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Intermetallic Lithium−Magnesium Hexamethyldisilazide: Synthesis and Structure, Discovery of an Oxygen-Centered Variant, and a Reaction with Benzonitrile That Produces a Novel Amidinate Cage Compound with a Trigonal Bipyramidal Li_4MgO Core

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Abstract: Intermetallic lithium−magnesium hexamethyldisilazide $[\{(Me_3Si)_2N\}_3LiMg]$, **1**, has been synthesized from a nonstoichiometric 2:1 ratio of LHMDS and $Mg(HMDS)_2$ in hexane/toluene solution. Its crystal structure reveals a simple dinuclear arrangement based on a near-planar $\overline{\mathrm{NMgNLi}}$ ring: the Mg center occupies a distorted trigonal planar environment of three N atoms, while the Li center occupies a distorted tetrahedral N_2C_2 environment due to two additional C−Li interactions with the μ-$N(SiMe_3)_2$ substituents. This structure appears to be retained in arene solution on the basis of the evidence of ^1H NMR spectral data. In the presence of trace amounts of oxygen, the surprising peroxide−oxide variant $[\{(Me_3Si)_2N\}_4\ Li_2Mg_2(O_2)_x(O)_y]$ preferentially crystallizes from solution. X-ray crystallography has established that its structure contains peroxide predominantly [$x = 0.715(7)$; $y = 0.285(7)$], the presence of which induces an aggregation state increase relative to **1**: the four indistinguishable metal centers, held in a square-planar arrangement, side-on-coordinate to the peroxide molecule and bind to two N atoms. The oxygen-scavenging ability of this system has been exploited further in a reaction with benzonitrile. This has yielded a third intermetallic lithium−magnesium crystalline compound, having the composition $[\{PhC(NSiMe_3)_2\}_4Li_4Mg(O)]$. X-ray crystallography has revealed its remarkable cage structure built around an unprecedented distorted trigonal bipyramidal Li_4MgO core, at the center of which lies a μ_5-O atom. Interestingly, all the metal centers lie out of the benzamidinate NCN ligand planes to indicate a significant degree of π-bonding. One NCN ligand also adopts an unusual face-capping mode to a Li_3 triangle, the like of which has previously only been observed in transition metal cluster compounds.

Introduction

The thirst for knowledge of lithium amides continues unabated with an annual flood of publications documenting their synthesis, structures, and chemical utilities.[1,2] Against this, the literature on magnesium amides represents no more than a trickle, though interest in them has recently been growing steadily.[3] However, it is in the area of mixed (intermetallic) lithium−magnesium amide chemistry that a true drought of information exists. This is surprising given the considerable synthetic potential offered by such composite species. Without detailed studies, possible synergic effects of combining more reactive lithium with less reactive magnesium in a molecular amide can only be guessed at; not withstanding, data are available on certain nonamide compounds (such as alkyls, with respect to their performance in Ziegler alkylation reactions of pyridine[4]) which show that mixed lithium−magnesium compositions can exhibit unique chemical behavior compared to their unimetallic component parts. Only as recently as 1993 was the first crystallographic characterization of a mixed lithium−magnesium amide:[5] the structure of $[\{PhCH_2(Me_2NCH_2CH_2)N\}_4Li_2Mg]$ is notable for a 2:1 Li/Mg stoichiometry and intramolecular (tertiary amine) N−Li coordinations which circumvents

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the need for donor solvent ligands. A year later followed the structures of two dibenzylamine derivatives, $[\{(PhCH_2)_2N\}_4Li_2Mg]$ and $[\{(PhCH_2)_2N\}_3LiMg\cdot pyridine]$,[6] the latter of which introduced a new 1:1 Li/Mg stoichiometry. While studies of the dibenzylamine system have played a major part in the advancement of lithium amide structural chemistry, the role of the amine in synthesis[7] has been limited (it is, however, a convenient source of 2-azaallyl anions[8]). Therefore, it is unlikely that the mixed dibenzylamido systems will be any more important in this respect. Thus, there remains a requirement for a mixed lithium−magnesium analogue of a known synthetically useful lithium amide reagent. We now report such a compound. The hindered steric nature of lithium bis(trimethylsilyl) amide $[\{(Me_3Si)_2NLi\}_n]$ (also commonly referred to as lithium hexamethyldisilazide, LHMDS) makes it valuable as a deprotonating agent in organic synthesis in the general mould of LDA,[9] though its chemistry can sometimes deviate from that expected of a conventional lithium amide base.[10] This compound was also the first alkali metal amide to be structurally characterized (by powder diffraction in 1969;[11] by single-crystal diffraction in 1978),[12] so its detailed structure ($n = 3$) is available for comparison; it has also been widely studied in solution[13] and computationally.[14] In this paper the preparation and crystal structure of the mixed lithium−magnesium analogue $[\{(Me_3Si)_2N\}_3LiMg]$, **1**, is described. Also, in a surprising development, we have found that the reaction solutions from which **1** is obtained act as highly efficient oxygen scavengers. Evidence of this ability is provided by an oxygen-contaminated variant of **1**, which contains both oxide and peroxide anions within its crystal structure. Furthermore, we have utilized this oxygen-scavenging ability in a reaction with benzonitrile to afford an unprecedented amidinate cage compound built on a mixed-metal Li_4MgO core. Previously reported unimetallic lithium and magnesium amidinate crystal structures are surveyed in the discussion.

Results and Discussion

Synthesis and Structure of New Intermetallic Amide. From its formula, **1** can be regarded as a 1:1 mixture of the lithium and magnesium salts of bis(trimethylsilyl)amine. However, despite repeated efforts, no isolable products could be obtained from such a mixture. When the relative stoichiometry of the lithium amide component was doubled, colorless crystals of **1** grew at freezer temperatures (ca. −30 °C). These proved troublesome to isolate since they dissolve readily in the mother liquor on removing the Schlenk tube from the freezer. Consequently, the yield of collected **1** was always rather low (<10%). It is important to make the magnesium bis(amide) reactant, $[\{(Me_3Si)_2N\}_2Mg]$, in a pure crystalline form prior to reacting it with the corresponding lithium amide. This is done by heating a 2:1 bis(trimethylsilyl)amine/dibutylmagnesium mixture in heptane to reflux for 4 h (eq 1) (an alternative preparation via transmetalation of the corresponding tin(II) amide has been reported).[15] All the butyl ligands are converted into butane by this action, thus avoiding the possibility of the mono(amido) intermediate $[\{(Me_3Si)_2NMgBu\}_n]$, a known compound,[16] interfering in the subsequent reaction. In the final step, the magnesium bis(amide) crystals are dissolved in toluene, and added to the lithium amide which is generated in situ by lithiation of the parent amine (eq 2). Williard and Nichols previously used this method of reacting two unimetallic bis(trimethylsilyl) amides to form a heterobimetallic composite in their report of the series of isostructural alkali metal complexes $[\{(Me_3Si)_2N\}_2M^1M^2\cdot(THF)_3]$ (where $M^1 = Li$, $M^2 = Na$ or K; $M^1 = Na$, $M^2 = K$).[17]

$$\textit{n,sec}\text{-}Bu_2Mg + 2(Me_3Si)_2NH \longrightarrow [\{(Me_3Si)_2N\}_2Mg] + 2BuH \qquad (1)$$

$$\begin{tikzcd} 2\textit{n}\text{-}BuLi + 2(Me_3Si)_2NH \arrow[r] & 2[(Me_3Si)_2NLi] + 2BuH \arrow[d, "{[\{(Me_3Si)_2N\}_2Mg]}"] \\ & {[\{(Me_3Si)_2N\}_3LiMg] + [(Me_3Si)_2NLi]} \end{tikzcd} \qquad (2)$$

