DALTON
FULL PAPER

Structural chemistry of monodentate donor-solvated mixed lithium–magnesium secondary amide complexes

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Received 2nd January 2001, Accepted 20th March 2001
First published as an Advance Article on the web 10th April 2001

The monodentate donor-solvated intermetallic lithium–magnesium amide complexes [$Mg(HMDS)_3Li\cdot(THF)$] **1** [HMDS = $N(SiMe_3)_2$], [$Mg(HMDS)_3Li\cdot(Pyr)$] **2** and [$Mg\{N(Cy)_2\}_3Li\cdot(THF)$] **3** [$N(Cy)_2$ = dicyclohexylamide] have been prepared and characterised by NMR spectroscopy and X-ray crystallography. Synthesis was achieved by the reaction of equimolar amounts of *n*-BuLi and *n*,*sec*-Bu_2Mg with three equivalents of the appropriate amine in hexane/donor solution. The molecular structures of **1**, **2** and **3** are essentially isostructural containing a central, planar LiNMgN four-membered ring: two amide units bridge to the metal centres whilst the third binds exclusively to magnesium in the terminal position to complete a three-coordinate distorted trigonal planar geometry. The lithium achieves a similar geometry with solvation from a single monodentate donor molecule. Three co-crystalline by-products were also isolated from solution and are included for completeness: [$Mg(HMDS)_2(Bu)Li\cdot Pyr$] **4**, [$(LiHMDS\cdot Pyr)_2$] **5** and [$Mg(HMDS)_2\cdot(Pyr)_2$] **6**. Complex **4** exhibits a similar structure to **1**, **2** and **3** with an alkyl group (consisting of disordered *n*- and *sec*-butyl groups) replacing the terminal amido functionality. Complex **4** is produced by a similar method to **2** *via* incomplete amination in the presence of two equivalents of hexamethyldisilazane (HMDS(H)). In contrast, **5** and **6** are simple homometallic amides formed when an excess of pyridine is introduced into the reaction system. To conclude the study a series of reactions were undertaken in which the stoichiometry of both amine and donor was altered systematically. The results from this study imply that intermetallic aggregation is hindered by the presence of excess donor solvent.

Introduction

In 1978 lithium hexamethyldisilazide became the first lithium amide to be characterised crystallographically.[1] Since then a large number of synthetically useful secondary amides of lithium have been prepared.[2] Due to their relatively low nucleophilicity and strong Brønsted basicity lithium amides have become invaluable tools for the synthetic chemist, second only in popularity to simple alkyllithium compounds. They have found use as deprotonating reagents in modern synthetic chemistry and also as transmetallating agents for the production of transition metal amides.[3]

By comparison the field of magnesium amide chemistry has received far less attention with only limited synthetic and structural data available.[4] This oversight has only recently begun to be corrected with particular attention focussing on the use of compounds such as $Mg(HMDS)_2$[5] in the fields of aldehyde/ketone reduction,[4a,b] and magnesium bis-(*R*)-*N*-benzyl-α-methylbenzylamide[4c] in asymmetric synthesis. Magnesium amides can exhibit different selectivities to that of their lithium counterparts and can be utilised under somewhat harsher conditions due to their greater thermal stability.

Given the number of synthetic applications to which lithium and magnesium amides can be applied, it is perhaps surprising that only a small number of amide complexes containing both metals have been prepared. Since the report of [$Mg\{PhCH_2(Me_2NCH_2CH_2)\}_4Li_2$] in 1993[6] only seven such complexes have been crystallographically characterised (although others have been prepared and patented for their potential application as initiators in anionic polymerisation[7]). These include some simple structures such as [$Mg(NBz_2)_4Li_2$] and the two simple tris-amides [$Mg(NBz_2)_3Li\cdot Pyr$][8] and $Mg(HMDS)_3Li$.[9] More complicated structures have also been prepared such as the inverse crown ethers [$Mg_2(HMDS)_4Li_2\cdot(O_2)_x(O)_y$][9] and [$Mg_2(TMP)_4Li_2\cdot(O)$][10] (TMP = 2,2,6,6-tetramethylpiperidide) and the dimeric mixed-metal, mixed-amide complex [$Mg\{(CH_2SiMe_2)NSiMe_3\}Li(TMP)]_2$.[11] Most recently Gade *et al.* have produced the latest addition to the series [1,8-$C_{10}H_6(NSiMe_3)_2Li\cdot(THF)MgBr\cdot(THF)$].[12] A number of amide complexes containing a different combination of metal types have also been reported including [$Ca(HMDS)_3Li\cdot(THF)$],[13] [$Na(HMDS)_3Y$],[14] and [$Mn(HMDS)_3Li\cdot(THF)$].[15] The remaining members of the inverse crown family which include [$Mg_2(HMDS)_4Na_2(O_2)_x(O)_y$],[10] [$Mg_2(TMP)_6Na_4\{C_6H_3(CH_3)\}$],[16] [$\{Mg_2(HMDS)_4K_2(O_2)\}_\infty$],[17] [$Mg_6(TMP)_{12}K_6(C_6H_5)_6$],[18] [$Zn_2(HMDS)_4Na_2(O)$][19] and [$\{Zn_2(HMDS)_4K_2(O_2)_x(O)_y\}_\infty$][19] should also be considered. Although data from certain non-amide complexes show that there is great synthetic potential to be found in mixed lithium–magnesium complexes (*e.g.* in the fields of Ziegler alkylation[20] and halide transfer reactions[21]) the potential synergic effects of coupling magnesium with more reactive lithium in an amide complex have yet to be explored in any depth. This is partly due to the fact that $Mg(HMDS)_3Li$, the compound which is of most interest synthetically due to its close relationship to the homometallic reagents LiHMDS and $Mg(HMDS)_2$ is not easy to prepare in good yields. This complex is of additional interest as it is also suspected to be the precursor for the aforementioned inverse crown ether [$Mg_2(HMDS)_4Li_2\cdot(O_2)_x(O)_y$].[9]

