Supplementary Material (ESI) for Chemical Communications

Manganese(II)-lithium and -sodium inverse crown ether (ICE) complexes

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Experimental Section

General Methods:

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. *n*-Hexane was dried by heating to reflux over sodium and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C. GC-MS examinations were recorded on a Trace GC (ZBS-ms column; 30m, 0.25x0.25 mm^2)/ Thermo Finnegan Polaris Q. Data for X-ray crystal structure determination were obtained with a Nonius Kappa CCD using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), elemental analyses were carried out on a Perkin Elmer 2400 elemental analyzer.

Crystal data for 1: $C_{36}H_{72}Li_2Mn_2N_4O$, M_r = 700.74, monoclinic, *space group C2/c*, a = 16.9678(6), b= 17.0135(6), c= 15.7137(5) Å, β= 118.803(2) °, V = 3975.0(2) Å^3, Z = 4, λ = 0.71073 Å, μ = 0.666 mm^{-1}, T = 173 K; 28348 reflections, 3894 unique, R_{int} 0.080; final refinement to convergence on F^2 gave R = 0.0437 (F, 2648 obs. data only) and R_w = 0.0993 (F^2, all unique data), *GOF* = 1.040.

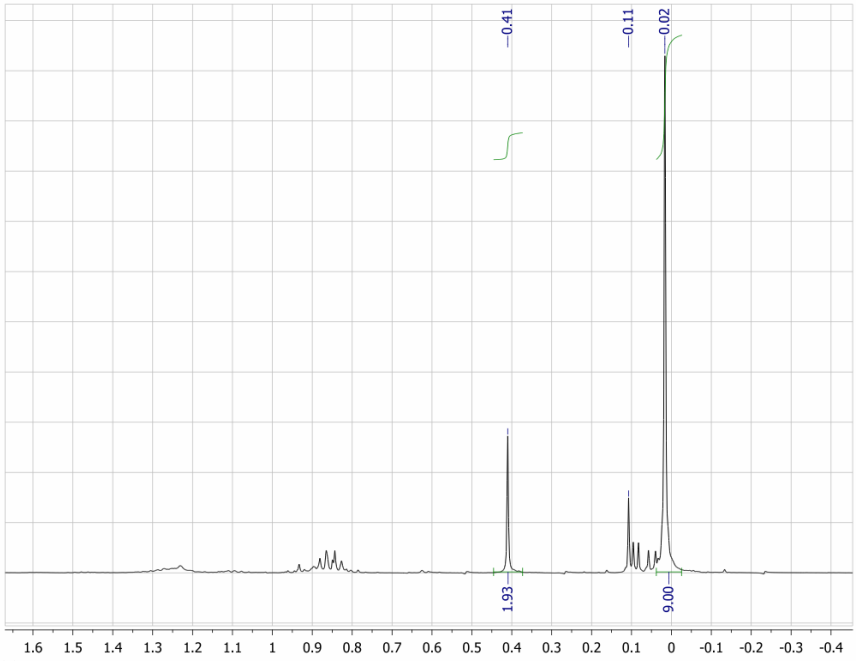
Synthesis of Na(HMDS)$_2$Mn(CH$_2$SiMe$_3$) 4: To a suspension of Na-*n*Bu (0.16g, 2.0 mmol) in 20 ml *n*-hexane two equivalents of HMDS(H) (0.84 mL, 4.0 mmol) were added to form a 1:1 mixture of NaHMDS and HMDS(H). Then Mn(CH$_2$SiMe$_3$)$_2$ (0.46 g, 2.0 mmol) was added, and the colour of the suspension changed from orange to colourless. Heating afforded a transparent colourless solution. On cooling at 0°C pale pink

crystals were obtained (0.72 g, 74.1%). Elemental analysis: Found: C, 39.25; H, 10.2; N, 5.7. Calc. for $C_{16}H_{47}MnN_2NaSi_5$: C, 39.55; H, 9.75; N, 5.8.
Crystal data for 4: $C_{16}H_{47}MnN_2NaSi_5$, M_r = 485.94, triclinic, *space group* $P\bar{1}$, a = 10.2226(3), b= 11.9296(3), c= 12.0857(3) Å, α= 97.180(1), β= 100.700(1), γ= 93.377(1) °, V = 1431.78(7) Å^3, Z = 2, λ = 0.71073 Å, μ = 0.690 mm^{-1}, T = 150 K; 32095 reflections, 6576 unique, R_{int} 0.051; final refinement to convergence on F^2 gave R = 0.0329 (F, 5179 obs. data only) and R_w = 0.0774 (F^2, all unique data), GOF = 1.021.

