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Reactions of chelating alkali metal amides with the Grignard reagent $^{n}BuMgCl$: crystal structures and solution ^{1}H NMR spectroscopic studies of the expected mono(amido)-product $[PhCH_2(Me_2NCH_2CH_2)NMg^{n}Bu]_2$ and the unexpected bis(amido)-product $\{[Ph(2\text{-}Pyr)N]_2Mg \cdot (THF)_2\}$

Kenneth W. Henderson, Robert E. Mulvey
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL (UK)

William Clegg and Paul A. O'Neil
Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU (UK)

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Abstract

Chelating alkali metal amides derived from metallation of the secondary amines $PhCH_2(Me_2NCH_2CH_2)NH$ and Ph(2-Pyr)NH, react with the Grignard reagent $^{n}BuMgCl$ in 1:1 molar ratios to afford mono(amido) $[PhCH_2(Me_2NCH_2CH_2)NMg^{n}Bu]_2$ **1** and bis(amido) $\{[Ph(2\text{-}Pyr)N]_2Mg \cdot (THF)_2\}$ **2** (where THF = tetrahydrofuran) respectively. X-Ray crystallography shows **1** to be dimeric having an (amido N–Mg)$_2$ ring, the central one of a fused tricyclic core, with the other two arising from internal complexation by the tertiary amine nitrogen atoms. Butyl ligands complete the pseudo-tetrahedral coordination of the magnesium atoms. Variable temperature ^{1}H NMR spectroscopic studies indicate that this structure retains its compact, highly rigid nature in arene solution, rendering it resistant to external complexation by THF. In contrast, the crystal structure of **2** is monomeric, with a pseudo-octahedral magnesium centre coordinated by two bidentate Ph(2-Pyr)N^{-} anions and two THF molecules. Bis(amido) **2** appears to result from the THF-induced disproportionation of alkyl(amido) $[Ph(2\text{-}Pyr)NMg^{n}Bu]_2$, a dimer akin to **1**, but decidedly more flexible sterically and therefore susceptible to attack by external donor molecules.

Introduction

Surprisingly few magnesium amides of formula $[(R^1R^2N)_2Mg \cdot (L)_x]_n$, bis(amido) magnesium compounds, whether uncomplexed (*i.e.* with $x = 0$) or complexed, have been reported [1]. Amination of bis(alkyl) magnesium compounds, $(R_2Mg)_n$, gives

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Correspondence to: Dr. R.E. Mulvey.

alkyl(amido) magnesium products, $[(R_2N)MgR]_n$, which often resist further amination, so mixed compounds of this type are more common, as are Grignard-type formulations $(R_2NMgX)_n$ where X is a halogen. The ionic lattice structure of the inorganic amide derived from ammonia, $[(H_2N)_2Mg]_\infty$, was characterised crystallographically more than twenty years ago [2]. Crystal structure determinations of amidomagnesium compounds derived from organic amines have hitherto been mainly confined to species containing silyl substituents. The simplest, $\{[(Me_3Si)_2N]_2Mg \cdot (THF)_2\}$, where THF = tetrahydrofuran, is monomeric, with a four-coordinate, pseudo-tetrahedral magnesium centre [3], as is $\{[(Me_3Si)(8\text{-quinolyl})N]_2Mg\}$, which utilises quinolyl nitrogen atoms as internal complexants to attain the same coordination [4]. This basic coordination geometry is repeated in two dimers derived from diamine [RN(H)R'N(H)R] molecules, $[Me_2Si(N^tBu)_2Mg \cdot (THF)]_2$ [5] and $\{[o\text{-}(Me_3Si)NC_6H_4(SiMe_3)N]Mg \cdot (OEt_2)\}_2$ [6]. Four-coordinate magnesium is also found in silicon-free alkyl(amido) structures, in the t-butyl substituted carbazole derivative $[(C_{28}H_{40}N)MgC_2H_5 \cdot (THF)_2]$, which is prevented from associating by the steric bulk of its fused heterocyclic ring system [7], and in the dimer $[Me(Me_2NCH_2CH_2)NMgMe]_2$ with its two distinct types of nitrogen-magnesium coordination [8]. Another alkyl(amido) dimer, $[(Me_3Si)_2NMg^sBu]_2$, marks a departure from the norm, having sterically-imposed, three-coordinate magnesium centres [9]. However, despite its novel composition, in the amido(nitrido) species $[(^tBuNH)_9(N)Mg_6]$ all six of the magnesium atoms occupy normal, four-coordinate, tetrahedral sites [10].

