

Synthesis and structure of cationic guanidinate-bridged bimetallic $\{\text{Li}_7\text{M}\}$ cubes (M = Mn, Co, Zn) with inverse crown counter anions†

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The reactions of the heteroleptic lithium amide $[\text{Li}_3(\mu\text{-hmds})_2(\mu,\mu\text{-hpp})]$ (**1**), where $[\text{hmds}]^-$ = hexamethyldisilazide and $[\text{hpp}]^-$ = hexahydropyrimidopyrimidide, with MnCl_2 , CoCl_2 or ZnBr_2 result in the formation of the separated ion-pairs $[\text{MLi}_7(\mu_8\text{-O})(\mu,\mu\text{-hpp})_6]^+[\text{A}]^-$, which each consist of a $\{\text{MLi}_7\}$ oxo-centred cube structural motif (M = Mn **2**, Co **4**, Zn **5**), with each face of the cube being bridged by an $[\text{hpp}]^-$ ligand. In the case of M = Mn and Co, the counter ion, $[\text{A}]^-$, is the pentagonal anionic inverse crown $[\{\text{Li}(\mu\text{-hmds})\}_5(\mu_5\text{-Cl})]^-$ (**3**), whereas the reaction with M = Zn produces the known tris-amido zincate $[\text{Zn}(\text{hmds})_3]^-$ counter anion.

Introduction

Serendipitous assembly is a successful method for the synthesis of polymetallic cage compounds.¹ With this method, a pro-ligand with molecular symmetry and structure likely to encourage cage formation is combined with a simple metal-containing precursor, such as a metal halide, in an appropriate solvent. The reaction between the various components then proceeds such that specific outcomes are not targeted. Rather, the chemical and physical conditions of the reaction result in the product self assembling to give a stable arrangement of ligands and metal atoms. The strategy has been put to particularly effective use in the synthesis of transition metal cages, based predominantly on μ -(*O*-donor) ligands.² Not only are the structures of the self-assembled compounds intrinsically interesting, the reliability and scope of the synthetic method, most notably in the case of transition metals, has allowed such cage compounds to be developed as single molecule magnets and as magnetic refrigerants.^{3,4}

The importance of the serendipitous assembly method for the synthesis of oxygen-bridged transition metal cages has prompted us to combine our interests in this area with our interests in the structures of alkali metal complexes of functionalized amido ligands.⁵ Here, our aim is to select N–H acidic nitrogen-containing heterocyclic ligands whose structures should encourage metal cage formation, and then to metallate these heterocycles with alkali

metals. Subsequently, the alkali-metallated heterocycles can be used as ligand sources in salt metathesis reactions with transition metal halides, allowing access to nitrogen-bridged polymetallic transition metal cages. In addition to the new structural chemistry of transition metal amides that could be developed, this method also potentially allows access to a range of cage compounds with magnetic properties that are influenced by μ -amido ligands rather than by μ -(*O*-donor) ligands.

Results and discussion

We now report the synthesis and structure of the heteroleptic trilithium complex $[\text{Li}_3(\mu\text{-hmds})_2(\mu,\mu\text{-hpp})]$ (**1**) ($[\text{hmds}]^-$ = hexamethyldisilazide, $[\text{hpp}]^-$ = hexahydropyrimidopyrimidide), and its reaction with d-block metal(II) halides, namely manganese(II) chloride, cobalt(II) chloride and zinc bromide. The reactions of **1** with MnCl_2 or with CoCl_2 result in the formation of separated ion-pairs consisting of the guanidinate-bridged, oxo-centred cationic metal cubes $[\text{MLi}_7(\mu_8\text{-O})(\mu,\mu\text{-hpp})_6]^+$ (M = Mn **2**, M = Co **4**), which in the case of each transition metal is accompanied by formation of the new anionic inverse crown $[\{\text{Li}(\mu\text{-hmds})\}_5(\mu_5\text{-Cl})]^-$ (**3**). The reaction of **1** with ZnBr_2 produces a separated ion pair consisting of the cage complex $[\text{ZnLi}_7(\mu_8\text{-O})(\mu\text{-hpp})_6]^+$ (**5**), which is isostructural to **2** and **4**, and the known tris(amido) zincate counter anion $[\text{Zn}(\text{hmds})_3]^-$.

