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cis-2,6-Dimethylpiperidide: a structural mimic for TMP (2,2,6,6-tetramethylpiperidide) or DA (diisopropylamide)?†

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Four novel heterobimetallic ate complexes containing *cis*-2,6-dimethylpiperidide (*cis*-DMP) have been prepared and characterised. Two contain one *cis*-DMP ligand, namely the bisalkyl-amido lithium, and sodium zincates [(TMEDA)·MZn(*cis*-DMP)(^{t}Bu)$_2$] (M = Li for **1**, Na for **2**). Both **1** and **2** are synthesised by co-complexation of the respective alkali metal amide with di-*tert*-butylzinc in the presence of a molar equivalent of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in a hydrocarbon medium. The third complex, containing two *cis*-DMP ligands, is the alkyl-bisamido sodium zincate [(TMEDA)·NaZn(*cis*-DMP)$_2$(^{t}Bu)] **3**. Complex **3** is prepared from **2** *via* a disproportionation reaction where the by-product is [(TMEDA)·NaZn(^{t}Bu)$_3$]. Another alkyl-diamido sodium zincate, [(TMEDA)·NaZn(DIBA)$_2$(^{t}Bu)] **4** is synthesised by utilising diisobutylamine [DIBA(H)]. This reaction emphasises the generality of this disproportionation process. Complex **5** contains three *cis*-DMP ligands and is a tris-amido sodium magnesiate [(TMEDA)·NaMg(*cis*-DMP)$_3$]. It is prepared by treating an equimolar mixture of butylsodium and dibutylmagnesium with three and one molar equivalents of *cis*-DMP(H) and TMEDA respectively, in hydrocarbon solution. By comparison of **1–5** with appropriate complexes from the literature, it has been possible to experimentally determine that the steric bulk of *cis*-DMP closely resembles that of DA but is considerably less bulky than 2,2,6,6-tetramethylpiperidide (TMP).

Introduction

There is currently worldwide interest surrounding the chemistry of alkali metal zincates and magnesiates.[1–3] Depending on the reaction stoichiometry employed in the preparation of the metall(ate) complexes and/or dynamic solution behaviour, various compositions of simple alkyl/amido-containing bimetallic ates are possible including: solvated and unsolvated $M^IM^{II}(R)_3$, $M^IM^{II}(NR_2)(R)_2$, $M^IM^{II}(NR_2)_2(R)$ and $M^IM^{II}(NR_2)_3$ (where: M^I is an alkali metal; M^{II} is Zn or Mg; R is an alkyl group; and NR_2 is an amido group). Predominantly, due to steric factors, "higher" zincate and magnesiate formulations (where the Zn or Mg atom is coordinated to four anions) have also been isolated.[4–8] From a reactivity perspective, many of these complexes have been utilised as highly effective regioselective reagents which have high functional group tolerance at ambient temperatures.[2] Often their performance outshines that of their parent organo–alkali metal reagent (either alkyl or amide) or Grignard-type (or organozinc) reagent. Thus far, the amides which have drawn the most interest in these ate compositions are the synthetically-important diisopropylamide (DA), 2,2,6,6-tetramethylpiperidide (TMP) and hexamethyldisilazide (HMDS) (Fig. 1), the homometallic lithium compounds of which have long been utility reagents in organic synthesis. Focusing on zincates, [(THF)·LiZn(TMP)(^{t}Bu)$_2$],[9,10] [(TMEDA)·LiZn(TMP)(^{n}Bu)$_2$],[11] [LiZn(TMP)$_3$][12–14] and [(TMEDA)·NaZn(TMP)(^{t}Bu)$_2$][15] (TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) have been shown to efficiently zincate (and sometimes even regioselectively multi-zincate) several key aromatic substrates such as benzene,[15,16] naphthalene,[17] aryl amides,[18] nitriles,[19] anilines,[20] and also metallocenes.[11] In addition, [(TMEDA)·LiZn(DA)(^{t}Bu)$_2$] and its sodium congener [(TMEDA)·NaZn(DA)(^{t}Bu)$_2$] have been shown to metallate alkynes.[21,22] Turning to the HMDS-containing lithium zincates, [(TMTA)·Li(HMDS)Zn(CH$_2$SiMe$_3$)$_2$][23] and [(PMDETA)·LiZn(HMDS)(Me)$_2$][24] (TMTA is 1,3,5-trimethyl-1,3,5-triazinane and PMDETA is *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine) have recently been prepared and characterised, and unusually the amido ligand in the latter occupies a terminal position in the solid-state. The proposed potassium zincate "KZn(HMDS)$_3$" reacts with toluene to yield the benzyl-trapped zincate [{KZn(HMDS)$_2$(CH$_2$Ph)}$_\infty$], a

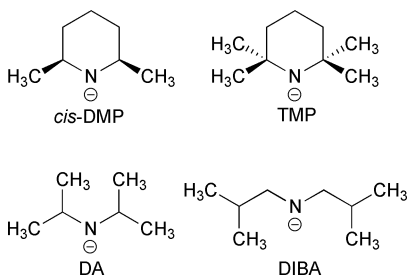

Fig. 1 Structural comparison of *cis*-DMP with common utility amides.

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surprising result since its magnesium relative ["$KMg(HMDS)_3$"] is completely inert under the same conditions even though Mg amides are considered to be more reactive than Zn amides.[25] Recently, the first lithium alkyl/amido zincates containing a primary amide (2,6-diisopropylphenylamide) have come to the fore.[26]

Turning to the magnesiates, several bimetallic alkyl/amido examples have been structurally characterised and utilised in synthesis.[4,5,27–42] Perhaps the most comprehensively studied is the sodium magnesiate $[(TMEDA)\cdot NaMg(TMP)_2(^n Bu)]$[43] which has recently been shown to selectively metallate benzene,[43] toluene[44] and metallocenes.[45,46] Also $[LiMg(DA)_3]$ and its sodium congener $[NaMg(DA)_3]$ have been shown to smoothly magnesiate alkynes.[47]

