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Synthesis of the mixed lithium–magnesium, mixed amide (*R,R/S,S*)-[$\{LiMg(TMP)[CH_2Si(Me)_2N(SiMe_3)]\}_2$]: a conformationally-locked structure of five fused rings inducing two stereogenic nitrogen centres

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Reaction of the magnesium amide $Mg(TMP)_2$ with the lithium amide LiHMDS is accompanied by an unexpected, sterically-promoted hydrogen transfer/amine elimination process, to yield the novel title compound which is the first such heterometallic composition to contain a heteroleptic amide ligand set.

Lithium amide compounds have been long-standing friends to the synthetic chemist, especially sterically encumbered types which find widespread use in regio-, stereo- and enantioselective deprotonation applications.[1] By comparison, magnesium amides are much more recent acquaintances, but they too are beginning to make an impression as specialist reagents,[2] most notably in the asymmetric arena.[3] While these mainstream homonuclear compounds have been commanding most attention, the effect of pairing a lithium (or another alkali metal) amide with a magnesium amide, in the same molecular package,[4] is also under scrutiny. Could this mixing promote a useful synergy, giving rise a new chemistry and novel structures, not known or not possible with the conventional homonuclear compounds? Studies directed towards answering this intriguing question are still at a preliminary stage; however, initial signs appear promising. For example, the idea of 'inverse crown ether' complexes was conceived from this heterobimetallic approach. These are eight-membered $(MNMgN)^{2+}$ rings (M = Li, Na or K)[5] which act as polymetallic hosts to oxygen-based O^{2-} or $(O_2)^{2-}$ dianions. Larger twelve-membered $(NaNMgNNaN)_2^{2+}$ or twenty four-membered $(KNMgN)_6^{2+}$ variants,[6,7] which function as single or multiple traps for larger arene-based anions, have also been introduced. In all of these mixed-metal macrocycles there is only one type of amido bridge, belonging to either 1,1,1,3,3,3-hexamethyldisilazide (HMDS) or 2,2,6,6-tetramethylpiperidide (TMP) ligands. Similarly, the few other mixed lithium–magnesium amides in the literature are also homoamido in composition. Therefore we set out to prepare the first mixed lithium–magnesium, mixed amide compound. As reported herein, while this aim has been achieved through the synthesis of [$\{LiMg(TMP)[CH_2Si(Me)_2N(SiMe_3)]\}_2$], **1**, which contains both TMP and HMDS ligands, surprisingly it is not an inverse crown ether and furthermore it is accompanied by an unexpected deprotonation of one of the Me groups attached to Si in the latter ligand. Interest is heightened by the fact that the molecular structure is chiral, as determined by X-ray crystallographic studies on representative crystals of **1**. This stereochemical outcome can be explained by an intramolecular hydrogen transfer, promoted by the sterically crowded, conformationally locked heteronuclear structure expected to form initially on mixing the component homonuclear amides.

We first observed **1** on attempting to prepare the homonuclear amides *in situ* by adding, in order, Bu^nLi (5 mmol) in hexane, HMDS(H) (5 mmol), Bu_2Mg (5 mmol) in heptane, and TMP(H) (10 mmol). The reaction mixture was subsequently heated to reflux for 90 min. A mutually coupled pair of doublets (^2J, 13.1 Hz) in the negative region of the ^1H NMR spectrum of a C_6D_6 solution of the product,† alerted us to the presence of the metal bound CHH′ group (a point later verified by X-ray crystallography). This surprising finding prompted us to try an alternative direct approach, preparing and isolating $Mg(TMP)_2$ (as an oil)[8] and LiHMDS (as a crystalline solid)[9] separately (to ensure all butyl anions had been consumed, a point confirmed by NMR studies), before adding them together in a 1 : 1 stoichiometry in hydrocarbon solution. Stirred and gently warmed for a few min but not heated to reflux, this solution also afforded pale yellow crystals of **1**.† Absolute yields could not be determined due to the high solubility of **1** which makes the low temperature filtration/isolation procedure problematical; however, in one attempt 30% was collected, though the true yield was considerably greater.

