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PAPER

Synthesis and structural chemistry of alkali metal tris(HMDS) magnesiate complexes containing chiral diamine donor ligands†

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Six alkali metal tris(HMDS) magnesiate complexes (HMDS, 1,1,1,3,3,3,-hexamethyldisilazide) containing chiral diamine ligands have been prepared and characterised in both the solid- and solution-state. Four of the complexes have a solvent-separated ion pair composition of the form $[[M \cdot (\text{chiral diamine})_2]^+ \{Mg(HMDS)_3\}^-]$ [$M = \text{Li}$ for **1** and **3**, Na for **2** and **4**; chiral diamine = (–)-sparteine for **1** and **2**, (*R,R*)-TMCDA for **3** and **4**, (where (*R,R*)-TMCDA is *N,N,N',N'*-(1*R,2R*)-tetramethylcyclohexane-1,2-diamine)] and two have a contacted ion pair composition of the form $[[K \cdot \text{chiral diamine}]^+ \{Mg(HMDS)_3\}^-]$ [chiral diamine = (–)-sparteine for **5** and (*R,R*)-TMCDA for **6**]. In the solid-state, complexes **1–4** are essentially isostructural, with the lithium or sodium cation sequestered by the respective chiral diamine and the previously reported anion consisting of three HMDS ligands coordinated to a magnesium centre. As such, complexes **1–4** are the first structurally characterised complexes in which the alkali metal is sequestered by two molecules of either of the chiral diamines (–)-sparteine (**1** and **2**) or (*R,R*)-TMCDA (**3** and **4**). In addition, complex **4** is a rare (*R,R*)-TMCDA adduct of sodium. In the solid state, complexes **5** and **6** exist as polymeric arrays of dimeric $[[K \cdot \text{chiral diamine}]^+ \{Mg(HMDS)_3\}^-]_2$ subunits, with **5** adopting a two-dimensional net arrangement and **6** a linear arrangement. As such, complexes **5** and **6** appear to be the only structurally characterised complexes in which the chiral diamines (–)-sparteine (**5**) or (*R,R*)-TMCDA (**6**) have been incorporated within a polymeric framework. In addition, prior to this work, no (–)-sparteine or (*R,R*)-TMCDA adducts of potassium had been reported.

Introduction

Alkali metal magnesiate chemistry has attracted increasing interest since the first magnesiate, lithium triphenylmagnesiate, “ LiMgPh_3 ”, was reported by Wittig in 1951.¹ Ate complexes often display a unique synergic chemistry completely distinct from that of their parent organo-alkali metal reagent (either alkyl or amido) or Grignard-type reagent. For instance, recently they have been shown to effect deprotonative metallation regioselectively on a range of organic substrates (such as benzene,² toluene,^{2a,3} furan,⁴ metallocenes⁵ and alkynes⁶) at ambient temperatures. As such, due to the requirement of the presence of an alkali metal for these metallations to succeed, where the departing hydrogen in the substrate is replaced by magnesium, these mixed-metal reactions have been termed alkali-metal-mediated magnesiations (AMMMg).^{1b–d} Previously, several alkali metal alkyl/amido magnesiates have been structurally characterised with donor ligands

such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and these have been utilised in synthesis.^{2–3,5–7} However, thus far the scope has been largely restricted to achiral donor systems. In this work chiral relatives have been studied. A naturally occurring alkaloid, (–)-sparteine (Fig. 1), has been synonymous with asymmetric synthesis since the seminal studies from the groups of Hoppe and Beak in the early 1990s.⁸ The chiral diamine can be isolated in significant quantities from the extraction of certain *papilionaceous* plants such as *Cytisus scoparius* (Scotch Broom),⁹ and is generally

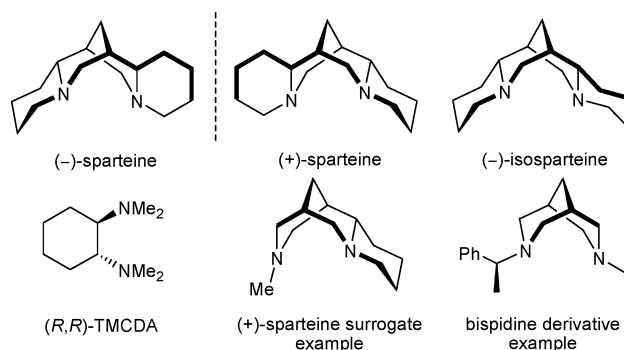


Fig. 1 Chiral diamines (–)-sparteine and (*R,R*)-TMCDA, along with other common chiral diamine auxiliaries.

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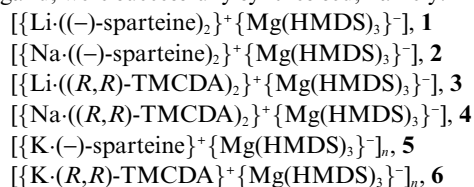
the chiral auxiliary of choice due to its ability to effect the enantioselective metallation of many key organic substrates¹⁰ generally in conjunction with alkylolithiums such as *n*-BuLi.¹¹ These reagents commonly give products in high enantiomeric excess and yield, with the efficiency and breadth of application of these (–)-sparteine alkylolithium systems thus far unsurpassed, achieving high levels of reactivity and stereoselectivity in deprotonation, oxidation, reduction and addition reactions.¹² Until 2009, (–)-sparteine was readily available from most chemical suppliers at relatively low expense (approximately £1.80 per mL);¹³ however, it has now been withdrawn from sale by many chemical suppliers. Other chiral diamine auxiliaries have been prepared in an attempt to better the performance of (–)-sparteine in enantioselective deprotonation. These include; (+)-sparteine,¹⁴ (–)-isosparteine,¹⁵ *N,N,N',N'*-(1*R*,2*R*)-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCDAs],¹⁶ (–/+)-sparteine surrogates¹⁷ and bispidine derivatives^{17c} (Fig. 1). It has recently been emphasised that altering the chiral diamine in an asymmetric deprotonation can have a drastic effect on the outcome of the reaction.¹⁸

From a structural perspective, (–)-sparteine and (*R,R*)-TMCDAs have been exploited by Strohmann to prepare several chiral classical organolithiums. This work includes a series of papers on the structural elucidation of (–)-sparteine and (*R,R*)-TMCDAs adducts of the commonly used alkylolithium bases *t*-butyllithium¹⁹ and isopropyllithium,²⁰ (–)-sparteine-coordinated *n*-butyllithium^{20a} and (*R,R*)-TMCDAs-coordinated *s*-butyllithium^{20b} and methylolithium.^{20b} Surprisingly, the synthetic and structural chemistry of chiral diamine complexes of alkali metal amides and alkali metal magnesiates has thus far been largely neglected. Addressing this deficiency, we reported the synthesis and structural characterisation of a (–)-sparteine coordinated mixed alkyl/amido sodium magnesiate, namely [(–)-sparteine·NaMg(TMP)₂][–]Bu], in 2008,²¹ and a year later, (–)-sparteine adducts of lithium and sodium HMDS along with a highly unusual hydroxyl-incorporated solvent-separated hexanuclear sodium sodiate, [(–)-sparteine·Na(μ-HMDS)Na(–)-sparteine]⁺[Na₄(μ-HMDS)₄(OH)][–],²² which are related to inverse crown ether structures.^{7d,23} Striving to develop a new chiral avenue in the area of alkali metal magnesiate chemistry we herein report the synthesis and structural characterisation of a series of HMDS alkali metal magnesiates featuring the chiral diamines, (–)-sparteine or (*R,R*)-TMCDAs as supporting ligands.