Compound **1** was synthesized by adding three equivalents of $[\text{Li}(\text{hmds})]$ to one of hppH in toluene. A standard work-up of the reaction followed by storage of a concentrated toluene solution at -4°C produced pale yellow crystals of **1** (Scheme 1). X-ray diffraction revealed that two independent molecules of **1**, **1a** and **1b**, are found in the unit cell. The structures of **1a** (Fig. 1) and **1b** are essentially identical, and that of **1b** is shown in Fig. S1.† The pyramidal coordination environments of Li(1/1A) in **1a** consist of one $[\text{hmds}]^-$ nitrogen and both nitrogens of the $[\text{hpp}]^-$ ligand,

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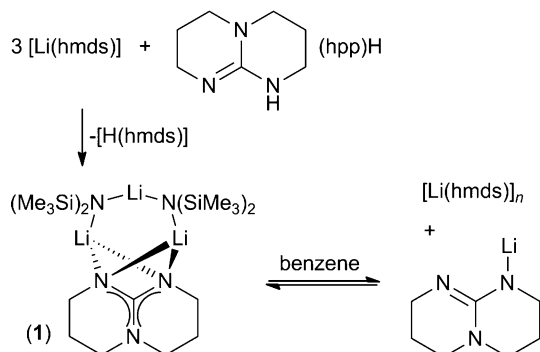
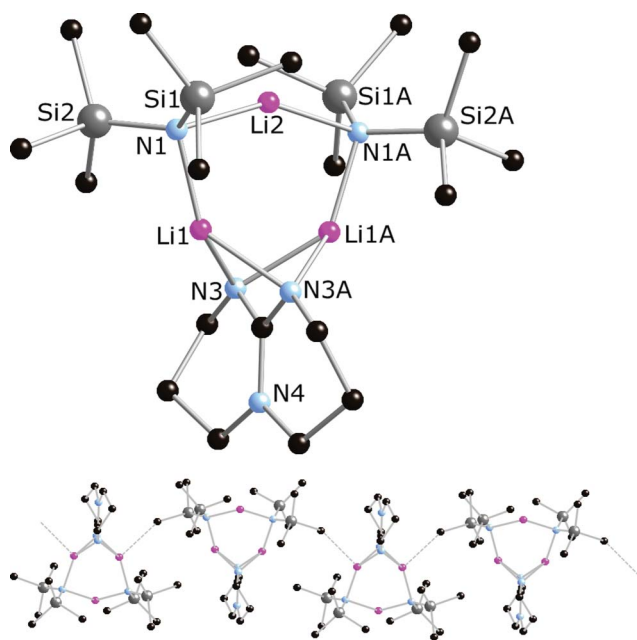
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Table 1 Metal–ligand bond distances [Å] for **1a** and for the cations **2**, **4**, and **5**

	1a	2	4	5
Li/M–O	—	2.072(10)–2.192(7)	2.0371(14), 2.0298(15)	1.983(5)–2.072(7)
Li/M–N	—	1.999(8)–2.192(7)	1.990(3)–2.092(3)	1.970(7)–2.169(7)
Li–O	—	—	2.001(3), 2.065(3)	—
Li–N	1.959(17)–2.091(13)	—	2.054(4)–2.082(2)	—

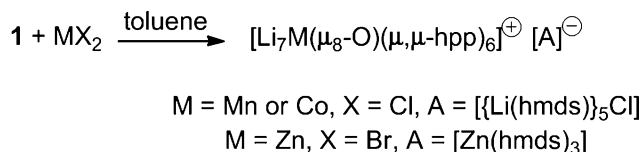
**Scheme 1****Fig. 1** Molecular structure of **1a** (upper), and the interactions between **1a** and **1b** (lower). Li = pink, N = blue, Si = grey.

