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Solid state and solution studies of lithium tris(*n*-butyl)magnesiates stabilised by Lewis donors†‡

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Several Lewis base adducts of the synthetically important lithium tris(*n*-butyl)magnesiate $LiMg(^nBu)_3$ have been prepared and structurally characterised. The complexes were prepared by a co-complexation approach *i.e.*, by combining the monometallic ^nBuLi and $^nBu_2Mg$ reagents in hydrocarbon solution before adding a molar equivalent of a donor molecule (a bidentate amine, tridentate amine or cyclic ether). The lithium magnesiates all adopt variants of the "Weiss motif" structure, *i.e.*, contacted ion pair dimers with a linear arrangement and metals connected by butyl anions, where tetrahedral magnesium ions are in the central positions and the lithiums occupy the outer region, solvated by a neutral Lewis donor [(donor)-Li(μ-$^nBu)_2$Mg(μ-$^nBu)_2$Mg(μ-$^nBu)_2$Li(donor)]. When TMPDA, PMDETA or (*R*,*R*)-TMCDA [TMPDA = *N*,*N*,*N*′*N*′-tetramethylpropanediamine; PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine; and (*R*,*R*)-TMCDA = (*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine], are employed, dimeric tetranuclear lithium magnesiates are produced. Due to the tridentate nature of the ligand, the PMDETA-containing structure (**2**) has an unusual 'open'-motif. When TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) is employed, a *n*-butoxide-containing complex [(TMEDA)Li(μ-^nBu)(μ-O$^nBu)Mg_2(^nBu)_2$(μ-^nBu)(μ-O^nBu)Li-(donor)] has been serendipitously prepared and adopts a ladder conformation which is commonly observed in lithium amide chemistry. This complex has also been prepared using a rational methodology. When 1,4-dioxane is employed, the donor stitches together a polymeric array of tetranuclear dimeric units (**6**). The hydrocarbon solution structures of the compounds have been characterised by ^1H, ^7Li, ^{13}C NMR spectroscopy; **2** has been studied by variable temperature and DOSY NMR.

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Introduction

Despite the first organolithium compounds being reported almost 100 years ago,[1] they are without doubt, still one of the most widely utilised classes of reagents in modern synthetic chemistry. This is primarily due to their versatility and their ease of use. The metallation reaction (*i.e.*, transforming a relatively inert C–H bond to a more reactive, more useful C–Metal bond) is fundamental to many synthetic procedures and is commonly achieved by reacting an organic substrate with an organolithium reagent. The resultant organometallic compound can then be electrophilically quenched, to furnish new organic molecules.[2] However, lithium organometallics often promote side reactions as a result of their high polarity/reactivity (including reacting with solvents such as THF and diethyl-ether) and they often require cryogenic temperatures to encourage selectivity. Alternative methods have been established using magnesium reagents, which generally offer a better functional group tolerance; however, their drawbacks include they generally have low solubility in common solvents and due to their sluggish reactivity there is often a need for an excess of the base to be used to give adequate yields.[3] As energy efficiency is becoming a key driver in modern synthesis,[4] it is important to develop protocols where chemistry can be performed at temperatures close to ambient. Over the past couple of decades, a new category of bimetallic alkali metal magnesiates, which often exhibit reactivities that cannot be replicated by the monometallic agents on their own, has been investigated.[5] In many cases, they can be used under mild reaction conditions and can display unusual deprotonation regioselectivities.[6] Magnesiates have recently received a high degree of attention from the synthetic chemist in a large part due to the work of Knochel.[7] His group has discovered that simply adding one equivalent of lithium chloride to a conventional Grignard or Hauser (amidomagnesium halide) reagent can have a marked difference in selectivity and reactivity. These lithium magnesiate reagents have been coined as 'turbo Grignard'[8] and 'turbo-Hauser'[9] [with general formulae

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† In memory of Professor Ken Wade, a truly inspirational man.

‡ Electronic supplementary information (ESI) available: NMR spectra for **1–6**. CCDC 1046063–104067. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00435g

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RMgCl·LiCl and (NR_2)MgCl·LiCl respectively]. The alkyl magnesiate RMgCl·LiCl is a useful reagent for inducing halogen–magnesium exchange in unactivated functionalised aryl and heteroaryl bromides in high yields, working at non-cryogenic temperatures with good group tolerance.[10] The amido containing (TMP)MgCl·LiCl (where TMP is 2,2,6,6-tetramethylpiperidide) is an efficient base for the hydrogen–magnesium exchange of aromatics and heteroaromatics substrates.[11] Homoleptic alkyllithium magnesiates, which depending on their stoichiometry can be grouped as (lower-order) triorganomagnesiates $LiMgR_3$ or (higher-order) tetraorganomagnesiates Li_2MgR_4, have also been established as useful synthetic reagents.[12] Both, homoleptic and heteroleptic alkyllithium magnesiates have been broadly employed in organic synthesis, so much so that $LiMg^nBu_3$ and $LiMg^iPr^nBu_2$ are commercially available as mixtures in hexane–diethyl ether. In 1951, Wittig employed a lithium magnesiate, $[LiMgPh_3]$[13] – prepared by combining phenyllithium with diphenylmagnesium – in addition reactions across ketones. Since this first report, lithium magnesiates has been established as useful reagents for nucleophilic additions.[13,14] They have also been found to be excellent bases for the deprotonation of aromatic substrates[15] such as fluoroaromatics,[15d] furans[15g] or pyridine carboxamides.[15h] The most common reagent employed in these reactions is $[LiMg^nBu_3]$. This complex has also been shown to have high activity in halogen–magnesium exchange reactions. Oshima treated dibromomethylsilanes with the magnesiate to prepare α-silylalkyl-magnesium compounds,[16] and Iida and Mase used it to carry out selective-monosubstitution of dibromoarenes.[17] Many other magnesiate systems have been employed, establishing lithium magnesiates as important reagents for halogen–magnesium exchange reactions.[16–18] Surprisingly, despite these extensive applications just a few examples of 'simple' homoleptic lithium magnesiates have been structurally characterised to date.[19] The structure of the pioneering Wittig's lithium magnesiate was elucidated by Weiss by adding TMEDA to the magnesiate mixture.[20] With respect to the lower order species, Weiss isolated and crystallised two different dimeric forms, firstly the contacted ion pair $[(TMEDA{\cdot}Li(\mu\text{-}Ph)_2Mg(\mu\text{-}Ph)]_2$ and the solvent separated ion pair $[(TMEDA)_2Li]^+[Ph_2Mg(\mu\text{-}Ph)]^-$. He also reported several other homoleptic organolithiums by using methyl,[21] benzyl,[22] or alkynyl[22] ligands. More recently, Power,[23] Hevia[24] and Westerhausen[25] have made further contributions by incorporating the 2,4,6-$iPr_3C_6H_2$, $CH_2Si(CH_3)_3$ (methyl(trimethylsilyl)) and C_4H_6 (butane-1,4-diide) anion respectively. In most cases, the lithium magnesiates adopt what has become known as the "Weiss-motif" with a tetrahedrally-disposed magnesium in the central positions and the alkali-metal occupying the outer region, solvated by neutral Lewis donors. With the exception of one compound (**5**), only homoleptic alkyl (or aryl) lithium magnesiates have been considered in this work but this is not a prerequisite as magnesiates also exist with combinations of different functional groups (heteroleptic) including oxide[26] or amido groups.[27]