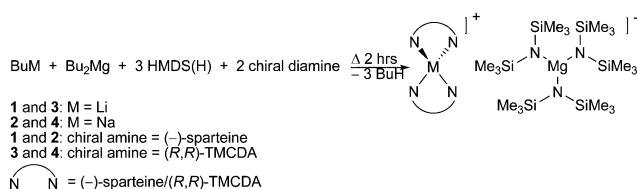
Results and discussion

Synthesis of new complexes 1–6

Four new *solvent-separated* and two new *contacted* ion pair alkali metal tris(HMDS) magnesiates each containing a chiral diamine ligand, were successfully synthesised, namely:



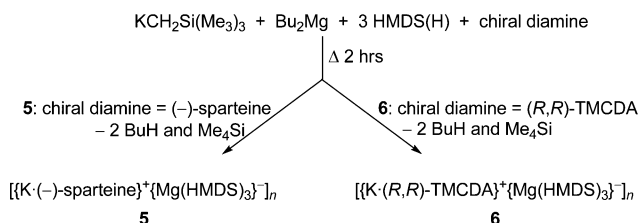
The synthetic routes to **1–4** are summarised in Scheme 1. *n*-Butyllithium (for **1** and **3**) or *n*-butylsodium (for **2** and **4**) was mixed with one molar equivalent of di-*n*-butylmagnesium in hexane



Scheme 1 Synthesis of **1–4**.

solution, and reacted with three molar equivalents of HMDS(H). To ensure complete amination of the *s*-block organometallics, these mixtures were heated to reflux before two molar equivalents of (–)-sparteine (for **1** and **2**) or of (*R,R*)-TMCDAs (for **3** and **4**) were added, causing the precipitation of a white solid from solution. For **1**, **3** and **4**, the addition of toluene was required to produce a homogeneous solution and for **2**, a neat toluene solution was required to achieve homogeneity. Colourless crystals of the product grew from the solution at ambient temperature for **1** and by slowly cooling the Schlenk tube to ambient temperature from a hot water-filled Dewar flask for **2–4** (crystalline yields of **1–4**, 80, 79, 61 and 81% respectively). The same products (**1–4**) were isolated when only one equivalent of the respective chiral diamine was utilised, albeit in a much reduced yield.

Scheme 2 summarises the synthetic routes to **5** and **6**. An equimolar mixture of (trimethylsilylmethyl)potassium and di-*n*-butylmagnesium was reacted with three molar equivalents of HMDS(H) in hexane solution. These mixtures were heated to reflux for two hours before one molar equivalent of (–)-sparteine (for **5**) or of (*R,R*)-TMCDAs (for **6**) was added, precipitating a white solid from solution. The precipitate dissolved on heating for **6**; however, for **5**, the addition of toluene was required to produce a homogeneous solution. In both cases (**5** and **6**), colourless crystals grew from the solution by slowly cooling the Schlenk tube using the aforementioned technique (crystalline yields of **5** and **6**, 85 and 52%, respectively).



Scheme 2 Synthesis of **5** and **6**.

Solid-state structures

Due to the solvent-separated ion pair composition of complexes **1–4**, the cation and anion of **1** will be discussed independently. Thereafter, only the cation will be discussed for **2–4**, owing to the generality of the anion in this series of complexes. Full crystallographic details are given in the ESI.†

X-ray crystallographic studies reveal that **1** crystallises in the orthorhombic system, with space group *P*2₁2₁2₁. The molecular structure of its cation (Fig. 2) is composed of two (–)-sparteine molecules which coordinate in their usual bidentate fashion to the lithium centre.^{20a,24} To the best of our knowledge, no (–)-sparteine adducts of the alkali metals have been prepared thus far in which the metal centre is sequestered by two (–)-sparteine molecules;

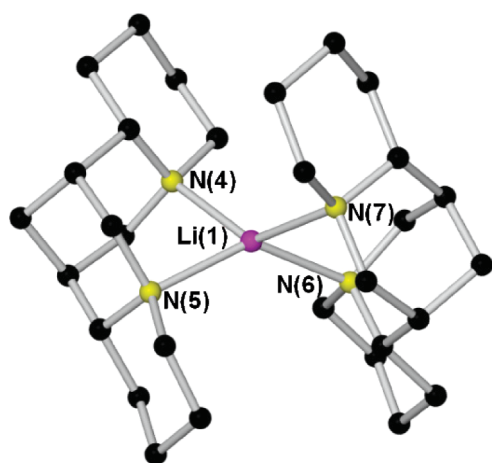


Fig. 2 Molecular structure of the cation of **1**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): Li(1)–N(4), 2.206(4); Li(1)–N(5), 2.205(4); Li(1)–N(6), 2.211(4); Li(1)–N(7), 2.271(4); N(4)⋯N(5), 2.970(2); N(6)⋯N(7), 2.993(2); N(4)⋯N(7), 4.139(2); N(4)⋯N(6), 3.684(2); N(5)⋯N(6), 4.093(2); N(5)⋯N(7), 3.721(2); N(4)–Li(1)–N(5), 84.65(13); N(4)–Li(1)–N(6), 113.04(2); N(4)–Li(1)–N(7), 135.2(2); N(5)–Li(1)–N(6), 135.9(2); N(5)–Li(1)–N(7), 112.5(2); N(6)–Li(1)–N(7), 83.8(1).

hence the cation of **1** as well as that of **2** are unique in this respect. Complexes in which one (–)-sparteine molecule coordinates to a lithium centre have recently been reported by Strohmman *et al.*,^{20a,24} including the first monomeric butyllithium complex [BuLi(–)-sparteine],^{19a} and by Stalke *et al.* whom, on forming the dimer structure [(–)-sparteine]·LiCH₂SiMe₃,²⁵ were able to deaggregate the hexameric aggregate of trimethylsilylmethyl lithium.²⁶ The mean Li–N bond distance within cation **1** (2.223 Å) lies in the range of those of the complexes where the Li centre is only coordinated to one (–)-sparteine molecule (2.006–2.234 Å)^{19a,20a,24–25} and as expected the greatest distortion from a perfect tetrahedral geometry for the Li centre (sum of angles, 665.05°; mean, 110.84°) arises due to the (–)-sparteine–Li bite angles (mean angle, 84.22°). This is in agreement with the mean bite angles of the aforementioned complexes independently characterised by Strohmman and Stalke, which also have distorted tetrahedral environments for their Li centres (range 82.22–87.74°).^{19a,20a,24–25}

The anion of **1** is composed of three HMDS ligands which coordinate to a magnesium centre. This anion is known, having previously been incorporated within the contacted ion pairs [{LiMg(HMDS)₃}],^{7d} [{THF·LiMg(HMDS)₃}],^{7g} and [{pyridine·LiMg(HMDS)₃}],^{7g} and the solvent-separated ion pair [{Li₂(μ-HMDS)(μ-TEMPO)·2TEMPO}]⁺[Mg(HMDS)₃][–],²⁷ and therefore does not merit any further discussion. A toluene solvated phase of **1** was also isolated and characterised by single-crystal diffraction. No significant structural differences were observed between the molecular geometries of the two phases and so detail on the solvated phase is included only in the ESI.†