A ^1H NMR spectrum of **1** in C_5D_5N was uninformative as it revealed only a single resonance in the alkyl region. When rerecorded in $C_6D_5CD_3$, two signals of relative integral 2:1 appeared in this region. The ^{13}C NMR spectrum run in the same solvent confirmed the presence of the two distinct methyl (Me_3Si-) groups. As discussed below this observation fits the structure found in the solid state: two chemically equivalent $(Me_3Si)_2N-$ groups bridge the pair of metal centers, while another binds terminally to the Mg center. Any exchange between these bridging and terminal amido groups must be slow as the spectra were recorded at ambient temperature. It therefore appears that the intermetallic structure remains intact in arene solution, where there is no competition from donor solvent molecules for coordination sites.

In terms of molecular architecture, the crystal structure of **1** (Figure 1) is as one would have predicted for a 1:1 Li/Mg stoichiometry. With respect to the N anions, the Li center occupies a two-coordinate bent geometry while the Mg center occupies a three-coordinate trigonal planar geometry. This coordination arrangement is centered on a $\overline{\text{LiNMgN}}$ ring which is essentially planar (RMS deviation 0.023(3), 0.022(2), 0.021(2), and 0.022(3) for Li1, N1, Mg1, and N2, respectively). The same N_3LiMg motif occupies the structure of the aforementioned $[\{(PhCH_2)_2N\}_3LiMg\cdot pyridine]$[6] (though note the additional presence of the solvent ligand which raises the lithium coordina-

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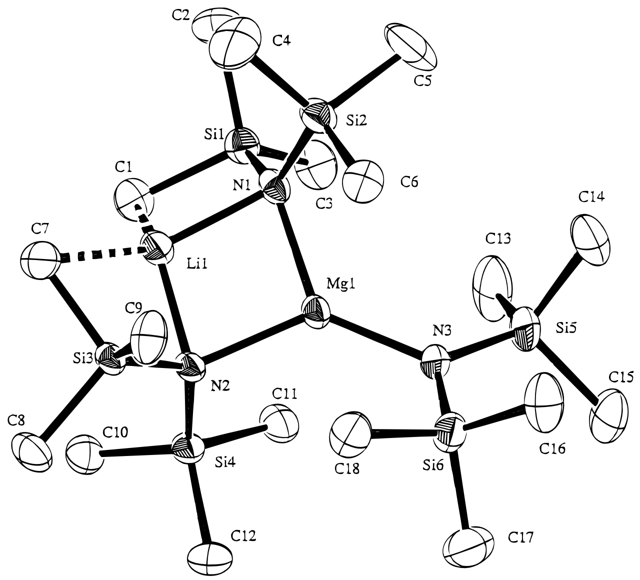

Figure 1. Thermal ellipsoid plot of **1** at 50% probability, showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. The Me⋯Li agostic-type interactions are highlighted as broken bonds.

tion number to three), while a carbon analogue has been reported in the structure of the bulky substituted aryl complex [(2,4,6-i-$Pr_3C_6H_2)_3LiMg\cdot0.6THF\cdot0.4Et_2O$].[18] Having a mean value of 2.019 Å, the N−Li bond lengths in **1** show little variation from those in the all-lithium trimeric complex [{$(Me_3Si)_2NLi$}$_3$] (2.00 Å),[12] the Li and N centers of which are similarly both two-coordinate; however, this comparison ignores the fact that the associated NLiN bond angles are markedly different [102.8(4)° in **1**, cf. 147(3)°], such that the coordinative deficiency is more surprising in **1** since it offers a much wider coordination arc for the possible docking of a solvent ligand. This point is reinforced by comparison with the dimeric THF[16,19] and ether[20] complexes of lithium bis(trimethylsilyl) amide, which in terms of angular dimensions (NLiN bond angles 106.3 and 104.9°, respectively) bear a closer resemblance to **1**. Although the Li centers in these solvates have a higher formal coordination number (three) than that in **1**, their N−Li bonds are only marginally longer at 2.025 and 2.055 Å, respectively. This suggests that the Li center in **1** must be receiving extra stabilization from atoms other than N. Prime candidates for this role are C1 and C7 belonging to the methyl groups on Si1 and Si3, respectively, which lie on opposite sides of the NLiNMg ring. The C1⋯Li1 and C7⋯Li1 distances are extremely short [2.294(10) and 2.320(9) Å, respectively]. This places them in the same category as formal, electron-deficient, C−Li bonds in alkyllithiums such as [$(EtLi)_4$][21] and [(t-$BuLi)_4$][22] (mean lengths 2.25 and 2.246 Å, respectively). Two hydrogen atoms attached to C1 (H1A, H1C) and two hydrogen atoms attached to C7 (H7B, H7C) also form short contacts with Li1 (respective distances 2.195, 2.173, 2.266, and 2.160 Å). Pseudoagostic interactions of this type are common for alkali metals with low coordination numbers when highly-polarized $Si^{\delta+}-CH_3^{\delta-}$ units are available within the structure. Such interactions can be intramolecular (as here) or intermolecular, as recently discussed in the context of a family of alkali metal hypersilanides.[23] The mean μN−Mg bond length in **1** (2.114 Å) is in good agreement with that previously found in the alkylamido dimer [{$(Me_3Si)_2NMg$$sec$-Bu}$_2$] (2.118 Å).[16] Predictably, the terminal N−Mg bond in **1** is shorter at 1.998(4) Å. By contrast the corresponding N−Mg bonds in the analogous N_3LiMg motif of [{$(PhCH_2)_2N$}$_3LiMg\cdot$pyridine][6] are all significantly shorter (by 0.069 and 0.053 Å for the bridging and terminal type, respectively) than those in **1**. This diminution in bond length can be attributed to the lesser steric demands of the dibenzylamido anion versus that of the bis(trimethylsilyl) one. Such steric factors probably explain why the 2:1 Li/Mg ratio employed in the reaction mixture does not produce a complex of the same stoichiometry, i.e., [{$(Me_3Si)_2N$}$_4Li_2Mg$], as this would require four anions to surround the Mg center (in a tetrahedral manner) instead of the three found in **1**. While the dibenzylamido anion can achieve this tetrahedral packing in [{$(PhCH_2)_2N$}$_4Li_2Mg$],[6] it appears to be only just small enough to do so, for the higher coordination cannot be sustained when the Li centers are replaced by Mg and thus [{[$(PhCH_2)_2N]_2$-Mg}$_n$] is dimeric (n = 2), not polymeric.[24] Hitherto, the size differential between these anions has been inconsequential as their metal complexes are often isostructural; for example, the lithium structures are cyclic trimers when solvent free, and cyclic dimers when solvated by THF or ether. As with the bond lengths, the endocyclic bond angle at Mg [99.5(2)°] also reflects the slight difference in size between the anions being 2.9° smaller in **1** than in [{$(PhCH_2)_2N$}LiMg·pyridine].[6] Other selected dimensions in **1** are listed in Table 1.