In this work we set out to produce a donor-solvated equivalent of $Mg(HMDS)_3Li$ in good yield with a view to producing a viable synthetic reagent containing both metals. A series of reactions were carried out using THF and pyridine with the aim of producing dative O–Li and N–Li bonds respectively that would replace the agostic bonding between the lithium centre and the methyl groups of the bridging HMDS groups found in

DOI: 10.1039/b100052g

$LiMg(HMDS)_3$. Two new donor-solvated mixed-metal tris-amide structures and a number of side products are described along with a suggested reaction equilibrium. Interestingly it is found through ^1H NMR spectroscopic studies and X-ray analysis that the concentration of donor present during the preparation has a profound effect on the intermetallic aggregation of the products formed. Also included is a hitherto unreported lithium–magnesium tris-dicyclohexylamide structure that is related structurally to the HMDS systems.

Results and discussion

Syntheses

Four new intermetallic lithium–magnesium amide complexes have been produced over the course of this study: the tris-amides $[Mg(HMDS)_3Li\cdot(THF)]$ **1**, $[Mg(HMDS)_3Li\cdot(Pyr)]$ **2** and $[Mg\{N(Cy)_2\}_3Li\cdot(THF)]$ **3**, and the alkyl-amido $[Mg(HMDS)_2(Bu)Li\cdot Pyr]$ **4**. In addition two pyridine-solvated homometallic amides $[(LiHMDS\cdot Pyr)_2]$ **5** and $[Mg(HMDS)_2\cdot(Pyr)_2]$ **6** were also produced as co-crystalline by-products. Subsequently **5** and **6** were both re-prepared individually by more rational methods. The ^1H NMR and X-ray crystallographic study of the products coupled with the low yields obtained for **2** and **4** suggested that in each reaction mixture a complex equilibrium is involved. This equilibrium will be discussed in conjunction with the NMR spectroscopic data obtained. A series of reactions were subsequently carried out using varying stoichiometries of both pyridine and HMDS(H) to examine the equilibrium properties of the system. This study showed that in the presence of excess donor solvent, intermetallic products were less likely to form. The main products in these cases were found to be mixtures of **5** and **6** whereas when less donor was present **2** and **4** were able to form albeit in poor yields. Complexes **1–3** were synthesised using the same methodology and so will be discussed together. In each case an equimolar mixture of *n*-BuLi and *n*,*sec*-Bu_2Mg (commercially available dibutylmagnesium or DBM contains a mixture of *n*- and *sec*-butyl groups) was prepared using commercially available reagents. The mixture was then chilled to 0 °C. To this chilled solution was added three equivalents of the appropriate secondary amine resulting in an exothermic reaction with the evolution of butane gas and the formation of a colourless solution. Upon addition of one equivalent of donor solvent a white precipitate formed which re-dissolved upon gentle heating. The solutions were then placed in a refrigerator at 0 °C, whereby crystallisation occurred over a period of 24 hours (see eqn. 1). Yields for **1** were reasonable (64%) whereas **2–4** were produced in more modest yields of 30% and under.

$$n\text{-BuLi} \cdot n,sec\text{-}Bu_2Mg + 3R_2NH \cdot Donor \rightarrow Donor{-}Li(NR_2)_2Mg{-}NR_2 - 3BuH \quad (1)$$

Carrying out the reaction using one equivalent of pyridine with two equivalents of HMDS(H) resulted in incomplete amination to form compound **4**, which contains a butyl chain bound to magnesium. This is not an unexpected result due to the reaction stoichiometry being such that there are three equivalents of butyl groups for only two equivalents of available N–H atoms from HMDS(H). Compound **4** is poorly resolved by X-ray crystallography due to disorder of the butyl functionality. This disorder is caused by the presence of both *n*- and *sec*-butyl groups (arising from the dibutylmagnesium used).

Molecular structures

Compounds **1–3** are isostructural intermetallic amides (Figs. 1–3) and thus will be considered together. The structure of **4** (Fig. 4) will also be discussed briefly in this initial section as it exhibits the same basic structural motif. In each case the molecular structures of **1–3** are dinuclear with a lithium : magnesium ratio of 1 : 1. The lithium centres occupy a three-coordinate distorted trigonal planar geometry bound to two

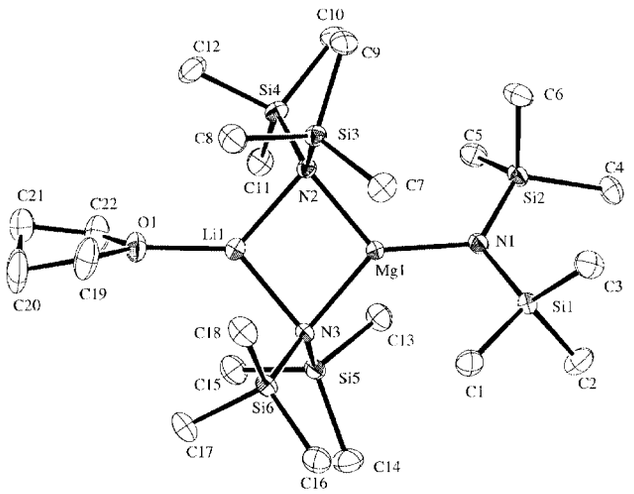


Fig. 1 Molecular structure of **1** showing the principle atom labels. Hydrogen atoms are omitted for clarity.