resulting in Li(1)–N(1) and Li(1)–N(3) bond distances of 1.959(17) and 2.091(13) Å, respectively (Table 1). The bent, two-coordinate environment of Li(2) consists of two [hmnds][−] ligands, with the Li(2)–N(1) distance being 1.998(8) Å, and the N(1)–Li(2)–N(1A) angle 148.9(12)°. The molecular structure of **1a** (and of **1b**) can be regarded as being formed by substitution of an [hmnds][−] ligand in the unsolvated cyclic trimeric rings of [Li(hmnds)]₃⁶ with an [hpp][−] ligand from the guanidine-solvated dimer [Li(hpp){hpp(H)}]₂.⁷ In the extended structure of **1** (Fig. 1), molecules of **1a** and **1b** interact *via* CH⋯Li pseudo-agostic interactions involving the SiMe₃ substituents. This type of interaction has precedent in

the structure of methyllithium itself¹³ and in the structures of trimethylsilyl-containing organolithiums.⁹

The room-temperature ¹H NMR spectrum of **1** in benzene-d₆ consists of broad, overlapping resonances in the range δ(¹H) = 1.38–3.35 ppm, and a broad singlet at 0.22 ppm (Fig. S2–S4†). Although these resonances can be assigned to the ¹H environments in **1**, it is clear that a dynamic process is occurring. A variable-temperature ¹H NMR spectroscopic study revealed that the dynamic process can be suppressed on cooling toluene solutions to −40 °C, such that the solid-state molecular structure of **1** is observed intact. On warming to +70 °C, the resonances coalesce and sharpen, implying a dynamic equilibrium, probably involving dissociation of **1** into [Li(hpp)] and [Li(hmnds)] (Scheme 1, Fig. S5†).

The ease with which **1** can be synthesized, combined with the known ability of the [hpp][−] ligand to encourage cage formation,^{10,11} make this ligand a promising candidate for use in the synthesis of transition metal cages. To test this hypothesis, the reactions of **1** with anhydrous manganese(II) chloride, cobalt(II) chloride and zinc bromide were carried out. Addition of **1** to MnCl₂ produced an amber-coloured solution after stirring, and following hot filtration of the reaction mixture and then storage of the solution, amber crystals of [MnLi₇(μ₈-O)(μ,μ'-hpp)₆][{Li(μ-hmnds)}₅(μ₅-Cl)]·(2 toluene), **[2][3]**·(2 toluene), formed. The same method using either CoCl₂ or ZnBr₂ produced large blue crystals of [CoLi₇(μ₈-O)(μ,μ'-hpp)₆][{Li(μ-hmnds)}₅(μ₅-Cl)]·(2 toluene), **[4][3]**·(2 toluene), or yellow crystals of [ZnLi₇(μ₈-O)(μ,μ'-hpp)₆][Zn(hmnds)₃], **[5][Zn{N(SiMe₃)₂]₃**, respectively (Scheme 2).

**Scheme 2**

The structures of the [MLi₇(μ₈-O)(μ,μ'-hpp)₆]⁺ cations (M = Mn, Co, Zn) are essentially identical, hence only **4** will be discussed in detail. Key bond lengths for **2**, **4** and **5** are shown for comparison in Table 1, and the structures of **2** and **5** are shown in Fig. S6 and S7.† The structure of **4** (Fig. 2) consists of a μ₈-oxo-centred {CoLi₇} cube, and each face of the cube is bridged by two nitrogens of an [hpp][−] ligand. Four of the eight metal positions in **4** are mixed positions of cobalt and lithium, *i.e.* Co(1)/Li(1) and Co(2)/Li(2), both in a ratio of one quarter to three quarters. Each metal atom in **4** resides in a distorted tetrahedral environment that consists of the oxo ligand and three [hpp][−] nitrogens. The mixed position Li(1)/Co(1)–O(1) bond lengths are 2.0371(14) and 2.0298(15) Å, and the Co/Li–N bond lengths are in the range 1.990(3)–2.092(3) Å (average 2.042 Å).

