Supporting Information

Rare-earth-metal trimethylsilylmethyl ate complexes

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NMR Spectra



Figure S1. ¹H NMR spectrum (500 MHz) of $Li_3Y(CH_2SiMe_3)_6$ (1) in C_6D_6 at 26 °C. The solvent residual signal is marked with an asterisk, + denotes emerging SiMe₄ as the decomposition product.



Figure S2. ¹³C{¹H} NMR spectrum (125 MHz) of $Li_3Y(CH_2SiMe_3)_6$ (**1**) in [D₈]toluene at 26 °C. The solvent residual signals are marked with asterisks, + denotes residual Et₂O.



Figure S3. VT ¹H NMR spectrum (500 MHz) of $Li_3Y(CH_2SiMe_3)_6^{-1}$ (1) in [D₈]toluene, # denotes emerging decomposition product SiMe₄.





Figure S4b. ⁷Li VT NMR spectra (116 MHz) of Li₃Y(CH₂SiMe₃)₆ (1) in [D₈]toluene.



Figure S5. ²⁹Si INEPTND NMR spectrum (99 MHz) of $Li_3Y(CH_2SiMe_3)_6$ (1) in [D₈]toluene at 26 °C.



Figure S6a. ${}^{1}H{}^{89}Y$ NMR spectrum (25 MHz) of Li₃Y(CH₂SiMe₃)₆ (**1**) in [D₈]toluene at 26 °C. The solvent residual signals are marked with asterisks, **+** denotes residual Et₂O and # decomposition product SiMe₄.



Figure S6b. ${}^{1}H-{}^{89}Y$ NMR spectrum (25 MHz) of Li₃Y(CH₂SiMe₃)₆ (**1**) in [D₈]toluene at -40 °C. The solvent residual signals are marked with asterisks, **+** denotes decomposition product SiMe₄.





Figure S8. ⁷Li NMR spectrum (194 MHz) of decomposition products of **1** in C_6D_6 at 26 °C, # denotes LiCH₂SiMe₃.





in C_6D_6 at 26 °C, # denotes LiCH₂SiMe₃.



Figure S11. ${}^{1}H{}^{-89}Y$ HSQC NMR spectrum (25 MHz) of decomposition products of **1** in C₆D₆ at 26 °C. Solvent residual signal is marked with an asterisk, # denotes LiCH₂SiMe₃.



Figure S12. ¹H NMR spectrum (400 MHz) of the reaction of decomposition products of **1** with benzophenone in C_6D_6 at 26 °C.



Figure S13. ¹H NMR spectrum (500 MHz) of $[LiOC(CH_2SiMe_3)(Ph)_2]_4$ (**4**) in C₆D₆ at 26 °C, solvent residual signal is marked with an asterisk.



Figure S14. ¹³C{¹H} NMR spectrum (126 MHz) of $[LiOC(CH_2SiMe_3)(Ph)_2]_4$ (4) in C₆D₆ at 26 °C. The solvent residual signals are marked with an asterisk.



Figure S16. ²⁹Si DEPT45 NMR spectrum (99 MHz) of $[LiOC(CH_2SiMe_3)(Ph)_2]_4$ (4) in C₆D₆ at 26 °C.



Figure S17. ¹H NMR spectrum (500 MHz) of the reaction of $Li_3Y(CH_2SiMe_3)_6$ (1) with 6 equivs. benzophenone in [D₈]toluene at 26 °C, solvent residual signal is marked with asterisks.



Figure S18. ⁷Li NMR spectrum (194 MHz) of the reaction of $Li_3Y(CH_2SiMe_3)_6$ (1) with 6 equivs. benzophenone in [D₈]toluene at 26 °C. The main peak at 0.4 ppm corresponds to [LiOC(CH₂SiMe₃)(Ph)₂]₄ (4).



Figure S19. ${}^{1}H{}^{-89}Y$ HSQC NMR spectrum (25 MHz) of the reaction of Li₃Y(CH₂SiMe₃)₆ (1) with 6 equivs. benzophenone in [D₈]toluene at 26 °C, solvent residual signal is marked with asterisks.