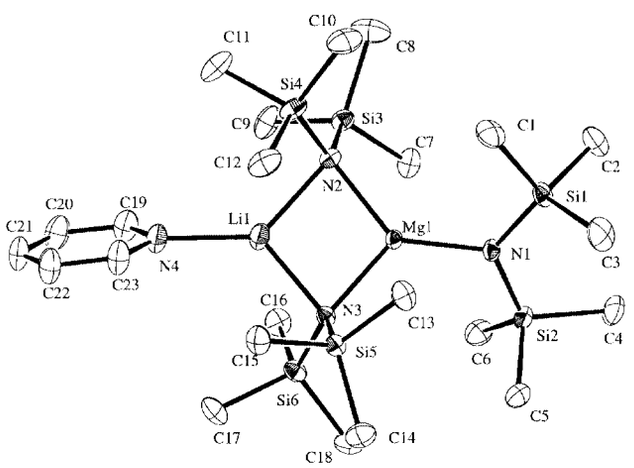


Fig. 2 Molecular structure of **2** showing the principle atom labels. Hydrogen atoms are omitted for clarity.

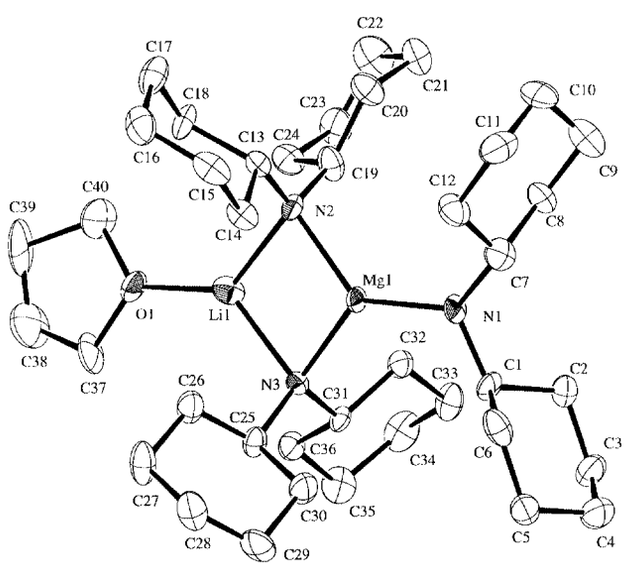


Fig. 3 Molecular structure of **3** showing the principle atom labels. Hydrogen atoms are omitted for clarity.

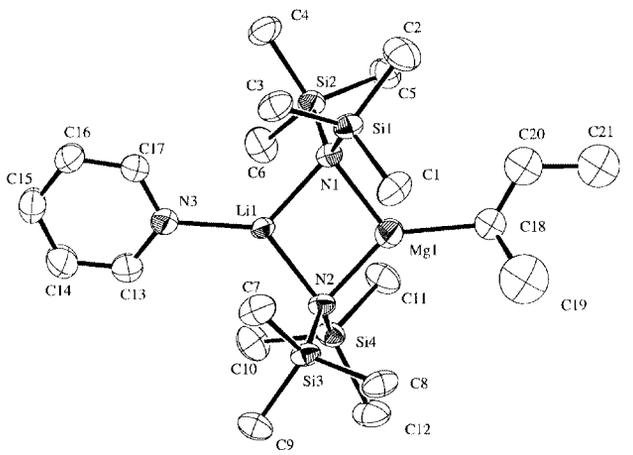


Fig. 4 Molecular structure of **4** (with *sec*-butyl group on Mg) showing the principle atom labels. Hydrogen atoms and disorder components are omitted for clarity.

bridging secondary amido units (HMDS in **1** and **2** and Cy_2N in **3**) and a terminal monodentate donor solvent molecule (either THF in **1** and **3** or pyridine in **2**). The magnesium centres also occupy a three-coordinate, distorted trigonal planar environment made up exclusively of secondary amide ligands, two bridging and one terminal. The three complexes are based around an approximately planar four-membered LiNMgN ring system (rms deviations from planarity are 0.0313, 0.0411 and 0.0221 Å respectively). Having mean values of 2.109, 2.124 and 2.082 Å for **1–3** respectively, the Li–N bond lengths are slightly longer than those of the simple all-lithium trimer lithium hexamethyldisilazide[1] (2.00 Å) and of the unsolvated lithium–magnesium hexamethyldisilazide analogue (2.019 Å).[9] The associated endocyclic N–Li–N bond angles are also markedly narrower with **1–3** exhibiting angles of 99.3(2), 98.8(1) and 98.3(4)° compared to 147° for lithium hexamethyldisilazide and 102.8° for the unsolvated Li–Mg analogue. These geometric changes are a direct result of the introduction of donor solvent molecules and the stabilising effect that this extra source of electron density has on the lithium centre. This effect can be confirmed by comparison with the geometric parameters of the dimeric THF[22,23] and diethyl ether[24] complexes of lithium hexamethyldisilazide. In these compounds the Li–N bond lengths have also been slightly extended from 2.00 to 2.025 and 2.055 Å respectively upon the addition of a donor solvent molecule. The N–Li–N bond angles of these solvates are also narrower at 106.3 and 104.9° respectively just as in **1–3**. The effect is slightly less pronounced in the case of **3** probably because dicyclohexylamido groups are much less sterically demanding than hexamethyldisilazide. The mean Mg–μ-N bond lengths are 2.095, 2.092 and 2.054 Å for **1–3** respectively. Predictably the terminal Mg–N distances are shorter at 2.004(3), 2.001(1) and 1.956(4) Å respectively. These values correspond well to those found in unsolvated $LiMg(HMDS)_3$ which are 2.114 and 1.998 Å (bridging and terminal respectively). The slight reduction in bond distances found between **3** and the others can once again be attributed to the lesser bulk of the dicyclohexylamide ligand. Similar endocyclic N–Mg–N bond angles are found for **1–3** of 100.2(1), 100.91(5) and 100.1(2)° respectively. The corresponding angle in $LiMg(HMDS)_3$[9] is smaller at 96.54°. Selected bond lengths and angles for **1–3** are collected in Tables 1–3 respectively. The presence of monodentate donor solvent molecules prevents the formation of the agostic-type interactions that are found between the lithium centre and adjacent methyl groups in $LiMg(HMDS)_3$. The effect of donor solvation is shown in eqn. 2.