Table 1. Selected Geometric Parameters (Å, deg) for **1**

Mg1−N1	2.125(4)	Mg1−N2	2.103(4)
Mg1−N3	1.998(4)	Li1−N1	2.021(8)
Li1−N2	2.017(9)	Li1⋯C1	2.294(10)
Li1⋯C7	2.320(9)	Mg1⋯C11	2.830(6)
N1−Mg1−N2	96.54(15)	N1−Mg1−N3	132.18(16)
N2−Mg1−N3	131.28(16)	N1−Li1−N2	102.8(4)
Mg1−N1−Li1	80.0(3)	Mg1−N2−Li1	80.6(2)

Surprising Oxidized Variant of New Intermetallic Amide. In examining other possible methods of preparing **1**, we carried out the reaction depicted in eq 3. Whereas the magnesium bis(amide) was preformed in the original preparation (eqs 1 and 2), here the metal alkyl reagents were mixed together in situ prior to the addition of the silylamine. Note the 1:1 Li/Mg stoichiometry used, which, in the original preparation, gave no isolable product. An immediate difference was discernible in the in situ method, as a small, but reproducible amount of solid product could be isolated from solution. However, unexpectedly, this turned out not to be **1**, but an oxygen-contaminated derivative of formula [{$(Me_3Si)_2N$}$_4Li_2Mg_2(O_2)_x(O)_y$], **2**. As discussed below, its precise composition, and in particular the relative quantities of peroxide and oxide present, could only be established through X-ray crystallographic studies. Refinement of the particular crystal reported here indicated that its oxygen content is mainly in the form of peroxide [i.e., with x = 0.715(7) and y = 0.285(7)]. On making this serendipitous discovery

$$n,sec\text{-}Bu_2Mg + n\text{-}BuLi + 3(Me_3Si)_2NH \xrightarrow{\text{trace of } O_2} z[\{(Me_3Si)_2N\}_4Li_2Mg_2(O_2)_x(O)_y] + zBuH + \text{other products} \quad (3)$$

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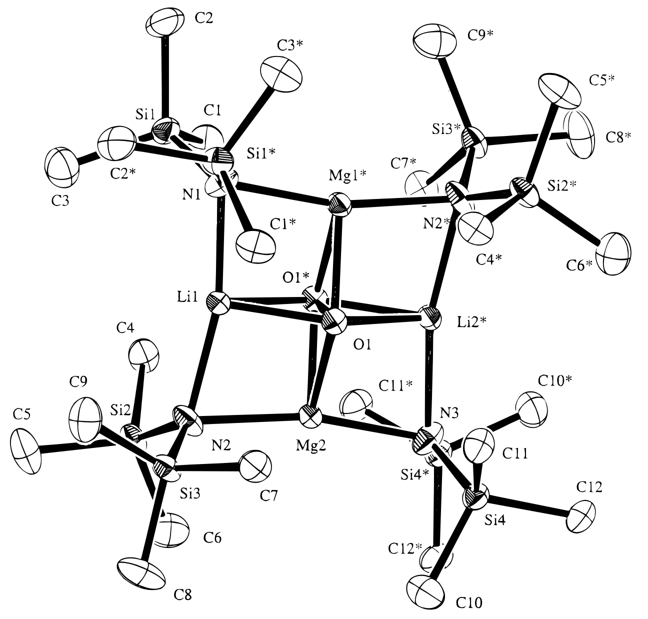

Figure 2. Molecular structure of **2** showing the atom-labeling scheme. Hydrogen atoms and minor disorder components have been omitted for clarity.

Table 2. Selected Geometric Parameters (Å, deg) for **2**[a]

M1−O1	2.023(2)	M1−O1*	2.013(2)
M1−O2	1.872(6)	M1−N1	2.113(2)
M1−N2	2.113(2)	M2−O1	2.012(2)
M2−O1*	2.024(2)	M2−O2	1.854(6)
M2−N2	2.135(2)	M2−N3	2.124(2)
O1−O1*	1.551(4)	N1−Mg1−N2	166.62(8)
N2−Mg2−N3	166.89(8)	M1−N1−M1*	77.31(10)
M1−N2−M2	76.58(7)	M2−N3−M1*	76.69(10)

[a] Where M1 is the Mg1/Li1 site and M2 is the Mg2/Li2 site. * = 3/2 − *x*, *y*, 1/2 − *z*.

of **2**, our first action was to check its reproducibility. This proved to be satisfactory. Five different batches of **2** were prepared following the same in situ procedure. Their authenticity was confirmed by checking the unit cell parameters of several crystals by X-ray diffraction. Yields of isolated **2** were consistently low, ranging from 1 to 5% maximum. No other solid products were obtained from the filtered solutions. Though colorless like **1**, crystals of **2** can be distinguished from their oxygen-free counterpart by a melting point analysis: reflecting a significantly larger molecular structure (see below), the latter melts over 80° higher at 203−205 °C. Recorded in $C_6D_5CD_3$ solution, the ^1H NMR spectrum of **2** establishes definitely that it does not contain lithium bis(trimethylsilyl) amide, magnesium bis[bis(trimethylsilyl) amide] or the mixed-metal analogue **1**. Two singlet resonances only 0.02 ppm apart, but clearly defined, are observable (at 0.29 and 0.27 ppm) in an approximate integration ratio of 2.5:1.0. Assuming the crystal structure of **2** is retained in solution, which is almost certain given the strength of the metal−oxygen core bonding, we tentatively assign these signals to the separate $(Me_3Si)_2N-$ groups associated with peroxide and oxide cores, respectively, noting that these dianions occur in the same 2.5:1.0 ratio in the crystal structure (i.e., $x = 0.715$, $y = 0.285$ in **2**). This view receives support from the ^{13}C NMR spectrum as it also displays two proximate signals at 6.20 and 6.10 ppm. A minute amount of free amine was also detected in the NMR solution of **2**.

The basic molecular structure of **2** without the oxide component is shown in Figure 2. Lying essentially in the same plane, the two Li and two Mg sites are indistinguishable from each other due to mutual substitution disorder. On free refinement, occupations of 51% Li and 49% Mg were obtained; thus, on the grounds of chemical sense, the occupancies of all metal sites were set to 50% Li/50% Mg. Occupying the core of the structure, the peroxide molecule is side-on-coordinated by all four metal centers. Not shown, the oxide atom replaces the peroxide molecule in approximately 30% of the molecules within the bulk lattice. Positioned at the center of the O(1)−O(1*) bond, this atom binds to the four metal centers in a square planar arrangement. Unfortunately, discussion of the dimensions of the metal−oxygen core is prejudiced by the two types of substitutional disorder observed. Relevant geometric parameters are listed in Table 2. The N heads bridge pairs of metal centers in the construction of a planar eight-membered $(NM)_4$ cyclic ring. In effect, the introduction of the oxygen components has induced a ring expansion in relation to the $(NM)_3$ cyclic structure of the parent lithium amide and an aggregation increase in relation to **1**. The Me_3Si tails of the amide groups occupy the periphery of the structure of **2**, to render it lipophilic. There is nothing remarkable about the Si−N and Si−C bond lengths (mean values 1.725 and 1.872 Å, respectively).