Figure S20. ¹H NMR spectrum (500 MHz) of the reaction of LuCl₃ with 4 equivs. of LiCH₂SiMe₃ after workup in C₆D₆ at 26 °C. Solvent residual signal is marked with an asterisk, diethyl ether with #.



Figure S21. ¹³C{¹H} NMR spectrum (126 MHz) of the reaction of LuCl₃ with 4 equivs. of LiCH₂SiMe₃ after workup in C₆D₆ at 26 °C. Solvent residual signal is marked with an asterisk, diethyl ether with #.



Figure S22. ⁷Li NMR spectrum (194 MHz) of LuCl₃ with 4 equivs. of LiCH₂SiMe₃ after workup in C₆D₆ at 26 °C.



Figure S23. ¹H NMR spectrum (500 MHz) of the reaction of LuCl₃ with 4 equivs. of LiCH₂SiMe₃ after workup and addition of excess diethyl ether in C₆D₆ at 26 °C. Solvent residual signal is marked with an asterisk, diethyl ether with #.



Figure S24. ¹H NMR spectrum (500 MHz) of the reaction of ScCl₃ with 6 equivs. of LiCH₂SiMe₃ after workup in C₆D₆ at 26 °C. Solvent residual signal is marked with an asterisk.



Figure S25. ⁷Li NMR spectrum (194 MHz) of ScCl₃ with 6 equivs. of LiCH₂SiMe₃ after workup in C₆D₆ at 26 °C.



Figure S26. ⁴⁵Sc NMR spectrum (122 MHz) of ScCl₃ with 6 equivs. of LiCH₂SiMe₃ after workup in C₆D₆ at 26 °C.



Figure S27. ¹H NMR spectrum (500 MHz) of the reaction of ScCl₃(thf)₃ with 2.9 equivs. of LiCH₂SiMe₃ in C₆D₆ at 10 °C. Solvent residual signal is marked with an asterisk.



Figure S28. ⁷Li NMR spectrum (194 MHz) of the reaction of $ScCl_3(thf)_3$ with 2.9 equivs. of LiCH₂SiMe₃ in C₆D₆ at 10 °C.



Figure S29. ²⁹Si INEPTND NMR spectrum (99 MHz) of the reaction of ScCl₃(thf)₃ with 2.9 equivs. of LiCH₂SiMe₃ in C₆D₆ at 10 °C.



Figure S30. ${}^{1}\text{H}-{}^{29}\text{Si}$ HSQC NMR spectrum (99 MHz) of the reaction of ScCl₃(thf)₃ with 2.9 equivs. of LiCH₂SiMe₃ in C₆D₆ at 10 °C. Solvent residual signal is marked with an asterisk, the resonance of Sc(CH₂SiMe₃)₃(thf)₂ is marked with #.



Figure S31. ⁴⁵Sc NMR spectrum (122 MHz) of the reaction of ScCl₃(thf)₃ with 2.9 equivs. of LiCH₂SiMe₃ in C₆D₆ at 10 °C.



of LiCH₂SiMe₃ in C₆D₆ compared with Sc(CH₂SiMe₃)₃(thf)₂ in [D₈]toluene. Solvent residual signals are marked with asterisks.



Figure S33. Stacked ⁴⁵Sc NMR spectra (122 MHz) of (from bottom to top) the reaction of $ScCl_3(thf)_3$ with 2.9 equivs. of $LiCH_2SiMe_3$, $ScCl_3$ with 6 equivs. of $LiCH_2SiMe_3$, $Sc(CH_2SiMe_3)_3(thf)_2$ and $[Li(thf)_4][Sc(CH_2SiMe_3)_4]$ in C_6D_6 .



Figure S34. ¹H NMR spectrum of $[Li(thf)_4][La(CH_2SiMe_3)_4(thf)]$ (**3**) (500.13 MHz, $[D_8]$ toluene, -40 °C). The solvent residual signals are marked with asterisks. Residual Et₂O is marked #.



Figure S35. ¹³C{¹H} NMR spectrum of $[Li(thf)_4][La(CH_2SiMe_3)_4(thf)]$ (**3**) (125.76 MHz, $[D_8]$ toluene, -40 °C). The solvent residual signals are marked with asterisks. Residual Et₂O is marked #.