In each case a dative bond is formed between the lithium centre and a monodentate donor molecule to give the aforementioned distorted trigonal planar geometry. This new, three-

Table 1 Selected geometric parameters (Å, °) for **1**

Li1–N3	2.120(6)	Mg1–N2	2.089(3)
Li1–N2	2.097(6)	Mg1–N3	2.101(3)
Li1–O1	1.932(6)	Mg1–N1	2.004(3)
N3–Mg1–N2	100.2(1)	N1–Mg1–N3	132.8(1)
N2–Mg1–N1	126.8(1)	N3–Li1–N2	99.3(2)
Mg1–N3–Li1	79.8(2)	Mg1–N2–Li1	80.5(2)
N3–Li1–O1	129.3(3)	N2–Li1–O1	131.2(3)

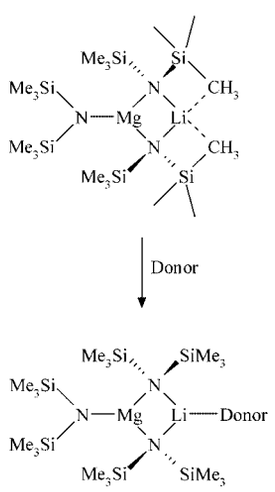
Table 2 Selected geometric parameters (Å, °) for **2**

Li1–N2	2.115(3)	Mg1–N1	2.001(1)
Li1–N3	2.132(3)	Mg1–N2	2.093(1)
Li1–N4	2.083(3)	Mg1–N3	2.090(1)
N2–Li1–N3	98.8(1)	N3–Li1–N4	129.3(2)
N2–Li1–N4	131.7(1)	N1–Mg1–N2	131.94(6)
N1–Mg1–N3	126.27(6)	N2–Mg1–N3	100.91(5)
Li1–N2–Mg1	80.12(9)	Li1–N3–Mg1	79.80(9)

Table 3 Selected geometric parameters (Å, °) for **3**

Li1–N3	2.079(12)	Mg1–N2	2.041(5)
Li1–N2	2.085(11)	Mg1–N1	1.956(4)
Li1–O1	1.945(10)	Mg1–N3	2.067(5)
N1–Mg1–N2	131.7(3)	N1–Mg1–N3	127.5(2)
N2–Mg1–N3	100.11(18)	N2–Li1–N3	98.3(4)
Mg1–N2–Li1	81.0(3)	Mg1–N3–Li1	80.5(3)
N2–Li1–O1	132.5(7)	N3–Li1–O1	129.2(6)

(2)



coordinate geometry stabilises the lithium centre electronically (and at the same time introduces additional steric bulk) thus removing the need to form agostic bonds. The results of solvation are illustrated by comparison of the average closest contact Li ··· C distances, 2.307 Å for $Mg(HMDS)_3Li$ compared with 2.981 and 2.877 Å for **1** and **2** respectively. The Li ··· C distances found in **1** and **2** are beyond the accepted threshold of conventional agostic bonding thus providing good evidence that the Li-donor bonding present in **1** and **2** removes the need for such Li ··· C interactions. Complex **4** is structurally similar to **1–3** and so will only be discussed briefly. Due to the disordered nature of the X-ray structure only a limited discussion of the structure can be included. Structurally **4** is almost identical to **2**, the only difference is that a butyl group (disordered in the X-ray structure) has replaced the terminal hexamethyldisilazide group. Once again the amide Li–N bond distances are longer than those of the unsolvated analogue with a mean length of 2.067 Å. The endocyclic N–Li–N bond angle is also reduced to 100.4(2)° in much the same way as for **1–3**. The mean Mg–μ-N bond distance is 2.076 Å with an endocyclic N–Mg–N bond angle of 99.87(11)°.

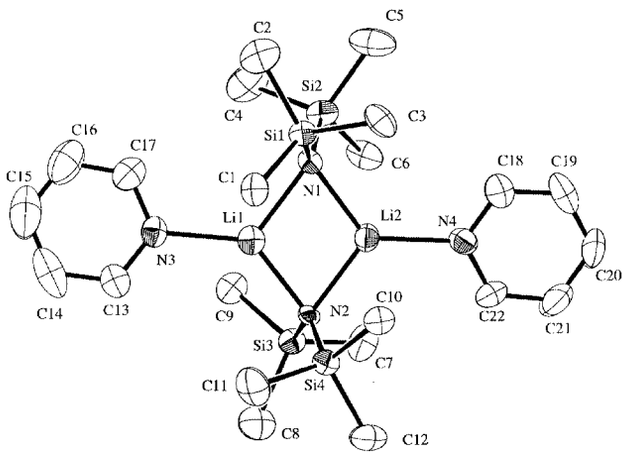


Fig. 5 Molecular structure of **5** showing the principle atom labels. Hydrogen atoms are omitted for clarity.

Table 4 Selected geometric parameters (Å, °) for **4**

Li1–N1	2.066(5)	Mg1–N1	2.090(3)
Li1–N2	2.068(5)	Mg1–N2	2.061(3)
Li1–N3	2.065(5)	Mg1–C18	2.132(9)
N1–Li1–N3	128.9(2)	N2–Li1–N3	130.4(3)
N1–Li1–N2	100.4(2)	N1–Mg1–C18	123.1(3)
N2–Mg1–C18	136.7(3)	N1–Mg1–N2	99.87(11)
Li1–N1–Mg1	80.15(16)	Li1–N2–Mg1	79.52(15)