As far as we can ascertain there is no precedent for the structure of **2**. It is the first crystal structure of a mixed lithium−magnesium, mixed amide−peroxide composition. In fact, main group element 1,2-*μ*-peroxide structures are extremely rare, being limited to a few elements such as Ba, Ge, and Sn.[25] No such magnesium peroxide species has been crystallographically characterized. Recently, however, a crystal structure of the lithium mixed peroxide−siloxide species $[(Me_3SiOLi)_4(Li_2O_2)\{(Me_3Si)_2NLi\}\cdot 2THF]$ has appeared.[26] Containing the same lithium amide as in **1** and **2**, and having its O_2^{2-} unit side-on-coordinated by three Li centers, this species was produced by air hydrolysis of the dilithium hydrazide $[(Me_3Si)_2N_2Li_2]$.

This leads us to consider the most important, but fundamentally the most perplexing, question to arise from the characterization of **2**: what is the source of the oxygen contamination? The problem of adventitious oxygen turning up in crystalline compounds studied by X-ray diffraction is not new. As long ago as 1964, Stucky reported the surprising structure of $Mg_4Br_6(O)\cdot 4Et_2O$,[27] a Grignard reagent oxidation product, made by allowing the solvent of a PhMgBr ether solution to slowly evaporate into the open atmosphere. Since then there have been a growing number of reports of oxygen contamination in early main group compounds. Especially pertinent to **2** is the mixed-metal cresylate $[R_7LiMg_4(O)\cdot 4THF]$ [R = *o*-$Me(C_6H_4)O^-$], where the O^{2-} anion sits at the center of a trigonal bipyramidal $LiMg_4$ cage.[28] Several barium oxide-containing cage species, of which the aryloxide $[(PhO)_{14}H_2Ba_8(O)_2\cdot 6HMPA\cdot 2PhMe]$[29] is representative, have also appeared in the literature. Reflecting the strong oxygen affinity of lithium, a number of structures formally containing "Li_2O" molecular units have been similarly elucidated. An early example is found in the dilithiosulfone

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complex $[\{[PhSO_2{-}C(SiMe_3)]Li_2\}_6Li_2O{\cdot}(THF)_{10}]$.[30] More recent examples from Group 15 with progressively larger cage sizes are the primary amide $[\{(c\text{-}C_5H_9)N(H)Li\}_{12}Li_2O]$,[31] the phosphanediide $[\{[i\text{-}Pr_2(Mes)Si]P\}_8Li_{16}{\cdot}Li_2O]$,[32] and the arsanediide $[\{[Me_2(i\text{-}PrMe_2C)Si]As\}_{12}Li_{24}{\cdot}Li_2O]$.[32] There is also the mixed oxide−alkoxide cage complex of $[(t\text{-}BuO)_8Li_8K_2(O){\cdot}(TMEDA)_2]$.[33] To complicate matters further, the oxygen contamination need not necessarily lead to O^{2-} incorporation. Hydroxides can be preferentially formed instead as illustrated by the heterotrianionic $[(C_6H_{11}O)_4(t\text{-}C_4H_9O)_4Li_4K_4{\cdot}KOH{\cdot}(THF)_5]$[34] and the heterobianionic $[(t\text{-}BuOLi)_{10}(LiOH)_6]$.[35] Note that the last three structures mentioned all contain lithium *tert*-butoxide molecules. As alluded to earlier, peroxide formation is another possibility, a further example being the barium diketonate $[(THD)_{10}Ba_6(O_2)(H_2O)_6]$ (HTHD = 2,2,6,6-tetramethylheptane-3,5-dione).[36] In all of the examples cited so far the source of the oxygen contamination is not known with any degree of certainty. The picture is not any clearer in the few selected cases where molecular oxygen has been deliberately introduced into reaction systems. Illustrative of this point, insertion of O_2 into alkyl−magnesium bonds gives on one hand alkoxide formation in the alkyl amide system $[Me_2Al(N\text{-}i\text{-}Pr_2)_2\text{-}Mg(OMe)]$,[37] and on the other alkyl peroxide formation in the tris(pyrazolyl)hydroborato system $[\{HB(3\text{-}t\text{-}Bu\text{-}pz)_3\}MgOOR]$ (R = Me, Et, *i*-Pr, *t*-Bu).[38] In the absence of crystal structures these latter compounds were characterized by ^{17}O NMR spectroscopic studies.

Returning to the specific system in question, the synthesis of **2** was carried out under what we believed to be strictly anhydrous conditions. Solvents were distilled under dry N_2 from sodium/benzophenone and used fresh. The amine reactant was triply distilled from calcium hydride onto fresh 4A molecular sieves. Obtained commercially from the Aldrich Chemical Co. Ltd., the metal alkyl solutions were not purified but used as supplied, following restandardization procedures. In general, moisture contamination of alkyllithium or dialkylmagnesium solutions leads to hydroxide formation. Since there is no evidence of hydroxide formation here, and in view of the precautions taken as mentioned above, we believe that the balance of probability lies with molecular oxygen being the contaminant, rather than traces of moisture. The interaction of organometallic compounds with oxygen is generally poorly understood, particularly when there is insufficient oxygen present to ultimately produce the stoichiometric metal oxide (note that some possible interactions of Li^+ with H_2O/O_2 have recently been the subject of an ab initio MO study[39]). Rarely do such reactions yield single products, as the indiscriminate reactivity of the radical intermediates involved encourages the formation of mixtures. The fact that both oxide and peroxide anions end up in **2** lends a degree of support to our view that molecular oxygen is involved in its formation. It is interesting that **2** should have a preponderance of the latter anion. From thermodynamic considerations, one would anticipate the oxide to be preferred in the presence of the small Li^+ and Mg^{2+} counterions. The peroxide incorporation step may therefore be a kinetic process. Shielding by the bulky amido groups could stabilize the resulting structure, and slow any bimolecular process whereby an oxygen atom is abstracted from the peroxide to convert it to an oxide. One can only speculate on how the peroxide might form: for example, it may derive from the direct insertion of O_2 into a metal−alkyl bond (cf. the Mg−O−O−R system mentioned previously). As yet, we have been unable to pinpoint the source of the oxygen. The first time **2** was synthesized, freeze−pump−thaw degassing cycles were not applied to the liquids concerned; however, they were used subsequently, but this did not prevent the crystallization of **2**. Of course, it is difficult to totally exclude oxygen from routine Schlenk work, as trace quantities can come from the glass or even from the commercial “oxygen-free” blanket gas which we did not purify further. Anyway, the important point in the present study is that irrespective of its source, any oxygen available in solution is quickly seized upon by this reaction system and subsequently precipitated in the form of the highly stable oxygen-centered bimetallic cage species **2**. However, it should be emphasized that **2** is a minor product, so the major product, presumably the intermetallic amide **1**, must remain in solution. The solution should also contain small amounts of an oxidized product such as the hydrazine $(Me_3Si)_2N{-}N(SiMe_3)_2$, as O_2 is formally being reduced. This possibility will be investigated in a follow-up study. In the total absence of oxygen, it is **1** that preferentially crystallizes.