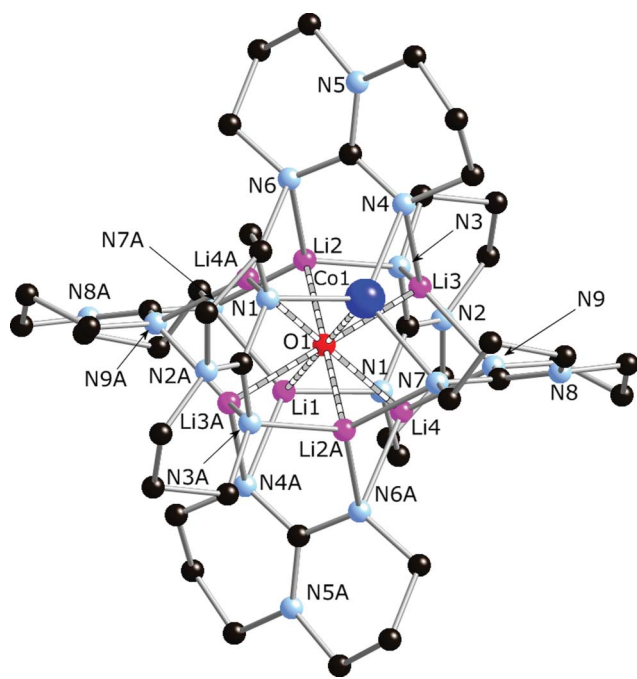


Fig. 2 Molecular structure of the cation **4**. Co = dark blue.

For the fully occupied lithium positions, the Li–O bond lengths are 2.001(3) and 2.065(3) Å, and the range of Li–N bond lengths is 2.054(4)–2.082(4) Å (average 2.065 Å). A thermal ellipsoid plot of **4** is shown in Fig. S11.†

The manganese atom in the cation **2** is disordered over the four sites of the asymmetric unit, i.e. all eight metal positions of the {MnLi₇} cube, with occupancies of 22, 16, 9 and 3 per cent. The zinc atom in **5** is disordered over all eight of the metal positions in the {ZnLi₇} cube, with occupancies of 31, 5, 25, 11, 14, 7, 1 and 6 per cent.

The anion **3** in **[4][3]** (Fig. 3) consists of a pentagonal arrangement of lithium cations bridged by a μ₅-chloro ligand, with each pair of adjacent lithiums being bridged by a μ-[hmds][−] ligand. The Li(5)–Cl(1) bond coincides with a mirror plane. The range of Li–Cl distances in **3** is 2.445(4)–2.458(7) (average 2.449 Å), and the Li–N

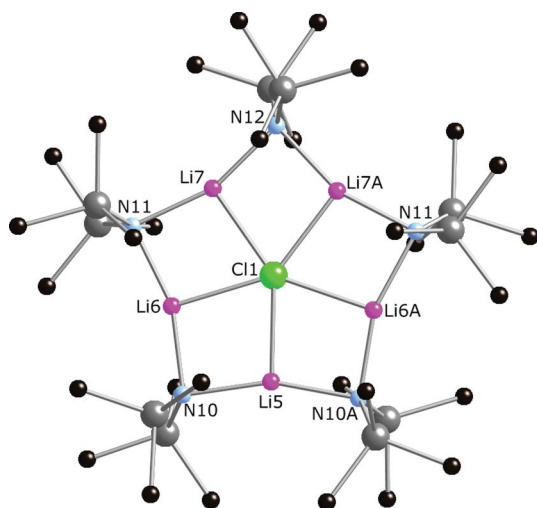


Fig. 3 Structure of the anion **3**. Chloride = green.

distances are in the range 2.050(5)–2.064(5) Å (average 2.058 Å). The chloride ion in **3** is co-planar with the lithium cations. The anion **3** in **[2][3]** is essentially isostructural with that in **[4][3]** (Fig. S7†).