X-ray crystallographic studies reveal that **2** crystallises in the orthorhombic system, with space group *P*2₁2₁2₁. Within the asymmetric unit of **2**, there are two independent sets of [{Na·(–)-sparteine}₂]⁺ and [{Mg(HMDS)₃}][–] ions. Due to the negligible differences in the dimensions of the two sets of ions, those associated with only one of the independent cations will be discussed. Fig. 3 shows the molecular structure and pertinent

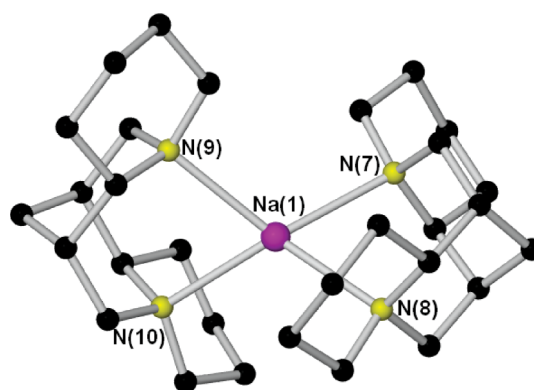


Fig. 3 Molecular structure of the cation of **2**. H atoms and solvent of crystallisation (toluene) have been omitted for clarity. Key bond distances (Å) and angles (°) (for one of the two cations found in the asymmetric unit): Na(1)–N(7), 2.476(3); Na(1)–N(8), 2.458(4); Na(1)–N(9), 2.448(4); Na(1)–N(10), 2.450(4); N(9)⋯N(10), 3.009(5); N(7)⋯N(8), 2.979(5); N(7)⋯N(9), 4.155(5); N(8)⋯N(9), 4.660(5); N(8)⋯N(10), 4.226(5); N(7)⋯N(10), 4.680(5); N(7)–Na(1)–N(8), 74.26(12); N(7)–Na(1)–N(9), 115.09(12); N(7)–Na(1)–N(10), 143.60(14); N(8)–Na(1)–N(9), 143.56(14); N(8)–Na(1)–N(10), 118.80(13); N(9)–Na(1)–N(10), 75.78(12).

dimensions of a cation of **2**, which bears a close resemblance to its lithium congener **1**, despite the difference in size between the alkali metals. Two (–)-sparteine molecules trap the sodium. Cation **2** is only the third complex to be reported thus far which incorporates both sodium and (–)-sparteine, the preceding two complexes, [(–)-sparteine·NaMg(TMP)₂]⁺ Bu]²¹ and the aforementioned hydroxyl-incorporated solvent-separated hexanuclear sodium sodiate, [(–)-sparteine·Na(μ-HMDS)Na·(–)-sparteine]⁺[Na₄(μ-HMDS)₄(OH)][–],²² (where in each complex the Na centre is only coordinated to one (–)-sparteine molecule) being reported previously by our group. The mean Na–N bond distance in the cation of **2** (2.458 Å) is in agreement with those in these complexes (2.499 Å and 2.426 Å, respectively).^{21–22} The Na centre adopts a distorted tetrahedral environment here (sum of angles around Na, 671°; mean angle 111.86°), as is the case for the sodium magnesiate, but different from that of the aforementioned sodium sodiate, which adopts a distorted trigonal planar arrangement. The mean M–N bond distance of cation **2** (2.461 Å) is greater than that of its lithium analogue **1** (mean bond distance, 2.223 Å), due to the larger size of the metal centre, and as expected the greatest distortion from a perfect tetrahedral geometry for the Na centre (sum of angles, 671.09°; mean angle 111.85°), arises due to the (–)-sparteine–alkali metal bite angles, which in keeping with the larger size of the metal centre, are approximately 9° more acute in **2** than in **1** (mean angles, 75.02° and 84.22°, respectively).

X-ray crystallographic studies reveal that **3** crystallises in the monoclinic system, with space group *P*2₁. As for **2**, within the asymmetric unit of **3**, there are two independent sets of [{Li·(R,R)-TMCDAs}₂]⁺ and [{Mg(HMDS)₃}][–] ions. Again as the differences in the dimensions of the two sets of equivalent ions are negligible, those associated with only one of the independent cations will be discussed. Fig. 4 shows the molecular structure and pertinent dimensions of a cation of **3**. Two (R,R)-TMCDAs molecules chelate in a terminal fashion to the lithium metal centre, akin to the arrangement often observed in alkali metal complexes

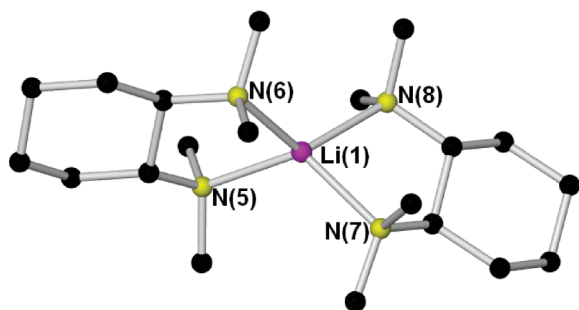


Fig. 4 Molecular structure of the cation of **3**. H atoms and solvent of crystallisation (toluene) have been omitted for clarity. Key bond distances (Å) and angles (°) (for one of the two cations found in the asymmetric unit): Li(1)–N(5), 2.153(5); Li(1)–N(6), 2.129(6); Li(1)–N(7), 2.133(6); Li(1)–N(8), 2.152(6); N(5)⋯N(6), 2.883(3); N(7)⋯N(8), 2.850(4); N(6)⋯N(8), 3.753(4); N(6)⋯N(7), 3.784(4); N(5)⋯N(7), 3.698(3); N(5)⋯N(8), 3.854(4); N(5)–Li(1)–N(6), 84.7(2); N(5)–Li(1)–N(7), 119.3(3); N(5)–Li(1)–N(8), 127.1(3); N(6)–Li(1)–N(7), 125.2(3); N(6)–Li(1)–N(8), 122.5(3); N(7)–Li(1)–N(8), 83.4(2).

of its achiral relative TMEDA.²⁸ On searching the Cambridge Crystallographic Database²⁹ we can find no precedent of a lithium centre (or indeed any alkali metal) binding simultaneously to two (*R,R*)-TMEDA ligands. Complexes in which one (*R,R*)-TMEDA molecule coordinates to a lithium centre have recently been reported by Strohmann *et al.*,^{20b,24d,30} including [BuLi·(*R,R*)-TMEDA],^{19b} which was the second structurally characterised alkyllithium monomer bearing a saturated hydrocarbon (the first being [BuLi·(–)-sparteine]).^{19a} Comparing the mean Li–N bond distance in the bis-chiral ligated cation **3** (2.142 Å) with its mono-ligated variants (range, 2.055–2.256 Å)^{19b,20b,24d,30} reveals no significant differences. As expected the greatest distortion from a perfect tetrahedral geometry for the Li centre in **3** (sum of angles, 662.20°) arises due to the (*R,R*)-TMEDA–Li bite angles (mean angle, 84.05°). In comparison to its (–)-sparteine analogue (cation **1**), the cation of **3** has a slightly shorter mean Li–N bond distance and a virtually identical amine–Li bite angle (2.142 Å *vs.* 2.223 Å; and, 84.05° *vs.* 84.22°, respectively). The difference in these parameters is perhaps due to the less sterically demanding nature of (*R,R*)-TMEDA when compared with (–)-sparteine.

