Alkaline Metal and Alkaline Metal Magnesiate Chemistry of the Bulky 2,6-Diisopropyl-\textit{N}\textendash(trimethylsilyl)anilino Ligand

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Abstract: Bulky amido ligands are precious in s-block chemistry, since they can implant complementary strong basic and weak nucleophilic properties within compounds. Recent work has shown the pivotal importance of the base structure with enhancement of basicity and extraordinary regioselectivities possible for cyclic alkaline metal magnesiates containing mixed \textit{n}-butyl/amido ligand sets. This work advances alkaline metal and alkaline metal magnesiate chemistry of the bulky arylsilyl amido ligand \textnormal{[N(SiMe\textsubscript{3})(Dipp)]}. \textsuperscript{(Dipp = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{4})} Infinite chain structures of the parent sodium and potassium amides are disclosed, adding to the few known crystallographically characterised unsolvated s-block metal amides. Solvation by \textit{N,N',N',N'}\textendashpentamethyldiethylenetriamine (PMDETA) or \textit{N,N',N,N'}\textendashtetramethylethlenediamine (TMEDA) gives molecular variants of the lithium and sodium amides; whereas for potassium, PMDETA gives a molecular structure, TMEDA affords a novel, semi-solvated infinite chain. Crystal structures of the first magnesiate examples of this amide in \textnormal{[MMg{N(SiMe\textsubscript{3})(Dipp)}\textsubscript{2}][\textit{\mu}\text{-nBu}]\textsubscript{n}} (\textit{M} = \textit{Na} or \textit{K}) are also revealed, though these breakdown to their homometallic components in donor solvents as revealed through NMR and DOSY studies.

Introduction

Alkaline metal amides of bulky secondary amines, \textnormal{[(MNR\textsubscript{2})\textsubscript{m}]}\textsuperscript{(m)}, are popular tools in many synthetic campaigns due to a complementary combination of strong deprotonating power and weak nucleophilicity. Most common are lithium 1,1,1,3,3,3-hexamethyldisilazide (LHMDS), lithium diisopropylamide (LDA) and lithium 2,2,6,6-tetramethyipiperidide (LiTMP), referred to collectively as the "utility amides".\textsuperscript{(1)} Though all these amides are useful in their monometallic form, the performance of the TMP anion in \textit{C}\textendash\textit{H} deprotonation applications can be significantly enhanced by incorporating it within multicomponent systems such as the turbo-Hauser base \textnormal{[TMMPmgCl\textsubscript{2}]}\textsuperscript{(2)} or magnesiate \textnormal{[(TMEDA)Na\textunderscore\textit{\mu}\textsubscript{TMP}\textunderscore\textit{\mu}\text-subscript{\textit{nBu}}Mg\textsubscript{2}(TMMP)]}\textsuperscript{(3)} (TMEDA = \textit{N,N',N',N'\textendash}tetramethylethlenediamine) or alternatively by administering LiTMP in combination with an organometallic (e.g., Al\textsubscript{2}(Bu\textsubscript{3})\textsubscript{4} (TMPP)Al\textsubscript{2}(Bu\textsubscript{3})\textsubscript{4},\textsuperscript{(5)} Zn(TMP)\textsubscript{2}\textsuperscript{(6)} or salt (MgCl\textsubscript{2}, ZnCl\textsubscript{2}, or CuCN\textsubscript{2}) trapping agent, which can drive equilibria to products by stabilising sensitive intermediates through lower polarity \textit{M}\textendash\textit{C} bonds (\textit{M} = Al, Mg, Zn). Curiosity in these new TMP-reagent mixtures is increased by the fact their chemistry can be considered cooperative in origin, implemented through distinct components working together through either synchronised or stepwise mechanisms. A leading example of the former is hexanuclear sodium magnesiate \textnormal{[Na\textsubscript{4}Mg\textsubscript{2}(TMMP\textsubscript{6}(nBu\textsubscript{3})\textsubscript{6}]}\textsuperscript{(8)} a bimetallic ring complex with two pendant butyl base units, in functioning as a template to effect ortho\textendash meta or meta\textendash meta deprotonation of a suite of aromatic substrates, superseding directed ortho-metallation (DoM),\textsuperscript{(9)} in reactions irreproducible by the separated monometallic components.