Utilizing the Oxidized Solution in the Synthesis of a Novel Mixed-Metal Amidinate. Originally our intention in this part of the work was to investigate the reactivity of the new intermetallic amide **1**. Specifically, by choosing an addition reaction rather than a deprotonation, we had hoped to harvest a product which retained both metal types (lithium and magnesium). To the best of our knowledge, there is no precedent in this branch of chemistry for using a mixed-metal reagent to generate a mixed-metal product. Subsequently, we pondered whether it would be possible to involve the oxidation product **2** in a similar process; i.e., could the oxide or peroxide anions be exploited in a further reaction? The low yield of **2** made it impractical to start this reaction from the bulk solid. Hence, deliberately omitting degassing procedures, **2** was reprepared in situ. Three molar equivalents of benzonitrile was then added to the solution. As revealed in eq 4, the reaction was

$$n,sec\text{-}Bu_2Mg + n\text{-}BuLi + 3(Me_3Si)_2NH + 3PhC{\equiv}N \xrightarrow{\text{trace of } O_2} x[\{PhC(NSiMe_3)_2\}_4Li_4Mg(O)] + yBuH + \text{other products} \quad (4)$$

successful, producing the tetralithium−monomagnesium mixed amidinate−oxide $[\{PhC(NSiMe_3)_2\}_4Li_4Mg(O)]$, **3**: thus, both of our objectives have been realized. However, we cannot be certain that **3** is formed directly from **2**, as the reaction solution may contain a mixture of several oxide-contaminated species.

Crystallizing as colorless needles, **3** was the only solid product to be obtained from the solution. Metal analysis of **3** by atomic absorption spectroscopy indicated a Li/Mg stoichiometry of 4:1. This was confirmed by X-ray crystallographic studies (see below) which established its precise composition and, in particular, the presence of the oxide. No peroxide molecules were detected. Complex **3** is only sparingly soluble in $C_6D_5\text{-}CD_3$. A ^1H NMR spectrum in this solvent revealed a compli-

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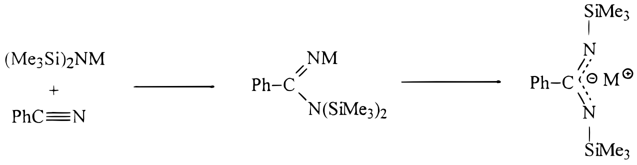
Scheme 1



cated series of overlapping SiMe$_3$ resonances centered at 0.16 ppm, and more than one set of Ph resonances (though in the dilute solution these were obscured by solvent peaks). Such complexity is consistent with the solid-state structure, which has two types of amidinate ligand. Repeated several times, the synthesis proved reproducible though yields of **3** were variable (maximum 13%—based on dibutylmagnesium consumption). No rationale can, as yet, be offered for the curious stoichiometry found in **3**. Equimolar amounts of lithium and magnesium were available in the reaction solution. Clearly, a mixture is formed in solution, of which **3** is the least soluble component. Built around a strongly bonded oxygen−metal core, its polynuclear cage structure (see below) suggests a high thermodynamic stability. The stoichiometry of **3** provides an amazing contrast with that in the aforementioned cresylate [R$_7$LiMg$_4$(O)·4THF],[28] in which the Li/Mg ratio is reversed, i.e., 1:4; here, as with **3**, the observed stoichiometry is in conflict with that originally employed in the reaction. The benzamidinate component of **3** arises from a well-known, two-step addition/migration process (Scheme 1). Metal amidinate chemistry has an extensive literature,[40] and trimethylsilyl-substituted examples of the type found in **3** have themselves been surveyed.[41] In earlier work, the two individual metal *N,N′*-bis(trimethylsilyl) benzamidinate components of **3** were prepared separately using this two-step method. The lithium system was first reported in 1973,[42] while benzonitrile and THF adducts of the magnesium system (bis(amidinates)) followed about 20 years later.[43] We therefore applied this same procedure to the combination of metal amides to afford intermetallic **3**.

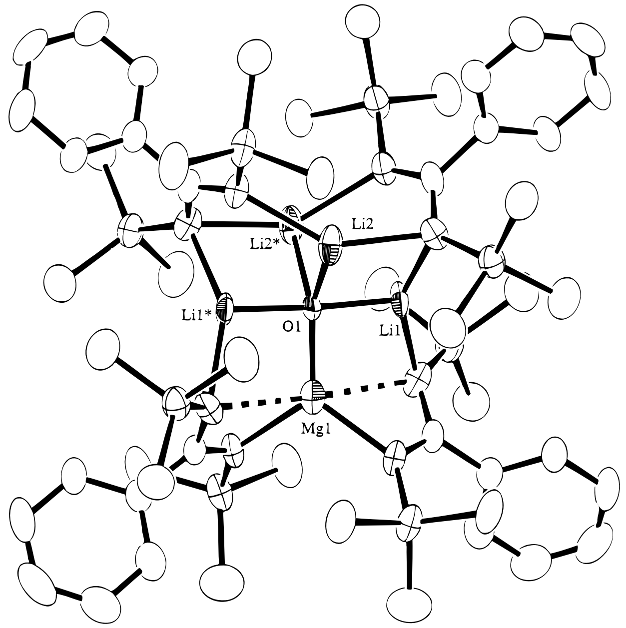


Figure 3. Molecular structure of **3** showing the atom-labeling scheme for the oxide−metal core. Hydrogen atoms are omitted for clarity.

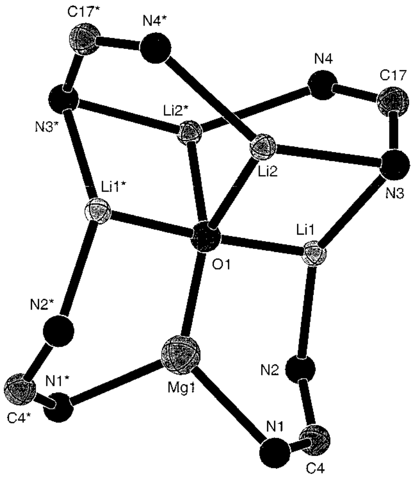


Figure 4. Metal−ligand core of **3** showing atom-labeling scheme.