We are currently exploring chiral avenues in zincate/magnesiate chemistry.[48] One direction which we are pursuing is the incorporation of chiral amides within the mixed-metal alkyl/amido metall(ate) framework. In this study the metall(ate) chemistry of achiral *cis*-2,6-dimethylpiperidide (*cis*-DMP) is explored (Fig. 1). Due to the fact that this amine is much less expensive than either of its two chiral *trans*-isomers, we decided to focus on this isomer as a prelude to work with its chiral isomers. Surprisingly, little attention has been paid to *cis*-DMP despite its similarity to DA and TMP. To the best of our knowledge, only two metal amide species of this ligand are known: the polymeric TMEDA-solvated lithium amide $[(TMEDA)\cdot Li(cis\text{-}DMP)]_\infty$;[49,50] and the dimeric amidoaluminium dihydride $[\{(cis\text{-}DMP)AlH_2\}_2]$.[51] Like DA, *cis*-DMP has two β-hydrogen atoms; and like TMP, *cis*-DMP is cyclic. Therefore *cis*-DMP can be regarded as a "tied-back" variant of DA, or a less sterically demanding version of TMP which lacks two of the four CH_3 limbs (Fig. 1). This begs the question: will *cis*-DMP function as a structural mimic of DA or TMP? In this article, we begin to answer this question by reporting the synthesis and structural elucidation of four new metall(ate) complexes which incorporate the *cis*-DMP anion, three new zincates and one new magnesiate, which gives some insight into the behaviour of *cis*-DMP in comparison to the much more comprehensively studied chemistry of DA and TMP.

Results and discussion

Synthesis of complexes 1–5

Four new zincates and one new magnesiate were successfully synthesised:

1 $(TMEDA)\cdot LiZn(cis\text{-}DMP)(^t Bu)_2$
2 $(TMEDA)\cdot NaZn(cis\text{-}DMP)(^t Bu)_2$
3 $(TMEDA)\cdot NaZn(cis\text{-}DMP)_2(^t Bu)$
4 $(TMEDA)\cdot NaZn(DIBA)_2(^t Bu)$
5 $(TMEDA)\cdot NaMg(cis\text{-}DMP)_3$

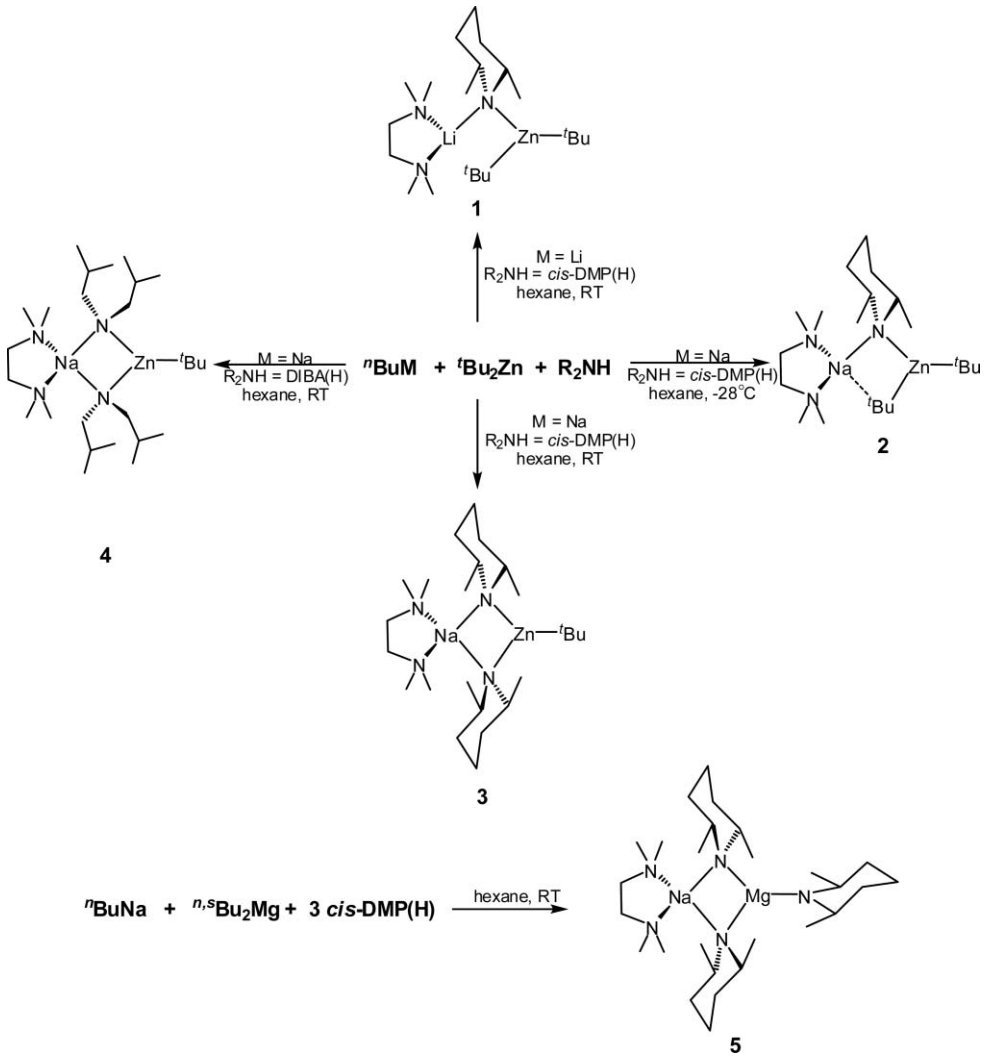
The synthetic routes to **1–5** are summarised in Scheme 1. For the zincate complexes, *n*-butyllithium (for **1**) or *n*-butylsodium (for **2–4**) was reacted with one molar equivalent of *cis*-DMP(H) [or DIBA(H) for **4**]. These mixtures were allowed to stir for around 30 min, before an equimolar quantity of $^t Bu_2Zn$ (in a hexane medium) was introduced *via* a cannula. In all cases (**1–4**) one molar equivalent of TMEDA was required to produce a homogeneous solution. Crystals precipitated from the hydrocarbon solution at ambient temperature for **1**, **3** and **4** and at −28 °C for **2**.