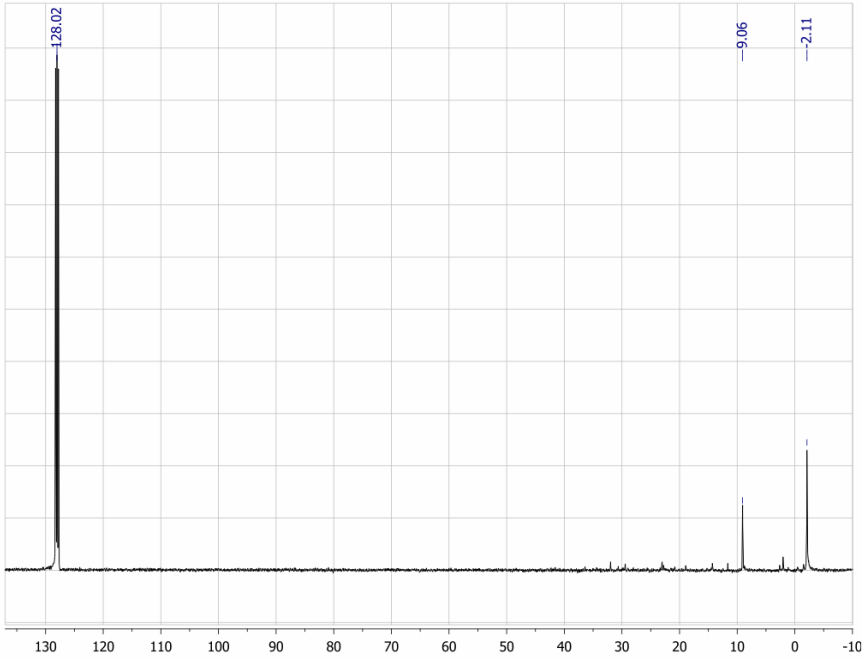
Synthesis of $Na_2Mn_2(HMDS)_4O$ 5: A suspension of **4** is prepared as explained above and under stirring air is allowed to enter for 1h through a drying tube filled with $CaCl_2$. The colour changes slowly to a dark green. When the stirring is stopped, a precipitation can be observed, which dissolves when the solution is heated. After cooling the solution pale pink crystals of **4** and pale green crystals of **5** can be obtained.
Crystal data for 5: $C_{24}H_{72}Mn_2N_4Na_2OSi_8$, M_r = 813.44, triclinic, *space group* $P\bar{1}$, a = 8.8889(2), b= 10.8003(3), c= 12.7193(4) Å, α= 95.656(1), β= 108.382(1), γ= 98.832(1) °, V = 1130.89(5) Å^3, Z = 1, λ = 0.71073 Å, μ = 0.812 mm^{-1}, T = 150 K; 29980 reflections, 7145 unique, R_{int} 0.042; final refinement to convergence on F^2 gave R = 0.0315 (F, 5578 obs. data only) and R_w = 0.0745 (F^2, all data), GOF = 1.029.