The molecular structure of **1** (Fig. 1)‡ is dimeric, composed of dinuclear (LiNMgN) monomeric fragments with pendant Me_2SiCH_2 arms which bind 'intramolecularly' through the methylene C atom to the Mg centre. Dimerisation is effected *via* 'intermolecular' bonds from the methylene C atom to the Mg centre of the other monomeric fragment. The Mg centres occupy distorted tetrahedral [80.80(10)–128.62(11)°] environments made up of two C and two N atoms. Formally occupying bent [104.3(2)°] geometries between two N atoms, each Li centre finds electronic relief through agostic interactions with one TMP [Li(1)···C(12), 2.565(6) Å; Li(2)···C(24), 2.585(6) Å] and one HMDS-Me group [Li(1)···C(4), 2.359(6) Å; Li(2)···C(28), 2.332(6) Å]. 'Intramolecular' Mg–C bonds are marginally longer than their 'intermolecular' counterparts (mean lengths, 2.320 and 2.258 Å, respectively). The $(MgC)_2$ ring they make, which represents the central component of a fivefold system of fused four-membered rings, is puckered

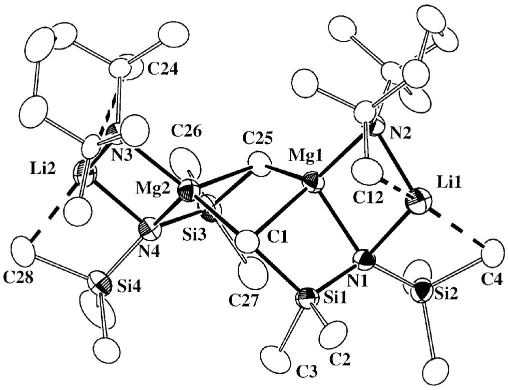

Fig. 1 Molecular structure of **1** showing agostic contacts as dashed lines. Hydrogen atoms are omitted for clarity. Selected dimensions (Å and °): Mg1–C1 2.319(3), Mg1–C25 2.252(3), Mg2–C1 2.264(3), Mg2–C25 2.321(4), Li1–N1 2.009(6), Li1–N2 1.990(6), Li2–N3 1.989(6), Li2–N4 2.012(6), Si1–N1 1.726(3), Si1–C1 1.875(3), Si3–N4 1.730(3), Si3–C25 1.877(3), Mg1–N4–Si1 92.0(1), N1–Si1–C1 105.4(1), Mg1–C1–Mg2 76.0(1), Mg1–C25–Mg2 76.2(1), Mg2–N4–Si3 91.9(1), N4–Si3–C25 105.4(1).

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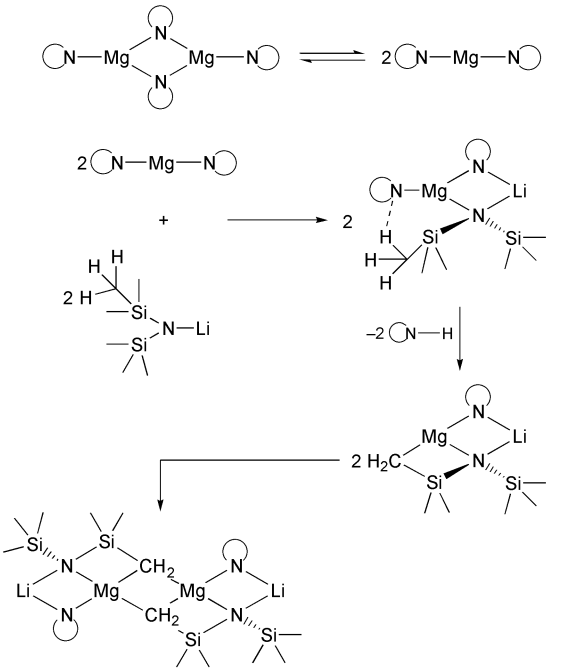

Scheme 1 Note that the stereochemistry shown here is idealized and not representative of that in **1**

(RMS deviation from planarity, 0.2138 Å). In contrast, the dinuclear (LiNMgN) rings at opposite ends of the structure are essentially planar. Mean Mg–N and Li–N bond lengths (2.104 and 2.000 Å, respectively) lie in the usual range for bonds of this type with the same connectivity. Also essentially planar, two (MgNSiC) rings complete the structure.