Casting the net wider for other bulky amides that might possess interesting cooperativity in magnesiate modifications our attention was drawn to the arylsilyl amido ligand \textnormal{[N(SiMe\textsubscript{3})(Dipp)]}\textsuperscript{(10)} which can drive equilibria to products by stabilising sensitive intermediates through lower polarity \textit{M}\textendash\textit{C} bonds (\textit{M} = Al, Mg, Zn). Curiosity in these new TMP-reagent mixtures is increased by the fact their chemistry can be considered cooperative in origin, implemented through distinct components working together through either synchronised or stepwise mechanisms. A leading example of the former is hexanuclear sodium magnesiate \textnormal{[Na\textsubscript{4}Mg\textsubscript{2}(TMMP\textsubscript{6}(nBu\textsubscript{3})\textsubscript{6}]}\textsuperscript{(8)} a bimetallic ring complex with two pendant butyl base units, in functioning as a template to effect ortho\textendash meta or meta\textendash meta deprotonation of a suite of aromatic substrates, superseding directed ortho-metallation (DoM),\textsuperscript{(9)} in reactions irreproducible by the separated monometallic components.

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has described two-coordinate \([\text{Mg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2]\) and the THF solvate \([\text{THF}]_2\text{Mg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))(\text{nBu})_2\) and \([\text{Mg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{OEt}_3)]\) was described by our group, to the best of our knowledge no alkali metal magnesiate has hitherto been reported. Therefore this study sets out to fill in important gaps in the alkali metal chemistry of \([\text{N}(\text{SiMe}_3)(\text{Dipp})]^-\) and to synthesise and characterise the first magnesiate examples as a prerequisite to determining whether this amide also possesses synergistic template base potential.

![Figure 1. Low-coordinate Ni and Fe complexes showing interaction of potassium with \(\pi\)-system as reported by Tilley.][1]

### Result and Discussion

#### Synthetic studies

A total of ten new crystalline compounds were prepared in this study. These comprise the solvent-free parent sodium and potassium amides \([\text{Na}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2\] (1) and \([\text{K}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2\] (2); the PMDETA \((\text{N},\text{N},\text{N}',\text{N}'\prime\)-pentamethyldiethylenetriamine) solvates \([\text{Li}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{PMDETA})\] (3), \([\text{Na}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{PMDETA})]\) (4) and \([\text{K}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{PMDETA})\] (5); the TMEDA \((\text{N},\text{N},\text{N}',\text{N}'\prime\)-tetramethylenediamine) solvates \([\text{Li}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{TMEDA})\] (6), \([\text{Na}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{TMEDA})]\) (7) and \([\text{K}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{TMEDA})]\) (8); and the heavier alkali metal magnesiates \([\text{NaMg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{nBu})_2]\) (9) and \([\text{KMg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{nBu})_2]\) (10). Polyamines PMDETA and TMEDA are popular chelating and solubility-enhancing ligands in alkali metal chemistry,[18] they generally help to deaggregate the parent unsolvated compounds as reflected here, though interestingly deaggregation has not occurred in the semi-TMEDA solvate 8.[18]

Monometallic complexes 1–8 were all synthesised by deprotonation of the starting amine \(\text{N}(\text{H})(\text{SiMe}_3)(\text{Dipp})\) by a metal alkyl reagent. In the lithium and sodium cases this was the relevant metal \(n\)-butyl reagent, whereas the lower stability of potassium alkyls necessitated switching to the more stable silylalkyl reagent \(\text{KCH}_2\text{SiMe}_3\), which unlike the \(n\)-butyl reagent does not possess any \(\beta\)-hydrogen atoms, and so avoids possible decomposition by such an elimination reaction. Ruhlandt-Senge[16] previously made \([\text{K}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2]\) (probably as a THF solvate) by deprotonation of the amine with potassium hydride in THF and used it in situ to generate Group 2 bis(salts) by salt metathesis with the relevant Group 2 metal iodide. Anwander[13] used a similar salt metathesis approach to make a series of rare earth metal amide complexes, during which he isolated \([\text{K}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2]\) in powder form and crystallised the tris(THF) solvate of \([\text{Li}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2]\) and determined its monomeric structure. In our study we observed no benefit in making the PMDETA solvates 4 and 5 through the salt metathesis of the lithium amide \([\text{Li}(\text{N}(\text{SiMe}_3)(\text{Dipp}))]\) with sodium tert-butoxide and potassium tert-butoxide, respectively, as crystalline yields of all the products were about 50% from both deprotonation and metathesis methods (Scheme 1). It is worth noting that irrespective of the method employed, \(^1\)H NMR monitoring of the filtrates from reaction solutions showed essentially quantitative conversions of the amine to amide in all cases. Both the starting metal reagent and, where relevant, the donor solvent employed in these reactions were added in slight excess compared to the parent amine.