Identification of $Me_3SiCH_2CH_2SiMe_3$ by ^{1}H- and ^{13}C-NMR spectroscopy and GC-MS (GC-MS were performed with the C_6D_6 solution used for NMR spectroscopy):

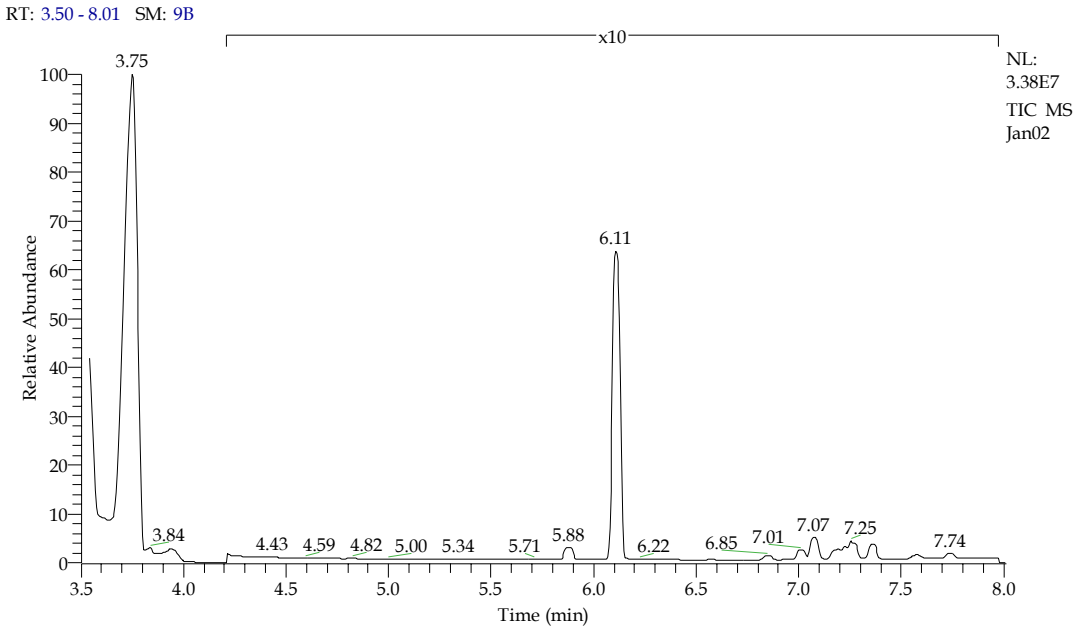
^{1}H-NMR spectrum of $Me_3SiCH_2CH_2SiMe_3$ in C_6D_6 solution:

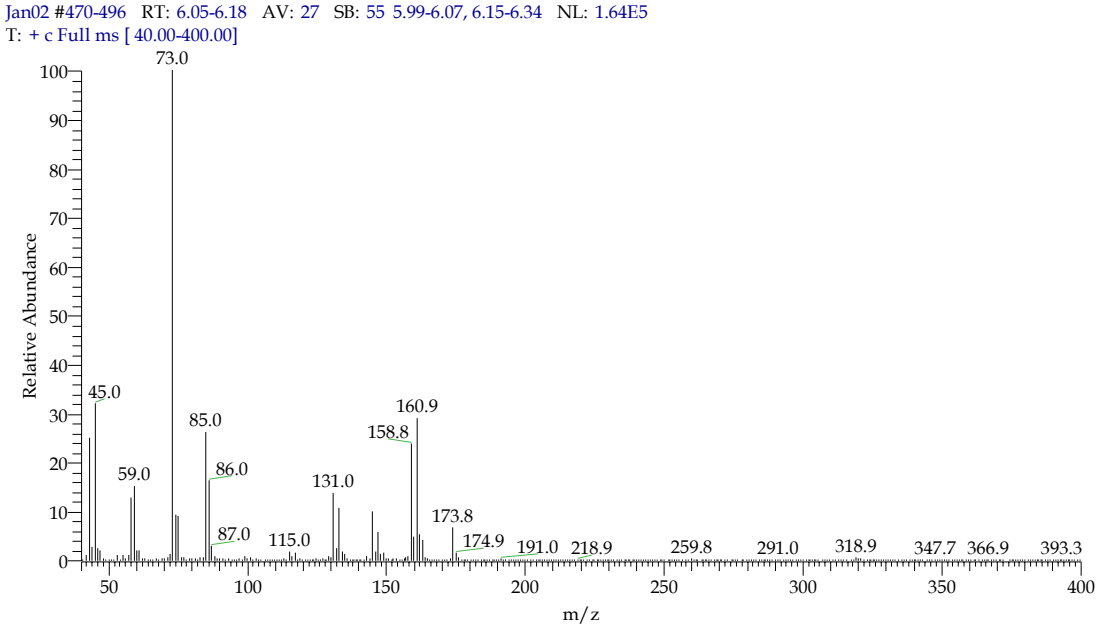


^{13}C-NMR spectrum of $Me_3SiCH_2CH_2SiMe_3$ in C_6D_6 solution:



