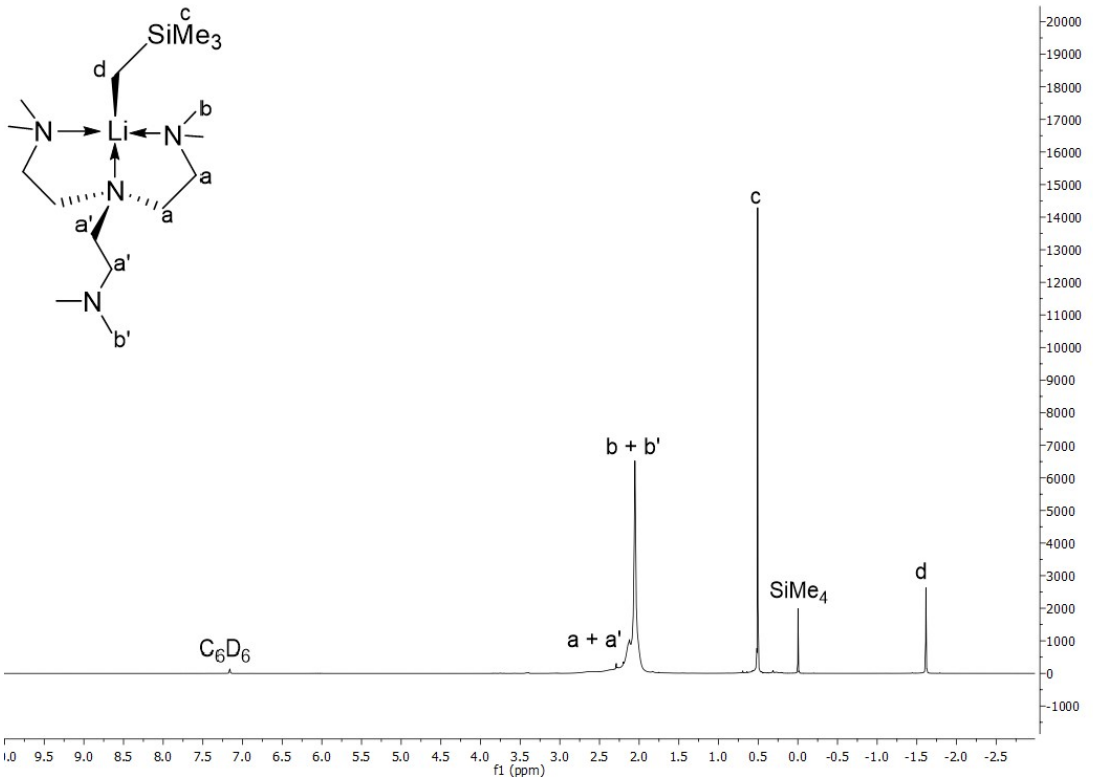

Figure S1: ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) of **1**.

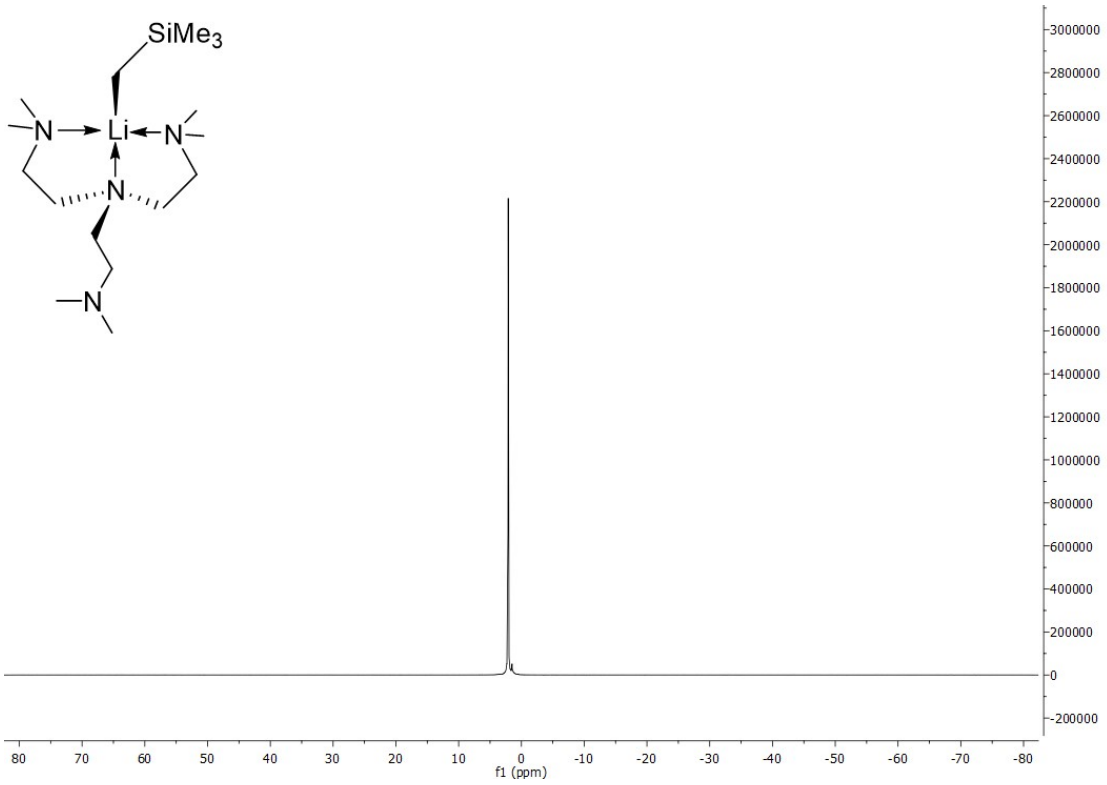

Figure S3: ^{7}Li NMR (d_6-benzene, 25 ˚C, 117 MHz) of **1**.