The synthetic approach and ultimate composition (that is an amido : alkyl ratio of 1 : 2) of **1** resembles that of Westerhausen's HMDS-containing lithium zincate.[23] For the Na zincates, the reactivity for *cis*-DMP(H), is more in line with that of DA(H) than of TMP(H). For instance, with TMP(H), only $[(TMEDA)\cdot NaZn(TMP)(^t Bu)_2]$[15] is isolated and a bis(TMP) zincate has never been detected. With DA(H), the reaction is more complex than anticipated. The aforementioned $[(TMEDA)\cdot NaZn(DA)(^t Bu)_2]$ is found to undergo a slow disproportionation-type reaction (over 48 h) to yield the bis(amido)alkyl zincate $[(TMEDA)\cdot NaZn(DA)_2(^t Bu)]$ (*cf.*, complex **3**), and the tris(alkyl) zincate $[(TMEDA)\cdot NaZn(^t Bu)_3]$.[21] Returning to **2**, this compound appears to exhibit identical behaviour to give **3** and $[(TMEDA)\cdot NaZn(^t Bu)_3]$ (observed by ^1H NMR spectroscopic studies of the resultant filtrate) at ambient temperature over a period of approximately two weeks. To elaborate, the ^1H NMR spectrum of the filtrate revealed a resonance at 1.41 ppm which was attributed to the $C(CH_3)_3$ H atoms in $[(TMEDA)\cdot NaZn(^t Bu)_3]$. Also **2** does not appear to react with an additional equivalent of *cis*-DMP(H) to yield **3**. In an attempt to reveal the generality of this disproportionation reaction, **4** was prepared in a similar fashion to **3**. Again, a bis(amido)alkyl zincate was forthcoming and **4** could not be prepared by a "rational" double amination route (*i.e.*, utilising two molar equivalents of amine).

Magnesiate **5**, was prepared by a similar mixed-metallation approach which was adopted for the preparation of its tris-DA analogue.[27] An equimolar mixture of BuNa and Bu_2Mg in hexane was treated with three molar equivalents of *cis*-DMP(H) and subsequently with one molar equivalent of TMEDA. In contrast to the zincate scenario, this led to the complete conversion of all the alkyl substituents to gaseous alkane, resulting in the formation of the desired TMEDA-solvated heterobimetallic tris(amido) complex **5**. In keeping with the aforesaid zincate reactions (**1–3**) the reactivity of *cis*-DMP(H) towards metallate species appears to resemble that of DA(H) more than that of TMP(H), as like its DA analogue, **5** is homoleptic with respect to its anionic ligands. When TMP(H) is utilised in the corresponding reaction full amination is not possible instead the bis(amide) species $[(TMEDA)\cdot NaMg(TMP)_2(^n Bu)]$ is formed.[43]

Solid-state structures

Fig. 2 shows the molecular structure and pertinent dimensions of **1**, which crystallises in the monoclinic system, space group $P2_1$. Each metal centre is three-coordinate. Due to the acute TMEDA–Li bite angle (N41–Li1–N44) of 85.62(10)°, the Li geometry is best described as pseudo-trigonal planar (summed angles at Li, 356.36°), whereas that of Zn is almost perfectly trigonal planar [range of angles and summed, 116.19(6)–122.61(6); and 359.86° respectively]. The $Li–N_{cis\text{-}DMP}$ bond distance [2.027(3) Å] in **1** is slightly shorter than the corresponding bond in $[(TMEDA)\cdot Li(cis\text{-}DMP)]_\infty$[49,50] [mean distance, 2.044 Å]; whilst the $Li–N_{TMEDA}$ bond distances are in turn longer [mean distance in **1** and $[(TMEDA)\cdot Li(cis\text{-}DMP)]_\infty$ are 2.205 and 2.161 Å respectively]. Zincate **1** has an open, curved Li–N–Zn–C1 motif [Li1 ··· C1 and Li1 ··· C13 distances are 3.545(3) and 2.813(3) Å respectively]. A similar scenario was encountered in the HMDS zincates $[(TMTA)\cdot Li(HMDS)Zn(CH_2SiMe_3)_2]$[23] and



Scheme 1 Syntheses of **1**–**5**.

[(PMDETA)·LiZn(HMDS)(Me)$_2$].[24] Presumably a "closed" motif for **1** is not possible due to the combined steric bulk of a TMEDA ligand, the bridging amide and a ^{t}Bu group. In the latter HMDS zincate,[24] a tridentate donor is utilised to sterically protect the Li centre; hence, reducing the need for an additional bridging ligand. In addition, the inclusion of PMDETA reverses the convention that an amide is a better bridging ligand than an alkyl group.

Fig. 3 shows the molecular structure and pertinent dimensions of **2**, which crystallises in the triclinic system, chiral space group *P*1. Akin to its lithium congener **1**, the structure of **2** is composed of the same basic building blocks—an alkali metal, a TMEDA ligand, a *cis*-DMP anion, a Zn centre, and two ^{t}Bu anions—the only difference being that one ^{t}Bu anion bridges to the Na atom rather than remaining terminally bound to the Zn atom. This results in the Zn centre in **2** having an almost identical coordination sphere [range of angles and total angle around the Zn centre, 117.8(2)–123.7(2); and 359.9° respectively] to that in **1**. The long Na1–C15 contact [2.845(10) Å] causes the coordination number of the alkali metal to increase from three to four and the formation of a five-membered, four-element (NaNZnCC) ring system. Discounting this undoubtedly weak Na–C interaction, the total for the angles around the Na centre is 354.26°, suggesting that with respect to the N atoms, the metal's coordination sphere is much closer to planar (360°) than pyramidal (328.5°). Including the Na1–C15 interaction suggests that the geometry is therefore distorted trigonal pyramidal rather than tetrahedral. In keeping with the larger size of the metal centre, the TMEDA bite-angle [75.93(18)°] is approximately 10° more acute in **2** than in **1**. Complex **2** is a *cis*-DMP analogue of [(TMEDA)·NaZn(TMP)(^{t}Bu)$_2$]. As mentioned previously, this latter complex has proven to be a useful utility base in the deprotonation of arenes[15] and metallocenes[11] and indeed as a ^{t}Bu nucleophile towards benzophenone.[52] The bond distances within the respective five-membered bimetallic rings for **2** and the TMP analogue differ significantly. For instance, the shortest Na–C contact [2.845(7) Å] in **2** is longer (by 0.095 Å) than that in the TMP-containing complex [2.750(10) Å]. This may be as a consequence of the shorter Na–N$_{amide}$ and to a lesser extent the Zn–C$_{bridging}$ distances in **2** [Na–N$_{amide}$ and Zn–C$_{bridging}$ bond distances in the TMP-containing complex are 2.412 and 2.149 Å respectively].