X-ray crystallographic studies revealed the unique structure of **3** (Figure 3), which has crystallographic C_2 symmetry. Four Li$^+$ and one Mg^{2+} cations are fixed in a distorted trigonal bipyramidal arrangement by a central oxide anion. Li1 and Li1* define the axial sites, and Mg1/Li2/Li2* define the equatorial plane (Figure 4). There is some disorder, as discussed in the Experimental Section, which limits the precision of bond lengths and bond angles within the structure (listed in Table 3). Confronted by this Li$_4$MgO foundation, the benzamidinate ligands build up an unprecedented amidinate cage structure by attaching themselves to this core through bonds with considerable π character, foregoing their more usual σ-bonding to these cations. In purely σ-bonded systems, the NCN−metal fragments are planar or nearly so, but in **3** each metal atom lies well above or below the NCN plane to which it is attached. As shown in Figure 5, there are two distinct types of NCN−metal attachment. In the first type, the NCN moiety assumes a bridging mode, with each N atom (N1, N2) coordinating to a single metal center (Mg1 and Li1, respectively). The torsion angles of Mg1N1C4N2 [15.0(5)°] and LiN2C4N1 [49.6(6)°] confirm the nonplanarity. The second type of NCN ligand exhibits an even more unusual triangular-face capping mode, where N3 bridges a pair of lithium centers [Li1 and Li2, with torsion angles Li1N3C17N4 = 36.3(6)° and Li2N3C17N4 = −36.6(6)°], while N4 binds terminally to a unique third lithium center [Li2*: torsion angle Li2*N4C17N3 = 10.3(8)°, * = $-x$, y, $-z + 0.5$]. Overall, therefore, bridging N3 has a unique four-coordinate, distorted tetrahedral geometry. The remaining N atoms are three-coordinate, but whereas N1 and N4 are distorted trigonal planar, N2 is more pyramidal (sum of bond angles 359.6°, 359.7°, and 350.4°, respectively). Alternatively, the geometry of N2 could be considered four-coordinate, distorted tetrahedral, if a long-range contact to Mg1 [2.471(4) Å] was deemed significant. However, the vast majority of N−Mg bond lengths in the Cambridge Crystallographic Database[44] lie between 1.95 and 2.3 Å (mean length overall 2.151 Å); longer contacts tend to involve highly coordinated Mg centers bonded to polydentate ligands (e.g., 2.396 Å for the heptacoordinated Mg center in Mg$_2$EDTA·9H$_2$O).[45] On this basis, the N2−Mg1 contact would appear to be extremely weak, and is probably an enforced consequence of N2 approaching Li1. Disregarding N2, the

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Table 3. Selected Geometric Parameters (Å, deg) for **3**[a]

Mg1−O1	1.850(6)	Mg1−N1	2.099(4)
Mg1···N2	2.471(4)	Li1−O1	1.799(11)
Li1−N2	2.105(10)	Li1−N3	2.076(9)
Li2−O1	1.919(11)	Li2−N3	2.118(10)
Li2−N4*	2.207(10)	N1−C4	1.337(6)
N2−C4	1.331(6)	N3−C17	1.327(6)
N4−C17	1.328(6)	O1−Mg1−N1	124.40(13)
N1−Mg1−N1*	111.2(3)	O1−Li1−N2	102.4(4)
O1−Li1−N3	105.2(4)	N2−Li1−N3	148.9(4)
O1−Li2−N3	99.4(5)	O1−Li2−N4*	101.8(4)
N3−Li2−N4*	143.7(6)	Mg1−O1−Li1	92.0(3)
Mg1−O1−Li2	141.7(3)	Li1−O1−Li1*	176.0(7)
Li1−O1−Li2	83.2(4)	Li1−O1−Li2*	93.6(4)
Li2−O1−Li2*	76.7(7)	Mg1−N1−Si1	134.3(2)
Mg1−N1−C4	97.4(3)	Li1−N2−Si2	104.8(3)
Li1−N2−C4	115.8(4)	Li1−N3−Li2	72.2(4)
Li1−N3−Si3	118.3(3)	Li1−N3−C17	98.6(4)
Li2−N3−Si3	122.8(3)	Li2−N3−C17	97.0(4)
Li2*−N4−Si4	103.8(3)	Li2*−N4−C17	128.7(4)
Li1−N3−C17−N4	36.3(6)	Li2−N3−C17−N4	−36.6(6)
Li2*−N4−C17−N3	10.3(8)	Mg1−N1−C4−N2	15.0(5)
Li1−N2−C4−N1	49.6(6)	N1−C4−C5−C6	−107.5(6)
N3−C17−C18−C19	82.7(6)		

[a] * = −*x*, *y*, 1/2 − *z*.

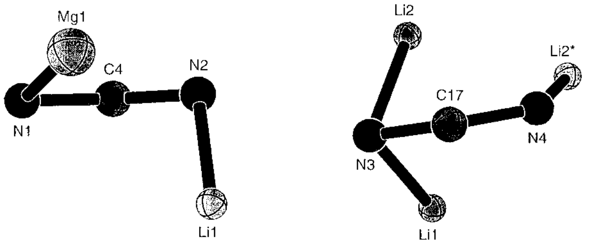

Figure 5. Orientations of metal centers in **3** with respect to the planes of their attached NCN ligands.

solitary Mg center occupies a three-coordinate, distorted trigonal planar environment. Both types of Li centers are also three-coordinate. However, equatorial Li2 has considerably greater pyramidal character than axial Li1 (sum of bond angles 344.9° and 356.5°, respectively). This, in part, reflects the sharper equatorial−equatorial Li2O1Li2* bond angle [76.7(7) Å, cf. 83.2(4)° for Li1O1Li2], as well as the awkward asymmetrical fit of each NCN ligand. An almost uniform delocalization is suggested by the near-equivalent C−N bond lengths within each half of the benzamidinate ligand [1.337(6)/1.331(6) Å for N1C4N2; 1.327(6)/1.328(6) Å for N3C17N4]. This is indicative of a substantial ionic contribution to the ligand−metal bonding, which would be enhanced by the strong polarizing effect of the attached trimethylsilyl substituents. Close to the ideal value of 120°, the bond angles within these sp^2-hybridized, three-atom units [119.2(4)° for N1C4N2; 121.9(4)° for N3C17N4] also suggest that the π-bonding is maximized. The high steric demands of the attached trimethylsilyl substituents appear to be satisfied at the most open peripheral points of the cage, so that disruption to the N−C−N bonding is minimized. Likewise, the phenyl rings lie almost orthogonal to the NCN planes to reduce steric interactions [N1C4C5C6 = −107.5(6)° and N3C17C18C19 = 82.7(6)°]. On the basis of this criteria, the description "diazaallyl system" clearly applies to these NCN ligands.

Turning to a comparison with other relevant structures, the μ_5-OLi$_4$Mg core of **3** can be contrasted with the structurally related μ_5-OLiMg$_4$ core of the aforementioned cresylate [R$_7$-LiMg$_4$(O)·4THF].[28] Bond lengths involving the oxide [O−Mg, 2.002(4) and 2.041(2) Å; O−Li, 1.89(2) Å] and coordination numbers (three for Li; five for Mg) in the latter intimate that the lithium-rich polyhedron is more compact. Still, there is enough steric similarity between the two polyhedra to speculate that an analogous amidinate cage could be built around this alternative OLiMg$_4$ core. Almost certainly, however, the need to accommodate seven amidinate ligands for charge balance would rule this out. There may be a possible clue here as to the curious metal stoichiometry found in **3**, in that, oxygen-centered polyhedra with Li/Mg ratios smaller than 4:1 will be much more sterically restricted due to valency considerations. This effect will be exacerbated when the ligands are hindered and bifunctional as here.