During this study two homometallic secondary amides **5** and **6** were also prepared and characterised. The lithium complex **5** (Fig. 5) is a simple dimeric lithium secondary amide. The structure consists of a central planar $(LiN)_2$ ring where each lithium adopts a three-coordinate distorted trigonal planar environment (exocyclic N–Li–N angles range from 121.9(6)–132.5(6)° with endocyclic angles of 105.7(5) and 106.7(5)°). Each lithium centre is bound to two bridging hexamethyldisilazide groups and one pyridine molecule in the terminal position. The structure is therefore essentially identical to the aforementioned THF and diethyl ether solvates. The three rings in the complex (two pyridine rings and the central $(LiN)_2$ ring) almost share the same plane with N–Li–N–C (C = pyridine α carbon atom) torsion angles of 6.3(9), 175.2(7), −170.6(6), −168.5(7), −174.3(6), 2.0(10), 8.0(10) and 4.6(10)°. The mean Li–μ-N bond distance is 2.04 Å and the mean Li–terminal N bond distance is 2.06 Å. The values for the bridging bonds correspond well to those found in unsolvated lithium hexamethyldisilazide. The terminal Li–N bond distances are of comparable size to the bridging bonds. This is unsurprising given the dative nature of the bonding between the lithium centre and pyridine nitrogen. The final complex to be isolated, **6**, is a simple monomeric magnesium amide (Fig. 6). The magnesium centre exhibits a stable four-coordinate geometry and is bound to two hexamethyldisilazide groups and solvated by two molecules of pyridine to give a distorted tetrahedral arrangement. The structure is almost identical to the THF-solvated variety reported by Bradley *et al.*[25] and the 2-picoline/2,3,5-collidine analogues reported by Winter *et al.*[26] The N–Mg bond distances are unremarkable with mean values of 2.029 Å for the hexamethyldisilazide groups and 2.205 Å for the metal-donor bonds compared with 2.0467 and 2.259 Å in the aforementioned 2-picoline solvated analogue. Once again it can be seen that long dative bonds are formed between the metal centre and the solvating pyridine groups. Selected bond lengths and angles for **4–6** are collected in Tables 4–6 respectively. The crystallographic data for **1–6** are provided in Table 7.

NMR spectroscopic studies

Each of the new complexes **1–6** has also been characterised by

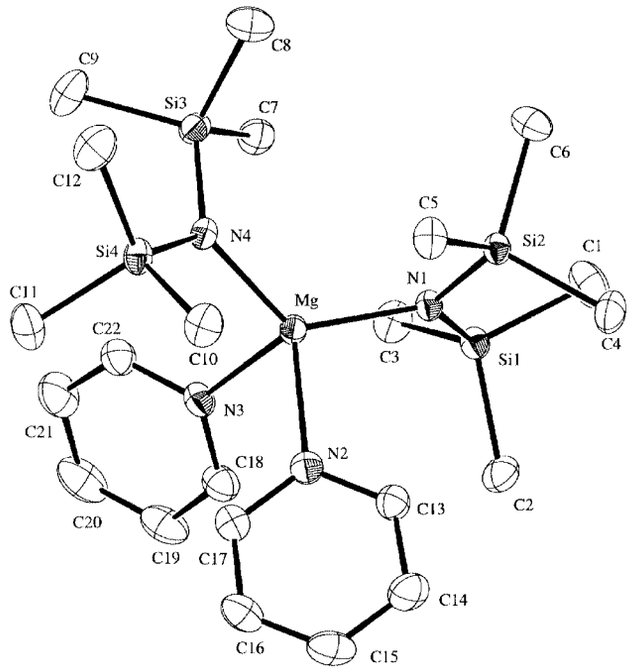


Fig. 6 Molecular structure of **6** showing the principle atom labels. Hydrogen atoms are omitted for clarity.

Table 5 Selected geometric parameters (Å, °) for **5**

Li1–N1	2.06(1)	Li1–N2	2.04(1)
Li1–N3	2.07(1)	Li2–N1	2.02(1)
Li2–N2	2.05(1)	Li2–N4	2.05(1)
Li1–N1–Li2	73.8(5)	Li1–N2–Li2	73.8(5)
N1–Li1–N3	121.9(6)	N2–Li1–N3	132.5(6)
N1–Li2–N4	129.3(6)	N2–Li2–N4	124.0(6)
N1–Li1–N2	105.7(5)	N1–Li2–N2	106.7(5)

Table 6 Selected geometric parameters (Å, °) for **6**

Mg1–N1	2.031(1)	Mg1–N2	2.190(2)
Mg1–N3	2.219(1)	Mg1–N4	2.026(1)
N1–Mg1–N2	100.74(5)	N1–Mg1–N3	116.75(5)
N1–Mg1–N4	126.75(6)	N2–Mg1–N3	87.84(5)
N2–Mg1–N4	117.42(6)	N3–Mg1–N4	101.21(5)

^{1}H and ^{13}C NMR spectroscopic studies in d_6 benzene solution. In the cases of **1**, **3**, **5** and **6** the spectra recorded at room temperature are consistent with the empirical formulae of the compounds as determined by X-ray crystallography. However in the cases of **2** and **4** the ^{1}H NMR spectra revealed that a mixture of products had co-crystallised. As a result of this it was decided to embark upon a systematic study of the products formed by varying the concentration of pyridine used during the reaction. Although **4**, **5** and **6** were prepared by the rational methods reported, it was during this study that they were first observed. By examining the integration ratios belonging to the peaks in the ^{1}H NMR spectra it was possible to investigate how the ratios of products changed with the concentration of pyridine. The spectra belonging to **1**, **3**, **5** and **6** will be discussed first due to their relative simplicity. In the case of **1** the spectrum recorded in d_6 benzene shows only four signals. Two signals are observed at 3.57 and 1.19 ppm for the solvating THF group and two signals at 0.34 and 0.32ppm in a 2 : 1 ratio for the two distinct types of HMDS groups (bridging and terminal). The integrals of 4 : 4 : 36 : 18 tally exactly with the empirical formula of **1**. The spectra recorded in d_6 benzene for **5** and **6** are both very similar. In each case three pyridine signals are observed in the region of 9–6.5 ppm in a ratio of 2 : 1 : 2 with a singlet integrating to 18H representing HMDS at 0.44 and 0.41