An initial X-ray experiment suggested that **3** had the structure shown in Scheme 1. Its overall composition is also confirmed by NMR spectroscopic studies. The main difference between **3**

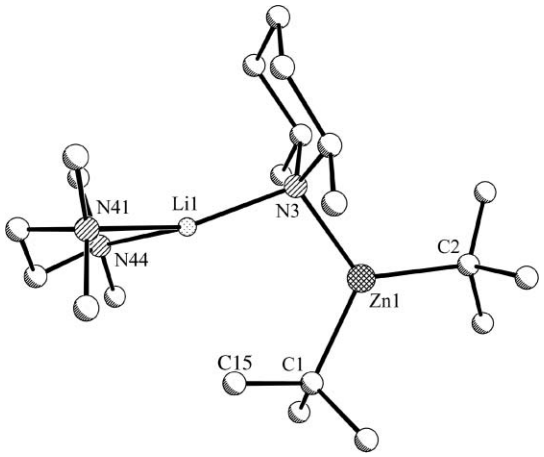


Fig. 2 Molecular structure of **1**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): Li1–N3, 2.027(3); Li1–N41, 2.211(3); Li1–N44, 2.198(3); Zn1–N3, 2.0622(12); Zn1–C1, 2.0476(15); Zn1–C2, 2.0510(15); N3–Li1–N41, 137.52(14); N3–Li1–N44, 133.22(14); N41–Li1–N44, 85.62(10); N3–Zn1–C1, 116.19(6); N3–Zn1–C2, 121.06(5); C1–Zn1–C2, 122.61(6); Li1–N3–Zn1, 106.16(6).

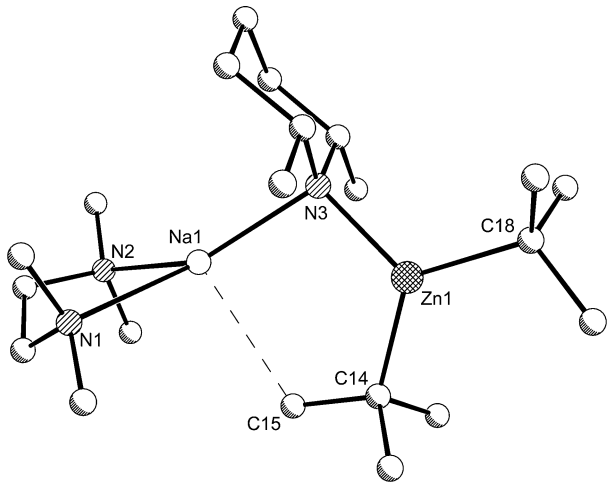


Fig. 3 Molecular structure of **2**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): Na1–N1, 2.452(5); Na1–N2, 2.462(6); Na1–N3, 2.342(5); Na1–C15, 2.845(10); Zn1–N3, 2.039(5); Zn1–C14, 2.048(5); Zn1–C18, 2.063(6); N1–Na1–N2, 75.93(18); N1–Na1–N3, 137.69(19); N2–Na1–N3, 140.64(18); N3–Zn1–C14, 118.4(2); N3–Zn1–C18, 117.8(2); C14–Zn1–C18, 123.7(2).

and the other new *cis*-DMP zincates, is that it has a diamido-alkyl constitution. Previously, the only example with such a composition is the DA zincate [(TMEDA)·NaZn(DA)$_2$(^{t}Bu)].[21] Due to the poor quality X-ray data for **3**, we decided to prepare another diamido-alkyl zincate (so to prove further the generality of the disproportionation reaction). By using diisobutylamine [DIBA(H)] (Fig. 1), we successfully prepared and grew X-ray quality crystals of [(TMEDA)·NaZn(DIBA)$_2$(^{t}Bu)], **4**. Fig. 4 shows the molecular structure of **4** and its key bond distances and angles. Complex **4** crystallises in the monoclinic system, space group $P2_1/n$. In keeping with zincates **1–3**, **4** is an ion-contacted zincate containing a four atom ring; however, in this case it is a (Na–N–Zn–N) ring, whereby the two metals are linked by two bridging DIBA ligands. The Zn centre's coordination sphere is

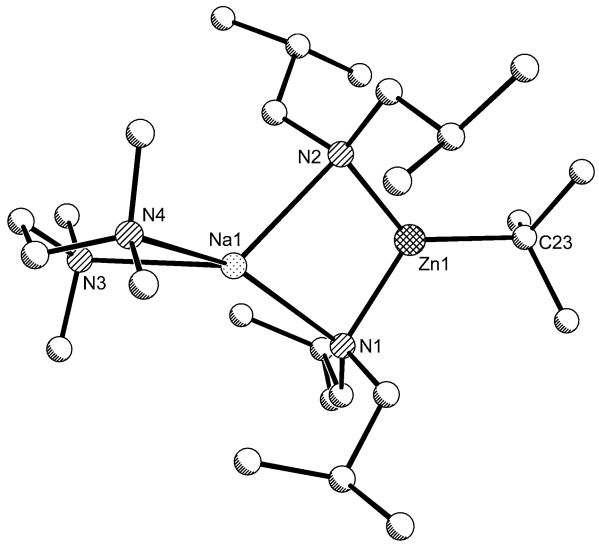


Fig. 4 Molecular structure of **4**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): Zn1–N2, 1.9830(14); Zn1–N1, 2.0281(14); Zn1–C23, 2.0330(17); Na1–N1, 2.4444(14); Na1–N2, 2.4460(15); Na1–N3, 2.5540(16); Na1–N4, 2.5927(16); N2–Zn1–N1, 102.58(6); N2–Zn1–C23, 132.44(6); N1–Zn1–C23, 123.83(6); N1–Na1–N2, 79.59(5); N1–Na1–N3, 123.56(5); N2–Na1–N3, 125.04(5); N1–Na1–N4, 150.54(5); N2–Na1–N4, 113.02(5); N3–Na1–N4, 72.35(5) Na1–N1–Zn1, 88.42(5); Na1–N2–Zn1, 89.41(5).

completed by coordination to a terminal ^{t}Bu group which results in this metal adopting a distorted trigonal planar environment. The key bond dimensions of **4** are essentially identical to those in its DA analogue.[21] The Na atom is bound solely to N atoms (two each from the amide and TMEDA). As expected, the shortest of these distances is for the metal-anion (Na–N_{amide}) contacts (mean, 2.445 Å, *cf.*, 2.573 Å for Na–N_{TMEDA} bonds). The N_{TMEDA}–Na–N_{TMEDA} bite angle in **4** is 72.35(5)°, which is approximately 3.5° wider than that in **2**. This possibly indicates that in the latter complex, the TMEDA can obtain better access to the metal's coordination shell due to the more open nature of the zincate. This is further corroborated by comparison of the mean Na–N_{TMEDA} distance in **2** and **4** (2.457 and 2.573 Å, respectively).