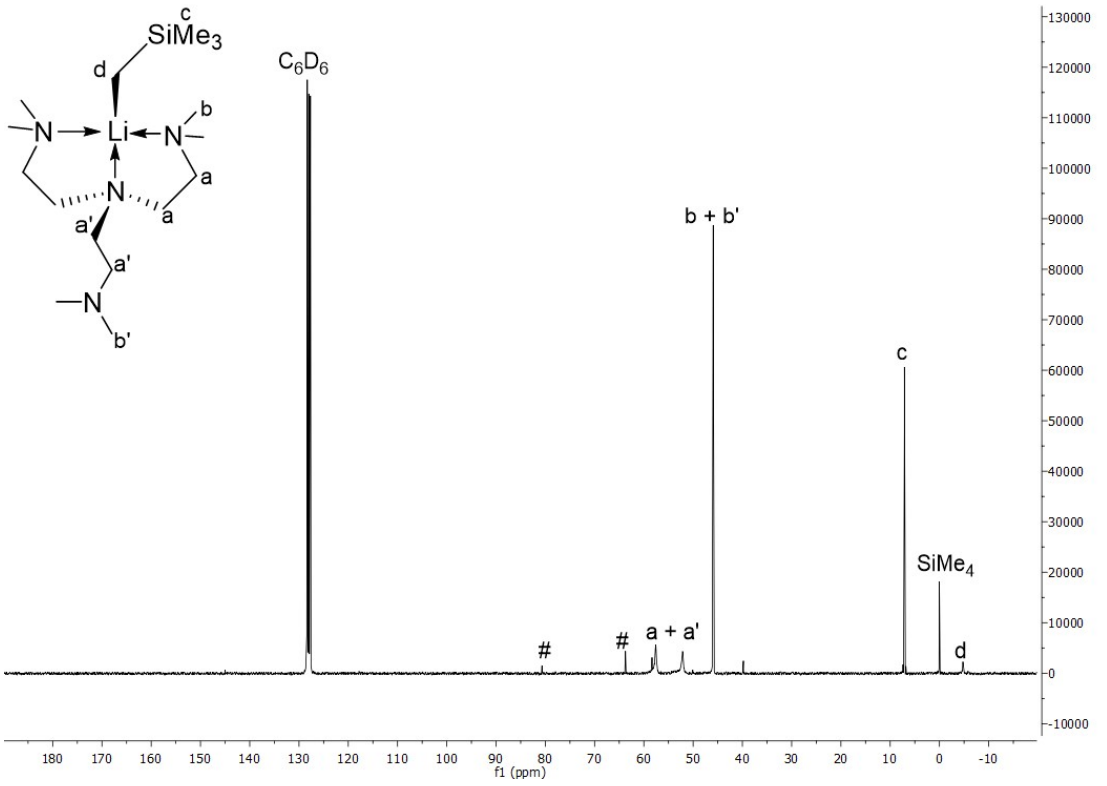

Figure S2: ^{13}C{^{1}H} NMR (d_6-benzene, 25 ˚C, 75 MHz) of **1**. # = Decomposition products (**2**).

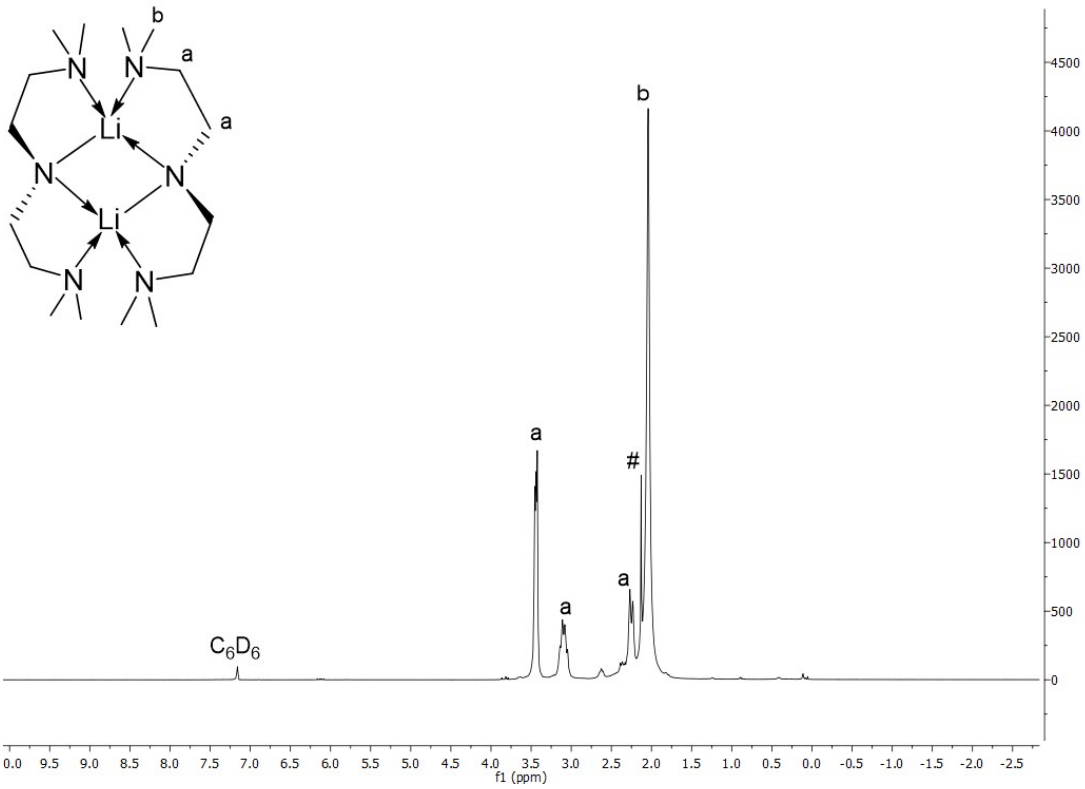

Figure S4: ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) of **2**. # = Unidentified impurities.