Table 7 Crystallographic data

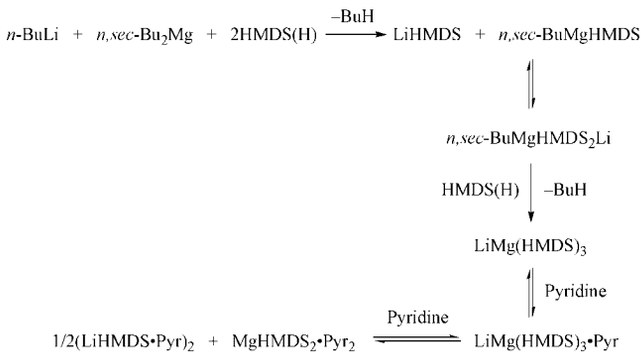
Compound	**1**	**2**	**3**[a]	**4**[a]	**5**	**6**
Formula	$C_{22}H_{62}LiN_3OSi_6Mg$	$C_{23}H_{59}MgLiN_4Si_6$	$C_{40}H_{47}LiMgN_3O$	$C_{21}H_{50}LiMgN_3Si_4$	$C_{22}H_{46}N_4Si_4Li_{24}$	$C_{22}H_{46}MgN_4Si_4$
M	584.51	591.50	644.27	488.25	985.71	503.28
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}1$	Cc	$P2_1/n$	$P\bar{1}1$	$P2_1/c$
a/Å	11.681(2)	11.509(3)	11.014(4)	8.754(2)	10.429(2)	13.000(2)
b/Å	19.297(3)	11.967(3)	18.998(6)	19.804(4)	16.806(5)	11.784(2)
c/Å	17.052(2)	15.833(3)	19.317(4)	17.956(4)	20.411(6)	20.239(4)
α/°	—	105.56(2)	—	—	108.98(2)	—
β/°	108.79(1)	90.11(2)	99.70(5)	94.685(19)	98.27(2)	90.49(2)
γ/°	—	117.47(2)	—	—	103.58(2)	—
V/Å^3	3638.6(8)	1843.6(8)	3984(2)	3102.5(12)	3192(1)	3100.2(10)
Z	4	2	4	4	4	4
D_c/g cm^{-3}	1.067	1.056	1.074	1.045	1.025	1.08
μ/mm^{-1}	0.26	0.255	0.077	0.224	0.201	0.228
Reflections measured	6944	8865	7277	6504	9236	7412
Unique reflections	6605	8447	3704	6096	8877	7106
Reflections used	3865	7303	3704	6069	6773	5165
R_{int}	0.050	0.017	0.0695	0.0227	0.039	0.035
No. of refined parameters	369	316	415	286	577	465
ωR	0.036	0.035	0.2023	0.1847	0.085	0.029
R	0.041	0.053	0.0686	0.0590	0.099	0.038
Max., min. e$^-$ density/e Å^{-3}	0.32, −0.25	0.52, −0.46	0.456, −0.338	1.121, −0.706	0.56, −0.67	0.27, −0.19

[a] For **3** and **4** wR is based on all reflections and on F^2, for all other structures wR is based on those reflections with $I > 2\sigma(I)$ and on F.

Table 8 Results of systematically altering the stoichiometries of HMDS(H) and pyridine in reaction of *n*-BuLi + DBM + HMDS(H) + pyridine

Equivalents of HMDS(H)	Equivalents of pyridine	Isolated products
1	1	**2** and **4**
2	1	**2** and **4**
3	1	**2** and **4**
4	1	**2** and **4**
1	2	**5** and **6**
2	2	**5** and **6**
3	2	**5** and **6**
4	2	**5** and **6**
1	4	**5** and **6**
2	4	**5** and **6**
3	4	**5** and **6**
4	4	**5** and **6**

ppm respectively for **5** and **6**. These correspond well to the empirical formulae of the two complexes and prove that in both **5** and **6** there is only one type of pyridine and HMDS environment. The overall integrals found in the ^{1}H NMR spectrum of **3** are also entirely consistent with the empirical formula. Once again two signals integrating to four hydrogen atoms each are observed at 3.83 and 2.52 ppm which correspond to the solvating THF group. Although the rest of the spectrum is quite complex the collection of signals found in the region 1.90–0.99 ppm integrate to approximately the correct value for four cyclohexyl groups. The presence of these groups was confirmed by X-ray crystallography. The assignment of ^{1}H NMR signals for **2** and **4** was made more difficult because a mixture of both products was obtained each time either was prepared. The pyridine signals for both **2** and **4** were found to overlap in the region from 8.59 to 6.55 ppm and exhibited the usual 2 : 1 : 2 signal ratios. A large number of signals with variable splittings were observed in the region from 2.11–0.83 ppm and these signals were assigned to the *n*- and *sec*-butyl groups found within the crystal lattice in **4**. Due to the overlapping of these peaks only one signal could be assigned with any degree of certainty. This was the unique doublet corresponding to the C*H*$_3$CH- group of the *sec*-butyl group at 1.21 ppm. The two equivalent HMDS groups of **4** were assigned to the singlet at 0.38 ppm by comparison of the integrals of the combined butyl peaks and each of the other singlets. It was this signal that was found to give the correct approximate ratio of 1 : 4. The remaining two signals exhibited an integral ratio of 2 : 1 and so were attributed to the bridging and terminal groups of **2** respectively. Complexes **2** and **4** cannot with any degree of certainty be distinguished by their ^{7}Li NMR spectra with **2** appearing at a slightly higher frequency (2.33 ppm compared to 2.28 ppm for **4**). It is unlikely that such a small difference could be reproducibly measured. The assignments were supported by the X-ray crystallographic data. During a reaction to re-prepare **2** as the sole product of the reaction the amount of pyridine was increased to two equivalents in order to alter the solubility properties of the reaction mixture. As a result it was found that rather than forming **2** or **4** a mixture of **5** and **6** was formed with these complexes being the only isolable products. After a number of repetitions of this reaction under various conditions it was postulated that increasing the concentration of donor solvent above one equivalent was responsible for retarding the formation of the desired intermetallic products. Donor solvents are well known to influence (usually reduce) the state of aggregation in lithium amide chemistry[27] and so it seems logical that the same properties can be extended to intermetallic amide systems. In order to test this idea a series of control reactions were carried out in which the concentration of both HMDS(H) (as a control) and pyridine was altered relative to the concentration of *n*-BuLi and Bu_2Mg and to each other. In each case a solid product was obtained from the reaction and examined by X-ray crystallography and ^{1}H NMR spectroscopy. The results are summarised in Table 8. It was found that as the number of equivalents of pyridine was raised from one to two the products obtained changed from small quantities of intermetallic **2** and **4** (isolated yields were generally less than 10%) to homometallic **5** and **6**. The same observations were made upon increasing the amount of pyridine to three, four and six equivalents. These results indicate that this reaction system almost certainly exists as a complex equilibrium in solution, along the lines of that shown in Scheme 1.