**Method A**

\[
\text{Na}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{L}) \rightarrow \text{Na}[\text{N}(\text{SiMe}_3)(\text{Dipp})](\text{L})_2 4
\]

**Method B**

\[
\text{Li}[\text{N}(\text{SiMe}_3)(\text{Dipp})](\text{L})_2 \rightarrow [\text{M}[\text{N}(\text{SiMe}_3)(\text{Dipp})](\text{L})_n] 5
\]

\(\text{L} = \text{PMDETA}\)

**Scheme 1. Alternative methods to prepare complexes 4 and 5.**

Deprotonation was utilised also in the syntheses of magnesiates 9 and 10 (Scheme 2). \(n\)-Butylsodium and trimethylsilylmethylpotassium were utilised as above to generate the respective heavier alkali metal amide from the amine, which in turn was reacted in a co-complexation approach with the \(n\)-butoxide and magnesium amide to afford the monoalkyl–bisamidomagnesiate \(\text{NaMg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{nBu})_2\) and \(\text{KMg}(\text{N}(\text{SiMe}_3)(\text{Dipp}))_2(\text{nBu})_2\), still afforded 9 and 10 as the main products. To the best of our knowledge these are the first alkali metal magnesiates of 2,6-diisopropyl-N-(trimethylsilyl)aniline to be synthesised, isolated from solution and crystallographically characterised (vide infra). However, sodium and potassium Group 13 ate complexes are known for aluminium.[20]

### Crystallographic characterisation

Tables S7 and S8 in the Supporting Information list the crystal data for all ten new compounds, while Table S9 compares selected metric data across the series.

In the absence of interrupting donor molecules, the parent sodium amide 1 and potassium amide 2 adopt infinite chain structures, though each has a distinctive propagation (Fig-
ures 2 and 3, respectively). The former has a linear arrangement with the amido substituents syn with respect to the [MLn] chain and hence eclipsing each other along the chain, whereas the latter has an anti conformation with the Dipp substituent on one molecular unit facing the SiMe3 substituent of the adjacent unit. Structure 1 is a channel solvate with both the solvent channels and the one-dimensional polymers propagating parallel to the a direction. For 2 the one-dimensional polymeric chains propagate parallel to c and neighbouring chains link through Me–K agostic interactions. Such interchain agostic interactions are not observed in 1. The strongest metal–ligand bond in each case is to the amido N atom (Na1–N1 2.2585(16) Å; K1–N1 2.6755(12) Å), but as these can only provide the alkali metal with a coordination number of one, the Dipp substituents also engage with the metal. The propagating interactions between monomeric units in 1 are Na contacts to the para and meta/meta’ Dipp C atoms (2.696(2) and 2.7514(16) Å) making the Dipp unit η1-bound, though there is an additional intramolecular Na1–C1 contact (3.1279(18) Å) to the ipso-C atom within the monomeric unit. Possessing the larger, softer K cation, 2 propagates through η4–C–K engagement (centroid length, 2.81 Å; range of K–C lengths, 3.1014(14)–3.1647(16) Å) and there is an additional close intramolecular contact (K–C1, 3.0735(14) Å) presumable of a centroid (K–C, 3.0735(14) Å). The N1-K1-centroid angle is 154.53° reflecting the bulky heteroleptic nature of the substituents attached to the amido nitrogen atom. Crystallographically characterised polymeric sodium and potassium amides are comparatively rare.[51]

PMDETA deaggregates the polymer of 1 all the way down to a monomer within 4 (Figure 4). Accompanied by the amido N, the tridentate solvent surrounds the Na centre within a distorted (N×4) tetrahedron in which the shortest bond is to the amido N atom (Na–N1, 2.3206(12) Å) with the PMDETA bonds to Na spanning the range 2.4188(14)–2.5201(14) Å. There is an additional Na–ipso-C contact (Na–C1, 3.0937(14) Å), presumably an unavoidable artefact of the short Na–N1 bond, though this is longer than that in polymeric 1, intimating that PMDETA is more effective than the η1-bound Dipp bonding to Na, a point reinforced by an increased C1-N1-Si1 bond angle (140.09° cf. 123.85(19)° in 2). As reported by Westerhausen, less bulky sodium amides can still dimerise in the presence of PMDETA in [Na(NPPh3)(PMDETA)]+. Unsurprisingly, the PMDETA lithium congener 3 is also monomeric (Figure 5) with a short Li1–(amido)N1 bond (2.020(3) Å) and three longer bonds to PMDETA N atoms (Li1–N2 2.314(3); Li1–N3 2.148(3); Li1–N4 2.216(3); mean value, 2.226 Å). Note that 3 and 4 are isomorphic and isostructural. The much crowded distorted tetrahedral environment about the smaller Li compared to that of Na in 4 is reflected in a less obtuse C1-N1-Si1 bond angle (128.77(11)°). Andrews has reported a monomeric lithium amide PMDETA complex in [Li(NPPhMe)(PMDETA)].[22]