Fig. 5 shows the molecular structure of **5** and contains its pertinent bond distances and angles. Complex **5** crystallises in the monoclinic system, space group $P2_1/n$. Unlike the previously discussed zincate structures, the anions in magnesiate **5** are solely *cis*-DMP ligands (*i.e.*, full amination has occurred without retention of any alkyl groups). This is in line with magnesium's greater affinity for nitrogen anions. The metal–N core of the structure is a planar $NaN_{amide}MgN_{amide}$ ring (sum of internal ring angles, 359.91°). Three of the internal angles are acute and range from 81.09(4)–86.59(4)°. The remaining internal angle (N1–Mg1–N3) is significantly wider (108.74°), to accommodate the distorted trigonal planar geometry of the Mg centre. The Na atom is four coordinate (akin to those in **2** and **3**), bound only to N atoms (two belong to anions and two to the bidentate TMEDA ligand). The coordination environment around Na is best described as highly distorted tetrahedral (sum of angles, 665.14°). As expected, the majority of this distortion is caused by the tight TMEDA bite-angle [71.13(4)°]. Turning to the bond distances, the Mg–$N_{bridging}$ bonds are longer (mean length, 2.050 Å) than the Mg–$N_{terminal}$ one

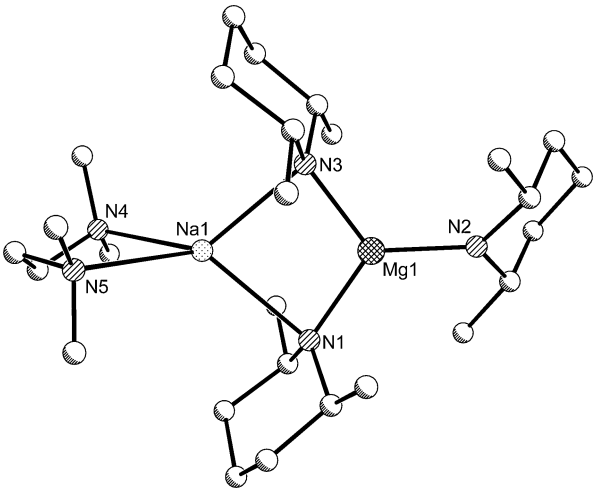


Fig. 5 Molecular structure of **5**. H atoms have been omitted for clarity. Key bond distances (Å) and angles (°): Na1–N1, 2.6263(12); Na1–N3, 2.4982(12); Na1–N4, 2.6117(13); Na1–N5, 2.6406(12); Mg1–N1, 2.0441(12); Mg1–N2, 1.9840(11); Mg1–N3, 2.0560(12); N1–Na1–N3, 81.09(4); N1–Na1–N4, 129.20(4); N1–Na1–N5, 128.02(4); N3–Na1–N4, 125.90(4); N3–Na1–N5, 129.62(4); N4–Na1–N5, 71.13(4); N1–Mg1–N2, 125.83(5); N1–Mg1–N3, 108.74(5); N2–Mg1–N3, 125.43(5).

[length, 1.9840(11) Å]; this is in accordance with the coordination number (C.N.) difference between the bridging N1/N3 atoms (C.N. is four) and terminal N2 atom (C.N. is three). Perhaps counterintuitively, the two Na–$N_{bridging}$ bonds (Na1–N1 and Na1–N3) have very different lengths [2.6263(12) and 2.4982(12) Å respectively; hence, $\Delta = 0.1281$ Å]. Indeed, this former bond is essentially identical in length to the Na–N_{TMEDA} dative bonds (mean distance, 2.6262 Å). On comparing the Na–$N_{bridging}$ bonds, with their aforementioned Mg–$N_{bridging}$ counterparts, the latter are much more uniform (difference in length, 0.0119 Å) and are shorter (by on average 0.512 Å) implying that they are stronger. Complex **5** can be compared with the other structurally-characterised sodium–magnesium tris(amide) complexes [(TMEDA)·NaMg(DA)$_3$], and its bis(amide) cousin [(TMEDA)·NaMg(TMP)$_2$(^{n}Bu)]. Like DA, when *cis*-DMP(H) is utilised, a tris(amide) sodium magnesiate was forthcoming, potentially giving clues to the eventual reactivity of **5** and its TMEDA-free complex with certain organic substrates and metallocenes. As the reaction of "(TMEDA)·NaMgBu$_3$" with excess TMP(H) only yielded the bis(amido) magnesiate (presumably due to steric-crowding around the metal centres) it can be concluded that the steric bulk of the TMP ligand is far greater than that of the *cis*-DMP ligand which is similar to that of DA. The key structural parameters of [(TMEDA)·NaMg(DA)$_3$] are similar to those of **5**; however, there are two noticeable differences. Firstly, although the Na–$N_{bridging}$ bonds in the former are still asymmetric (difference in length, 0.065 Å), they are considerably more uniform than those in **5**, and secondly, the mean Na–N_{TMEDA} distance in the DA complex (2.5505 Å) is shorter than that in **5** (2.6262 Å). This second point possibly suggests that in **5** the chelating TMEDA ligand is more restricted in its approach to the Na centre, indicating that the steric demands of three *cis*-DMP ligands is actually greater than that of three DA anions. At this juncture it is appropriate to note that the metal atoms in **1–5** do not appear to require supplementary M · · · C agostic-type interactions to increase their stability and the *cis*-DMP six-membered ring adopts a chair conformation, in which the methyl limbs occupy equatorial positions.

By comparing the solid-state structures of **1–5** and some key examples from the literature, it is possible to determine experimentally the relative steric bulk of the amide ligands *cis*-DMP, TMP, DA and DIBA. Undoubtedly, and unsurprisingly, the most sterically demanding ligand of this set is TMP, as *contacted* tris(TMP) zincate or magnesiate complexes with this amide have not yet been detected, although a *solvent-separated* tris(TMP) sodium magnesiate has recently been reported.[53] Due to the similar reactivity of *cis*-DMP(H) and DA(H) [*i.e.*, to yield both mono- and bis(amido) zincates[21] and tris(amido) magnesiates[27]] it can be concluded that they have similar steric properties.[54] However, when **5** is compared with [(TMEDA)·NaMg(DA)$_3$], from a steric perspective it appears that *cis*-DMP is slightly more sterically encumbered than DA as the Na–N_{TMEDA} interactions in **5** are longer than those found in the DA derivative. Finally, when [(TMEDA)·NaZn(DA)$_2$(^{t}Bu)][21] (mean Na–N_{TMEDA} distance is 2.6195 Å) is compared with **4** (mean Na–N_{TMEDA} distance is 2.5733 Å), it can be tentatively deduced that since the bidentate ligand makes a slightly closer approach to the metal in **4**, from a steric point of view, DA appears larger than DIBA. In summary, it can be concluded that the order of the amides with decreasing steric bulk is: TMP ≫ DMP > DA > DIBA.