Figure S1. ⁷Li NMR spectrum of $[Li(thf)_4][La(CH_2SiMe_3)_4(thf)]$ (**3**) (194.37 MHz, $[D_8]$ toluene, -40 °C). LiCl is marked with # and unknown impurities are marked with ~.



Figure S37. ¹H NMR spectra of $[Li(thf)_4][La(CH_2SiMe_3)_4(thf)]$ (**3**) at -40 °C (bottom) after 1 h at ambient temperature (middle) and after 5 d at ambient temperature (top), (bottom 500.13 MHz, [D₈]toluene, -40 °C), (middle 500.13 MHz, [D₈]toluene, 26 °C), (top 400.11 MHz, [D₈]toluene, 26 °C). SiMe₄ is marked with #.



Figure S38. ¹H NMR spectra of LiCH₂SiMe₃ at -40 °C (bottom) and at ambient temperature (top), (bottom 500.13 MHz, [D₈]toluene, -40 °C), (top 500.13 MHz, [D₈]toluene, 26 °C) solvent residual signals are marked with asterisks.



Figure S39. ⁷Li NMR spectra of LiCH₂SiMe₃ at -40 °C (bottom, 194.37 MHz, [D₈]toluene) and at 26 °C (top, 194.37 MHz, [D₈]toluene).

X-Ray Crystallography

Table S1. Crystallographic Data for Compound 1, 2 and 3

	1	2 ^[d]	3
formula	C ₂₄ H ₆₆ Li ₃ Si ₆ Y	$C_{48}H_{120}Li_2O_4Sc_2Si_8$	C ₃₆ H ₈₄ LaLiO ₅ Si ₄
CCDC	2215408	2215407	2215409
M _r [g mol ⁻¹]	633.03	1089.95	855.24
colour	colourless	colourless	colourless
crystal dimensions [mm]	0.194 x 0.142 x 0.067	0.306 x 0.288 x 0.260	0.542 x 0.359 x 0.298
cryst syst	Monoclinic	Triclinic	Monoclinic
space group	Сс	P1	P21/c
a [Å]	18.9631(17)	13.0921(6)	17.4785(18)
b [Å]	10.3876(10)	13.0811(6)	15.0572(16)
c [Å]	40.329(4)	21.0745(15)	20.279(2)
α [°]	90	90.0230(13)	90
β [°]	96.829(2)	90.093(14)	112.9880(10)
γ [°]	90	90.071(9)	90
<i>V</i> [Å ³]	7887.8(13)	3609.2(3)	4913.2(9)
z	8	2	4
<i>T</i> [K]	100(2)	100(2)	100(2)
$ ho_{calcd}$ [g cm ⁻³]	1.066	1.003	1.156
μ [mm ⁻¹]	1.672	0.353	0.999
F (000)	2736	1200	1824
θ range [°]	2.034/26.464	1.555/22.241	2.051/29.706
unique reflns	16149	13964	13924
collected refins	53733	17319	84117
$R_1^{[a]}/wR_2(I>2\theta)^{[b]}$	0.0433 /0.0795	0.0894/0.2093	0.0349/0.0775
R1 ^[a] /wR2(all data) ^[b]	0.0685/0.0875	0.1113/0.2272	0.0520/0.0868
GOF ^[c]	0.884	1.037	1.021

 $\frac{[c]}{[c]}GOF = [\Sigma w(Fo^2 - Fc^2)^2 / (no - np.)]^{1/2} \cdot \frac{[a]}{[a]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[a]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[a]}{[c]}R1 = \Sigma (||Fo| - |Fc||) / \Sigma |Fo|, Fo > 4\sigma(F0) \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2)^2]\}^{1/2} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2]} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2] \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2]} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2]} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2] \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2]} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)^2]} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo^2 - Fc^2)^2 / \Sigma [w(Fo^2 - Fc^2)]} \cdot \frac{[c]}{[c]}wR2 = \{\Sigma [w(Fo$

^[d] Metric seems to be tetragonal, but refinement was not possible (wR₂ = 0.70). The crystals had poor quality and only reflections up to 0.93 Å could be collected. Additional disorder was found but could not be resolved reliably due to the missing high resolution data.