A single tridentate PMDETA ligand is not sufficient to coordinatively saturate the K centre of the amide 5, which therefore exists as a centrosymmetric dimer (Figure 6). Dimerisation is manifest by a long K1–C13’ intermolecular interaction (3.2272(17) Å) involving a methyl of the SiMe3 group,[23] which closes a eight-membered (KNSiC)2 ring similar to that found by Coles and Cloke in [K(N(SiMe2C6H4-2-OMe)2)] with an analogous K–C intermolecular interaction of 3.222(2) Å.[24] The primary K coordination sphere of 5 is composed of four N atoms, with the shortest bond being to the amido N1 (2.7174(13) Å) with those to PMDETA (N2, N3, N4) having a mean length of 2.8913 Å. This intramolecular tetratomic coordination brings K into close proximity to both the ipso-C1 of the Dipp substituent and one terminal Me of the PMDETA ligand (lengths of 2.9806(14) Å and 3.2166(2) Å, respectively). Small PMDETA bite angles dictate that this KN4 coordination sphere is far removed from the perfect tetrahedron (range of bond angles, 60.58(4)° to 127.56(4)°; mean 103.57°). Only with the lithium amide is a monomeric structure retained upon substituting PMDETA by the smaller TMEDA ligand. The resulting structure, 6, is shown in Figure 7. There is...
disorder present which somewhat compromises the Li–N (TMEDA) metric data, but the primary coordination about Li is unequivocal comprising three nitrogen atoms—one amido and two TMEDA types.

In contrast the larger sodium centre in 7 cannot be coordinatively satisfied by the amide/TMEDA combination so akin to the case of the K PMDETA complex 5 dimerisation takes place through Na–C–Si interactions to close a (NaNSiC)₂ ring (Figure 8). Na approaches the anionic amido N atom more closely (2.2847(14) Å) than the neutral TMEDA N atoms (mean length, 2.4668 Å), giving rise to a trigonal pyramidal primary NaN₃ coordination (sum of bond angles, 339.08°), but as in 5 this crowded coordination brings the metal into close proximity with intramolecular C1–8 (2.9379(16) Å) and intermolecular C14–2.869(2) Å, making it five-coordinate overall.

The crystallographic determination of potassium amide 8 (Figure 9) established it as a hemi-TMEDA solvate though the reaction was carried out using a 1:1 K/TMEDA stoichiometric ratio. Note that this structure contains two crystallographically independent molecules within the asymmetric unit cell, with...
Figure 7. Molecular structure of \([\text{LiN(SiMe}_3\text{(Dipp)})\text{(TMEDA)}]\). (6). Thermal ellipsoids are displayed at 35% probability, hydrogen atoms, and the disordered component of TMEDA ligand and two methyl groups of one \(\text{iPr}\) unit are omitted for clarity. Selected bond lengths [Å] and angles [°]: \(\text{Li}1\)-\(\text{N1} 1.905(4); \text{N1}-\text{C1} 1.388(2); \text{Si}1-\text{N1} 1.6756(17); \text{Si1-N1-Li1} 121.50(15); \text{C1-N1-Si1} 108.20(17); \text{C1-N1-Si1} 130.30(13).

Figure 8. Molecular structure of \([\text{NaN(SiMe}_3\text{(Dipp)})\text{(TMEDA)}]\). (7). Thermal ellipsoids are displayed at 30% probability and hydrogen atoms have been omitted for clarity. Dashed lines illustrate the Na–C contacts. Symmetry operation to generate equivalent atoms denoted \(\times \cdot \text{symmetry operations} \)

\[\begin{align*}
\text{K1} & \rightarrow \text{K1} + (1/2, 0, 0) \\
\text{K2} & \rightarrow \text{K2} + (1/2, 0, 0) \\
\text{Na1} & \rightarrow \text{Na1} + (0, 1/2, 0) \\
\text{Na2} & \rightarrow \text{Na2} + (0, 1/2, 0) \\
\end{align*}\]

Selected bond lengths [Å] and angles [°]: \(\text{K1}–\text{C1} 2.780(3); \text{K1}–\text{N1} 1.905(4); \text{Na1}–\text{N2} 2.3613(19)\).

Figure 9. a) Asymmetric unit of the structure of \([\text{KN(SiMe}_3\text{(Dipp)})\text{(TMEDA)}]\). (8). b) Section of extended framework structure showing atom connectivity between the metal and the \([\text{NISiMe}_3\text{(Dipp)}]\) ligand. Thermal ellipsoids are displayed at 35% probability and hydrogen atoms have been omitted for clarity. Dashed lines denote the K–aryl contacts. Symmetry operation to generate equivalent atoms denoted \(\times \cdot \text{symmetry operations} \)

\[\begin{align*}
\text{K1} & \rightarrow \text{K1} + (1/2, 0, 0) \\
\text{K2} & \rightarrow \text{K2} + (1/2, 0, 0) \\
\text{Na1} & \rightarrow \text{Na1} + (0, 1/2, 0) \\
\text{Na2} & \rightarrow \text{Na2} + (0, 1/2, 0) \\
\end{align*}\]

Selected bond lengths [Å] and angles [°]: \(\text{K1}–\text{C1} 2.7909(8); \text{K1}–\text{C14} 2.793(2)\).