Turning to **4**, it crystallises in the orthorhombic system, space group *P*2₁2₁1. Fig. 5 shows the molecular structure and pertinent dimensions of its cation, which akin to its lithium congener **3**, is composed of two (*R,R*)-TMEDA molecules which chelate terminally to the sodium. As expected the mean M–N bond distance of cation **4** (2.327 Å) is greater than that of its lithium analogue **3** (mean bond distance, 2.142 Å) and as expected the greatest distortion from a perfect tetrahedral geometry for the Na centre (sum of angles, 666.59°) arises due to the (*R,R*)-TMEDA–M' bite angles, which in keeping with the larger size of the metal centre, are approximately 8° more acute in **4** than in **3** (mean angles, 75.95° and 84.05°, respectively). In comparison to its (–)-sparteine analogue (cation **2**), the cation of **4** has a shorter mean Na–N bond distance and a slightly more open amine–Na bite angle (2.327 Å *vs.* 2.461 Å and 75.95° *vs.* 75.22°, respectively), again emphasising the slightly reduced steric demands of (*R,R*)-TMEDA *versus* (–)-sparteine.

Focusing on **5**, it crystallises in the monoclinic system, space group *P*2₁. Fig. 6 shows its molecular structure and

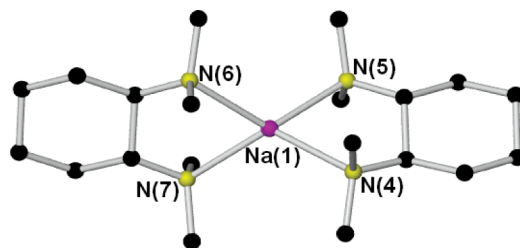


Fig. 5 Molecular structure of the cation of **4**. H atoms and solvent of crystallisation (toluene) have been omitted for clarity. Key bond distances (Å) and angles (°): Na(1)–N(4), 2.310(5); Na(1)–N(5), 2.312(3); Na(1)–N(6), 2.357(3); Na(1)–N(7), 2.329(3); N(6)⋯N(7), 2.880(3); N(4)⋯N(5), 2.847(3); N(5)⋯N(6), 4.081(3); N(4)⋯N(6), 4.281(3); N(4)⋯N(7), 4.076(3); N(5)⋯N(7), 4.316(4); N(4)–Na(1)–N(5), 76.05(12); N(4)–Na(1)–N(6), 133.06(14); N(4)–Na(1)–N(7), 122.95(15); N(5)–Na(1)–N(6), 121.84(10); N(5)–Na(1)–N(7), 136.84(10); N(6)–Na(1)–N(7), 75.85(9).

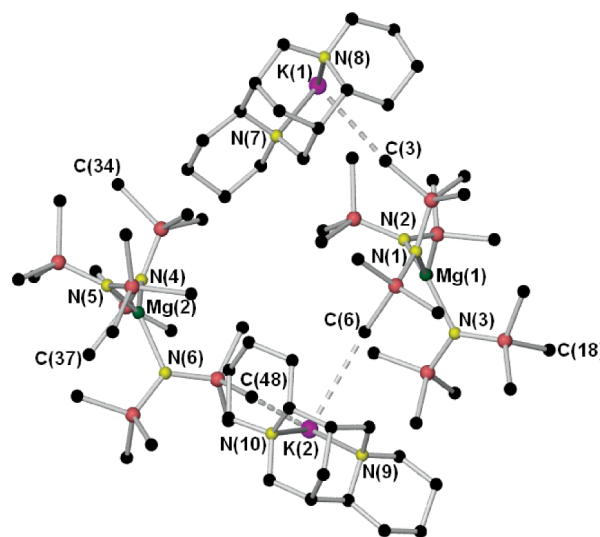


Fig. 6 Asymmetric unit of **5**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): K(1)–N(7), 2.789(2); K(1)–N(8), 2.877(2); K(1)–C(3), 3.222(3); K(2)–N(9), 2.768(2); K(2)–N(10), 2.813(2); K(2)–C(6), 3.448(3); K(2)–C(48), 3.255(3); Mg(1)–N(1), 2.038(2); Mg(1)–N(2), 2.019(2); Mg(1)–N(3), 2.032(2); Mg(2)–N(4), 2.027(2); Mg(2)–N(5), 2.011(2); Mg(2)–N(6), 2.037(2); N(7)–K(1)–N(8), 62.75(6); N(7)–K(1)–C(3), 93.85(6); N(8)–K(1)–C(3), 112.71(7); N(9)–K(2)–N(10), 63.41(6); N(9)–K(2)–C(6), 87.35(7); N(9)–K(2)–C(48), 177.33(7); N(10)–K(2)–C(6), 105.00(7); N(10)–K(2)–C(48), 118.99(6); C(6)–K(2)–C(48), 90.79(7); N(1)–Mg(1)–N(2), 118.80(9); N(1)–Mg(1)–N(3), 119.59(9); N(2)–Mg(1)–N(3), 121.57(9); N(4)–Mg(2)–N(5), 118.6(1); N(4)–Mg(2)–N(6), 119.25(9); N(5)–Mg(2)–N(6), 122.15(9). The asymmetric unit of **5** polymerises through K(1)–C(18), 3.407(3); K(1)–C(37), 3.297(3); and K(2)–C(34), 3.248(3) Å. These interactions are not shown in the figure for clarity.

pertinent dimensions, which in marked contrast to the previously discussed complexes, is a *contacted* ion pair alkali metal magnesiate. Its asymmetric unit contains two [{K·(–)-sparteine}⁺{Mg(HMDS)₃}[–]] ion pairs linked by an agostic-type interaction [K(2)–C(6)] involving a Me(SiMe₂)N unit (Fig. 6). Both Mg(HMDS)₃ anions interact with the two potassium atoms (again through K–CH₃ agostic interactions) within the asymmetric unit and a third neighbouring K atom (*i.e.*, the anions act

as μ_3 -bridges) thus promoting the formation of a polymeric array. In this polymer, each K atom is five-coordinate and bound to two (–)-sparteine N atoms [mean K–N distance, 2.812 Å], and three CH₃ groups [range of K–C distances, 3.222(3)–3.448(3) Å]. Interestingly, there are no K–N_{amide} interactions. The extended structure exists as a two-dimensional net (Fig. 7). Each ring of the net consists of 22 atoms and incorporates three [$\{K(\text{–})\text{-sparteine}\}^+ \{Mg(\text{HMDS})_3\}^-$] units. To the best of our knowledge, no complexes (alkali metal or indeed any metal) have been prepared thus far in which the chiral diamine (–)-sparteine has been incorporated within a polymeric framework, and in addition, no (–)-sparteine adducts of potassium have been reported thus far; hence **5** is unique in both of these respects. Both solvent-separated and contacted ion pair potassium magnesiate have been previously reported by Mulvey *et al.* These include, arene- or metallo-arene incorporated contacted ion pair complexes such as [$\{K(\text{benzene})_2\}^+ \{Mg(\text{HMDS})_3\}^-$]³¹ or [$\{K[(C_6H_6)_2Cr]_2\}^+ \{Mg(\text{HMDS})_3\}^-$]_∞³² and the ferrocene-containing solvent separated system, [$\{K(\eta^5\text{-ferrocene})_2(\eta^3\text{-toluene})_2\}^+ \{Mg(\text{HMDS})_3\}^-$]_∞³³. Despite the $Mg(\text{HMDS})_3^-$ anion being a part of the contacted ion pair structure of **5** the range of N–Mg–N angles [118.6(1)–122.15(9)°] is essentially identical to that found in the solvent separated structure of **1**.