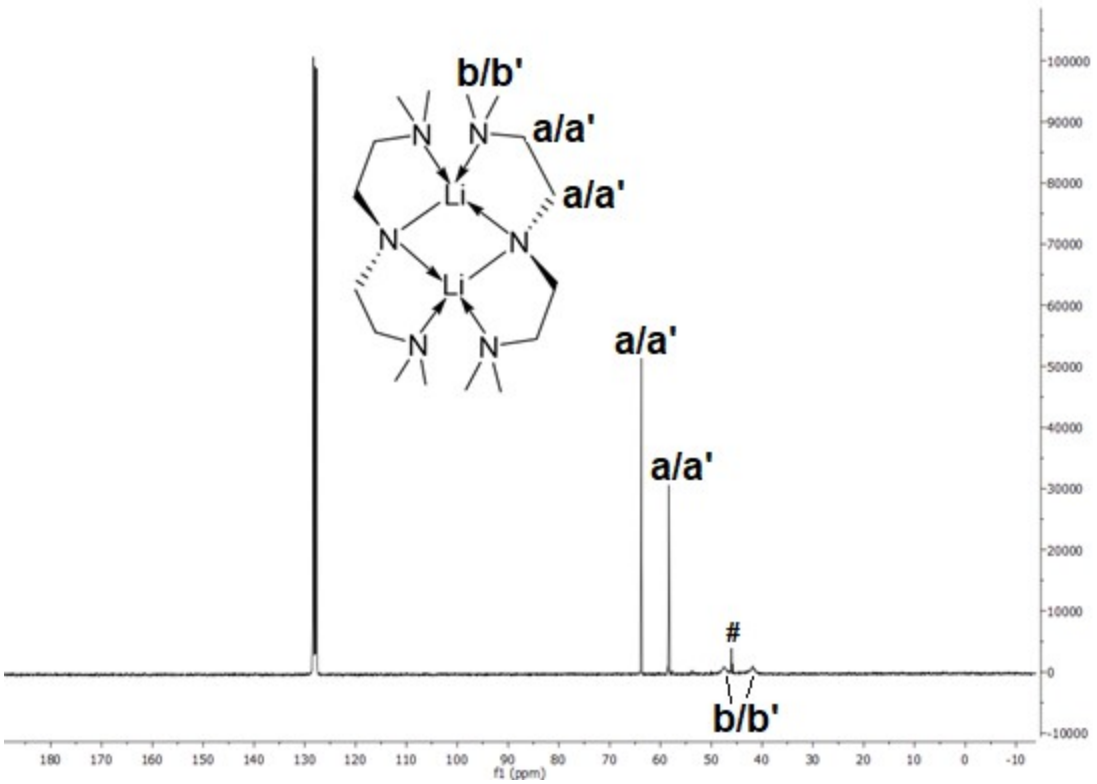

Figure S5: $^{13}C\{^{1}H\}$ NMR (d_6-benzene, 25 ˚C, 75 MHz) of **2**. # = Unidentified impurities.

Figure S6: ^{7}Li NMR (d_6-benzene, 25 ˚C, 117 MHz) of **2**.