Magnesiates 9 and 10, which both have a 2:1 amido/butyl stoichiometric ratio different to the 3:1 ratio in the aforementioned pre-inverse-crown template base \([\text{Na}_2\text{Mg_2(TMPP)}_2\text{(nBu)}_4]\), were expected to adopt different structural architectures from this TMP derivative. X-ray crystallographic determinations duly confirmed this expectation. The salient difference is that both 9 and 10 have infinite helical chain structures (Figures 10–13) and not the ring architecture that appears to be the key feature behind the special templating metallation ability of \([\text{Na}_2\text{Mg_2(TMPP)}_2\text{(nBu)}_4]\).

Sodium magnesiates 9 displays two distinct types of (half occupancy) Na atom separated by a magnesiate anion, neither of which engage with the amido N atom. Na1 lies upon a twofold rotation axis and bonds to two symmetrically equivalent butyl C atoms (C16/C16’, 2.779(2) Å) and two symmetrically equivalent aryl groups (C4/C4’ and C5/C5’) at the para/meta positions (2.793(2) Å and 2.913(2) Å, respectively), making it six-coordinate overall. The next shortest distance between Na1 and the aryl group is to C3 (at 3.2535(20) Å), which seems too long, so the hapticity of the aryl substituent is best regarded as \(\eta^1\). Lying on a crystallographic inversion centre sandwiched between two aryls from neighbouring magnesiates ion, Na2 binds in a \(\eta^6\) arrangement to both of them (range of \(\text{Na}_2–\text{C}^\beta\) bond lengths, 2.684(2)–3.1565(18) Å; Na–nC-centroid distance 2.5311(1) Å; centroid-na-centroid angle, 180.0°). Propagation of this contacted ion pair structure into an infinite helical chain (Figure 12) is through these different types of Na–C interaction. Mg1 occupies a \(\text{nC}_7\) distorted trigonal planar coordination (sum of bond angles; 359.69°) comprising two amide ligands (mean Mg–N–distance, 2.0328 Å) and one butyl ligand (Mg1–C16, 2.1533(19) Å). The helical chain structure of 10 (Figure 13) is less intricate than that of 9 as it contains only one alkali metal (K) site. Sandwiched between two aryl rings (K1–cent-
Solution NMR spectroscopic characterisation

All the new compounds 1–10 were also characterised in solution by $^1$H and $^{13}$C($^1$H) NMR spectroscopy recorded at ambient temperature. Assignments were aided by $^1$H,$^1$H-COSY and $^1$H,$^{13}$C-HSQC experiments. In general, the data obtained (see the full experimental details in the Supporting Information) supported the formulae established by X-ray crystallography of the solid samples.

Figure 12. Part of the polymeric helical chain of [NaMg{N(SiMe$_3$)(Dipp)}$_2$(μ-nBu)$_n$]$_{10}$ (9) that propagates parallel to the crystallographic c-axis.
Since the polymeric solids 1 and 2 were poorly soluble in arene solvents, their solutions were made up in a mixture of C₆D₆ and [D₈]THF solvents. This meant we were viewing THF solvates instead of the pure, unsolvated parent amides. All the expected resonances of the amides such that they could dissolve well in C₆D₆ without the addition of polar THF. The ⁷Li NMR spectrum of 3 revealed a single species at 25 °C. Its ¹H NMR spectrum showed one methine CH resonance and two distinct Me resonances for the Dipp substituent, consistent with one type of amido group. The aforementioned quaternary C atom bound to N appears at 157.5 ppm in the ¹³C spectrum, essentially identical to those in the THF solvates of 1 and 2, and to those in the PMDETA solvates of the sodium and potassium amide 4 and 5 (at 157.8 ppm and 157.0 ppm, respectively). There are differences but surprisingly only modest ones for the PMDETA resonances across the series 3–5. For example, the CH₄ resonances appear at 46.0/44.9 ppm, 45.3/43.9 ppm, and 44.9/40.9 ppm for terminal/central positions respectively in the ¹³C NMR spectra. Both the Li and Na TMEDA solvates 6 and 7, being molecular solids, dissolve in C₆D₆ in contrast to the polymeric hemi-TMEDA solvate 8, which requires some [D₈]THF to exhibit solubility in the arene. Consistent with the monomeric structure in the crystal, the ³¹P NMR spectrum of 6 shows a solitary resonance. TMEDA is bound to the Li as evidenced by the chemical shift and order of the TMEDA resonances in the ¹H NMR spectrum (Me, 1.61 ppm; CH₃, 1.44 ppm), which bear a close resemblance to those in the Na TMEDA solvate (1.57 ppm and 1.49 ppm, respectively). As anticipated, the mixed solvent solution of 8 contains free TMEDA, with the order of its resonances reversed in comparison (CH₃, 2.12 ppm; Me, 1.97 ppm), as [D₈]THF will now be solvating the larger alkali metal.