Three magnesium amidinate structures are available for comparison with **1**: the bis(amidinate) [{PhC(NSiMe)$_2$}$_2$Mg·N$\equiv$CPh][43] and two isostructural mixed aluminum−magnesium complexes [Me$_2$A1(*i*-Pr$_2$N)Mg{RNC(Me)NR′}] (R = R′ = *t*-Bu or *p*-tolyl).[46] Optimum (amidinate) N−Mg (σ, σ) bonding is observed in each structure, with the amidinate ligands disposed in a chelating manner. This more efficient orbital overlap is apparently counterbalanced by higher Mg coordination numbers (five and four, respectively); hence, the bond lengths involved (range 2.06−2.13 Å) are in the same general area as those in **3**. In light of these monomagnesium structures, it is clear that the N−Mg bonding in **3** is compromised by the steric imposition of the trigonal bipyramidal metal framework.

A recent surge of interest has established crystallographically-characterized examples of lithium amidinate monomers, dimers, and one trimer, but there is no precedent for a structure with four lithium centers. The monomeric benzamidinates [PhC-(NPh)$_2$Li·base] [base = TMEDA, (Me$_2$NCH$_2$)$_2$, or PMDETA, (Me$_2$NCH$_2$)$_2$NMe][47] resemble their magnesium counterparts, with symmetrical (σ, σ) N−Li bonding contained within planar, four-membered NCNLi rings, the anions of which are diazaallylic (N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N) in nature. This confirms the type of electronic structure favored when steric constraints are at a minimum. Upon dimerization, steric factors come more into play so greater electronic and structural variety is observed. Most interestingly, the benzamidinate dimer [{PhC(NPh)$_2$Li·HMPA}$_2$] [HMPA, (Me$_2$N)$_3$P=O][47] exhibits a more localized N=C−N fragment, attributed to the unequal distribution of N−Li bonds (one N atom binds to two Li centers, while the other binds to one Li center). On this basis, it might be expected that the N3C17N4 fragment in **3** would show a similar nonuniform delocalization as its N atoms also coordinate to unequal numbers of Li centers; however, this is not the case. This apparent conflict can be rationalized if the σ/π nature of the ligand−metal bonding is considered: in the HMPA dimer, two N−Li bonds are pure σ, and the other has a high degree of π-character; whereas in **3**, all the bonds are π-based. Hence, the electronic distribution within N3C17N4 is more symmetrical. Dimerization in two closely related methyl-substituted benzamidinates [{4-XC$_6$H$_4$C(NSiMe$_3$)$_2$Li·base}$_2$] (X = Me, base = THF[48] or *p*MeC$_6$H$_4$C$\equiv$N)[49] is achieved differently from that in the HMPA system. Essentially, one NCN unit engages two Li centers in a (σ, σ) manner, while the other engages them in a (π, π) manner. To effect this, the dihedral angle between the distinct NCN planes is approximately 90°. The symmetrical nature of the NCN ligation thus leads to a pair of diazaallyl N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N

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Table 4. Crystallographic Data

	1	2	3
formula	$C_{18}H_{54}LiMgN_3Si_6$	$C_{24}H_{72}Li_2Mg_2N_4O_{1.72}Si_8$	$C_{52}H_{92}Li_4MgN_8OSi_8$
formula weight	512.4	731.5	1122.1
Crystal size mm	0.20 × 0.20 × 0.20	0.60 × 0.55 × 0.25	0.60 × 0.24 × 0.15
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2/n$	*Pbcn*
color	colorless	colorless	colorless
a, Å	8.994(2)	9.161(3)	10.317(3)
b, Å	11.440(5)	13.785(5)	26.138(15)
c, Å	16.620(4)	18.139(4)	24.986(14)
α, deg	98.33(2)	90	90
β, deg	92.57(2)	91.17(2)	90
γ, deg	105.00(3)	90	90
max 2θ, deg	50.0	51.1	50.0
U, Å^3	1628.3(8)	2290.1(12)	6738(6)
Z	2	2	4
R,[a] Rw[b]	5.81, 17.24	3.57, 9.97	5.71, 17.83
GOF	1.015	1.007	0.956

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections having $I > 2\sigma(I)$. [b] $Rw = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

bridges. Yet another mode of dimerization is seen in the acetamidinate $[\{MeC(NPh)_2Li{\cdot}HMPA\}_2]$:[47] two HMPA molecules bridge two Li centers to form a central $(OLi)_2$ ring. From the perspective of the anion, this structure simply constitutes two joined monomers, each with the familiar planar NCNLi ring. Unusual in terms of its aggregation state, the trimeric benzamidinate $[\{PhC(NSiMe_3)_2Li\}_3{\cdot}N{\equiv}CPh]$[50] has no special NCN ligating features: one unit binds in a (σ, σ) manner to two Li centers, and two others bind in a chelating (π, π) manner to each of two Li centers. Rather the novelty arises because a unique benzonitrile-solvated Li center experiences the latter type of bonding from two separate NCN ligands, making it five-coordinate overall. This survey found no example of the triangular-face capping linkage observed for the N3C17N4 ligand in **3**. On reflection, this is not suprising as it is the three-dimensional cage nature of the structure which facilitates the opportunity for such a linkage. Reinforcing this point, one has to look to transition metal clusters to find a possible analogy for this type of linkage. The X-ray structure of $[Os_3(\mu\text{-}H)(CO)_9\{PhNC(Ph)NH\}]$[51] provides such an example, as it shows the amidinide ligand capping one triangular face of osmium atoms, and formally donating five electrons to the cluster. However, the analogy is limited since the metal triangles involved are fundamentally different. In the transition metal case, there is osmium−osmium bonding, the bond lengths are equivalent within experimental error (2.79 Å), and the bond angles are almost that of an equilateral triangle (range 59.4−60.4°), whereas, there is no metal−metal bonding in the Li_3 triangle, and its geometry is highly asymmetrical [edge lengths 2.381(19), 2.470(13), and 2.712(12) Å; internal angles 54.5(4), 57.6(4), and 68.0(4)°].

Experimental Section

Reactions were performed in Schlenk tubes under an argon atmosphere, and the crystalline products were transferred to an argon-filled glovebox for storage and subsequent characterization. Pure shield argon was purchased from BOC Gases. Solvents were distilled over sodium/benzophenone until blue and directly placed over fresh 4A molecular sieves. Benzonitrile was dried over $CaSO_4$ and distilled from P_2O_5. The amine was distilled from CaH_2. In general (see Results and Discussion), the above liquids were degassed three times before employed in reactions. Metal alkyl solutions were obtained commercially from Aldrich. *n*-BuLi was restandardized prior to use by titration with diphenylacetic acid.[52] Bu_2Mg was restandardized prior to use by titration with *sec*-butanol in xylene using 1,10-phenanthroline as indicator.[53] NMR spectral data were recorded on a Bruker AMX 400 spectrometer operating at 400.13 MHz for ^1H, 100.61 MHz for ^{13}C, and 155.50 MHz for ^7Li. ^1H and ^{13}C chemical shifts are given relative to external $SiMe_4$; ^7Li chemical shifts are given relative to external LiC1 in D_2O. All spectra were recorded at ambient temperature. C, H, and N analysis was performed by use of a Perkin-Elmer 2400 elemental analyzer, and metal analysis was carried out by atomic absorption spectroscopy using a PU 9100 Philips spectrometer.