In contrast to the reactions of **1** with MnCl₂ and CoCl₂, the reactions of **1** with ZnBr₂ produce a cation-anion pair in which the anion is the trigonal planar tris(amido) zincate [Zn(hmds)₃][−] (Fig. S18†), the structure of which has been reported previously by others.¹² In terms of the counter anion, we attribute the different outcome in the case of **[5][Zn(hmds)₃]** to the greater radius of the bromide anion, which presumably is too great to enable it to act as a template in the formation of a crown based on [Li(hmds)] units.

Analytically pure samples of **[2][3]**, **[4][3]** and **[5][Zn(hmds)₃]** were obtained by placing the crystalline materials under vacuum. In the case of **[2][3]** and **[4][3]** the lattice toluene was evaporated. The Q-band EPR spectrum of **[2][3]** (Fig. S10†) recorded at 5 K features a broad resonance centred on 11963 G (*g* = 2.001). The resonance is a six-line multiplet with a separation of 80 G between the components of the multiplet. The EPR spectrum is consistent with high-spin manganese(II). The X- and Q-band EPR spectra of **[4][3]** at 5 K show resonances at 1062 G (full width at half-maximum = 89 ± 1.5 G) and 3650 G (full width at half-maximum = 228 ± 4 G), respectively, consistent with *g*' = 6.518 ± 0.058, and there is an inflection in the X-band spectrum at 12040 G (*g*' = 0.588) (Fig. S15 and S16). These *g*-values fall within a typical range for low-symmetry Co(II) coordination environments.¹³

The paramagnetism of **[2][3]** resulted in the ¹H NMR spectrum of this compound consisting of a series of broad, overlapping resonances approximately in the region δ(¹H) = 0.9–3.6 ppm (Fig. S8†). These resonances are likely due to be due to the [hpp][−] protons, and the two sharp singlets at δ(¹H) = 0.29 and 0.10 ppm can be assigned to the SiMe₃ substituents (Fig. S9†). The ⁷Li NMR spectrum of **[2][3]** consists of three sharp resonances at δ(⁷Li) = 1.52, 1.92 and 2.39 ppm, and a broad resonance approximately in the range δ(⁷Li) = −0.5–3.5 ppm, centred on 1.71 ppm (Fig. S9†). Structural assignments based on the paramagnetic NMR spectra of **[2][3]** cannot be completely free from ambiguity, however the ⁷Li NMR spectrum may indicate that the compound exists as two components in benzene: one type that contains manganese(II) and one that does not, although there is no evidence to suggest that the solid-state structure of **[2][3]** is preserved in solution. Similarly, the paramagnetism of **[4][3]** resulted in the ¹H NMR spectrum of this compound consisting of a series of broad, low-intensity resonances in the region δ(¹H) = 0.79–4.45 ppm assignable to the hpp protons, two sharp singlets at δ(¹H) = 0.62 and 0.01 ppm assignable to the SiMe₃ substituents, and seven resonances at lower field with δ(¹H) = 15.14–44.72 ppm (Fig. S13†). The ⁷Li NMR spectrum of **[4][3]** consists of four sharp resonances in the region δ(⁷Li) = 2.33–2.86 ppm, and six broad, overlapping resonances in the region δ(⁷Li) = −0.06–2.17 ppm (Fig. S14†). As with **[2][3]**, the NMR spectroscopic data may again indicate that **[4][3]** exists as a cobalt(II)-containing component and a lithium-only component.

The ¹H and ¹³C NMR spectra of **[5][Zn(hmds)₃]** in benzene show environments characteristic of the [hpp][−] and [hmds][−] ligands (Fig. S19 and S20†). Thus the ¹H NMR spectrum consists of group of mutually coupled resonances in the region δ(¹H) = 3.43–1.54 ppm corresponding to the [hpp][−] environments and sharp singlets at 0.81 and 0.10 ppm corresponding to the SiMe₃ substituents. The ¹³C NMR spectrum has the [hpp][−] environments at δ(¹³C) = 25.42,

45.46, 49.66 and 162.11 ppm and a trimethylsilyl resonance at $\delta(^{13}\text{C}) = 2.62$ ppm.