Results and discussion

Syntheses

By combining (co-complexing) the monometallic reagents ^{n}BuLi and $^nBu_2Mg$ in hexane solution, a white suspension of the homoleptic mixture $[LiMg^nBu_3]$ was produced. On the addition of one molar equivalent of the corresponding Lewis base the suspension is solubilised. For **1**, one equivalent of TMPDA (*N*,*N*,*N*′*N*′-tetramethylpropanediamine) was added to $[LiMg^nBu_3]$ in hexane affording a colourless solution. Crystallisation at −35 °C resulted in colourless crystals of dimeric $[(TMPDA){\cdot}Li(\mu\text{-}^nBu)_2Mg(\mu\text{-}^nBu)]_2$ (**1**) in 67% yield. In contrast, addition of PMDETA (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) in an equimolar ratio results in the formation of a yellow oil in the bulk hexane. Concentration of the hexane solution and storage at −35 °C resulted in colourless crystals of $[(PMDETA){\cdot}Li(\mu\text{-}^nBu)(^nBu)Mg(\mu\text{-}^nBu)]_2$ (**2**) in 35% yield. When the chiral auxiliary ligand (*R*,*R*)-TMCDA [(*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine] was added to an equimolar mixture of *n*-butyllithium and di-*n*-butylmagnesium in hexane, a white suspension was produced which on gently heating it dissolves in the reaction medium. Storage at −35 °C for 36 hours deposited dimeric crystalline **3**, $[\{(R,R)\text{-TMCDA}\}{\cdot}Li(\mu\text{-}^nBu)_2Mg(\mu\text{-}^nBu)]_2$, in high yield (82%). Compound **5**, $[(TMEDA){\cdot}Li(\mu\text{-}^nBu)(\mu\text{-}O^nBu)Mg(^nBu)]_2$, can be synthesised by the equimolar reaction of lithium-*n*-butoxide (synthesised *in situ* by reacting *n*-butyllithium with *n*-butanol) with an equimolar quantity of di-*n*-butylmagnesium and TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (33%). The synthesis of the homoleptic *n*-butyllithium magnesiate stabilised by TMEDA produced crystalline material (**4**) in 59%. Disappointingly, and despite repeated attempts at the analysis, the crystals degraded before the data collection was completed (at 123 K). Due to the synthetic importance of the bimetallic mixture $[LiMg^nBu_3]$ in ethereal solution,[14d,15d–i] we decided to study the role of oxygen donors such as THF or diethylether. $[LiMg^nBu_3]$ was dissolved in hexane and the Lewis base was added in stoichiometric and substoichiometric amounts, and also in excess; however, no crystalline material was obtained. Next, it was decided to focus on the bidentate donor 1,4-dioxane by adding one molar equivalent of the cyclic ether to an equimolar mixture of *n*-butyllithium and di-*n*-butylmagnesium in benzene. Precipitation of a white solid suggested the formation of a new adduct. Toluene was added to the resultant white solid, which redissolved the complex on strong heating. Cooling the solution slowly to ambient temperature afforded a crop of colourless needles of polymeric $[(dioxane){\cdot}LiMg^nBu_3]_\infty$, **6** (47%).

X-ray crystallography

The TMPDA-solvated lithium magnesiate **1** crystallises in the space group *Pbca* (Fig. 1). **1** was found to be a dimer with the classical 'Weiss-type' motif (Scheme 1) in which six butyl anions bridge the four metals (two Li and two Mg atoms), giving rise to three four-membered rings (*i.e.*, two Li–C–Mg–C rings and one Mg–C–Mg–C ring). The former rings are fused

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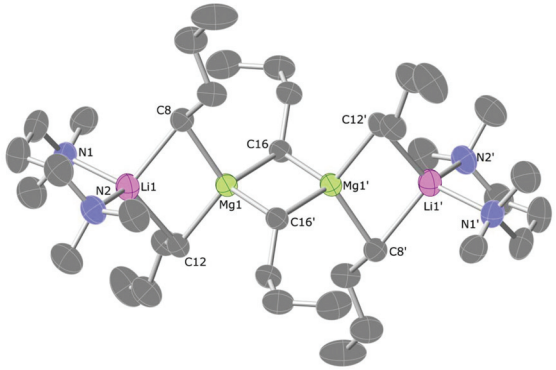
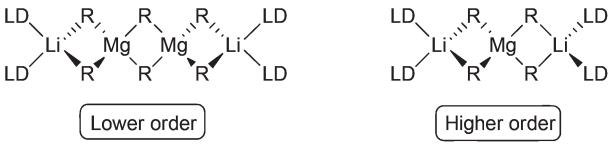
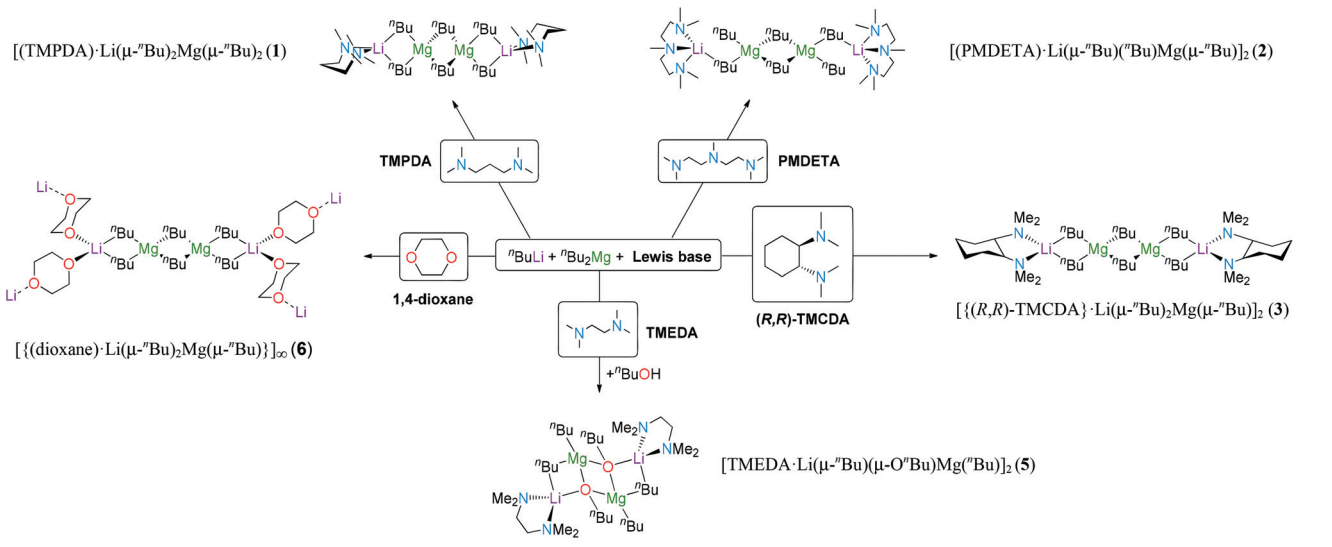