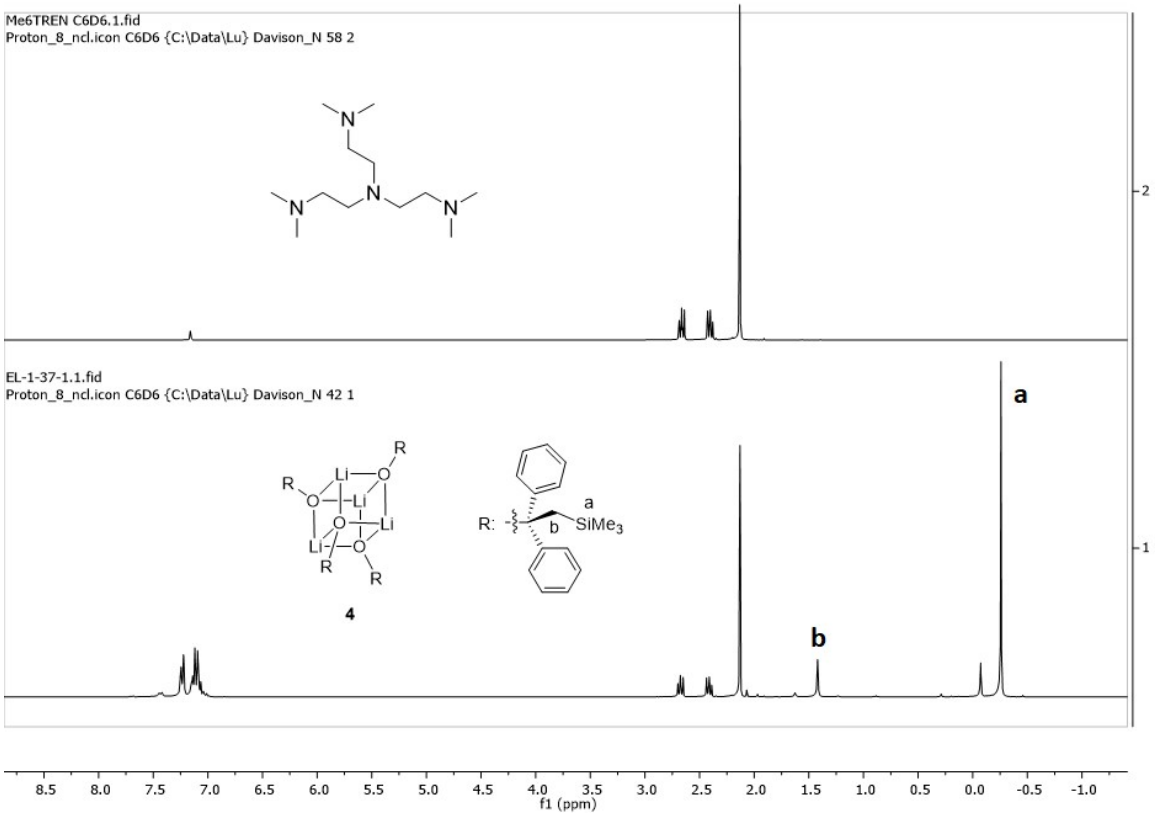

Figure S7: ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) of a mixture of **4** and Me^{6}Tren.

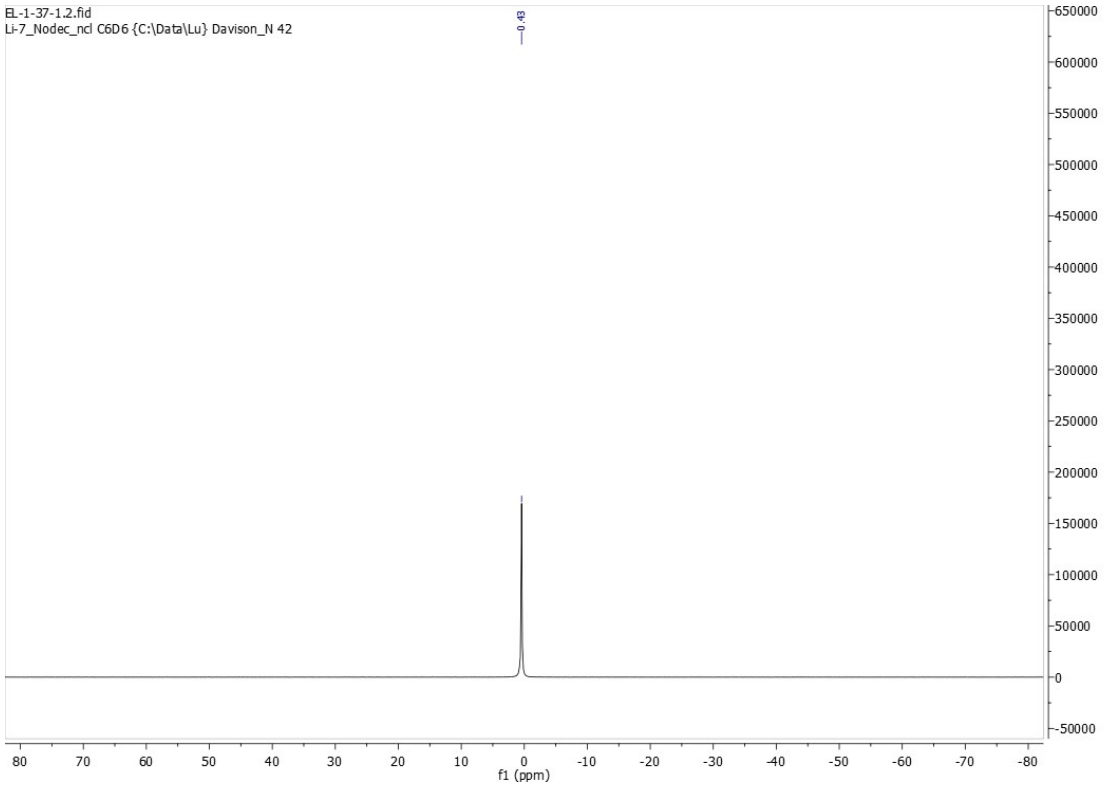

Figure S8: ^{7}Li NMR (d_6-benzene, 25 ˚C, 117 MHz) of a mixture of **4** and Me^{6}Tren.