Scheme 1

Increasing the amount of donor solvent present in the system serves to push the equilibrium towards forming larger quantities of the pyridine solvated homometallic amides **5** and **6** rather than their intermetallic cousins **2** and **4**. This is understandable as the breakdown of the intermetallic **2** to its homometallic precursors **5** and **6** involves a change of 1 mole of pyridine to three moles. Increasing the amount of HMDS(H) present in the reaction mixture resulted in a reduction in the amount of solid product produced (from around 10% to 5% or less) at low pyridine concentrations (1 equivalent). This can be attributed to the change in the solubility properties of the reaction solution upon the addition of excess amine. At higher concentrations of pyridine increasing the amount of amine present led to an increase in the amount of crystalline material produced (although with two or more equivalents of pyridine present in the reaction mixture **5** and **6** were the only products formed). Yields of 50% and above were noted for the formation of **5** and **6** in the presence of four equivalents each of HMDS(H) and pyridine compared with around 10% for a 1 : 2 ratio of HMDS(H) to pyridine. This increased yield can be attributed to the poor hexane solubility of **5** and **6** coupled with the fact that more of the pyridine and HMDS(H) present in the reaction mixture is used in the formation of highly coordinated **5** and **6**. The amount of free amine and uncomplexed pyridine left unreacted in solution is likely to be too low to substantially affect the solvation properties of the reaction mixture.

Experimental

Syntheses and characterisation

All reactions were performed in Schlenk tubes under an inert atmosphere of dry, oxygen-free argon gas. *n*-Butyllithium and *n*,*sec*-dibutylmagnesium were purchased from Aldrich and standardised prior to each use using the diphenylacetic acid reagent indicator[28] and xylene–*sec*-butanol with 1,10-phenanthroline indicator methods[29] respectively. 1,1,1,3,3,3-Hexamethyldisilazane, dicyclohexylamine and pyridine were distilled from CaH_2, degassed using a freeze–pump–thaw methodology[30] and stored over 4A molecular sieves until required. Hexane and THF were distilled from Na–benzophenone, degassed using the same methodology and stored over 4A molecular sieves.

NMR spectral data were obtained using a Bruker DPX 400 spectrometer operating at 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and 155.50 MHz for ^{7}Li. Chemical shifts are reported relative to TMS at 0.00 ppm (for ^{1}H and ^{13}C) and to LiCl in D_2O at 0.00 ppm (for ^{7}Li).

Compound 1. A mixture of *n*-BuLi (10 mmol) and *n*,*sec*-Bu_2Mg (10 mmol) in hexane was chilled to 0 °C using an ice bath, the chilled solution was subsequently treated with HMDS(H) (30 mmol) resulting in the evolution of heat and gas (BuH). 10 mmol of THF was then added dropwise. Cooling of the solution to 4 °C overnight afforded colourless crystals of **1**. Yield 64%, mp 96–98 °C. ^{1}H NMR (400.13 MHz in d_6 benzene at 300 K) δ 3.57 (t, 4H, CH_2O of THF), 1.19 (m, 4H, CH_2CH$_2$O of THF), 0.34 (s, 36H, SiCH_3, bridging HMDS), 0.32 (s, 18H SiCH_3, terminal HMDS) and 0.10 (s, 9H, free HMDS(H)). ^{7}Li NMR δ 3.79 (s). ^{13}C NMR δ 69.87 (s, CH$_2$ of THF), 25.50 (CH$_2$ of THF), 6.46 (SiCH$_3$ bridging HMDS), 6.39 (SiCH$_3$, terminal HMDS).

Compound 2. A mixture of *n*-BuLi (5 mmol) and *n*,*sec*-Bu_2Mg (5 mmol) in hexane was chilled to 0 °C using an ice bath. The chilled solution was subsequently treated with HMDS(H) (30 mmol) resulting in the evolution of heat and gas (BuH). 10 mmol of pyridine was added dropwise to this chilled solution resulting in the formation of a white precipitate which dissolved to give a clear solution upon further heating. Upon slow cooling of this solution in a Dewar of warm water a small crop of colourless crystals were produced. These were found to be a co-crystalline mixture of compounds **2** and **4**. Overall yield of **2** < 5%, due to the mixture of products isolated no melting point was obtained. ^{1}H NMR (400.13 MHz in d_6 benzene at 300 K) δ 8.59 (s, 2H, α-pyridine), 6.82 (m, 1H, γ-pyridine), 6.55 (m, 2H, β-pyridine), 2.11–0.83 (various, <1H total 5H, *n*- and *sec*-butyl), 0.42 (s, 13.8H, **2** bridging HMDS), 0.38 (s, 6.25H, **4**), 0.33 (s, 6.25H, **2** terminal HMDS). ^{7}Li NMR δ 2.33 (**2**), 2.28 (**4**). ^{13}C NMR δ 150.37 (pyridine), 138.8 (pyridine), 125.18 (pyridine), 7.24 (HMDS of **4**), 7.17 (bridging HMDS of **2**), 7.12 (terminal HMDS of **2**), butyl signals for **4** were too weak to be observed. Larger quantities of **2** (32% yield) can also be produced using LiHMDS and $Mg(HMDS)_2$ although small amounts of **5** and **6** were also produced as by-products using this method.