Magnesiates 9 and 10 conform to the pattern seen with the other polymeric solids 1, 2 and 8 in requiring the addition of [D₈]THF for their dissolution in C₆D₆. Hence, the solutions will contain THF solvates. The reduced solubility of the donor-free compounds in hydrocarbon solvents such as methylvyclohexane immediately signalled that we were dealing with structures distinct from that of the cyclic hexanuclear sodium magnesiates [Na₄Mg₃(TMP₃)(μ-nBu)₉]₉, which shows excellent solubility in hydrocarbon media. The ¹H and ¹³C NMR spectra of 9 show two distinct types of amido group. For example, the former shows two p-CH-Ar triplet resonances at 6.85 and 6.64, two CH(CHO₂)₂ septets at 4.27 and two Si(CHO₂)₂ singlets at 0.30 ppm and 0.25 ppm. This could be due to two distinct amido groups within the same molecule or alternatively two distinct amido-containing molecules. The chemical shift of the CH₂-nBu multiplet appearing at ~0.26 ppm indicates that this ligand is more likely to be attached to Mg as it would appear more upfield if attached to the more electropositive metal Na (for example, the same resonance appears in C₆D₆ solutions of [(Mg(TMP)(μ-nBu))ₐ] at 0.05 ppm²⁷ and [Mg(TMP)(μ-nBu)-IPr] (IPr = 1,3-bis-(2,6-disopropylphenyl)imidazol-2-ylidine) at ~0.42 ppm).²⁸ Due to the ambiguity of these spectra we turned to diffusion-ordered spectroscopy (DOSY)²⁹ to attempt to find a resolution. For an accurate molecular weight (MW) determination we utilised the external calibration curve (ECC) approach with normalised diffusion coefficients that has recently been developed by the Stalke group.³⁰ This novel approach takes into account the shape of the molecule allowing accurate MW predictions with a maximum error of less than 9%. The beauty of this approach is that only one internal reference (that also can be the solvent) is necessary, whereas previous approaches required multiple references. In this case tetramethylsilane was employed. DOSY determined MWs of species in solution were estimated using the diffusion coefficient values for 9 in [D₈]THF (Figure S1, Tables S2–S3 in the Supporting Information). Two distinct diffusion coefficients were obtained consistent with two distinct species. The best fit for these were found to be the homometallic THF solvates [[(D₈)THF]₉Mg(N(SiMe₃)(Dipp))(μ-nBu)] ⁹a (surprisingly the error when for x = 1, −6%, was found to be much less than that for x = 2, −21%, a result at odds with the aforementioned crystal structure, which contained two THF ligands) and [[(D₈)THF]₉Na(N(SiMe₃)(Dipp))] ⁹b with the error from their calculated MWs being −6% and −7%, respectively. Significantly the heterometallic like 9 would have an error of 36% if unsolvated, or 43% if solvated by one THF ligand. Clearly the magnesiates that crystallise from hydrocarbon/arene solution breaks down to homometallic species in the presence of the strong Lewis base THF (Scheme 3).³¹ Organomagnesium compounds are synonymous with redistribution reactions, most notably the Schlenk equilibrium. Unsurprisingly, the potassium...
magnesiate 10 was found to undergo the same disproportionation reaction in [D₈]THF (Scheme 3), with the corresponding DOSY data consistent with the two homometallic species [[([D₈]THF)Mg(N(SiMe₃)(Dipp))(μ-nBu)] 10a and [[([D₈]THF)K(N(SiMe₃)(Dipp))][Mg{N(SiMe₃)(Dipp)}(nBu)] 10b with small errors of –4 % and +1 %, respectively, versus the calculated MWS. Supporting evidence that 9a and 10a are the same solution species comes from the close similarity of their chemical shifts (for example: 1H, CH₂-nBu at –0.26 ppm and –0.22 ppm, respectively; Si(CH₃)₃ at 0.30 ppm in both; 13C, CH₂-nBu at 9.3 ppm and 9.0 ppm, respectively; (α-C=Ar) appearing at 145.1 ppm in both). Ruhlandt-Senge also reported [[(THF)₉Mg(N(SiMe₃)(Dipp))(nBu)] and NMR data are consistent with that found in 9a and 10a (e.g., CH₂-nBu at 9.4 ppm in neat C₆D₆).

Scheme 3. Breakdown of the complexes 9 and 10 in [D₈]THF.