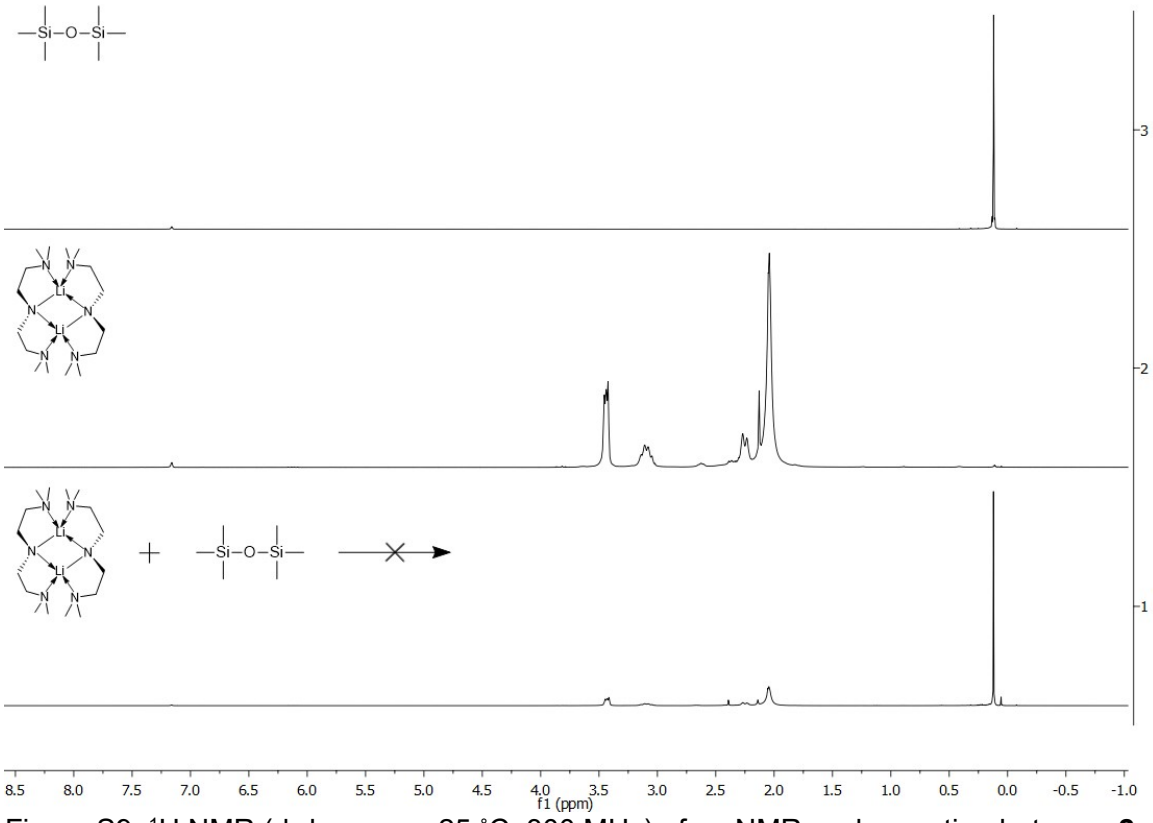

Figure S9: ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) of an NMR scale reaction between **2** and hexamethyldisiloxane and ^{1}H NMR of both starting materials.

Kinetic NMR experimental procedure.

$LiCH_2SiMe_3$ (0.0753g, 0.8 mmol), Me_6Tren (0.1846g, 0.8 mmol), cyclohexane (0.0673 g, 0.8 mmol) and C_6D_6 (1.9016g, 2 ml) were placed into separate vials. The C_6D_6 was split and 1 ml was added to each of the $LiCH_2SiMe_3$ and cyclohexane. The solution of cyclohexane in C_6D_6 was added to the Me_6Tren. The solution of $LiCH_2SiMe_3$ was added to the mixed solution of Me_6Tren and cyclohexane at room temperature and the time of mixing was recorded. 0.5570g of the resulting solution was placed in a J Young NMR tube in glove box.

The concentration of **1** was obtained from the area of the signal at 0.46 ppm (9H, $-SiMe_3$), the concentration of **2** from the area of the signal at 3.38 ppm (8H, NCH_2CH_2N), the concentration of vinyl dimethyl amine from the area of the signal at 6.03 ppm (1H, =CH-N) and the concentration of tetramethylsilane from the area of the signal at 0.00 ppm (12H), using cyclohexane (12H, 1.40 ppm) as the internal standard. The MestReNova™ NMR software was used to process the spectrum and obtain accurate integrations.