The most interesting aspect of the structure is the chiral nature of the HMDS N atoms N(1) and N(4). Each binds to one Li and one Mg centre, and to one $SiMe_3$ and one $SiMe_2CH_2$ group. Only the enantiomeric *R*,*R* and *S*,*S* pair has been observed. The *R*,*S* diastereoisomer has not been detected. Based on knowledge of related magnesium and mixed lithium–magnesium amide structures, it is possible to construct a structural pathway (Scheme 1) to rationalise the formation of **1**. Though not yet confirmed crystallographically, the structure of $Mg(TMP)_2$ is almost certainly either a monomer or a loosely-associated dimer. These two structural types co-exist in solutions of $Mg(HMDS)_2$,[10] so it is likely that solutions of $Mg(TMP)_2$ would contain an even more significant preponderance of monomer given the greater steric bulk of TMP. In the first step of the pathway, it is envisioned that a $Mg(TMP)_2$ monomer would approach a molecule of LiHMDS (formally a trimer in the solid state, but here shown as a monomer for simplicity). This should result in a heteronuclear arrangement, akin to that known for $LiMg(HMDS)_3$,[5a] but more sterically crowded and with a mixed TMP-HMDS bridge. A close contact between a C–H bond on the bridging $Me(SiMe_2)N$ group and the N atom of the terminal TMP ligand could then trigger hydrogen transfer and subsequent loss of TMPH. Concomitantly, a new Mg–C bond and fixed stereogenic N centre are formed. Relief of steric crowding around the Mg centre then allows dimerisation to proceed in the final step, thus increasing the coordination number of the Mg centre from 3 to 4. It is pertinent to note that no analogous pathway is possible in a homonuclear LiHMDS–LiTMP system, as from valency considerations no terminal TMP ligand would be available for subsequent displacement.

Though rare, it is known that certain transition metal (Ti,[11] V,[12] Zr[13]) HMDS-containing complexes can for steric reasons lose a hydrogen atom to generate $CH_2Si(Me)_2NSiMe_3$ ligands through direct metallation with a strong base (Bu^nLi, LiHMDS, NaHMDS), but these reactions afford only achiral products. A more interesting analogy is provided by a mixed Sb–Ga *geminal* organodimetallic complex[14] in which a $(2\text{-}C_5H_4N)C(SiMe_3)_2$ ligand is converted to $(2\text{-}C_5H_4N)C(SiMe_3)Si(Me)_2CH_2$ with generation of a new stereogenic C centre. Thermally induced *via* an intramolecular MeH elimination (*cf.*, the amine elimination here), this deprotonation is facilitated by a Me–Ga bond (*cf.*, the R_2N–Mg bond here) within the cyclic precursor.

Finally, given that **1** retains a bulky amide ligand within a conformationally-locked ring structure, as well as a bifunctional C, N-alkide, amide ligand, it will be of interest to ascertain whether it and similar heterometallic complexes have a future as companion reagents to the conventional homometallic bases and nucleophiles.

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Notes and references

† NMR data for **1** revealed an unusual asymmetrical pattern for the TMP ligand which we attribute to a fixed, rigid environment. δ_H (400.13 MHz, C_6D_6) –0.75 (d, 2 H, C*H*H′), –0.40 (d, 2 H, CH*H′*), 0.19 (s, 18 H, Si*Me*$_3$), 0.39 (s, 6 H, Si*Me*Me′), 0.61 (s, 6 H, SiMe*Me′*), 0.65/0.78/1.53 (m, 8 H, *β-CH*$_2$, TMP), 1.12 (s, 6 H, *Me*-TMP), 1.28 (s, 6 H, *Me′*-TMP), 1.46 (s, 12 H, 2*Me″*-TMP), 1.53/1.82 (m, 4 H, *γ-CH*$_2$, TMP); δ_C (100.61 MHz, C_6D_6) 5.03 (Si*Me*$_3$), 6.11 (*C*HH′), 9.20 (Si*Me*Me′), 9.89 (SiMe*Me′*), 19.81 (*γ-C*, TMP), 32.21/34.93/38.19/38.98 (4*Me*-TMP), 43.62 (*β-C*, TMP), 52.24/52.62 (*α-C*, TMP). Assignments were verified by COSY, DEPT and ^1H, ^{13}C HMQC experiments. Crystals of **1** start to decompose at 146 °C and finally melt at 164–166 °C.

‡ *Crystal data* for **1**: $C_{30}H_{70}Li_2Mg_2N_4Si_4$, $M = 661.76$, orthorhombic, space group $Pna2_1$, $a = 11.6682(2)$, $b = 16.8825(4)$, $c = 20.9980(4)$ Å, $V = 4136.3(2)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.197$ mm^{-1}, $T = 150$ K, $R = 0.0504$ for 6153 reflections with $I > 2\sigma(I)$, $R_w = 0.1181$ for 9097 unique reflections. 30186 reflections measured ($R_{int} = 7.86\%$) to a $2\theta_{max}$ of 54.96°. Refinement on F^2 with SHELXL gave a final maximum residual electron density of 0.318 e Å^{-3}. CCDC 182/1734. See http://www.rsc.org/suppdata/cc/b0/b004317f/ for crystallographic files in .cif format.

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