The structures of the cationic cubes **2**, **4** and **5** are similar to that of μ_8 -hydride-containing cation $[\text{Li}_8(\mu_8\text{-H})(\text{hpp})_6]^+$, which has been reported with several different counter anions, including $[\text{Zn}^+\text{Bu}_3]^-$.¹⁴ The observation of μ_8 -oxo ligands in molecular compounds is rare. A search of the Cambridge Structural Database reveals that the few previously reported μ_8 -oxo compounds are based entirely on alkali metals,¹¹ meaning that the cations **2**, **4** and **5** are the first d-block metal complexes of μ_8 -oxo ligands. The oxygen-scavenging ability of alkali metal organometallics is well known.¹⁵ Indeed, several examples of oxo-containing lithium organozincates are known in which μ_n -oxo ligands ($n = 3\text{--}6$) derive either from molecular oxygen or from adventitious water from the reaction solvent.¹⁶ A lithium-manganese(II) amido inverse crown ether has also been shown to be able to accommodate a μ_4 -oxo ligand.¹⁷ The oxygen scavenging ability of bimetallic alkali metal organometallics is seen consistently with the synthesis of **[2][3]**, **[4][3]** and **[5][Zn(hmds)₃]**. Molecular oxygen is unlikely to be the source of the oxo ligands in the three $\{\text{MLi}_7\}$ cubes because performing the syntheses using rigorous anaerobic conditions either with a Schlenk line or in an efficient glove box (dioxygen levels less than 0.5 ppm) does not affect the outcome. The μ_8 -oxo ligand in the structure of the cation **2** therefore most likely derives from the presence of adventitious water in the toluene solvent. To test this hypothesis, a small amount of degassed water was added to rigorously dried toluene (approximately 50 μL in 15 mL) and stirred vigorously for 30 min, and the mixture then subsequently added to MX_2 . A dry toluene solution of **1** was then added to the suspension of MX_2 , and following the same reaction time and workup conditions as in the case of the serendipitous formation of the oxo-centred cubes, formation of crystalline **[2][3]**, **[4][3]** and **[5][Zn(hmds)₃]** was again observed, but in slightly higher yields.

The structural chemistry of lithium amido zincates^{16,18,19} and, to a lesser extent, lithium amido manganates^{9,17,20,21} has been investigated in some detail. In recent years, interest in both types of amido metallate has increased substantially owing to their applications as superbasic metallating reagents.^{19,21,22} Somewhat surprisingly, the cation **4** in **[4][3]** provides the first crystallographically characterized example of a lithium amido cobaltate.

Lithium amide/halide co-complexes are widely used to enhance the efficiency of key organic syntheses, such as the aldol reaction,²³ however crystallographically characterized examples such as **3** are rare. The anion **3** is also a new member of the s-block metal inverse crown family, a term describing complexes consisting of a macrocyclic arrangement of metal amide units that host an anionic guest within the crown.²⁴ The majority of inverse crowns are heterobimetallic combinations of an alkali metal with a less polar divalent metal, so it is notable that the inverse crown in **3** is a cyclic pentamer of $[\text{Li}(\text{hmds})]$.²⁵ The solid-state structure of lithium hexamethyldisilazide is the cyclic trimer $[\text{Li}(\text{hmds})]_3$, however in hydrocarbon solution a tetramer-dimer equilibrium has been observed.²⁶ To account for the formation of **3**, an aggregation process involving $[\text{Li}(\text{hmds})]_n$ units with $n = 1, 2, 3$ or 4 templating around the nascent chloride ion can be envisaged, although proof for this cannot be obtained by NMR spectroscopy owing to the paramagnetism of **[2][3]** and **[4][3]**. A mechanism qualitatively similar to that which we propose for **3** is thought to account for the formation of the anionic phospho(V)zane cyclic

pentamer $[\{\text{P}(\mu\text{-N}^t\text{Bu})_2(\mu\text{-NH})\}_5(\text{HCl})]$, in which the chloride ion templates the formation of the macrocycle *via* a series of hydrogen bonds.²⁷ A pentameric structural motif related to **3** was also observed in the mercury-based inverse crown $[\{(\text{F}_3\text{C})_2\text{CHg}\}_5(\mu_5\text{-Cl})_2]$, although in this instance the macrocycle was pre-synthesized and the chloride guest added subsequently.²⁸