NMR spectroscopic studies

Complexes **1–5** are highly soluble in arene solvents, hence, C_6D_6 solutions of the complexes were subjected to ^{1}H and ^{13}C NMR spectroscopic analysis (results in Tables 1 and 2). Two-dimensional (COSY and HSQC) techniques were used to aid in the assignment of the data. For comparison, data on the amine *cis*-DMP(H) in C_6D_6 solution is also included in this discussion. Due to the chair conformation adopted by *cis*-DMP(H), four resonances are observed for the four chemically distinct β- and γ-H atoms (Fig. 6,

Table 1 ^{1}H NMR spectroscopic data (400.13 MHz, 300 K, C_6D_6) for *cis*-DMP(H) and **1–3** and **5**

	cis-DMP(H)	TMEDA	**1**	**2**	**3**	**5**
α-C*H*	2.45	—	3.32	3.40	3.21	3.12
β-CH_2	1.43, 1.00	—	1.67, 0.39	1.70, 0.15	1.68, 0.76	1.76, 0.79
γ-CH_2	1.65, 1.24	—	1.83, 1.72	1.82, 1.71	1.95, 1.72	2.00 1.76
CH_3	0.96	—	1.05	1.07	1.26	1.41
N*H*	0.75	—	—	—	—	—
TMEDA (CH_3)	—	2.12	1.66	1.66	1.84	1.81
TMEDA (CH_2)	—	2.36	1.48	1.56	1.78	1.71
^{t}Bu (CH_3)	—	—	1.59	1.61 (br)	1.71	—

Table 2 ^{13}C NMR spectroscopic data (100.62 MHz, 300 K, C_6D_6) for *cis*-DMP(H) and **1–3** and **5**

	cis-DMP(H)	TMEDA	**1**	**2**	**3**	**5**
α-*C*	52.7	—	57.2	56.4	60.3	58.0
β-*C*	34.6	—	38.0	39.2	38.9	38.6
γ-*C*	25.6	—	27.2	26.8	27.3	27.4
CH_3	23.4	—	25.9	27.0	28.9	27.2
TMEDA (*C*H_3)	—	46.0	46.9	45.8	46.3	47.0
TMEDA (*C*H_2)	—	58.4	57.2	56.8	57.3	57.6
^{t}Bu (*C*H_3)	—	—	35.7	35.7	35.2	—
^{t}Bu (*C*)	—	—	[a]	[a]	[a]	—

[a] The quaternary *C* resonance was not observed in the spectrum.

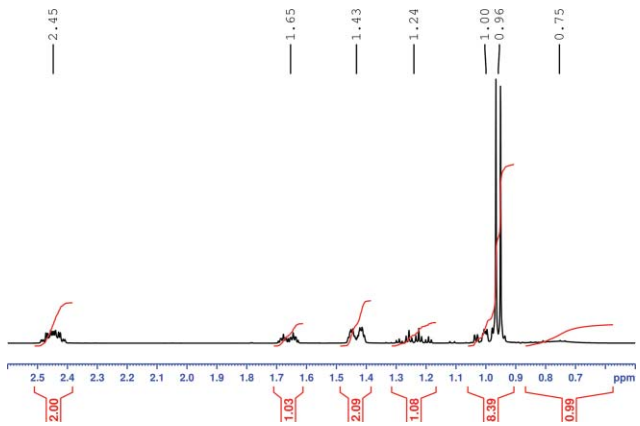


Fig. 6 ^1H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of *cis*-DMP(H).

Table 1). In general when deprotonated and incorporated within a bimetallic framework, the resonances associated with *cis*-DMP broaden and a systematic downfield shift of the α-*H*, C*H*$_3$, one β-*H* and one γ-*H* atoms, and upfield shift of the other β-*H* and γ-*H* atoms is observed. The corresponding ^{13}C NMR spectra reveal that all the *cis*-DMP chemical shifts are shifted downfield with respect to the free amine. The two ^1H and two ^{13}C resonances associated with the TMEDA ligand in **1–5** are different from those encountered in the free diamine indicating that in all cases it remains coordinated to the alkali metal in arene solution. The resonance for the ^{t}Bu quaternary *C* atom could not be located in the ^{13}C NMR spectra for the solutions of **1–3**.

Assuming that the ^{t}Bu groups in **1** are allowed to freely rotate, the ^1H NMR spectrum for a C_6D_6 solution of **1** appears to indicate that the solid state structure is maintained in solution (see ESI†). The resonances for the *cis*-DMP hydrogen atoms in **1** are significantly broader than those observed in the free amine and their chemical shifts are consistent with those reported for the D_8-THF solution of aforementioned [(TMEDA)·Li(*cis*-DMP)]$_\infty$.[50] Turning to the arene solution of **2**, its ^1H and ^{13}C NMR spectra essentially resemble that of **1**, except that the resonances associated with the two ^{t}Bu groups are extremely broad (see the ESI†). This is possibly indicative of a significantly slower rotation of the alkyl units in **2** (when compared with **1**). As expected, the ^{t}Bu resonances in the spectra for the C_6D_6 solutions of **3** are sharper, suggesting that this group does not undergo a dynamic exchange process to occupy a bridging position, presumably due to the retention of the strong Na–N bonding. The NMR spectra of solutions of **4** are not directly comparable to those of **1–3** as it contains DIBA and no *cis*-DMP; however, the ^{t}Bu resonances in the NMR spectra for arene solutions of **3** and **4** are identical. Turning to the C_6D_6 solution of magnesiate **5**, only one set of broad amido signals (chemical shifts are not concentration dependent) are present in the ^1H NMR spectrum suggesting that its solid-state structure may not be retained in solution (two distinct sets of signals, due to the bridging and terminal amido ligands, would have been expected). This observation suggests that the chemically distinct *cis*-DMP ligands in **5** undergo a dynamic fast exchange process in arene solution, or **5** forms a solvent-separated ion pair consisting of [Na·(arene)$_x$]$^+$ and [Mg(*cis*-DMP)$_3$]$^-$. To gain more insight into the solution behaviour of **5**, a low temperature ^1H NMR spectroscopic study of the magnesiate in D_8-toluene was conducted. The focus of our study was the resonance for the α-C*H* atom (Fig. 7). At 300 K, the resonance (3.05 ppm) was relatively broad. On cooling to 273 K, the resonance (3.03 ppm) broadened further without any sign of decoalescence. However, at 253 K, two distinct resonances (3.43 and 2.96 ppm) are present in a 1 : 2 ratio which can be attributed to terminal and bridging *cis*-DMP ligands respectively. This data suggests that in arene solution, **5** does indeed undergo a fast dynamic exchange at ambient temperature, which is sufficiently slowed on cooling to 253 K.