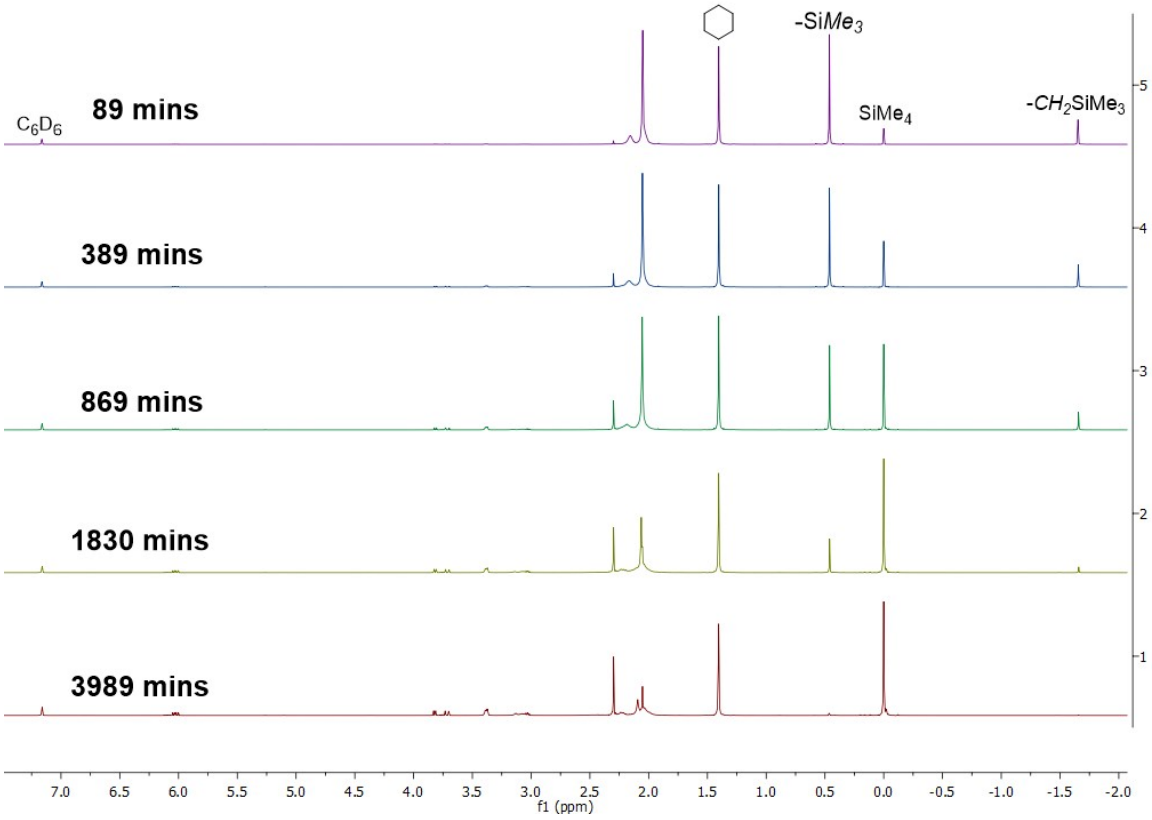

Figure S10: ^1H NMR (d_6-benzene, 25 ˚C, 500 MHz) of **1**. Internal standard (I) = cyclohexane. $[C]_0$ = 0.4 M, [I] = 0.4 M.

UV-Vis Spectra of Complex 1, Me^6Tren and $[LiCH_2SiMe_3]_6$

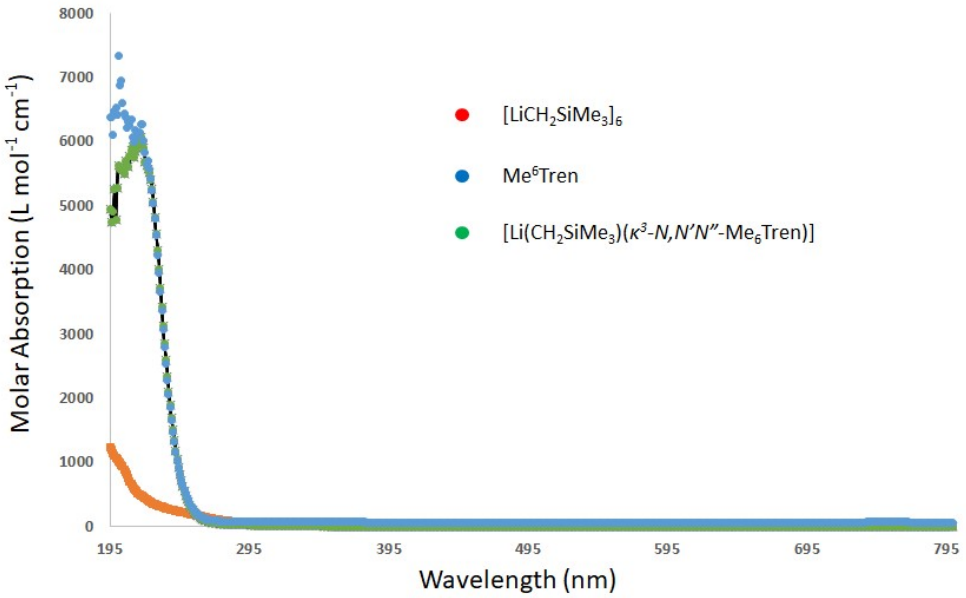

Figure S11. UV Absorption spectra of complex **1**, Me^6Tren and $[LiCH_2SiMe_3]_6$ in *n*-hexane. Concentration: 0.5 mmol L^{-1}. Temperature: 25 °C.

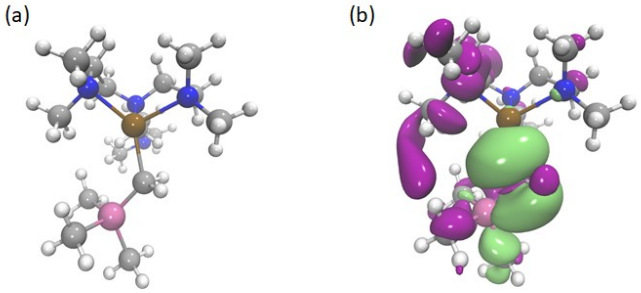

Figure S12. (a) Geometry optimisation of complex **1**; (b) the electron density difference analysis associated with a possible absorption band at 214.8 nm (Table S3). Colour codes for (b): green (loss in electron density); purple (gain in electron density).

Single Crystal X-ray Diffraction Details

Data for the structures of **1**-**3** were collected 150 K on a Rigaku Oxford Diffraction Xcalibur, Atlas, Gemini ultra diffractometer equipped with an Oxford Cryosystems CryostreamPlus open-flow N_2 cooling device using copper radiation ($\lambda_{CuK\alpha}$ = 1.54184 Å). The intensities were corrected for absorption empirically using spherical harmonics. Cell refinement, data collection and data reduction were undertaken via the software CrysAlisPro[1]; solved using XT[2] and refined by XL[3] using the Olex2 interface[4]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned with idealised geometry and their atomic displacement parameters (ADP) constrained to be an appropriate multiple of the parent atom.

The macrocyclic molecule in the structure was observed to be disordered and was hence modelled in two discreet orientations with appropriate restraints applied to ADPs and bond geometry.