Fig. 1 Molecular structure of **1**. Ellipsoids are displayed at 30% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li1–N1, 2.092(4); Li–N2, 2.085(4); Li–C8, 2.348(4); Li1–C12, 2.303(4); Mg1–C8, 2.205(6); Mg1–C12, 2.225(2); Mg1–C16 2.298(2); N1–Li1–N2, 99.8(2); N1–Li1–C8, 106.9(2); N1–Li1–C12, 120.4(2); N2–Li1–C8, 107.4(2); N2–Li1–C12, 117.1(2); C8–Li1–C12, 104.5(1); C8–Mg1–C12, 112.2(1); C8–Mg1–C16, 104.1(1); C8–Mg1–C16′, 112.6(1); C12–Mg1–C16, 110.1(1); Li1–C8–Mg1, 70.5(1); Li1–C12–Mg1, 71.0(1).



Scheme 1 Weiss-motifs of a lower order $[(donor)\cdot LiMgR_3)]_2$ (left) and a higher order lithium magnesiate $[(donor)_2\ Li_2MgR_4]$, (right). LD = Lewis donor.

to the latter at different Mg atoms. Each Mg atom is bound solely to (four) C atoms, and each Li atom binds to two C atoms and their coordination sphere is completed with the ancillary ligand forming a six-membered Li–N–C–C–C–N ring. The Li–C distances range from 2.348(4) to 2.303(4) Å and the Mg–C distances from 2.205(6) to 2.298(2)Å are as expected for such species. A search in the Cambridge Structural Database[28] reveals that only four lithium complexes stabilised by TMPDA have been crystallographically characterised, bearing anionic groups such as phenylacetylene,[29] isocyanate,[30] borataben-zene[31] or benzyl.[32] Li–N distances of **1**, [2.085(4) to 2.092(4) Å], are similar to those found for other lithium compounds stabilised by chelating TMPDA. Diamines have proven being a key additive in the field of alkali metal-mediated magnesiation, dramatically modifying both structural pattern and reactivity,[33] so different nitrogen-donors were employed in this work (Scheme 2). Apart from lithium magnesiates, tridentate ligand PMDETA has been used to chelate lithium zincates like PMDETA·$LiZn(HMDS)Me_2$,[34] PMDETA·$LiZnMe_3$[35] or PMDETA·$LiZn(CH_2SiMe_3)$.[36] The employment of the tridentate ligand PMDETA causes the lithium magnesiate to crystallise as dimeric **2** whereby the lithium atoms bind in the usual way to the ancillary ligand crystallising in space group $P2_1/n$ (Fig. 2). The same methodology was used by Hevia *et al.* to produce $[(PMDETA)LiMg(CH_2SiMe_3)_3]$.[24] *n*-Butyl's less sterically demanding nature in comparison to methyl(trimethylsilyl) presumably results in two key differences between the structures. While the lithium magnesiate containing methyl(trimethylsilyl) groups was found to be a monomer, compound **2** can be described as an 'open dimeric' motif, in which the lithium and magnesium atoms are bridged by only one butyl group so the angle Li–C20–Mg1 is more open than in the closed structures, which contain Li–C–Mg–C four-membered rings. This angle is also affected by the nature of the anionic group, being 83.31° in the *n*-butyllithium magnesiate dimer and 149.4° for Hevia's monomer.[24] Complex **2** resembles the dimer obtained by Weiss and co-workers when they employed the alkynyl ligand with TMEDA, although the structure found by them is



Scheme 2 Synthesis of homoleptic *n*-butyllithium magnesiates.

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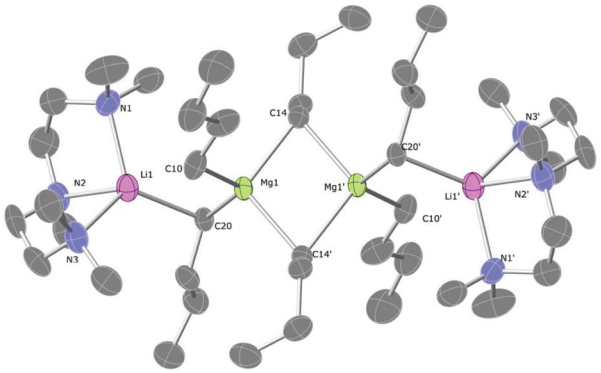

Fig. 2 Molecular structure of **2**. Ellipsoids are displayed at 30% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li–N1, 2.178(5); Li–N2, 2.273(5); Li–N3, 2.161(5); Li1–C20, 2.271(5); Li1···C10, 3.161(1); Mg1–C10, 2.186(3); Mg1–C20, 2.237(3); Mg1–C14, 2.321(3); N1–Li–N2, 82.3(2); N1–Li–N3, 120.0(2); N2–Li1–N3, 83.3(2); N1–Li1–C20, 117.3(2); N2–Li1–C20, 108.1(2); N3–Li1–C20, 122.7(2); C10–Mg1–C14, 107.4(1); C10–Mg1–C20, 121.2(1); C14–Mg1–C20, 105.5(1).