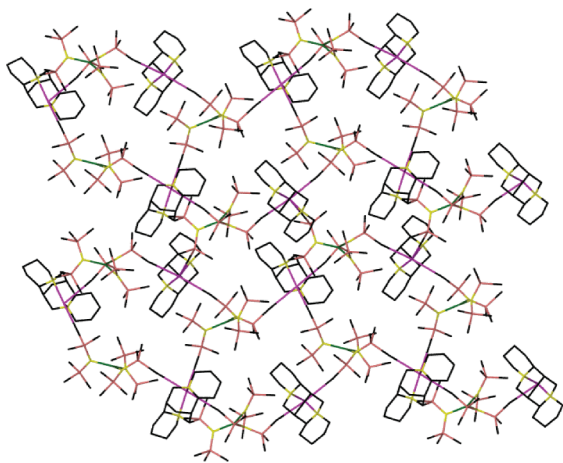


Fig. 7 Extended view of supramolecular **5**, showing its two dimensional net arrangement, with each ‘hole’ in the net consisting of 22 atoms and incorporating three [$\{K(\text{–})\text{-sparteine}\}^+ \{Mg(\text{HMDS})_3\}^-$] units.

X-ray crystallographic studies reveal that **6** crystallises in the triclinic system, space group *P1*. Fig. 8 shows the molecular structure and pertinent dimensions of **6**, which as is the case with **5** is a contacted ion pair potassium magnesiate. Also akin to **5**, the asymmetric unit of **6**, contains two crystallographically unique anion–cation pairs this time of the composition [$\{K((R,R)\text{-TMCD})^+ \{Mg(\text{HMDS})_3\}^-$]. Four K–CH₃ agostic interactions [K(1)–C(5), K(1)–C(29), K(2)–C(1) and K(2)–C(32)] result in the asymmetric unit adopting a 12-membered K₂C₄N₂Si₄ ring motif (Fig. 8). Each K atom is five-coordinate bound to two (*R,R*)-TMCD N atoms [mean K–N distance, 2.779 Å, which is slightly shorter than the mean K–N bond distance in **5**, (2.812 Å), perhaps due to the less sterically demanding nature of (*R,R*)-TMCD when compared with (–)-sparteine], and three CH₃ groups [range of K–C distances, 3.112(2)–3.684(4) Å]. Mirroring the situation in **5**, there are no K–N_{amide} interactions. Both

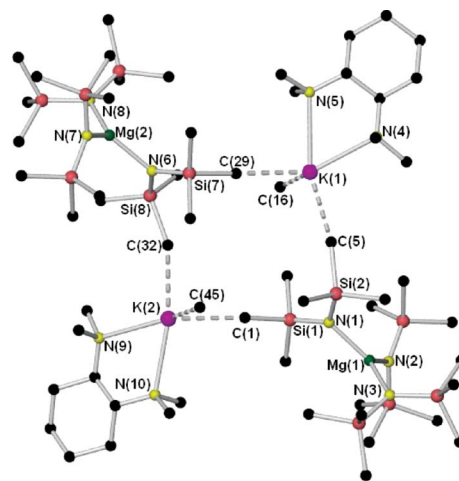


Fig. 8 Asymmetric unit of **6**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): K(1)–N(4), 2.727(2); K(1)–N(5), 2.849(2); K(1)–C(5), 3.368(2); K(1)–C(29), 3.075(2); K(2)–N(9), 2.767(2); K(2)–N(10), 2.771(2); K(2)–C(1), 3.112(2); K(2)–C(32), 3.684(4); Mg(1)–N(1), 2.0276(19); Mg(1)–N(2), 2.024(2); Mg(1)–N(3), 2.036(2); Mg(2)–N(6), 2.0322(19); Mg(2)–N(7), 2.026(2); Mg(2)–N(8), 2.008(2); N(4)–K(1)–N(5), 62.35(5); N(4)–K(1)–C(5), 90.83(6); N(4)–K(1)–C(29), 130.01(6); N(5)–K(1)–C(5), 136.16(6); N(5)–K(1)–C(29), 88.11(6); C(5)–K(1)–C(29), 81.14(7); N(9)–K(2)–N(10), 63.44(5); N(9)–K(2)–C(1), 126.09(6); N(9)–K(2)–C(32), 84.14(7); N(10)–K(2)–C(1), 95.49(6); N(10)–K(2)–C(32), 126.60(7); C(1)–K(2)–C(32), 69.70(7); N(1)–Mg(1)–N(2), 118.83(8); N(1)–Mg(1)–N(3), 118.84(9); N(2)–Mg(1)–N(3), 122.32(8); N(6)–Mg(2)–N(7), 119.91(9); N(6)–Mg(2)–N(8), 118.69(9); N(7)–Mg(2)–N(8), 121.38(9). The asymmetric unit of **6** polymerises through K(1)–C(16) [3.257(4) Å] and K(2)–C(45) [3.202(4) Å].

$Mg(\text{HMDS})_3^-$ anions interact with the two potassium atoms (*via* K–CH₃ agostic interactions) within the asymmetric unit and a third neighbouring K atom (*i.e.*, the anions act as μ_3 -bridges) thus promoting polymerisation. The extended structure exists as a linear polymeric framework (Fig. 9) consisting of alternating ‘small’ 12-atom (K₂C₄N₂Si₄) and ‘large’ 16-atom (K₂Mg₂C₄N₄Si₄) fused rings. Complex **6** is the first (*R,R*)-TMCD adduct of

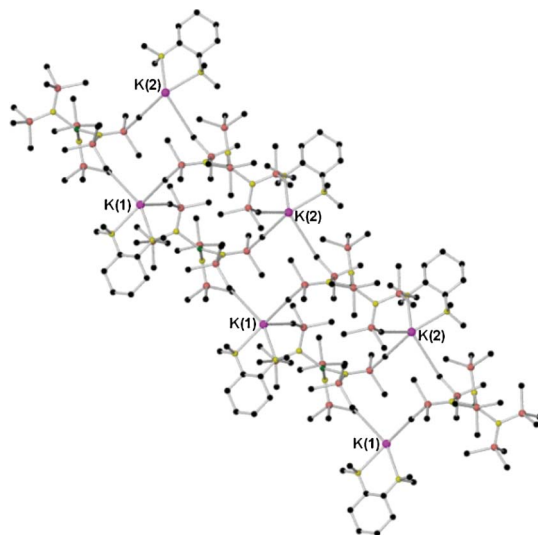


Fig. 9 Extended view of supramolecular **6**, showing the linear arrangement of three asymmetric units, with alternating large and small rings.

potassium and it also appears to represent the only example of a coordination polymer involving this chiral diamine.