Table S1. Crystal Structure Refinement Details for Complexes

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{16}H_{41}LiN_4Si$	$C_{16}H_{40}Li_2N_6$	$C_{20}H_{52}Li_2N_6O_2Si_2$	$C_{68}H_{84}Li_4O_4Si_4$
Formula weight	324.56	330.42	478.73	1105.47
Temperature/K	150.0(2)	150.0(2)	150.0(2)	150.0(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c	C2/c	$P2_1/c$
a/Å	10.8910(3)	15.6022(3)	16.9028(5)	12.7436(2)
b/Å	18.7942(5)	10.0920(2)	8.8805(3)	22.0133(3)
c/Å	10.9483(3)	14.6868(3)	19.9387(7)	23.1214(4)
α/°	90	90	90	90
β/°	94.108(3)	111.323(2)	108.353(4)	94.5910(10)
γ/°	90	90	90	90
Volume/Å^3	2235.22(11)	2154.24(8)	2840.67(17)	6465.40(18)
Z	4	4	4	4
ρ_{calc}g/cm^3	0.964	1.019	1.119	1.136
μ/mm^{-1}	0.919	0.467	1.328	1.193
F(000)	728.0	736	1056	2368.0
Crystal size/mm^3	0.23 × 0.22 × 0.13	0.31 × 0.2 × 0.12	0.35 × 0.25 × 0.18	0.22 × 0.12 × 0.04
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.366 to 133.246	10.672 to 133.228	9.346 to 133.322	7.672 to 133.268
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 22, -13 ≤ l ≤ 12	-15 ≤ h ≤ 18, -11 ≤ k ≤ 12, -17 ≤ l ≤ 17	-20 ≤ h ≤ 20, -10 ≤ k ≤ 9, -23 ≤ l ≤ 23	-15 ≤ h ≤ 15, -26 ≤ k ≤ 24, -27 ≤ l ≤ 26
Reflections collected	17538	14540	10127	59102
Independent reflections	3923 [R_{int} = 0.0870, R_{sigma} = 0.0627]	1902 [R_{int} = 0.0459, R_{sigma} = 0.0223]	2503 [R_{int} = 0.0751, R_{sigma} = 0.0452]	11344 [R_{int} = 0.0810, R_{sigma} = 0.0511]
Data/restraints/parameters	3923/345/266	1902/0/115	2503/0/151	11344/784/733
Goodness-of-fit on F^2	1.067	1.045	1.052	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.1466	R_1 = 0.0398, wR_2 = 0.1065	R_1 = 0.0447, wR_2 = 0.1161	R_1 = 0.0544, wR_2 = 0.1340
Final R indexes [all data]	R_1 = 0.0805, wR_2 = 0.1637	R_1 = 0.0444, wR_2 = 0.1110	R_1 = 0.0533, wR_2 = 0.1262	R_1 = 0.0726, wR_2 = 0.1486
Largest diff. peak/hole / e Å^{-3}	0.29/-0.31	0.17/-0.14	0.31/-0.35	1.06/-0.34

Computational Details

General

Optimizations were carried out with the $B3LYP^5$ *x-c* functionals as implemented in the ORCA quantum chemistry software[6]. Grimme's D3 dispersion correction was added to account for weak interactions. Throughout optimizations were carried out with the def2-TZVP[7] basis set. In order to speed up the calculations the RI-J and COSX (RIJCOSX) were used respectively for Coulomb integrals and numerical integration for HF exchange. During the geometry optimisations, the total SCF energy was set to converge within 10^{-6} a.u., while the gradient converged to 10^{4-} a.u. Single point calculations with DLPNO-CCSD and a def2-TZVP basis set were also performed using ORCA quantum chemistry software.

Table S2. Cartesian coordinates of optimized structure of **1**.

Coordinates from ORCA-job Li

N	6.77101640109436	2.62960348839574	3.95658682451567
N	4.51459113621450	0.49931143417387	6.18363760799703
C	7.39393395696241	4.16424050115539	7.50941651348532
C	8.09923288944361	2.32848522562653	3.39083244062769
H	8.03558671005258	1.64964945743952	2.49944267882872
H	8.65489679905843	1.76842231163746	4.17000700591144
C	5.85956284175626	3.28143612932315	2.99276064177843
H	5.05090518799869	2.58460788110379	2.66775693198714
H	6.42111829327072	3.51627826810565	2.06387441472349
C	6.18866817776041	1.43548435394794	4.60440239850109
H	6.98410647919169	0.97112831496169	5.22157911697039
H	5.88638995815812	0.67126464675633	3.84422534327307
Li	7.31739607603433	4.17938058977509	5.42721420893417
N	8.97422285335186	4.60025049690959	4.05748541347467
N	11.86263420060305	3.52712307432334	6.28629051641428
C	8.59021073751397	5.94752831673058	3.60090160316143
H	9.24876599354782	6.31569736341916	2.76891859759731
H	8.75741356870364	6.63302094007135	4.45578273653333
C	8.90686522293756	3.57771558315267	2.99445404125159
H	9.92753881562713	3.24979427278903	2.68631025145232
H	8.47073003691846	4.02950203607047	2.07936585893088
C	10.26890492616497	4.63456549502231	4.76539149478022