again a closed dimer.[22] Strohmann crystallographically characterized a Mg–C four-membered rings. This angle is also affected by the ^{n}BuLi adduct stabilised by PMDETA, where the tetranuclear dimer [(^{n}BuLi)$_2$PMDETA]$_2$ is produced.[37] This dimer is structurally related to compound **2** as both can be interpreted as a dimer with two outer PMDETA·^{n}BuLi units linked to a dimeric core of (^{n}BuLi)$_2$ for Strohmann's complex or (^{n}Bu$_2$Mg)$_2$ for **2**. Strohmann's lithium dimer presents longer Li–C interatomic distances for the outer unit [2.498(6) Å] than compound **2** [2.271(5) Å] suggesting a stronger interaction between the outer PMDETA·^{n}BuLi and the central ring in **2**. The C–Mg distance [2.237(3) Å] is within the range of typical bond lengths in organomagnesiates. Next, a chiral bidentate donor was employed and produced the complex [{(*R*,*R*)-TMCDA}·Li(μ-^{n}Bu)$_2$Mg(μ-^{n}Bu)]$_2$ (**3**) which crystallises in space group $P2_1$ (Fig. 3). (*R*,*R*)-TMCDA solvates the triorganomagnesiate leading to a contacted ion pair dimer where the atoms in molecule are not related by any symmetry operations. Several alkali-metal magnesium amide complex stabilised by chiral

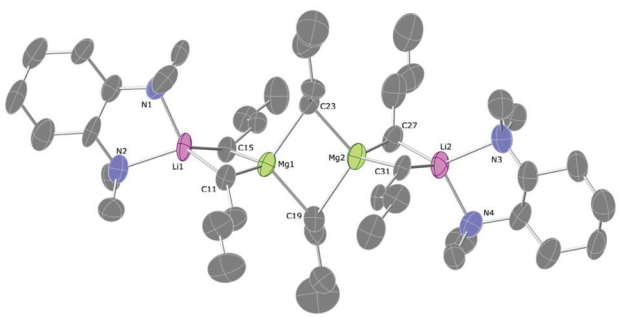

Fig. 3 Molecular structure of **3**. Ellipsoids are displayed at 30% probability and all hydrogen atoms are omitted for clarity.

donors[33c,38] [namely (–)-sparteine and (*R*,*R*)-TMCDA] have been characterised, but to the best of our knowledge, this is the first example of a crystallographically elucidated chiral tris-(alkyl)lithium magnesiate. When TMEDA was employed, crystals of **4** could be isolated; however, they could not be analysed by X-ray crystallography, even when low temperatures were employed (123 K). The crystals were found to degrade in the X-ray beam, presumably due to them undergoing a phase change. Although no solid-state structural data for **4** could be obtained, a hydrocarbon solution of the complex was studied by NMR spectroscopy (*vida infra*). In one of the attempts to analyse **4**, data was successfully collected and the structure was found to be [(TMEDA)·Li(μ-^{n}Bu)(μ-O^{n}Bu)Mg(^{n}Bu)]$_2$ (**5**). It is a heteroleptic dimer that contains both *n*-butyl and *n*-butoxide groups. In light of this serendipitous discovery, a rational synthetic procedure for the complex was employed (*vida supra*) involving the co-complexation of lithium-*n*-butoxide and di-*n*-butylmagnesium. Compound **5**, which crystallises in space group $P2_1/c$, is a dimer of [(TMEDA)·Li(O^{n}Bu)Mg^{n}Bu$_2$] units which bind through a Mg–O interaction exhibiting ladder-like features[39] (Fig. 4). Each unit is composed of a four-membered (C–Mg–O–Li) ring. Lithium is linked to magnesium *via* one butyl and one butoxide group and it completes its coordination sphere coordinating to TMEDA in order to have tetrahedral (sum of angles 657.44°) coordination.

Magnesium ions are linked to two butyl groups (one bridge and one terminal). A very close precedent can be found in the sodium (or potassium) magnesium alkoxides crystallographically

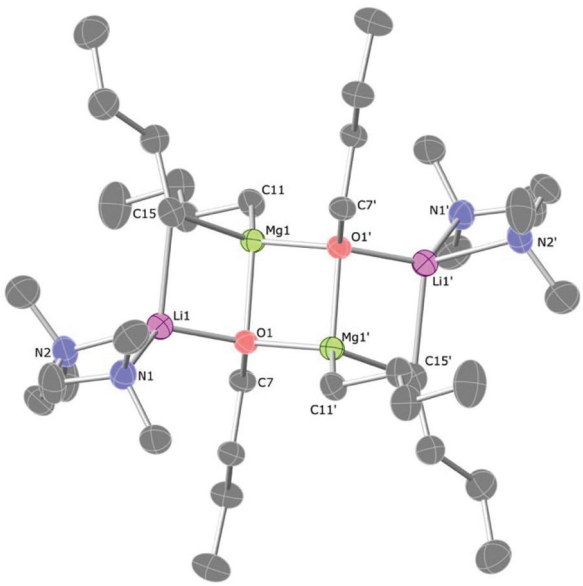

Fig. 4 Molecular structure of **5**. Ellipsoids are displayed at 30% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li1–N1, 2.114(3); Li1–N2, 2.191(3); Li1–C15, 2.343(3); Li1–O1, 1.946(3); Mg1–C11, 2.156(2); Mg1–C15, 2.211(2); Mg1–O1, 2.044(1); N1–Li1–N2, 86.5(1); N1–Li1–C15, 111.3(1); N1–Li–O1, 125.5(1); N2–Li1–O1, 123.7(1); N2–Li1–C15, 112.4(1); O1–Li1–C15, 98.1(1); C11–Mg1–C15, 118.3(1); C11–Mg1–O1, 115.5(1); C15–Mg1–O1, 99.0(1).

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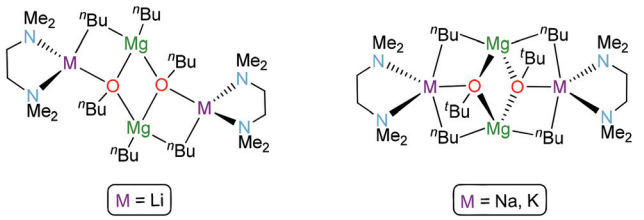

Fig. 5 ChemDraw representations for [(TMEDA)LiMg(^{n}Bu)$_2$(O^{n}Bu)]$_2$ (**5**) (left) and Mulvey's alkali metal alkoxide–magnesium bis(alkyl) dimers (inverse crowns) [(TMEDA)MMg(^{n}Bu)$_2$(O^{t}Bu)]$_2$, M = Na, K (right).