Figure S40. Comparison of the crystal structures of $Li_3Y(CH_2SiMe_3)_6$ (**1**, left) and hexameric [LiCH₂SiMe₃]₆ (right) (ellipsoids set to the 50 % probability level, hydrogen atoms omitted for clarity). Selected interatomic distances (Å) and angles (°) for complex **1**: Y1–C1 2.362(6), Y1–C5 2.628(7), Y1–C9 2.515(6), Y1–C17 2.467(7), Y1–C21 2.620(7), Y1–Li1 2.838(10), Y1–Li2 2.846(11), Y1–Li3 2.936(11), Li1–Li3 2.582(15), Li2–Li3 2.670(15), Li1–C5 2.259(14), Li1–C9 2.209(12), Li1–C13 2.244(12), Li2–C13 2.294(12), Li3–C13 2.163(13), Li2–C17 2.155(13), Li2–C21 2.267(13), Li3–C5 2.226(13), C1–Si1 1.842(6), C5–Si2 1.863(7), C9–Si3 1.861(7), C13–Si4 1.855(7), C17–Si5 1.858(7), C21–Si6 1.857(7); Y1–C1–Si1 128.4(3), Y1–C5–Si2 118.8(3), Y1–C5–Li1 70.5(3), Y1–C5–Li3 73.9(3), Y1–C9–Si3 120.3(3), Y1–C9–Li1 73.5(3), Y1–C17–Si5 153.8(4), Y1–C17–Li2 75.7(3), Y1–C21–Si6 159.0(3), Y1–C21–Li2 70.8(3), Y1–C21–Li3 74.6(3), Li1–Y1–Li2 81.0(3), Li1–Li3–Li2 89.3(5). Bottom: Illustration of distorted trigonal pyramid consisting of Li1–Li2–Li3–Y1 subunit of complex **1**.



Figure S41. Crystal structure of one of the crystallographically independent molecules of $[Li(thf)_4][LiSc_2(CH_2SiMe_3)_8]$ (2) (ellipsoids set to 50 % probability level). All hydrogen atoms and disorders were omitted for clarity. Carbon atoms of THF and the SiMe_3 groups were rendered as wireframes. Selected interatomic distances (Å) and angles (°): Sc1–C1 2.27(3), Sc1–C5 2.344(14), Sc1–C9 2.24(3), Sc1–C13 2.169(14), Sc2–C17 2.190(14), Sc2–C21 2.348(17), Sc2–C25 2.29(3), Sc2–C29 2.22(3), C1–Si1 1.84(3), C5–Si2 1.867(16), C9–Si3 1.80(3), C13–Si4 1.914(14), C17–Si5 1.891(15), C21–Si6 1.882(18), C25–Si7 1.78(3), C29–Si8 1.87(3), Sc1–Li1 2.80(2), Sc2–Li1 2.82(2), Li2–O1_1 1.82(3), Li2–O1_2 1.92(4), Li2–O1_3 1.87(4), Li2–O1_4 1.89(4); Sc1–C1–Si1 119.7(15), Sc1–C5–Si2 132.4(7), Sc1–C9–Si3 125.5(16), Sc1–C13–Si4 112.8(7), Sc2–C29–Si8 123.3(14), Sc1–Li1–Sc2 165.7(10).



Figure S42. Crystal structure of $[Li(thf)_4][La(CH_2SiMe_3)_4(thf)]$ (**3**) (ellipsoids set to 50% probability level). Hydrogen atoms and disorders of the THF groups are omitted for clarity. Selected interatomic distances (Å) and angles (°): La1–C1 2.598(3), La1–C5 2.605(2), La1–C9 2.605(2), La1–C13 2.614(2), La1–O1 2.6895(18), C5–La1–O1 176.18(7), C1–La1–C5 96.29(8), C9–La1–C5 97.48(7), C13–La1–C5 104.11(8), C1–La1–C9 111.84(8), C9–La1–C13, 121.47(8), C1–La1–C13 118.72(8).