Conclusions

In summary, the heteroleptic lithium amide **1** has been used as a precursor for the synthesis of the ion-separated compounds **[2][3]**, **[4][3]** and **[5][Zn(hmds)₃]**. The heterobimetallic cations **2**, **4** and **5** contain (μ_8 -oxo)-centred $\{\text{MLi}_7\}$ cubes ($M = \text{Mn}, \text{Co}, \text{Zn}$), with each face of the cube capped by a $\mu_4\mu'_4\text{-[hpp]}^-$ ligand. An additional serendipitous outcome was the formation of the anionic inverse crown **3**. The apparent ability of d-block metals to replace lithium in a structural type more commonly found in s-block chemistry may enable more extensive investigations of the less common coordination environment for the transition metals, such as tetrahedral cobalt(II), which would add to the considerable current interest in cage compounds of octahedral cobalt(II).²⁹ Our ongoing research in this area will also extend the synthetic method described for **[2][3]**, **[2][3]** and **[5][Zn(hmds)₃]** to other N–H acidic heterocycles.

Experimental

Synthesis of **1**

A solution of $\text{LiN}(\text{SiMe}_3)_2$ (0.50 g, 3.0 mmol) in toluene (15 mL) was added to hppH (0.14 g, 1.0 mmol) at -78°C and stirred for 30 min. The reaction was warmed to room temperature and stirred for 1 h, producing a colourless precipitate. Gentle heating of the reaction mixture produced a pale yellow solution, which was filtered and stored overnight at -4°C , resulting in the formation of **1** as pale yellow crystals (0.32 g, 66%). Elemental analysis calculated for $\text{C}_{19}\text{H}_{48}\text{N}_5\text{Si}_4\text{Li}_3$: C 47.56, H 10.08, N 14.60; found: C 47.42, H 9.93, N 14.51. Crystal data for **1**: $\text{C}_{19}\text{H}_{48}\text{N}_5\text{Si}_4\text{Li}_3$, $M = 479.80$, tetragonal, $P4_2bc$, $a = 16.4053(3)$, $c = 21.4837(10)$ Å, $V = 5781.99(31)$ Å³, $T = 100(2)$ K, $Z = 8$, 12200 reflections collected, 4177 independent reflections ($R_{\text{int}} = 0.0397$), 89.6% completeness to $\theta = 28.66^\circ$ ($\lambda = 0.71073$ Å), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0393$ and $wR_2 = 0.0989$, R indices (all data) $R_1 = 0.0551$, $wR_2 = 0.1060$.

Synthesis of **[2][3]**

A solution of **1** (0.48 g, 1.0 mmol) in toluene (10 mL) was added to a stirred suspension of MnCl_2 (0.06 g, 0.5 mmol) in toluene (15 mL) at room temperature. The pale pink reaction mixture was stirred overnight, resulting in a pale amber solution and a precipitate. Filtration of the hot reaction mixture (Celite, porosity 3) produced an amber solution, which was reduced in volume to approximately 5 mL and stored at -4°C . After two days, amber crystals of **[2][3]** formed. For spectroscopic and analytical studies, the nascent solvent was removed by syringe and the crystalline material then washed with hexane (2×5 mL), before being dried in vacuo, which resulted in evaporation of the lattice toluene to give **[2][3]** (0.05 g, 30% isolated yield). An alternative synthesis of **[2][3]**, using the same amounts of each reagent but with the suspension of MnCl_2 in toluene containing 50 μL of