characterised by Mulvey[40] (Fig. 5). The core of these examples and **5** is a O–Mg–O–Mg ring and the alkali metal is bonded to one oxygen atom and one molecule of TMEDA. While the tetrahedrally-disposed lithium atom is bridged to magnesium by one *n*-butyl chain in **5**, sodium and potassium atoms are penta-coordinated as they bond to two butyl groups to form a closed structure. Since 1998, this motif has been known as an inverse crown compound.[27c,41] All the *n*-butyl anions are bridging in the inverse crown molecules whereas two of these groups adopt terminal binding positions in **5**. The difference in the steric nature of *t*-butoxide *versus* *n*-butyl may be an explanation for this structural variation; however, it seems more likely that it is due to an alkali metal effect as it could be envisaged that bulkier alkoxide groups (albeit not at the α-position of the ligand) would more likely generate open structures. The cyclic ether 1,4-dioxane has been previously used to solvate different lithium 'ate' complexes.[24,42] When one equivalent is added to the unsolvated LiMg(^{n}Bu)$_3$, it was possible to crystallise polymeric **6**, which crystallises in space group *C*2/*c* (Fig. 6). Lithium magnesiate **6** comprises dimeric [(dioxane)$_2$-LiMg^{n}Bu$_3$]$_2$ units where two dioxane molecules bridge with lithium acting as a bridge between different dimers undergoing a three-dimensional polymeric structure. Unfortunately, a large amount of unresolved disorder adversely affects the precision of the *n*-butyl groups, dioxane and benzene molecules (present as crystallisation solvent in the unit cell) and therefore precludes discussion of any geometrical parameters, although its connectivity is unequivocal.

NMR spectroscopic studies

Complementing their solid-state characterization, lithium magnesiates **1–6** have also been examined using multinuclear (^{1}H, ^{7}Li and ^{13}C) NMR spectroscopy. In order to maintain the Lewis base coordination in solution, the solvent of choice was D^{12}-cyclohexane for all the complexes, except for **6**, which required D^8-toluene and an elevated acquisition temperature (353 K) because of its low solubility. A comparison of the resonances in the ^{1}H and ^{13}C NMR spectra belonging to the ancillary ligands of **1–6** with those observed for the free Lewis bases suggests that the donors remain coordinated to the metal centres in solution (see ESI‡ for full details). As a solid state structure for '[(TMEDA)LiMg(^{n}Bu)$_3$]$_2$' **4** was frustratingly not forthcoming, we examined hydrocarbon solutions of this compound. The ^{1}H NMR spectrum shows two singlets at 2.33 and 2.39 ppm while the signals for free TMEDA in *cyc*-C$_6$D$_{12}$ appear at 2.30 and 2.14 ppm. ^{1}H NMR spectra showed that both TMEDA and ^{n}Bu resonances were present (in an approximate 1 : 3 ratio) which is in agreement with a low order lithium magnesiate. Turning to ^{7}Li NMR resonances, the resonance for *n*-butyllithium is shifted upfield from 2.40 ppm to 1.01 ppm when it is co-complexed with the 'low polarity' di-*n*-butylmagnesium (Table 1). The further shift of this resonance after the addition of the donor also highlights that the Lewis base remains coordinated to the lithium in solution. Tridentate ligand PMDETA causes the most shielded resonance, appearing at 0.77 ppm for **2**. Although the structure parameters for **1–6**

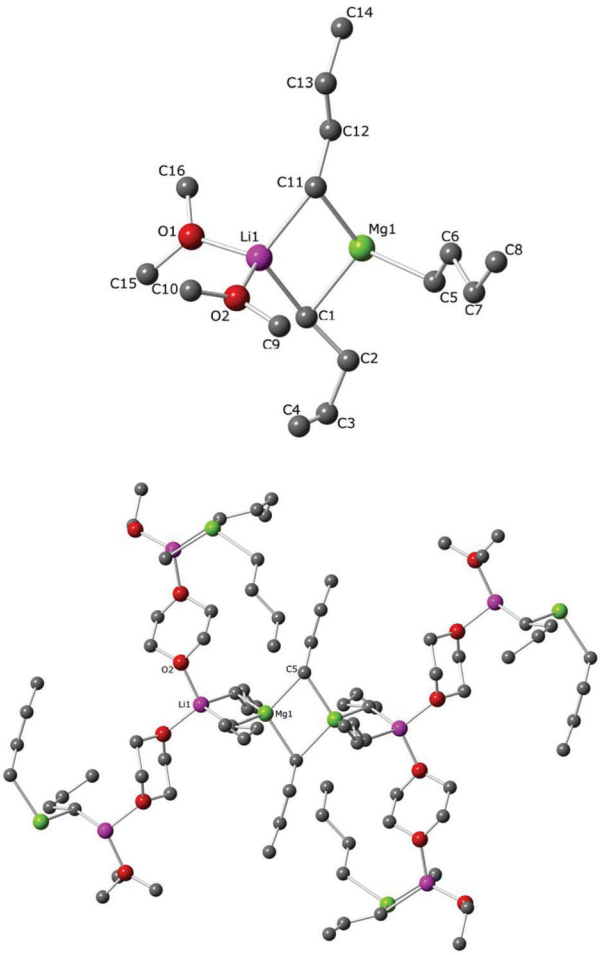

Fig. 6 Molecular structure of **6**, showing asymmetric unit; (top) and polymer propagation (bottom). All hydrogen atoms are omitted for clarity.

Table 1 Chemical shifts in the ^{7}Li spectrum in *cyc*-C$_6$D$_{12}$ at 300 K

Complex	^{n}BuLi	LiMg^{n}Bu$_3$	**1**	**2**	**3**	**4**	**5**
^{7}Li (ppm)	2.40	1.01	0.79	0.77	1.04	0.87	0.99

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show the presence of at least two chemically distinct *n*-butyl chains, the NMR spectroscopic studies at 300 K show only one set of signals for the alkyl groups in hydrocarbon solution is present. This fact suggests that rapid exchange of the alkyl positions occurs in solution, causing the signals for the *n*-butyl chains to become equivalent. In all cases (see ESI‡ for full details) the resonance for the CH_2–M resonance is broad. As a case study, we choose to probe further a D^8-toluene solution of **2** using a variable-temperature experiment in an attempt to decipher the three different *n*-butyl groups (one terminal, one bridging Li and Mg centres, and one bridging two Mg atoms) which exist in the solid state structure (*N.B.*, *cyc*-C_6D_{12} is solid below 268 K).The temperature was lowered to 240 K and ^{1}H NMR spectroscopic measurements were obtained every 10 K (Fig. 7). At the lowest temperature, the CH_2–M resonance decoalesces into two signals of an approximate integration of 1 : 2, not the three resonances that we expected. This seems to point to two possible scenarios. Firstly, in arene, the dimer stays intact but the terminal *n*-butyl group now adopts a bridging position (or is in rapid exchange between bridging and terminal with respect to the NMR timescale); or secondly, the dimer dissociates to a monomer in D^8-toluene and the resonances therefore correspond to two bridging and one terminal butyl chain (Scheme 3). In order to find out whether **2** retains its dimeric structure in solution, we performed ^{1}H NMR diffusion-ordered nuclear magnetic resonance spectroscopy (^{1}H-DOSY) to gain insight into its aggregation in D^8-toluene. DOSY measurements are useful to estimate molecular weights of species in solution,[43] as species with higher molecular weight diffuse slower that those with lower molecular weight. A relationship can be established between coefficient diffusion and molecular weight, which are inversely proportional. In our study we chose 1,2,3,4-tetraphenylnaphthalene (TPhN), 1-phenylnaphthalene (PhN), and tetramethylsilane (TMS) as internal standards, as they exhibit good solubility in toluene with minimal overlapping of signals and are inert to magnesiates.