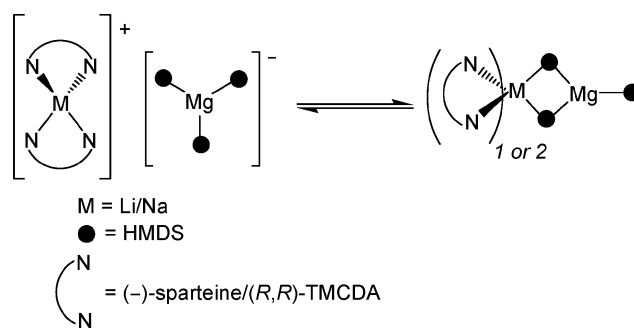
Collectively, the structural data presented for the complexes reported herein, indicate that only one molecule of the diamine [(–)-sparteine or (*R,R*)-TMCD] is necessary to saturate the K atom (complexes **5** and **6**). This is counterintuitive as the larger size of a K atom with respect to a Li and/or Na atom would seem to suggest that a K atom should require two or more molecules of the diamine to fill its substantially larger coordination sphere and not only one. However, due to the softer nature of K (*cf.*, Li and Na), more competition from agostic interactions arises, rendering additional K–N interactions unnecessary. Furthermore, the utility of either of the diamines (–)-sparteine or (*R,R*)-TMCD for complexes **1–4**, in which the metal centre is either Li or Na, does not produce connectivity differences for their corresponding alkali metal magnesiates; however, when K is the alkali metal (in complexes **5** and **6**), changing the diamine dramatically alters the final arrangement of the complex from a supramolecular point of view. Possibly the more sterically demanding nature of (–)-sparteine hinders the closure of the $K_2C_4N_2Si_4$ ring observed for **6** (Fig. 6) and therefore gives the final more open polymeric arrangement seen for **5** (Fig. 7).

NMR spectroscopic studies

Complexes **1–4** are soluble in both arene and ethereal solvents; whilst **5** and **6** are insoluble in arenes, but soluble in ethers such as THF. This permitted a NMR spectroscopic study on solutions of the complexes in d_8 -toluene (for **1–4**), and d_8 -THF (for **1–6**). Focusing on the (–)-sparteine complexes, **1** and **2** in arene solution, the 1H and ^{13}C NMR spectra obtained from the respective experiments were complex showing a forest of resonances due to the vast number of chemically distinct aliphatic hydrogen and carbon atoms present in the donor molecule (see ESI†). The key features associated with the diamine ligand in both sets of these spectra are that the resonances are broader than those for the free ligand, and the most downfield resonance of the free ligand (δ 2.78) is shifted slightly upfield on complexation (by 0.08 ppm for both **1** and **2**). Hence, (–)-sparteine appears to remain coordinated to the respective metal centres in arene solution. The HMDS region of these spectra are rather more complex than initially envisaged. If the solid state structures were to be retained in solution, then a single resonance should be observed. This is indeed the scenario which is encountered when d_8 -THF solution is used. Although the spectra appear to indicate that a solvent-separated ion pair structure is forthcoming it is obvious that the solid state structures are not retained in THF solution (Fig. S6–S8 and S14–15†). The resonances associated with the (–)-sparteine ligand exactly match those of free (–)-sparteine (indicating that the diamine has been displaced by d_8 -THF). This ligand disengagement therefore implies that the chiral information associated with the alkali metal centres has been lost. As only one $Si(CH_3)_3$ resonance is observed, the likely solution state structures of these complexes are $[M \cdot (d_8\text{-THF})_x]^+ [Mg(HMDS)_3]^-$ (where M is Li or Na for **1** and **2** respectively). In d_8 -toluene solution (300 K) at least three chemically distinct $Si(CH_3)_3$ resonances are observed, indicating much more complex solution dynamics. To shed light on these solution dynamics we undertook a variable temperature NMR spectroscopic study on a d_8 -toluene solution of **2** (Fig. S18†).

At high temperature (353 K) one sharp, distinct resonance (δ 0.26) was observed. On decreasing the acquisition temperature, a broadening of this resonance and a gradual downfield shift was noted (*e.g.*, at 313 K, δ 0.44). As alluded to earlier, at 300 K, the first sign of decoalescence was noted [resonances at 0.49, 0.54 (br) and 0.64]. On cooling the solution further (263 K), these signals sharpened (0.75, 0.72 and 0.64). We believe that these data may correspond to an equilibrium occurring between a solvent-separated and a contacted ion pair species. This will be discussed in more detail later during the discussion of the solution structures of **3** and **4**.

The solutions of (*R,R*)-TMCD-containing complexes **3** and **4**, behave similarly to their (–)-sparteine analogues. To emphasise, in d_8 -toluene solution, the 1H NMR spectra reveal three unique $Si(CH_3)_3$ resonances at 0.65, 0.39, 0.34 and 0.64, 0.39, 0.34 for **3** and **4**, respectively, and the diamine resonances are shifted from those of the free diamine (Fig. S30†). By comparing the 1H NMR spectra with a series of standards [*e.g.*, HMDS(H), LiHMDS, NaHMDS and $Mg(HMDS)_2$] we can exclude the formation of any of these compounds in our systems. The 7Li NMR spectra (d_8 -toluene) of **1** and **3** show that there are two Li species in solution (δ 1.34 and 1.08; and 1.48 and –0.62 for **1** and **3**, respectively). This fact coupled with the presence of three $Si(CH_3)_3$ resonances in its corresponding 1H NMR spectrum leads us to believe that a dynamic process is occurring in solution. Like **1** and **2**, the spectra for arene solutions of **3** and **4** showed that the (*R,R*)-TMCD resonances were broad. In addition, due to the simpler structure of the diamine, it was clear that only one type of (*R,R*)-TMCD ligand was present. It is likely that on dissolution in d_8 -toluene solution, the solvent separated species (**1–4**) exist in an equilibrium with its respective contacted ion pair, namely $[(\text{diamine})_x \cdot M(\mu\text{-HMDS})_2Mg(HMDS)]$ (Scheme 3).



Scheme 3 Possible equilibrium between solvent-separated ion pair (akin to structures of **1–4**) and contacted ion pair structures in d_8 -toluene solution.

The three different HMDS environments (*vide infra*) can be accounted for by one resonance corresponding to the three HMDS ligands present in the respective solvent-separated ion pair species, and the other two signals (which are in a 2 : 1 ratio) corresponding to the distinct bridging and terminal HMDS ligands present in the particular contacted ion pair structure. The most downfield resonance (0.65 for **3** and 0.64 for **4**, respectively) can be attributed to the solvent-separated ion pair structure. The ratio of the “solvent-separated” resonance to the other two resonances alters depending on the concentration of the solution. Interestingly and

surprisingly, for **3** this contacted ion pair structure appears to form solely in d_6 -benzene solution [*i.e.*, only two $\text{Si}(\text{CH}_3)_3$ resonances observed], with the seeming absence of the “solid state” solvent-separated species. This is corroborated by the ^7Li NMR spectrum of **3** which reveals a single Li environment (δ 1.45).

Turning to d_8 -THF solutions of **3**, **4** and **6**, the ^1H NMR spectra reveal a similar scenario to that encountered for their (–)-sparteine analogues; that is a solvent-separated structure is present, with the cation being coordinated to d_8 -THF molecules rather than the diamine ligands. As expected, the polymeric structures of **5** and **6** are not retained in solution.

Conclusions

In an effort to develop a new avenue in alkali metal magnesiate chemistry we have prepared and characterised four new solvent-separated HMDS alkali metal magnesiates and two new contacted ion pair HMDS potassium magnesiates all containing chiral diamine ligands. Complexes **1–4** are the first structurally characterised complexes in which the alkali metal is sequestered by two molecules of either the chiral diamine (–)-sparteine (in **1** and **2**) or the chiral diamine (*R,R*)-TMCDA (in **3** and **4**). Complex **4** is a rare (*R,R*)-TMCDA adduct of sodium. Prior to this work no potassium complexes containing (–)-sparteine or (*R,R*)-TMCDA had been prepared or structurally characterised. The new potassium complexes, **5** and **6** exist in the crystalline state as polymeric arrays. NMR spectroscopy revealed that the solution structures of **1–4** in arene solution were more complex than initially envisaged. It appears that the solvent separated species (akin to the solid state structures) are in an equilibrium with its respective contacted ion pair. Future studies will focus on extending this chemistry to different amide systems and assessing their efficacy in asymmetric synthesis.