degassed water, was also accomplished (0.06 g, 36% isolated yield). Elemental analysis for $C_{72}H_{162}N_{23}OSi_{10}ClLi_7Mn$: calculated C 48.42; H 9.14, N 18.04; found C 48.11, H 8.99, N 17.67. Crystal data for **1**: $C_{86}H_{178}N_{23}OSi_{10}ClLi_7Mn$, $M = 1988.96$, monoclinic, $C2/c$, $a = 20.1096(12)$, $b = 24.4769(15)$, $c = 24.9736(17)$ Å, $\beta = 105.769(6)^\circ$, $V = 11829.9(13)$ Å³, $T = 100(1)$ K, $Z = 4$, 21119 reflections collected, 7584 independent reflections ($R_{int} = 0.0906$), 99.7% completeness to $\theta = 21.00^\circ$ ($\lambda = 0.71073$ Å), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0857$ and $wR_2 = 0.1979$, R indices (all data) $R_1 = 0.1783$, $wR_2 = 0.2215$.

Synthesis of [4][3]

This compound was synthesized in an identical manner to [2][3] using a suspension of anhydrous $CoCl_2$ (0.11 g, 0.5 mmol) in toluene (10 mL) and a solution of **1** (0.24 g, 0.5 mmol) in toluene (10 mL). The resulting blue solution was stored overnight at room-temperature to result in blue crystals of [4][3]·(2 toluene). Drying the crystals *in vacuo* resulted in evaporation of the lattice toluene to give [2][3] (0.42 g, 24% isolated yield; with water 0.49 g, 28%). Elemental analysis calculated for $C_{72}H_{162}N_{23}OSi_{10}ClCoLi_7$: C 48.31; H 9.12, N 18.00; found C 47.82, H 8.98, N 17.51. Crystal data for **1**: the SQUEEZE function of PLATON was applied to two independent toluene molecules, which could not be refined owing to severe disorder at special positions,³⁰ $C_{86}H_{178}N_{23}OSi_{10}ClLi_7Co$, $M = 2009.07$, monoclinic, $C2/c$, $a = 20.1006(4)$, $b = 24.5598(4)$, $c = 24.9957(5)$ Å, $\beta = 105.786(2)^\circ$, $V = 11874.2(4)$ Å³, $T = 123(1)$ K, $Z = 4$, 43649 reflections collected, 12325 independent reflections ($R_{int} = 0.0275$), 98.8% completeness to $\theta = 76.56^\circ$ ($\lambda = 1.54178$ Å), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0629$ and $wR_2 = 0.1746$, R indices (all data) $R_1 = 0.0653$, $wR_2 = 0.1763$.

Synthesis of [5][3]

This compound was synthesized in an identical manner to [2][3] using anhydrous $ZnBr_2$ (0.11 g, 0.5 mmol) and **1** (0.24 g, 0.5 mmol). The resulting yellow solution stored overnight at room-temperature to result in yellow crystals of [5][3] (0.04 g, 32% isolated yield; with water 0.06 g, 48%). Elemental analysis calculated for $C_{60}H_{126}N_{21}OSi_6Li_7Zn_2$: C 47.93; H 8.31, N 19.56; found C 47.78, H 8.19, N 19.59. Crystal data for [5][3]: $C_{60}H_{126}N_{21}OSi_6Li_7Zn_2$, $M = 1505.70$, orthorhombic, $Pba2$, $a = 27.7860(13)$, $b = 24.4230(11)$, $c = 12.1310(7)$ Å, $V = 8232.3(7)$ Å³, $T = 100(2)$ K, $Z = 4$, 33772 reflections collected, 10107 independent reflections ($R_{int} = 0.1008$), 94.5% completeness to $\theta = 23.25^\circ$ ($\lambda = 0.71073$ Å), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0481$ and $wR_2 = 0.1150$, R indices (all data) $R_1 = 0.1317$, $wR_2 = 0.1268$.

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