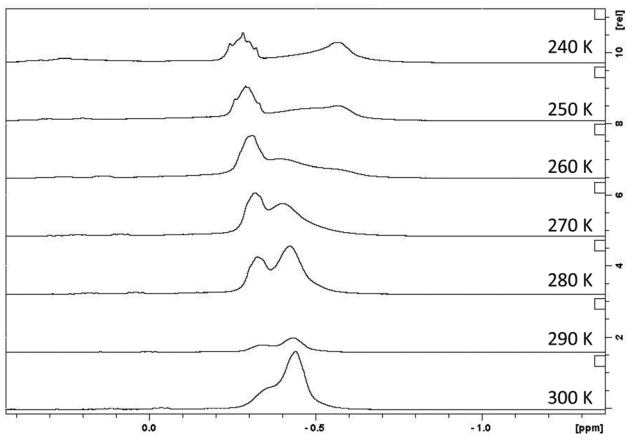
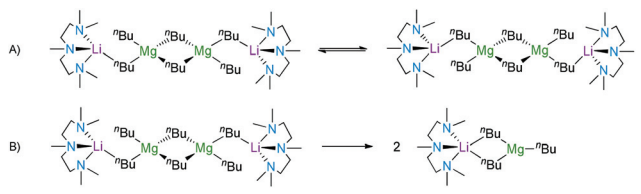


Fig. 7 Variable-temperature ^{1}H NMR experiment of **2** in D_8-toluene at 300 K.



Scheme 3 Representation of two different equilibrium processes of **2** in solution.

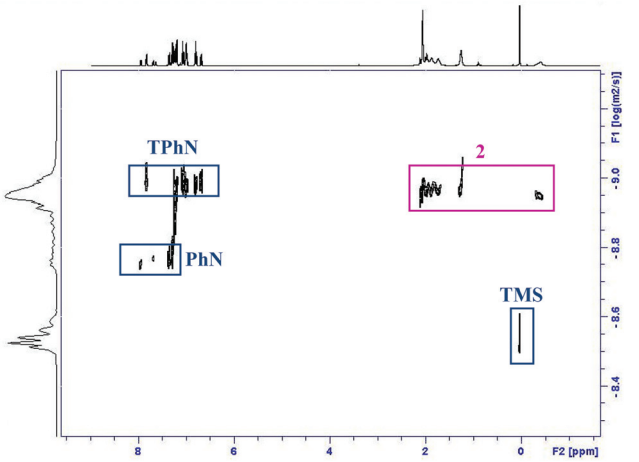


Fig. 8 ^{1}H DOSY NMR spectrum of complex **2** in D^8-toluene solution at 300 Kin the presence of inert standards 1,2,3,4-tetraphenylnaphthalene (TPhN), 1-phenylnaphthalene (PhN) and tetramethylsilane (TMS).

The ^{1}H-DOSY NMR spectrum of a mixture of **2** with these standards in D^8-toluene at 300 K showed only one set of signals for the lithium magnesiate confirming that there is only one species in solution and PMDETA remains attached to the lithium magnesiate in arene solvent (Fig. 8). A correlation between log *D* (average diffusion value, *D*, 7.2×10^{-10} m^2 s^{-1}) and log FW (FW = molecular weight) can be established (calibration curve obtained from the internal standards, $\log D = -0.698 \log FW - 7.358$; $r^2 = 0.995$). This correlation gave an experimental molecular weight which was estimated to be 370 g mol^{-1}, which differs in a 1.23% from the molecular weight for the monomer [(PMDETA)LiMg^{n}Bu$_3$]. Thus, analysis of this data suggests that the dimeric constitution of **2** in solid state is not retained in solution.

Conclusions

A systematic study of a series of *n*-butyllithium magnesiates in solid state and solution has been performed by employing neutral bidentate, tridentate and chiral Lewis bases. It is possible to rationally synthesise homoleptic dimers which adopt the 'Weiss motif' in solid state. Solution studies have shown that the Lewis bases remain attached to the lithium magnesi-

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ate species in aliphatic and arene solvents; however, there is evidence that the aggregation state can be lowered, even in the presence of potentially π-donating arene molecules. In future studies, we will look to utilise these compounds in organic transformations and compare the results with the previously published data.

Experimental

General methods

n-Hexane and toluene were distilled from sodium/benzophenone, 1,4-dioxane, TMEDA, TMPDA and PMDETA were distilled from CaH_2. (*R*,*R*)-TMCDA was synthesised according to the standard procedure.[44] *n*-Butyllithium was freshly standardised by titration against menthol–1,10-phenanthroline in THF at 0 °C $^nBu_2Mg$ was standardised with iodine in presence of an excess of LiCl, in THF at 0 °C. All synthetic work was carried out under argon by using standard Schlenk techniques. ^1H, ^{13}C NMR and ^7Li NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. All ^{13}C NMR spectra were proton decoupled. ^1H-DOSY experiments were performed in an NMR tube that was charged with 20 mg of **2**, TPhN (15 mg), PhN (13 μL), TMS (19 μL), and D^8-toluene up to 0.7 mL of solution, before NMR analysis. Data for X-ray crystal structure determinations were measured with Oxford Diffraction Xcalibur and Gemini A diffractometers using graphite monochromated radiation. All structures were refined using all unique reflections and against F^2 to convergence using SHELXL-97.[45] Disordered butyl groups in **1**, **2** and **6** were modelled over two sites with appropriate restraints and constraints applied. High degrees of motion were also observed for the dioxane and benzene solvents present in structure **6**. The sample used for structure **3** was twinned by a 180° rotation about 001. The raw data was processed to give an *hklf* 5 formatted reflection file. Refinement with this data gave a much improved model, but still required restraints to be added to the displacement parameters of atoms Li2, N3, N4, C36 and C41. Selected parameters are reported in Table 1 of ESI‡ and full details are available in cif format, see CCDC 1046063 to CCDC 1046067 contain the supplementary crystallographic data for this paper. Elemental analyses were attempted, but due to the extreme air sensitivity of the complexes variable results were obtained.