Experimental

General procedures

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. (–)-Sparteine was stored over 4 Å molecular sieves. *n*-Butyllithium (1.6 M solution in hexanes) and di-*n*-butylmagnesium (1 M solution in heptane) was purchased from Aldrich and used as received. *n*-Butylsodium,³⁴ (trimethylsilylmethyl)potassium³⁵ and *N,N,N',N'*-(1*R*,2*R*)-tetramethylcyclohexane-1,2-diamine^{16b} were prepared according to literature methods. NMR spectra were recorded on a Bruker AV400 spectrometer, operating at 400.03 MHz for ^1H , 100.60 MHz for ^{13}C and 155.47 MHz for ^7Li . Yields of products are based on the percentage consumption of the alkali metal reagent. Microanalytical data were generally inconclusive presumably due to the highly air- and moisture-sensitive nature of the complexes and due to the loss of entrained solvent of crystallisation. Correlations between hydrogen atoms and carbon atoms were obtained through COSY and HSQC NMR spectroscopic methods. Single-crystal X-ray diffraction data were recorded on an Oxford Diffraction Gemini S diffractometer at 123 K. Selected crystallographic and refinement parameters are given in Table 1. All structures were refined to convergence with SHELX-97.³⁶

Synthesis of $[\{\text{Li}\cdot(\text{–})\text{-sparteine}\}_2]^+[\text{Mg}(\text{HMDS})_3]^-$ (**1**)

A flame-dried Schlenk tube was charged with $^n\text{BuLi}$ (1.25 mL of a 1.6 M solution in hexanes, 2 mmol) and 5 mL of dried hexane. $^n\text{Bu}_2\text{Mg}$ (2 mL of a 1 M solution in heptane, 2 mmol) was then added followed by three molar equivalents of HMDS(H)

Table 1 Selected crystallographic and refinement parameters

Compound	1	2^b	3^b	4	5	6
Formula	$\text{C}_{48}\text{H}_{106}\text{LiMgN}_7\text{Si}_6$	$\text{C}_{58.5}\text{H}_{118}\text{NaMgN}_7\text{Si}_6$	$\text{C}_{45}\text{H}_{106}\text{LiMgN}_7\text{Si}_6$	$\text{C}_{45}\text{H}_{106}\text{NaMgN}_7\text{Si}_6$	$\text{C}_{33}\text{H}_{80}\text{KMgN}_5\text{Si}_6$	$\text{C}_{28}\text{H}_{76}\text{KMgN}_5\text{Si}_6$
Formula weight	981.19	1135.44	945.16	961.21	778.97	714.89
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$	$P1$
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>a</i> /Å	16.5576(2)	17.5291(5)	11.7763(3)	16.3363(4)	12.2778(3)	11.7004(3)
<i>b</i> /Å	18.5861(3)	23.5696(6)	35.6239(8)	17.3342(4)	20.7952(6)	12.1366(3)
<i>c</i> /Å	19.5813(3)	33.9026(9)	14.4655(3)	21.8477(5)	18.5454(6)	16.3796(5)
$\alpha/^\circ$	90	90	90	90	90	103.209(2)
$\beta/^\circ$	90	90	96.227(2)	90	91.334(3)	90.700(2)
$\gamma/^\circ$	90	90	90	90	90	92.796(2)
Volume/Å ³	6025.97(15)	14007.0(7)	6032.7(2)	6186.8(3)	4733.7(2)	2261.07(11)
<i>Z</i>	4	8	4	4	4	2
Refls. collected	35 383	48 737	29 468	25 964	45 075	27 798
2θ max.	52	52	52	58	54	62.68
Refls. unique	11 806	25 549	21 184	15 834	19 412	20 958
Refls. obs.	8728	12 053	14 010	10 128	13 133	15 659
R_{int}	0.0472	0.0735	0.0316	0.0298	0.0520	0.0205
Goodness of fit	0.872	0.801	0.801	0.927	0.798	0.889
$R [I > 2\sigma(I)]$, <i>F</i>	0.0358	0.0606	0.0418	0.0549	0.0421	0.0346
wR (all data), F^2	0.0587	0.0868	0.0638	0.1246	0.587	0.0699
Flack parameter ^a	0.01(6)	0.10(7)	–0.03(5)	–0.06(9)	–0.04(3)	0.01(3)

^a Absolute configuration confirmed by refinement of Flack parameter. ^b Toluene solvate.

(1.26 mL, 6 mmol) at ambient temperature, producing a clear solution. The solution was heated to reflux for two hours and whilst still warm, two molar equivalents of (–)-sparteine (0.92 mL, 4 mmol) was added, precipitating a white solid. Toluene (11 mL) was then introduced, with heating, to form a homogeneous pale yellow solution. After 24 h at ambient temperature, a crop of X-ray quality colourless crystals of **1** (1.57 g, 80%) precipitated from solution. ^1H NMR (300 K, d_8 -THF): δ 2.70, 2.67, 2.61, 2.59, 2.57, 2.49, 2.33, 2.11, 1.97, 1.90, 1.78, 1.68, 1.50, 1.45, 1.39, 1.29, 1.23, 0.98, 0.88, 0.06 (SiCH_3 , 54H, s). ^{13}C NMR (300 K, d_8 -THF): δ 67.31, 65.01, 62.83, 57.03, 56.26, 54.52, 37.68, 35.70, 34.45, 30.14, 28.37, 27.13, 26.78, 25.99, 25.85, 25.64, 6.93 (SiCH_3). ^7Li NMR (300 K, d_8 -THF): δ –2.29.

Synthesis of $[\{\text{Na}\cdot(\text{–})\text{-sparteine}\}_2]^+[\text{Mg}(\text{HMDS})_3]^-$ (**2**)

A flame-dried Schlenk tube was charged with freshly prepared $^n\text{BuNa}$ (0.16 g, 2 mmol) in a glovebox, after which 5 mL of dried hexane was added, and placed in an ultrasonic bath for 10 min. $^n\text{Bu}_2\text{Mg}$ (2 mL of a 1 M solution in heptane, 2 mmol) was then added at ambient temperature, producing a brown congealed mass. On the addition of three molar equivalents of HMDS(H) (1.26 mL, 6 mmol) the solution became cloudy white and some precipitate was observed. The solution was heated to reflux for two hours and whilst still warm, two molar equivalents of (–)-sparteine (0.92 mL, 4 mmol) was added. A cloudy white to pale yellow colour change was observed, along with the precipitation of a large quantity of white solid. Solvent was removed *in vacuo* and 5 mL of neat toluene added with heating, to form a homogeneous solution. The pale yellow solution was immediately placed in a hot water-filled Dewar flask and after 48 h, a crop of X-ray quality colourless crystals of **2** (1.08 g, 79%) precipitated from solution. ^1H NMR (300 K, d_8 -THF): δ 2.70, 2.66, 2.62, 2.59, 2.56, 2.51, 2.48, 2.34, 2.11, 1.99, 1.90, 1.78, 1.68, 1.51, 1.39, 1.32, 1.29, 1.26, 1.23, 1.20, 1.00, 0.98, 0.06 (SiCH_3 , 54H, s). ^{13}C NMR (300 K, d_8 -THF): δ 67.31, 65.00, 62.83, 57.03, 56.25, 54.52, 37.68, 35.70, 34.45, 30.14, 28.37, 27.13, 26.77, 25.99, 25.64, 6.93 (SiCH_3).