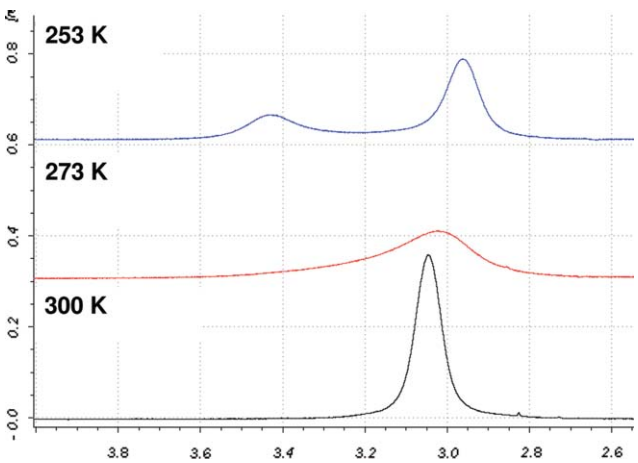


Fig. 7 Variable temperature ^1H NMR spectra (400.13 MHz, $C_6D_5CD_3$) of **5**.

Conclusions

In an effort to develop the metall(ate) chemistry of *cis*-DMP (a close relative to the synthetically important TMP and DA) we

Table 3 Selected crystallographic and refinement parameters

Compound	**1**	**2**	**4**	**5**
Formula	$C_{21}H_{48}LiN_3Zn$	$C_{21}H_{48}N_3NaZn$	$C_{26}H_{61}N_4NaZn$	$C_{27}H_{58}MgN_5Na$
Formula weight	414.93	430.98	518.15	500.08
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Wavelength/Å	0.71073	1.54180	1.54180	0.71073
a/Å	8.3990(3)	8.3370(4)	9.7987(1)	14.1862(4)
b/Å	16.7308(4)	9.6409(5)	19.5516(2)	15.1005(5)
c/Å	9.5282(4)	9.7024(4)	16.5289(2)	14.6621(4)
α/°	90	61.815(4)	90	90
β/°	108.761(4)	78.623(4)	91.279(1)	97.090(3)
γ/°	90	73.435(5)	90	90
Volume/Å^3	1267.78(8)	657.03(5)	3165.82(6)	3116.88(16)
Z	2	1	4	4
Refls. collected	12 776	6022	19 219	25 234
Refls. unique	6035	3312	5797	8635
Refls. obs.	5446	3302	4569	5421
R_{int}	0.0204	0.0418	0.0187	0.0370
Goodness of fit	0.975	1.060	1.002	0.949
$R\,[I > 2\sigma(I)]$, F	0.0252	0.0658	0.0304	0.0475
wR(all data), F^2	0.0512	0.1841	0.0791	0.1045

have prepared and characterised three new alkali metal zincates and one new magnesiate complex of *cis*-DMP. In addition we report the synthesis and structure of another closely related zincate containing the DIBA anion. By comparing the structural data reported here with other pertinent literature complexes, we have experimentally shown that the structural chemistry of *cis*-DMP mimics more closely that of DA, and in terms of decreasing steric bulk, the amido ligands can be ranked as TMP ≫ DMP > DA > DIBA. Future studies will examine the reactivity of **1–5** as bimetallic bases to determine whether the structural patterns observed here, profoundly affect reactivities.

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. *cis*-2,6-Dimethylpiperidine was stored over 4 Å molecular sieves. *n*,*s*-Dibutylmagnesium (1 M solution in heptane) and *n*-butyllithium (1.6 M solution in hexanes) was purchased from Aldrich and used as received. *n*-Butylsodium[55] and *t*-dibutylzinc[15] were prepared according to literature methods. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C. All data were collected on an Oxford Diffraction Gemini S instrument at 123 K. Selected crystallographic and refinement parameters are given in Table 3. All structures were refined to convergence with SHELX-97.[56]

Synthesis of [(TMEDA)·LiZn(*cis*-DMP)^{t}Bu$_2$] (1)

^{n}BuLi (0.63 mL of a 1.6 M solution in hexanes, 1 mmol) was added to 2 mL of dried hexane in a Schlenk tube. *cis*-DMP(H) (0.14 mL, 1 mmol) was introduced and the mixture was allowed to stir for 30 min. In a separate Schlenk tube, freshly prepared ^{t}Bu$_2$Zn (0.18 g, 1 mmol) was dissolved in 5 mL of hexane. This latter solution was transferred to the former *via* a canula, which was followed by the addition of TMEDA (0.15 mL, 1 mmol). This pale yellow solution was allowed to stand at ambient temperature. After 48 h, small colourless X-ray quality crystals of **1** were deposited (0.32 g, 78%). ^{1}H NMR (400.13 MHz, 300 K, C_6D_6): δ 3.32 (α-C*H*, 2H, m), 1.83 (γ-C*H*, 2H, m), 1.72 (γ-C*H*, 2H, m), 1.67 (β-C*H*, 2H, m), 1.66 (TMEDA CH_3, 12H, s), 1.59 (^{t}Bu, 9H, s), 1.48 (TMEDA CH_2, 4H, s), 1.05 (CH_3, 6H, d), 0.39 (β-C*H*, 2H, m). ^{13}C NMR (100.62 MHz, 300 K, C_6D_6): δ 57.2 (α-*C*), 57.2 (TMEDA *C*H$_2$), 46.9 (TMEDA *C*H$_3$), 38.0 (β-C), 35.7 (^{t}Bu *C*H$_3$), 27.2 (γ-*C*), 25.9 (*C*H$_3$). ^{7}Li NMR (155.47 MHz, 300 K, C_6D_6): δ 0.93.