Synthesis of [TMPDA·Li(μ-^{n}Bu)$_2$Mg(^{n}Bu)]$_2$ (1)

^{n}BuLi (0.25 mL, 4 mmol of 1.6 M solution in hexanes) was dissolved in 15 mL of dried hexane in an oven-dried Schlenk. 4 mmol of $^nBu_2Mg$ (4 mL of 1 M solution in heptanes) were added, turning the solution to slightly cloudy. After stirring for 30 minutes, 4 mmol of TMPDA (0.68 mL) were added. Gently heating gave a colourless solution. All volatiles were removed under vacuum and 10 mL of pentane were added. The solution was transferred to a freezer (−80 °C) affording colourless crystals after 24 hours. (0.89 g, 67%).

^1H NMR (400.13 MHz, 300 K, *cyc*-C_6D_{12}): δ −0.80 to −0.42 (12H, br, M–CH_2CH$_2$CH$_2$CH$_3$, ^{n}Bu), 0.85 (18H, t, $^3J_{HH}$ = 7.2 MHz, M–CH$_2$CH$_2$CH$_2$CH_3, ^{n}Bu), 1.22–1.32 (12H, m, M–CH$_2$CH$_2$CH_2CH$_3$, ^{n}Bu), 1.50–1.58 (12H, m, M–CH$_2$CH_2CH$_2$CH$_3$, ^{n}Bu), 1.66 (4H, br, N–CH$_2$CH_2CH$_2$–N, TMPDA), 2.25 (24H, s, N–CH_3, TMPDA), 2.45–2.47 (8H, t, $^3J_{HH}$ = 4.8 Hz, N–CH_2, TMPDA). $^{13}C\{^1H\}$ NMR (100.62 MHz, 300 K, *cyc*-C_6D_{12}): δ 9.99 (M–*C*H$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 13.26 (M–CH$_2$CH$_2$CH$_2$*C*H$_3$, ^{n}Bu), 23.34 (N–CH$_2$*C*H$_2$CH$_2$–N, TMPDA), 31.74 (M–CH$_2$*C*H$_2$CH$_2$CH$_3$, ^{n}Bu), 32.09, (M–CH$_2$CH$_2$*C*H$_2$CH$_3$, ^{n}Bu) 45.97 (N–*C*H$_3$, TMPDA), 60.82 (N–*C*H$_2$CH$_2$*C*H$_2$–N, TMPDA). ^7Li NMR (155.50 MHz, 300 K, *cyc*-C_6D_{12}): δ 0.79.

Synthesis of [PMDETA·Li(μ-^{n}Bu)Mg(^{n}Bu)(μ-^{n}Bu)]$_2$ (2)

^{n}BuLi (2.5 mL, 4 mmol of 1.6 M solution in hexanes) was dissolved in 15 mL of dried hexane in an oven-dried Schlenk tube. 4 mmol of $^nBu_2Mg$ (4 mL of 1 M solution in heptanes) were added and solution turned slightly cloudy. After stirring for 30 minutes, 4 mmol of PMDETA (0.84 mL) were added. Solution is gently heated to give a colourless solution with a yellow oil at the bottom of the Schlenk tube. It was and stored at −30 °C, affording colourless crystals after 1 day. (0.53 g, 35%).

^1H NMR (400.13 MHz, 300 K, *cyc*-C_6D_{12}): δ −0.82 to −0.62 (12H, br, M–CH_2CH$_2$CH$_2$CH$_3$, ^{n}Bu), 0.86 (18H, t, $^3J_{HH}$ = 7.2 MHz, M–CH$_2$CH$_2$CH$_2$CH_3, ^{n}Bu), 1.23–1.30 (12H, m, M–CH$_2$CH$_2$CH_2CH$_3$, ^{n}Bu), 1.50–1.56 (m, 12H, M–CH$_2$CH_2CH$_2$CH$_3$, ^{n}Bu), 2.29 (30H, s, N–CH_3 PMDETA), 2.44–2.53 (16H, br, N–CH_2, PMDETA). The relatively low solubility of **2** over prolonged periods of time in *cyc*-C_6D_{12} solutions precluded the collection of its $^{13}C\{1H\}$ spectrum. ^7Li NMR (155.50 MHz, 300 K, *cyc*-C_6D_{12}): δ 0.77.

Synthesis of [(*R*,*R*)-TMCDA·Li(μ-^{n}Bu)$_2$Mg(^{n}Bu)]$_2$ (3)

^{n}BuLi (2.5 mL, 4 mmol of 1.6 M solution in hexanes) was dissolved in 15 mL of dried hexane in an oven-dried Schlenk. 4 mmol of $^nBu_2Mg$ (4 mL of 1 M solution in heptanes) were added and solution turned slightly cloudy. After stirring for 30 minutes, 4 mmol of (*R*,*R*)-TMCDA (0.76 mL) were added. The mixture was gently heated to yield a transparent colourless solution. The solution was transferred to a freezer operating at −30 °C, affording colourless crystals after 24 hours. (1.22 g, 82%).

^1H NMR (400.13 MHz, 300 K, *cyc*-C_6D_{12}): δ −0.73 to −0.71 (12H, br, M–CH_2CH$_2$CH$_2$CH$_3$, ^{n}Bu), 0.86 (18H, t, $^3J_{HH}$ = 7.2 MHz, M–CH$_2$CH$_2$CH$_2$CH_3, ^{n}Bu), 1.07–1.13 (4H, m, γ-CH_2, (*R*,*R*)-TMCDA), 1.15–1.20 (4H, m, β-CH_2, (*R*,*R*)-TMCDA), 1.22–1.31 (12H, m, M–CH$_2$CH$_2$CH_2CH$_3$, ^{n}Bu), 1.50–1.56 (12H, m, M–CH$_2$CH_2CH$_2$CH$_3$, ^{n}Bu), 1.78–1.80 (4H, m, γ′-CH_2, (*R*,*R*)-TMCDA), 1.90–1.93 (4H, m, β′-CH_2, (*R*,*R*)-TMCDA), 2.18 (12H, s, N–CH_3, (*R*,*R*)-TMCDA), 2.39 (14H, s, N–CH_3 and α-C*H*, (*R*,*R*)-TMCDA). $^{13}C\{^1H\}$ NMR (100.62 MHz, 300 K, *cyc*-C_6D_{12}): δ 10.31 (M–*C*H$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 13.32 (M–CH$_2$CH$_2$CH$_2$*C*H$_3$, ^{n}Bu), 21.81 (γ-*C*H$_2$, (*R*,*R*)-TMCDA), 25.04 (β-*C*H$_2$, (*R*,*R*)-TMCDA), 31.56 (M–CH$_2$*C*H$_2$CH$_2$CH$_3$, ^{n}Bu), 32.22 (M–CH$_2$CH$_2$*C*H$_2$CH$_3$, ^{n}Bu), 37.06 (N–*C*H3, (*R*,*R*)-TMCDA), 44.63 (N–*C*H3, (*R*,*R*)-

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TMCDA), 64.07 (α-CH, (*R*,*R*)-TMCDA). ^{7}Li NMR (155.50 MHz, 300 K, *cyc*-C_6D_{12}): δ 1.04.