Synthesis of $[\{\text{Li}\cdot(\text{R,R})\text{-TMCDa}\}_2]^+[\text{Mg}(\text{HMDS})_3]^-$ (**3**)

A flame-dried Schlenk tube was charged with $^n\text{BuLi}$ (0.63 mL of a 1.6 M solution in hexanes, 1 mmol) and 10 mL of dried hexane. $^n\text{Bu}_2\text{Mg}$ (1 mL of a 1 M solution in heptane, 1 mmol) was then added followed by three molar equivalents of HMDS(H) (0.63 mL, 3 mmol) at ambient temperature, producing a clear solution. The solution was heated to reflux for two hours and whilst still warm, two molar equivalents of (R,R)-TMCDa (0.38 mL, 2 mmol) was added, precipitating a white solid. Toluene (30 mL) was added, with heating, to form a homogeneous pale yellow solution. The solution was immediately placed in a hot water-filled Dewar flask and after 48 h, a crop of X-ray quality colourless crystals of **3** (0.26 g, 61%) precipitated from solution. ^1H NMR (300 K, d_8 -THF): δ 7.11–7.18 (toluene $\text{CHo}/m/p$, m), 2.35 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 2.30 (toluene CH_3 , s), 2.27 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 24H, s), 1.78 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 1.67 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 1.13 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 1.13 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 0.06 (SiCH_3 , 54H, s). ^{13}C NMR (300 K, d_8 -THF): δ 64.99 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 40.81

($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 26.54 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 26.49 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 6.93 (SiCH_3). ^7Li NMR (300 K, d_8 -THF): δ –0.50.

Synthesis of $[\{\text{Na}\cdot(\text{R,R})\text{-TMCDa}\}_2]^+[\text{Mg}(\text{HMDS})_3]^-$ (**4**)

A flame-dried Schlenk tube was charged with freshly prepared $^n\text{BuNa}$ (0.08 g, 1 mmol) in a glovebox, after which 20 mL of dried hexane was added, and placed in an ultrasonic bath for 10 min. $^n\text{Bu}_2\text{Mg}$ (1 mL of a 1 M solution in heptane, 1 mmol) was then added at ambient temperature, producing a brown congealed mass. On the addition of three molar equivalents of HMDS(H) (0.63 mL, 3 mmol) the solution became cloudy white with precipitate observed. The solution was heated to reflux for two hours and whilst still warm, two molar equivalents of (R,R)-TMCDa (0.38 mL, 2 mmol) was added, precipitating a white solid. Toluene (15 mL) was added, with heating, to form a homogeneous pale yellow solution. The solution was immediately placed in a hot water-filled Dewar flask and after 48 h, a crop of X-ray quality colourless crystals of **4** (0.35 g, 81%) precipitated from solution. ^1H NMR (300 K, d_8 -THF): δ 7.10–7.18 (toluene $\text{CHo}/m/p$, m), 2.35 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 2.30 (toluene CH_3 , s), 2.27 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 24H, s), 1.78 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 1.67 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 1.12 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 1.12 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 4H, m), 0.06 (SiCH_3 , 54H, s). ^{13}C NMR (300 K, d_8 -THF): δ 129.67 (toluene), 128.91 (toluene), 64.99 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 40.81 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 26.54 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 26.51 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 6.93 (SiCH_3).

Synthesis of $[\{\text{K}\cdot(\text{–})\text{-sparteine}\}]^+[\text{Mg}(\text{HMDS})_3]^-$ (**5**)

A flame-dried Schlenk tube was charged with freshly prepared $\text{KCH}_2\text{Si}(\text{CH}_3)_3$ (0.32 g, 2.5 mmol) in a glovebox, after which 5 mL of dried hexane was added, and placed in an ultrasonic bath for 10 min. $^n\text{Bu}_2\text{Mg}$ (2.5 mL of a 1 M solution in heptane, 2.5 mmol) was then added at ambient temperature, producing a brown congealed mass. The solution remained the same on the addition of three molar equivalents of HMDS(H) (1.58 mL, 7.5 mmol). The solution was placed in an ultrasonic bath for 15 min, producing a cloudy creamy solution with precipitate observed. The solution was heated to reflux for two hours and whilst still warm, one molar equivalent of (–)-sparteine (0.58 mL, 2.5 mmol) was added. A cloudy white to yellow colour change was observed, along with the precipitation of a large quantity of white solid. Toluene (5 mL) was added, with heating, to form a homogeneous solution. The yellow solution was immediately placed in a hot water-filled Dewar flask and after 48 h, a crop of X-ray quality colourless crystals of **5** (1.65 g, 85%) precipitated from solution. ^1H NMR (300 K, d_8 -THF): δ 2.70, 2.67, 2.61, 2.59, 2.56, 2.51, 2.48, 2.34, 2.31, 2.11, 1.99, 1.96, 1.90, 1.78, 1.69, 1.50, 1.45, 1.39, 1.29, 1.23, 1.00, 0.97, 0.06 (SiCH_3 , 54H, s). ^{13}C NMR (300 K, d_8 -THF): δ 67.32, 65.01, 62.83, 57.04, 56.26, 54.52, 37.68, 35.71, 34.45, 30.14, 28.38, 27.13, 26.78, 26.00, 25.85, 6.93 (SiCH_3).

Synthesis of $[\{\text{K}\cdot(\text{R,R})\text{-TMCDa}\}]^+[\text{Mg}(\text{HMDS})_3]^-$ (**6**)

A flame-dried Schlenk tube was charged with freshly prepared $\text{KCH}_2\text{Si}(\text{CH}_3)_3$ (0.13 g, 1 mmol) in a glovebox, after which 10 mL

of dried hexane was added, and placed in an ultrasonic bath for 10 min. $n\text{-Bu}_2\text{Mg}$ (1 mL of a 1 M solution in heptane, 1 mmol) was then added at ambient temperature, producing a brown congealed mass. Upon the addition of three molar equivalents of HMDS(H) (0.63 mL, 3 mmol) the solution became cloudy white with precipitate observed. The solution was heated to reflux for two hours and whilst still warm, one molar equivalent of (*R,R*)-TMCDA (0.19 mL, 1 mmol) was added. A cloudy white to pale yellow colour change was observed, along with the precipitation of a large quantity of white solid. The precipitate dissolved on heating, forming a homogeneous solution. The pale yellow solution was immediately placed in a hot water-filled Dewar flask and after 48 h, a crop of X-ray quality colourless crystals of **6** (0.32 g, 52%) precipitated from solution. ^1H NMR (300 K, d_8 -THF): δ 2.35 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 2H, m), 2.27 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 12H, s), 1.78 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 2H, m), 1.67 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 2H, m), 1.12 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 2H, m), 1.12 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$, 2H, m), 0.06 (SiCH_3 , 54H, s). ^{13}C NMR (100.60 MHz, 300 K, d_8 -THF): δ , 64.99 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 40.81 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 26.53 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 26.51 ($\text{CH}_2\text{CH}_2\text{CH}\{\text{N}(\text{CH}_3)_2\}_2$), 6.93 (SiCH_3).

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