H	10.20750129753219	5.45735176797457	5.50880842632068
H	11.10826762802390	4.88756448820086	4.06765890466771
C	10.63073935832058	3.34238848379707	5.51600386027912
H	9.76380675983523	3.04478117525393	6.16009200988792
H	10.79240104283563	2.52200580142422	4.78590314494657
C	11.61997919077313	4.08376300295097	7.62540974407327
H	11.36513906991885	3.27364312666493	8.35918044509959
H	10.71261863713600	4.71979026808336	7.57244864619586
C	12.78683100554421	4.92187809761316	8.15472259329198
H	13.00177943708299	5.77009630712374	7.47369422661805
H	13.71891176573929	4.32742350076919	8.25499636510568
H	12.54898665678448	5.32837984553219	9.15908998890161
C	12.73631881231180	2.35242903177096	6.30020089088886
H	12.17731697984563	1.42297733089295	6.59876205814707
H	13.49602182857793	2.50948890155514	7.09342799318479
C	13.46737119190019	2.11627626823009	4.97545843637781
H	12.76432231828112	1.92013423271949	4.13887139117911
H	14.13863829919762	1.23558999965717	5.05018939619522
H	14.07591424794611	3.00243791126941	4.70142237056592
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N	5.56414764397206	8.31489767083215	6.63120946460770
C	5.19974308882505	4.56495552655586	3.52988402071026
H	4.59259337115782	5.02220264095001	2.70320446393050
H	4.48469406916285	4.29476514013664	4.33286921982583
C	7.12487295216752	6.05793049599840	3.14274838691357
H	6.91353404677116	7.12856506656243	2.91072011358662
H	6.99996626891499	5.53016764797598	2.17477524633895
C	5.45057766938443	6.56964649107841	4.88446523864108
H	4.70167312321306	6.05612305312889	5.52292427936882
H	4.88040453415656	7.26016178420161	4.21011168607548
C	6.35920861135965	7.40847262639181	5.79924775389660
H	6.99278818266961	6.71127279315261	6.40589828044300

H	7.04932969239415	8.01523483350193	5.17725860620730
C	5.12864376707160	7.69152439685673	7.89009066804487
H	5.93656822122045	7.74092253664549	8.66795033423146
H	4.97906673466381	6.60879194817876	7.70014974141614
C	3.82947997478788	8.28212558219440	8.44543154514820
H	3.00785509065650	8.18628428592885	7.70623322980524
H	3.93133249780155	9.35826084874004	8.69747563949853
H	3.53117073419482	7.75683286341760	9.37580104177230
C	6.17659941155579	9.63198196505668	6.82094575639122
H	7.24776834412690	9.54676382156747	7.15173926722113
H	5.64594447853820	10.13092467915969	7.65795122004891
C	6.08321643052699	10.53437910209486	5.58695192534015
H	6.61660244143903	10.10520299994562	4.71305944554328
H	6.53872618707704	11.52560227289421	5.79013574502430
H	5.02504948167791	10.68635829011812	5.29304244701867
H	7.97598095447897	3.33104340575201	7.98420531676968
H	6.40690976749872	4.12867648150157	8.04125408726193
H	7.88028415536917	5.08501276865207	7.93019175303274
C	4.99646169764614	1.72521602142107	5.53440346538930
H	5.32014324614273	2.48150757864335	6.28764886119885
H	4.16514912048845	2.19477617709207	4.95923994701959
C	4.73543451501161	0.46827543255688	7.63396132209232
C	6.21241798151963	0.45949623144873	8.03033576727479
H	4.24850264053936	-0.45504721699738	8.01623992238680
H	4.22016117264524	1.32471508375510	8.15029191420781
H	6.73360237523224	-0.41092430301402	7.57984099502246
H	6.31092100204329	0.39195227628824	9.13308403245015
H	6.73157561834027	1.38844945817038	7.71673538171415
C	3.15893755012772	0.11042205475934	5.79761706758141
C	3.03193801917339	-0.32065072046888	4.33421928880873
H	2.41049108533293	0.92534061128468	6.00913694045226
H	2.86313425255913	-0.74285075463194	6.44526177153015

H	3.27473614049432	0.50494902468398	3.63337530232056
H	1.99299437139018	-0.64053899382009	4.11205510645285
H	3.71604302014176	-1.16541476978385	4.11379298668716

Table S3. TD-DFT calculation results in the UV region

Note: The density difference in Figure 4 corresponds to the transition at 214.8 nm.

sWavelength (nm)	Oscillator Strength (arb. units)
384.6	0.000391632
288.1	0.003666203
277.4	0.000136559
275.0	0.026216805
256.9	0.006504681
257.3	0.002909365
244.0	0.002791437
238.0	0.004144694
216.0	0.002644470
229.0	0.001829772
210.4	0.005750149
222.1	0.030206657
214.8	0.060790309
216.4	0.005409655
212.0	0.005098303
204.3	0.031057306
203.1	0.021005109
196.2	0.003763692
200.6	0.000742650
197.5	0.031121178
203.9	0.018545091
195.6	0.002877630
198.0	0.000889426

Wavelength (nm)	Oscillator Strength (arb. units)
202.3	0.016137849
195.5	0.023372335
187.7	0.002101476
188.2	0.001260989
191.8	0.003287311
195.1	0.018168607
192.5	0.008828247

[1] CrysAlisPro, Rigaku Oxford Diffraction, Tokyo, Japan.
[2] Sheldrick, G.M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2015**, *71*, 3-8.
[3] Sheldrick, G.M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112-122.
[4] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[5] Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.
[6] Neese, F. "Software update: the ORCA program system, version 4.0." Wiley Interdisciplinary Reviews: Computational Molecular Science 8.1 (2018): e1327.
[7] Florian, W. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.