Synthesis of [TMEDA·LiMg^{n}Bu$_3$]$_x$ (4)

^{n}BuLi (2.5 mL, 4 mmol of 1.6 M solution in hexanes) was dissolved in 15 mL of dried hexane in an oven-dried Schlenk. 4 mmols of $^{n}Bu_2Mg$ (4 mL of 1 M solution in heptanes) were added and solution turned slightly cloudy. After stirring for 30 minutes, 4 mmol of TMEDA (0.60 mL) were added. The mixture was gently heated to yield a transparent colourless solution. The solution was transferred to a freezer operating at −35 °C, affording colourless crystals after 48 hours. (0.75 g, 59%).

^{1}H NMR (400.13 MHz, 300 K, *cyc*-C_6D_{12}): δ −0.75 to −0.31 (6H, br, M–C*H*$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 0.84 (9H, t, $^{3}J_{HH}$ = 7.3 MHz, M–CH$_2$CH$_2$CH$_2$C*H*$_3$, ^{n}Bu), 1.21–1.30 (6H, m, M–CH$_2$CH$_2$C*H*$_2$CH$_3$, ^{n}Bu), 1.46–1.54 (6H, m, M–CH$_2$C*H*$_2$CH$_2$CH$_3$, ^{n}Bu), 2.28 (12H, s, N–C*H*$_3$, TMEDA), 2.34 (4H, s, N–CH$_2$, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 300 K, *cyc*-C_6D_{12}): δ 10.81 (M–*C*H$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 14.23 (M–CH$_2$CH$_2$CH$_2$*C*H$_3$, ^{n}Bu), 32.39 (N–CH$_2$*C*H$_2$CH$_2$–N, TMPDA), 32.99 (M–CH$_2$*C*H$_2$CH$_2$CH$_3$, ^{n}Bu), 46.74, (N–*C*H$_3$, TMEDA) 57.93 (N–*C*H$_2$, TMEDA). ^{7}Li NMR (155.50 MHz, 300 K, *cyc*-C_6D_{12}): δ 0.84.

Synthesis of [TMEDA·Li(μ-^{n}Bu)(μ-O^{n}Bu)Mg(^{n}Bu)]$_2$ (5)

^{n}BuLi (3.35 mL, 5 mmol of 1.6 M solution in hexanes) was dissolved in 15 mL of dried hexane in an oven-dried Schlenk tube. 5 mmol of ^{n}BuOH were added (0.45 mL) at 0 °C and white solid immediately precipitates. 5 mmol of $^{n}Bu_2Mg$ (5 mL of 1 M solution in heptanes) were added and solution turned slightly cloudy. After stirring for 30 minutes, 5 mmol of TMEDA (0.75 mL) were added. Suspension is stirred for 2 hours and filtrated over celite with a filter stick. Solution is concentrated and stored at −35 °C, affording a crop of crystals after 24 hours (0.44 g, 33%).

^{1}H NMR (400.13 MHz, 300 K, *cyc*-C_6D_{12}): δ −0.94 to −0.46 (8H, br, M–C*H*$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 0.84–0.93 (18H, m, M–(O)–CH$_2$CH$_2$CH$_2$C*H*$_3$, ^{n}Bu and O^{n}Bu), 1.26 (12H, br, M–(O)–CH$_2$CH$_2$C*H*$_2$CH$_3$, ^{n}Bu and O^{n}Bu), 1.53 (12H, br, M–(O)–CH$_2$C*H*$_2$CH$_2$CH$_3$, ^{n}Bu and O^{n}Bu), 2.25 (24H, s, N–C*H*$_3$, TMEDA), 2.35 (8H, m, N–C*H*$_2$, TMEDA), 3.63 (8H, br, M–O–C*H*$_2$CH$_2$CH$_2$CH$_3$, O^{n}Bu), The relatively low solubility of **2** over prolonged periods of time in *cyc*-C_6D_{12} solutions precluded the collection of its ^{13}C{1H} spectrum. ^{7}Li NMR (155.50 MHz, 300 K, *cyc*-C_6D_{12}): δ 0.99.

Synthesis of [{(dioxane)·Li(μ-^{n}Bu)$_2$Mg(^{n}Bu)}$_2$]$_\infty$ (6)

^{n}BuLi (0.125 mL, 2 mmol of 1.6 M solution in hexanes) was dissolved in 5 mL of dried hexane in an oven-dried Schlenk. 2 mmol of $^{n}Bu_2Mg$ (2 mL of 1 M solution in heptanes) were added, turning the solution to slightly cloudy. After stirring for 30 minutes, 2 mmol of 1,4-dioxane (0.17 mL) were added. All the volatiles are removed under vacuum and the white precipitated is suspended in 5 mL of dried benzene. Addition of 2 mL of dried toluene and vigorously heating affords in a colourless solution. The flask containing the colourless solution was placed in a Dewar flask of hot water and allowed to cool slowly to room temperature affording colourless needles. (0.27 g, 47%).

^{1}H NMR (400.13 MHz, 343 K, D_8-toluene): δ −0.31 (12H, t, $^{3}J_{HH}$ MHz M–C*H*$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 1.09 (18H, t, $^{3}J_{HH}$ = 7.2 MHz, M–CH$_2$CH$_2$CH$_2$C*H*$_3$, ^{n}Bu), 1.52–1.61 (12H, m, M–CH$_2$CH$_2$C*H*$_2$CH$_3$, ^{n}Bu), 1.71–1.79 (12H, m, M–CH$_2$C*H*$_2$CH$_2$CH$_3$, ^{n}Bu), 3.39 (16H, s, dioxane). ^{13}C{^{1}H} NMR (100.62 MHz, 343 K, D_8-toluene): δ 9.66 (M–*C*H$_2$CH$_2$CH$_2$CH$_3$, ^{n}Bu), 14.35 (M–CH$_2$CH$_2$CH$_2$*C*H$_3$, ^{n}Bu), 23.34 (N–CH$_2$*C*H$_2$CH$_2$–N, TMPDA), 32.10 (M–CH$_2$*C*H$_2$CH$_2$CH$_3$, ^{n}Bu), 67.59, (M–CH$_2$CH$_2$*C*H$_2$CH$_3$, ^{n}Bu) 137.79 (dioxane). ^{7}Li NMR (155.50 MHz, 343 K, D_8-toluene): δ 0.67.

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