Reactivity studies

Our failure to synthesise a template ring complex as [Na₄Mg₂(TMP)(nBu)]₉ incorporating the arylsilyl amido ligand [N(SiMe₃)(Dipp)] in place of TMP reduced our expectation of realising enhanced or special reactivities, but for completeness we carried out some representative metallation–iodination reactions. Table S10 in the Supporting Information compiles the reactions between [Mg{N(SiMe₃)(Dipp)}(nBu)] and the same set of potential bases. In both cases the atropisomers dimerise by means of Na···C interactions. Table S10 also generates a monomeric lithium amide, but it is not sufficient to coordinatively saturate the K centre of the amide, which exists as a centrosymmetric dimer, with dimerisation expected by a long K–CH₃SiMe₃ intermolecular interaction that closes an eight-atom (KNSiC)₂ ring. Reducing the chelating capability of the donor solvent via TMEDA has little effect on the magnesium amide, which forms its inclusion here, though NMR studies confirmed its formula. Though monometallic 11 could result from a disproportionation of bimetallic ate 9, it is possible that 9 never formed in the hydrocarbon medium, but was in fact a mixture of 1 and [Mg{N(SiMe₃)(Dipp)}(nBu)], with 11 forming as a result of the latter deprotonating the oxazoline substrate. However, given that the yield of iodo product 12a using [Mg{N(SiMe₃)(Dipp)}(nBu)] on its own was 80 % at 25 °C, but is only 10 % using 9 as the base under the same conditions, this suggests that the presence of the sodium amide component significantly inhibits reactivity of the alkylmagnesium amide. Since it was clear that these magnesiates do not possess robust bimetallic structures like that of the cyclic hexanuclear sodium magnesiate [Na₄Mg₂(TMP)(nBu)]₉, it was deemed not worthwhile to explore their reactivity any further.

Conclusion

This study has uncovered a remarkable s-block complex structural diversity based on the amide [N(SiMe₃)(Dipp)]⁺ functioning as a ligand on its own or in combination with an n-butyl ligand. The parent sodium and potassium amides adopt infinite chain structures, with linear or zig-zag arrangements, respectively, adding to the relatively few known crystallographically characterised unsolvated s-block metal amides. Tridentate PMDETA deaggregates the sodium polymer to a monomer and also generates a monomeric lithium amide, but it is not sufficient to coordinatively saturate the K centre of the amide, which exists as a centrosymmetric dimer, with dimerisation expressed by a long K–CH₃SiMe₃ intermolecular interaction that closes an eight-atom (KNSiC)₂ ring. Reducing the chelating capability of the donor solvent via TMEDA has little effect on the lithium amide, which remains monomeric, but the sodium amide dimerises by means of Na–C–Si interactions mimicking the case of the PMDETA potassium amide. Refusing half a molar equivalent of TMEDA despite a 1:1 K/TMEDA stoichiometric ratio in the solution, the potassium amide crystallises as a hemi-TMEDA solvate. Its infinite chain structure has distinct K coordination environments, one occupying a N₃ site, the other

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sandwiched between aryl rings of two Dipp ligands, classifies it as a novel potassium potassiate.

Both crystalline sodium and potassium magnesiates display a 2:1 amido/butyl stoichiometric ratio in infinite helical chain structures conflicting with the 3:1 ratio of the template base [Na2Mg2(TMP)6(nBu)3], which inspired this study. Lack of hydrocarbon solubility denied any opportunity for these ates to display special reactivities like that of the template base. THF was needed for solubility but DOSY studies indicate that the donor promotes fragmentation of the magnesiates into homometallic moieties. The ring architecture is the key feature behind the special templating metalation ability of [Na2Mg2(TMP)6(nBu)3], but such architectures proved inaccessible with the [Ni(SiMe3)(Dipp)] ligand. Despite this disappointment the study is important, as it has clearly established that the presence of aryl groups can be an inhibiting factor to molecular ring formation as their π-faces can engage intermolecularly with alkali metals to help construct polymeric chains. Future work will focus on circumventing this solubilitystructural problem by using bulky lipophilic non-aryl ligands.