Preparation of $[\{(Me_3Si)_2N\}_3LiMg]$ (1). The magnesium bis(amide) precursor was prepared beforehand by reacting Bu_2Mg (5 mmol in heptane) with bis(trimethylsilyl)amine (10 mmol) and heating the mixture to reflux for 4 h. On cooling to ambient temperature, large colorless crystals of $[\{(Me_3Si)_2N\}_2Mg]$ were formed. These were washed with hexane, isolated by vacuum filtration, and set aside for later use. The lithium amide precursor was prepared in situ by treating the chilled amine (10 mmol) with *n*-BuLi (10 mmol) in hexane. In another Schlenk tube, the pure crystalline magnesium bis(amide) (5 mmol) was dissolved in toluene (10 mL), and the solution was transferred via cannula to the lithium amide solution. The mixture was stirred for 1 h at ambient temperature and then placed in a freezer (at ca. −30 °C). After 24 h, a modest crop of colorless crystals of **1** were obtained. Typical yield isolated: 8−10% [based on consumption of magnesium bis(amide)]. Mp 120 °C dec. ^1H NMR ($C_6D_5CD_3$): δ 0.21 (s, 2H, b $SiMe_3$), 0.28 (s, 1H, t $SiMe_3$). (C_5D_5N): 0.60 (s, $SiMe_3$). ^{13}C NMR (C_5D_5N): δ 7.66 ($^{13}C-^{29}Si$, ^1J 52 Hz). ^7Li NMR (C_5D_5N): δ 3.20 (s). Anal. Calcd for $C_{18}H_{54}N_3LiMgSi_6$: C, 42.2; H, 10.6; N, 8.2; Li, 1.4; Mg, 4.7; Si, 32.9. Found: C, 40.6; H, 9.3; N, 7.4; Li, 1.3; Mg, 4.0.

Preparation of $[\{(Me_3Si)_2N\}_4Li_2Mg_2(O_2)_x(O)_y]$ (2). Equimolar amounts (10 mmol:10 mmol) of the two metal alkyl solutions (in hexane/heptane) were mixed in a Schlenk tube and chilled. Bis(trimethylsilyl) amine (30 mmol) was then added, and a vigorous reaction ensued. The reaction mixture was stirred for 1 h and then placed in a refrigerator at 5 °C. Small colorless crystals of **2** formed overnight. Typical yield: 1−5% (based on consumption of *n*-BuLi). Mp 203−205 °C. ^1H NMR ($C_6D_5CD_3$): δ 0.08 (s, trace impurity of amine), 0.27 (s, 1H, $SiMe_3$ in oxide structure), 0.29 (s, ca. 2.5H, $SiMe_3$ in peroxide structure). ^{13}C NMR ($C_6D_5CD_3$): δ 6.10 ($SiMe_3$ in oxide structure), 6.20 ($SiMe_3$ in peroxide structure). ^7Li NMR (C_5D_5N): δ 2.97 (s). Anal. Calcd for $C_{24}H_{72}N_4O_{1.4}Li_2Mg_2Si_8$: C, 39.5; H, 9.9; N, 7.7; O, 3.7; Li, 1.9; Mg, 6.6; Si, 30.7. Found: C, 38.8; H, 9.7; N, 7.3; Li, 1.9; Mg, 6.9.

Preparation of $[\{PhC(NSiMe_3)_2\}_4Li_4MgO]$ (3). A solution containing *n*-BuLi, Bu_2Mg, and the amine (10 mmol:10 mmol:30 mmol)

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in hexane/heptane was prepared as in the synthesis of **2**. Benzonitrile (30 mmol) was slowly introduced into this chilled solution, resulting in a vigorous reaction which produced a pale orange solution. Colorless needle crystals of **3** were obtained on standing the solution at ambient temperature for several days. Typical yield: 10−13% (based on consumption of magnesium alkyl). Mp 178 °C dec. ^{1}H NMR (C_6D_5-CD_3): δ 0.12/0.13/0.15/0.17/0.20 (overlapping s, ca. 18H, $SiMe_3$), 7.03−7.13 (m, 3H, Ph), 7.34−7.42 (d + overlapping m, 2H, Ph). ^{13}C NMR (C_5D_5N): δ 3.63 ($SiMe_3$), 126.40 (*p*-Ph), 126.64 (*o*-Ph), 128.20 (*m*-Ph), 149.32 (*ipso*-Ph), 178.40 (NCN). ^{7}Li NMR (C_5D_5N): δ 3.41. Anal. Calcd for $C_{52}H_{92}N_8OLi_4MgSi_8$: C, 55.7; H, 8.26; N, 10.0; O, 1.4; Li, 2.5; Mg, 2.1, Si, 20.0. Found: C, 54.5; H, 8.27; N, 11.0; Li, 2.4; Mg, 2.0.

Crystallography. Crystal samples were mounted using oil-drop techniques. Crystal data and refinement parameters are given in Table 4, and selected geometric parameters are given in Tables 1−3.

Data Collection and Processing. Measurements were made at 123 K with Mo Kα radiation (λ = 0.710 69 Å) on a Rigaku AFC7S diffractometer fitted with a graphite monochromator. Intensities, *I*, were estimated from $\omega/2\theta$ scans for **1** and **2** and ω scans for **3**. Corrections were applied for Lorentz and polarization parameters, and equivalent intensities were then averaged.

Structure Analysis and Refinement. All structures were solved by direct methods[54] and the examination of subsequent difference synthesis. All non-hydrogen atoms, except those in the minor disordered conformations, were refined anisotropically. For **1** those H-atoms that approached the metal centers (those on C1, C7, and C11) were refined isotropically, and all others were placed in calculated positions in a riding mode. For **2** and **3** all H-atoms were placed in calculated positions using a riding mode. An occupancy parameter was refined for the peroxide/oxide disorder of **2**. After trial calculations the occupancy of each metal site was set at 50% Mg and 50% Li on the grounds of chemical sense. The Li_4MgO core of **3** is disordered by a rotation about the Li1O1Lil* axis. An occupancy parameter was refined as were *x*, *y*, and *z* of the minor positions. The temperature factors were, however, constrained such that $U_{iso}(Mg2) = 1.2U_{eq}(Mg1)$ and $U_{iso}(Li3) = 1.2U_{eq}(Li2)$ [occupancy 0.834(5):0.166(5)]. All methyl group orientations of all three structures were based upon the refinement of a rotational parameter about the Si−Me bonds. Final full-matrix, least-squares refinements[55] were on F^2 and converged to give a maximum shift/esd ratio of 0.001. All calculations were performed on a Silicon Graphics Indy R4600.

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Supporting Information Available: Full crystallographic details including atomic coordinates, thermal parameters, bond lengths and angles, and atomic displacement parameters for compounds **1**−**3** (12 pages, print/PDF or CIF). See any current masthead page for ordering information and Web access instructions.

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