Compound 3. A mixture of *n*-BuLi (5 mmol) and *n*,*sec*-Bu_2Mg (5 mmol) in hexane was chilled to 0 °C using an ice bath. To this mixture was added dicyclohexylamine (15 mmol). A vigorous reaction ensued whereby the solution turned from clear and colourless to yellow. To this solution was added THF (5 mmol), the solution was allowed to cool to 4 °C for 24 hours during which time a small crop of colourless crystals formed which were subsequently identified as **3**. Yield 14.9%, mp 100 °C (decomposition), 310–312 °C (melt). ^{1}H NMR (400.13 MHz in d_6 benzene at 300 K) δ 3.83 (m, 2H, OCH_2 of THF), 2.52 (m, 2H, CH_2 of THF), 1.90–0.99 (m, 33H, C_6H_{11}). ^{13}C NMR (^{1}H-decoupled, 100 MHz, d_8 toluene, 300 K) δ 66.5 (OCH$_2$ of THF), 26.4 (CH$_2$ of THF), 57.0–14.6 (C_6H_{11}).

Compound 4. A mixture of *n*-BuLi (10 mmol) and *n*,*sec*-Bu_2Mg (10 mmol) in hexane was chilled to 0 °C using an ice bath, the chilled solution was subsequently treated with HMDS(H) (20 mmol) to give a clear and colourless solution. To this solution pyridine (10 mmol) was added dropwise resulting in the formation of a white precipitate which dissolved upon heating. After cooling a small crop of colourless crystals was produced which were found to be a mixture of products **2** and **4**. Yield of **4** was very low <8%, due to the mixture of products isolated no melting point was obtained for **4**. ^{1}H NMR (400.13 MHz in d_6 benzene at 300 K) δ 8.59 (s, 2H, α-pyridine), 6.82 (m, 1H, γ-pyridine), 6.55 (m, 2H, β-pyridine), 2.11–0.83 (various, <1H total 5H, *n*- and *sec*-butyl), 0.42 (s, 13.8 H, **2** bridging HMDS), 0.38 (s, 16.25H, **4**), 0.33 (s, 6.25H, **2** terminal HMDS). ^{7}Li NMR δ 2.28 (**4**), 2.33 (**2**). ^{13}C NMR δ 150.27 (pyridine), 138.43 (pyridine), 125.63 (pyridine), from 40–15 (butyl of **4**, very weak), 7.23 (HMDS of **4**), 7.18/7.10 (weak signals, HMDS of **2**, bridging/terminal). This complex can also be produced by the reaction of LiHMDS with 1 equivalent each of HMDS(H) and *n*,*sec*-Bu_2Mg (although small amounts of **4** are still formed).

Compound 5. To a chilled solution of LiHMDS in hexane (10 mmol, produced by the literature method)[1] was added 10 mmol of pyridine, resulting in the formation of a white precipitate which re-dissolved upon heating. After cooling a large crop of colourless crystals were formed which were found to be **5**. Yield 67%, mp 164 °C. ^{1}H NMR (400.13 MHz in d_6 benzene at 300 K) δ 8.76 (d, 2H, α-pyridine), 6.87 (m, 1H, γ-pyridine), 6.62 (m, 2H, β-pyridine), 0.44 (s, 18H, Me_3Si), 0.09 (s, 0.1H, free HMDS(H)). ^{7}Li NMR δ 2.33. ^{13}C NMR δ 150.04 (pyridine), 137.85 (pyridine), 124.85 (pyridine), 6.95 (CH$_3$ of HMDS).

Compound 6. To a chilled solution of $Mg(HMDS)_2$ in hexane (10 mmol, produced by the literature method)[5] was added 20 mmol of pyridine resulting in the formation of a white precipitate which re-dissolved upon heating. After cooling a large crop of colourless plate-like crystals were formed which were found to be **6**. Yield 63%, mp 122 °C. ^{1}H NMR (400.13 MHz in d_6 benzene at 300 K) δ 8.60 (d, 2H, α-pyridine), 6.82 (m, 1H, γ-pyridine), 6.53 (m, 2H, β-pyridine), 0.41 (s, 18H, HMDS), 0.10 (s, negligible, free HMDS(H)). ^{13}C NMR δ 151.01 (α-pyridine), 139.37 (γ-pyridine), 124.97 (β-pyridine), 7.45 (CH$_3$ of HMDS).

Molecular structure determination

Crystalline samples of each of the six compounds were examined on a Rigaku AFC7S diffractometer at 150 K, with Mo-Kα radiation (λ = 71069 Å). Selected X-ray crystallographic data is presented in Table 7. Data were processed and the structures solved using the teXsan[31] package. Structures were refined to convergence against F for compounds **1**, **2**, **5**, and **6**[31] and against F^2 for **3** and **4**.[32]

CCDC reference numbers 155643–155648.

See http://www.rsc.org/suppdata/dt/b1/b100052g/ for crystallographic data in CIF or other electronic format.

Elemental analyses

Although elemental analyses (C, H, and N) were carried out for **1–6** the results were generally inaccurate. Each sample suffered from the loss of bound solvent during the analytical procedure, this variation in solvent content coupled with the fact that **2** and **4** were always formed as mixtures can be attributed as the cause of this inaccuracy.

Acknowledgements

We thank the EPSRC and the University of Strathclyde (Faculty studentship to P. J. A. R.) for sponsoring this research.

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