Experimental Section

General procedures: All reactions and manipulations were performed under a protective atmosphere of dry pure argon gas using standard Schlenk tube or glovebox techniques. Solvents were dried by heating to reflux over sodium benzophenone ketyl. Isolation and characterisation of metallated intermediate 11: Reaction mixture was allowed to cool down to ambient temperature. After a period of one week, colourless crystals of 11 grew from the reaction mixture. Attempts to analyse the crystalline material by X-ray diffraction studies were unsuccessful due to the highly disordered nature within the structure of 11. These were filtered, washed with n-hexane (3 x 4 mL) and dried under vacuum (unrefined yield: 290 mg, 0.60 mmol, 30%). The absolute yield was higher since the filtrate contained a mixture of the product 11 and starting material. The reaction was also studied using two and three molar equivalents of complex 9 and one equivalent of the substrate (2 mmol) giving the same compound 11. The NMR spectra of isolated crystalline 11 are in agreement with a 1:1 ratio of [Ni(SiMe3)(Dipp)][2-C6H4-1-(oxazoline)(Me)]] in 11. 1H NMR (400.13 MHz, C6D6/[D8]THF, 25°C): δ = 8.24 (ddd, J(H,H) = 6.8, 1.2, 0.8 Hz, 1H; m-CH-Ar), 7.99 (dt, J(H,H) = 7.6, 0.9 Hz, 1H; o-CH-Ar), 7.42 (td, J(H,H) = 7.2, 1.2 Hz, 1H; p-CH-Ar), 7.20 (td, J(H,H) = 7.5, 1.4 Hz, 1H; m-CH-Ar), 7.17 (d, 2H; CD2, over-lapping, m-CH-Ar, Dipp), 6.97 (t, J(H,H) = 7.5 Hz, 1H, CH-Ar, Dipp), 4.30 (br sept, J(H,H) = 6.7 Hz, 2H; -CH(CH2)3), 3.69 (s, 2H; -CH2), 1.43 (d, J(H,H) = 6.9 Hz, 6H; -CH(CH3)2), 1.28 (brd, J(H,H) = 6.5 Hz, 6H; -CH(CH3)2), 0.94 (brs, 6H; -(CH3)2), 0.33 ppm (s, 9H; -(Si(CH3)3)3). 13C{1H} NMR (100.6 MHz, C6D6/[D8]THF, 25°C): δ = 178.9 (C13-Mg), 176.0 (Cα-Ar), 152.5 (N-Cβ-Ar, Dipp), 145.0 (o-Cβ-Ar, Dipp), 140.1 (m-CH-Ar), 135.0 (Cβ-Ar), 131.0 (p-CH-Ar), 125.7 (o-CH-Ar), 125.1 (m-CH-Ar), 123.3 (m-CH-Ar, Dipp), 119.5 (p-CH-Ar, Dipp), 81.3 -(CH2), 64.5 (C8), 28.1 (br. -(CH3)2), 27.3 -(CH(CH3)2), 25.3 -(CH2CH3), 25.1 -(CH(CH3)2), 3.6 ppm -(Si(CH3)3). NMR spectra also revealed small amounts of methylcyclohexane (from crystallisation) as well as minute traces of 4,4-dimethyl-2-phenyl-oxazoline and [Ni(SiMe3)(Dipp)] as a result of unavoidable hydrolysis. Elemental analysis calc (%) for C29H38MgN2O Si: C 70.38, H 8.49, N 6.55.

Application of metallated compounds in organic synthesis by electrophilic addition reaction

General procedure: The aryl substrates 4,4-dimethyl-2-phenyl-oxazoline (12a) and N,N-diospropylenzymamide (12b) were treated with the appropriate metal complex in methylcyclohexane. All reactions were stirred at/for different temperatures/times and substrate base stoichiometries of 1:1 and 1:2 were probed. Following metalation, the corresponding 2-monoiodo derivatives 13a and 13b were obtained by in situ reaction with an iodine solution in tetrahydrofuran (1 M) at –78°C. The reaction mixture was allowed to warm up to ambient temperature over a period of 16 h. A saturated aqueous NH4Cl solution was added, followed by saturated aqueous Na2SO4 solution. Extraction of the organic crude with ethyl acetate (3 x 10 mL), then it was washed with brine (10 mL) and dried over anhydrous MgSO4. The solvent was removed under reduced pressure and the crude reaction product was dissolved in CDCl3, 1.10-Phenanthroline was added as internal standard, the yields being calculated by 1H NMR spectroscopy (see Tables S10 and S11 in the Supporting Information for details).

The aromatic substrate 12a or 12b (2 mmol) was added to a reaction mixture of the corresponding monometallic complexes 1, 2, [Mg(N(SiMe3)(Dipp))(nBu)] (2 mmol) in methylcyclohexane (15 mL) or the mixed-metal complexes 9/10 (2 mmol/4 mmol) in methylcyclo-
In situ synthesis of [Mg(N(SiMe3)(Dipp))(nBu)]: In a Schlenk tube, 2,6-dioisopropyl-N-(trimethylsilyl)aniline (499.0 mg, 2 mmol) was added to a solution of commercial nBu3Mg (2.1 mL, 1 M solution in n-hexane, 2.1 mmol) in bulk methylcyclohexane (15 mL). The reaction mixture was stirred for 1 h before the aromatic substrate was introduced.

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Broken promise: Rare examples of polymeric unsolvated alkali metal magnesiumates containing the bulky amide \([\text{NiSiMe}_3](\text{Dipp})\)\(^{-}\) (Dipp = 2,6-iPr\(_2\)-C\(_6\)H\(_4\)) are uncovered. Their structures show aryl groups can inhibit molecular ring formation, a requirement for template bases, as aryl \(\pi\)-faces can engage intermolecularly with alkali metals to construct chains (see figure), which break in donor solvents to homometallic species ruling out any synergistic reactivity.