Synthesis of [(TMEDA)·NaZn(*cis*-DMP)^{t}Bu$_2$] (2)

Freshly prepared *n*-butylsodium (0.08 g, 1 mmol) was suspended in 5 mL of dried hexane, and placed in an ultrasonic bath for 10 min. *cis*-DMP(H) (0.14 mL, 1 mmol) was introduced and the mixture was allowed to stir for 30 min. In a separate Schlenk tube, freshly prepared ^{t}Bu$_2$Zn (0.18 g, 1 mmol) was dissolved in 5 mL of hexane. This latter solution was transferred to the former *via* a canula, which was followed by the addition of TMEDA (0.15 mL, 1 mmol). The pale yellow solution was immediately placed in a freezer operating at –28 °C. After 48 h, small colourless X-ray quality crystals of **2** were deposited (0.10 g, 23%). ^{1}H NMR (400.13 MHz, 300 K, C_6D_6): δ 3.40 (α-C*H*, 2H, m), 1.82 (γ-C*H*, 2H, m), 1.71 (γ-C*H*, 2H, m), 1.70 (β-C*H*, 2H, m), 1.66 (TMEDA CH_3, 12H, s), 1.61 (^{t}Bu, 9H, br s), 1.56 (TMEDA CH_2, 4H, s), 1.07 (CH_3, 6H, d), 0.15 (β-C*H*, 2H, m). ^{13}C NMR (100.62 MHz, 300 K, C_6D_6): δ 56.8 (TMEDA *C*H$_2$), 56.4 (α-*C*), 45.8 (TMEDA *C*H$_3$), 39.2 (β-C), 35.7 (^{t}Bu *C*H$_3$), 27.0 (*C*H$_3$), 26.8 (γ-*C*).

Synthesis of [(TMEDA)·NaZn(*cis*-DMP)$_2$^{t}Bu] (3)

Freshly prepared *n*-butylsodium (0.08 g, 1 mmol) was suspended in 5 mL of dried hexane, and placed in an ultrasonic bath for 10 min. *cis*-DMP(H) (0.14 mL, 1 mmol) was introduced and the mixture was allowed to stir for 30 min. In a separate Schlenk tube, freshly prepared ^{t}Bu$_2$Zn (0.18 g, 1 mmol) was dissolved in 5 mL

of hexane. This latter solution was transferred to the former *via* a canula, which was followed by the addition of TMEDA (0.15 mL, 1 mmol). The pale yellow solution was left at ambient temperature and after 48 h, small colourless crystals of **3** deposited (0.14 g, 28% with respect to *cis*-DMP). ^{1}H NMR (400.13 MHz, 300 K, C_6D_6): 3.21 (α-C*H*, 2H, m), 1.95 (γ-C*H*, 2H, m), 1.84 (TMEDA CH_3, 12H, s), 1.78 (TMEDA CH_2, 4H, s), 1.72 (γ-C*H*, 2H, m), 1.71 (^{t}Bu, 9H, s), 1.68 (β-C*H*, 2H, m), 1.26 (CH_3, 6H, d), 0.76 (β-C*H*, 2H, m). ^{13}C NMR (100.62 MHz, 300 K, C_6D_6): δ 60.3 (α-*C*), 57.3 (TMEDA *C*H_2), 46.3 (TMEDA *C*H_3), 38.9 (β-C), 35.2 (^{t}Bu *C*H_3), 28.9 (*C*H_3), 27.3 (γ-*C*).

Synthesis of [(TMEDA)·NaZn(DIBA)$_2$(^{t}Bu)] (4)

Freshly prepared *n*-butylsodium (0.32 g, 4 mmol) was suspended in 10 mL of dried hexane, and placed in an ultrasonic bath for 10 min. ^{i}Bu$_2$NH (0.66 mL, 4 mmol) was introduced and the mixture was allowed to stir for 30 min. In a separate Schlenk tube, freshly prepared ^{t}Bu$_2$Zn (0.72 g, 4 mmol) was dissolved in 10 mL of hexane. This latter solution was transferred to the former *via* a canula, which was followed by the addition of TMEDA (0.60 mL, 4 mmol). X-Ray quality crystals of **4** precipitated from the solution at ambient temperature (yield of first batch, 0.65 g, 31%). ^{1}H NMR (400.13 MHz, 300 K, C_6D_6): δ 2.93 (NCH_2, 8H, d), 1.90 (NCH$_2$C*H*, 4H, sept.), 1.86 (TMEDA CH_3, 12H, s), 1.75 (TMEDA CH_2, 4H, s), 1.64 (^{t}Bu, 9H, s), 1.05 [NCH$_2$CH(CH_3)$_2$, 24H, d]. ^{13}C NMR (100.62 MHz, 300 K, C_6D_6): δ 67.5 (N*C*H$_2$), 57.2 (TMEDA, *C*H_2), 45.7 (TMEDA, *C*H_3), 35.2 (^{t}Bu), 31.2 (NCH$_2$*C*H), 22.2 [NCH$_2$CH(CH$_3$)$_2$].

Synthesis of [(TMEDA)·NaMg(*cis*-DMP)$_3$] (5)

Freshly prepared *n*-butylsodium (0.16 g, 2 mmol) was suspended in 4 mL of dried hexane, and placed in an ultrasonic bath for 10 min. *n*,*s*-Dibutylmagnesium (2 mL of a 1 M solution in hexane, 2 mmol) was added followed by three molar equivalents of *cis*-2,6-dimethylpiperidine (0.81 mL, 6 mmol) added dropwise, producing a cloudy yellow solution. The solution was vigorously stirred for 1 h and then TMEDA (0.3 mL, 2 mmol) was introduced dropwise, producing a transparent yellow solution. After 30 min, the solution was left to stand at room temperature for 48 h, producing a crop of colourless X-ray quality needle-like crystals of **5** (0.55 g, 55%). ^{1}H NMR (400.13 MHz, 300 K, C_6D_6): δ 3.12 (α-C*H*, 2H, m), 2.00 (γ-C*H*, 2H, m), 1.81 (TMEDA CH_3, 12H, s), 1.76 (γ-C*H*, 2H, m), 1.76 (β-C*H*, 2H, m), 1.71 (TMEDA CH_2, 4H, s), 1.41 (CH_3, 6H, d), 0.79 (β-C*H*, 2H, m). ^{13}C NMR (100.62 MHz, 300 K, C_6D_6): δ 58.0 (α-*C*), 57.6 (TMEDA *C*H_2), 47.0 (TMEDA *C*H_3), 38.6 (β-C), 27.4 (γ-*C*), 27.2 (*C*H_3).

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