GC-MS of $Me_3SiCH_2CH_2SiMe_3$ in C_6D_6 solution:





For this MS spectrum the MS library shows high possibilities for two compounds:
Me_3Si-CHMe-$SiMe_3$ and Me_3Si-CH_2CH_2-$SiMe_3$; in combination with the NMR spectra the second solution could be confirmed.

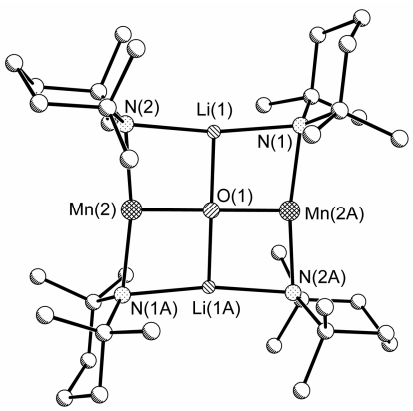


Fig. S1 Molecular structure of **1** with hydrogen atoms and minor disorder components omitted for clarity. Selected bond lengths (Å) and bond angles (°): Li(1)-O(1) 1.9334(6), Mn(2)-O(1) 1.9368(5), Li(1)-N(1) 2.1311(17), Li(1)-N(2) 2.1344(17), Mn(2)-N(1) 2.1266(18), Mn(2)-N(2) 2.0995(17), Li(1)-O(1)-Mn(2) 90.26(5), Mn(2)-O(1)-Mn(2A) 180.00(2), O(1)-Li(1)-N(1) 94.73(5), O(1)-Li(1)-N(2) 94.47(5), O(1)-Mn(2)-N(1) 94.78(5), O(1)-Mn(2)-N(2) 95.46(5).

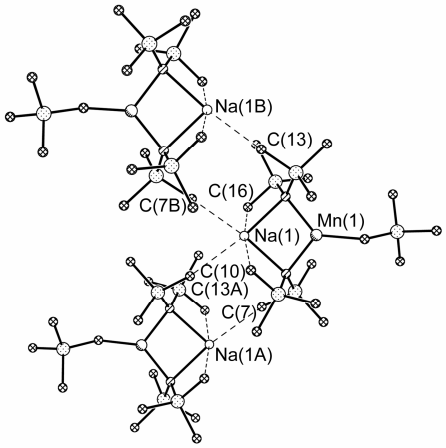


Fig. S2 Section of the polymeric chain structure of **4** showing intramolecular and intermolecular Na…Me contacts as broken lines.

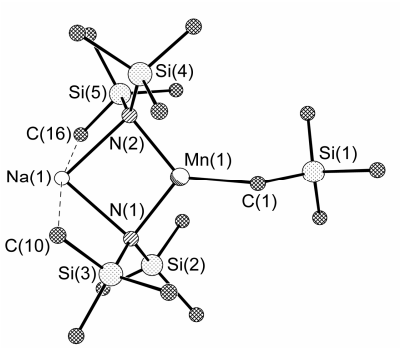


Fig.S3 Dinuclear unit of **4** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mn(1)-C(1) 2.117(2), Mn(1)-N(1) 2.1291(14), Mn(1)-N(2) 2.1345(14), Na(1)-N(1) 2.4493(15), Na(1)-N(2) 2.4655(15), Na(1)-C(10) 2.768(2), Na(1)-C(16) 2.734(2), Na(1)-C(13A) 2.882(2), Na(1)-C(7B) 3.121(2), N(1)-Mn(1)-N(2) 103.73(5), C(1)-Mn(1)-N(2) 122.66(10), C(1)-Mn(1)-N(2) 131.38(10), N(1)-Na(1)-N(2) 86.05(5).