The scant attention paid to magnesium amide structural chemistry contrasts with the wealth of information now available on lithium amide structures. Two reviews covering the structures of a range of lithium organonitrogen species, including lithium amide species, have recently appeared [11]. Recently there has also been a small, but significant growth in the numbers of reports of sodium amide and potassium amide structures. Chelating alkali metal amides, derived from the secondary amines phenyl(2-pyridyl)amine, Ph(2-Pyr)NH, and N'-benzyl-N,N-dimethylethylenediamine, $PhCH_2(Me_2NCH_2CH_2)NH$, provide the starting materials in the studies of magnesium amide species reported here. Both amido anions offer flexibility in the way they bind to metal centres. X-Ray crystallography has established that $[Ph(2\text{-Pyr})N]^-$ can assume chelation geometries (i) with both nitrogens terminal in $[Ph(2\text{-Pyr})NLi \cdot (HMPA) \cdot HN(2\text{-Pyr})Ph]$ [12], one isomer of $[Ph(2\text{-Pyr})NLi \cdot (HMPA)]_2$ [13], and $[Ph(2\text{-Pyr})NNa]_2 \cdot (HMPA)_3$ [14], (ii) with the amido-nitrogen bridging and the pyridyl-nitrogen terminal in the other isomer of $[Ph(2\text{-Pyr})NLi \cdot (HMPA)]_2$ [13], and (iii) with both nitrogens bridging in $[Ph(2\text{-Pyr})NNa \cdot (PMDETA)]_2$ [14] and $[Ph(2\text{-Pyr})NK \cdot (TMEDA)]_2$ [15] with respect to the alkali metal centres. The modes of attachment of $[PhCH_2(Me_2NCH_2CH_2)N]^-$ have not been so well studied, though a NMR spectroscopic/cryoscopic examination of $[PhCH_2(Me_2NCH_2CH_2)NLi]_n$ [16] suggests that the amido-nitrogens bridge pairs of lithium cations in a $(NLi)_3$ trimeric cycle, which may or may not involve intramolecular dimethylamidonitrogen · lithium $(Me_2N \cdot Li)$ coordinations.

As reported here, we have now incorporated these amido anions into magnesium-containing structures by treating the Grignard reagent $(^nBuMgCl)_n$ with $[Ph(2\text{-Pyr})NM]_n$ and with $[PhCH_2(Me_2NCH_2CH_2)NM]_n$ (M = Li or Na in each case) in 1:1 molar ratios. Reactions involving the latter amine proceeded as expected, to give mono(amido) $[PhCH_2(Me_2NCH_2CH_2)NMg^nBu]_2$ (1). Surprisingly, however, the bis(amido) complex $\{[\mathrm{Ph(2\text{-}Pyr)N}]_2\mathrm{Mg}\cdot(\mathrm{THF})_2\}$ (**2**) was produced from the former amine; this complex is believed to be formed via the intermediate $[\mathrm{Ph(2\text{-}Pyr)NMg^nBu}]_n$. X-Ray crystallographic studies and ^{1}H NMR spectroscopic studies of both **1** and **2** are described. Discussion centres on how the size and stereochemistry of the chelating bridge offered to the metal by the incoming amido anions, influences the structure and stability of the butyl(amido) magnesium species involved.

Results and discussion

The alkali metal precursors of **1**, $[\mathrm{PhCH_2(Me_2NCH_2CH_2)NLi}]_n$ and $[\mathrm{PhCH_2(Me_2NCH_2CH_2)NNa}]_n$, and of **2**, $[\mathrm{Ph(2\text{-}Pyr)NLi}]_n$ and $[\mathrm{Ph(2\text{-}Pyr)NNa}]_n$, were generated in hexane under protective argon blankets, and subsequently treated *in situ* with THF solutions of the Grignard chloride $(^n\mathrm{BuMgCl})_n$ (eq. 1). Use of lithium amides in synthesis is well known whereas sodium amides have been largely neglected in this area, but in our work they proved to be equally effective as amido transfer agents. All four alkali metal amides gave X-ray quality crystals of the amidomagnesium product in a similar (good) yield. Exactly equimolar proportions of $(\mathrm{R^1R^2NM})_n$ and $(^n\mathrm{BuMgCl})_n$ were employed in the expectation of obtaining n-butyl(amido) magnesium $(\mathrm{R^1R^2NMg^nBu})_n$ products (after removal of the LiCl or NaCl precipitates). Analysis of **1** confirmed the expected empirical formula $[\mathrm{PhCH_2(Me_2NCH_2CH_2)NMg^nBu}]_n$ but that of **2** revealed it, surprisingly, to be the bis(amido) species $\{[\mathrm{Ph(2\text{-}Pyr)N}]_2\mathrm{Mg}\cdot(\mathrm{THF})_2\}_n$. Complex **2** is probably formed by disproportionation of the intermediate $[\mathrm{Ph(2\text{-}Pyr)NMg^nBu}]_n$, the product expected from the 1:1 stoichiometry employed in the reaction. The other disproportionation product would be the known bis(organo)magnesium compound $(^n\mathrm{Bu_2Mg})_n$ or more precisely a THF solvate thereof (eq. 2). It is noteworthy that there is an earlier report of disproportionation of an alkyl(amido)magnesium species (eq. 3) [17]. Another distinction between **1** and **2** concerns the coordinating solvent THF, which is found only in the latter amide, although similar amounts were available to complex the magnesium centres in each reaction mixture. To find why these differences should arise the structures of the compounds involved were elucidated.

$$\mathrm{R^1R^2NM} + {}^n\mathrm{BuMgCl} \xrightarrow{\text{hexane,THF}} \mathrm{R^1R^2NMg^nBu} + \mathrm{MCl} \tag{1}$$

$$\mathrm{R^1R^2NMg^nBu} \xrightarrow{\text{hexane,THF}} 1/2\left[(\mathrm{R^1R^2N})_2\mathrm{Mg}\cdot(\mathrm{THF})_2\right] + 1/2\ {}^n\mathrm{Bu_2Mg}\cdot(\mathrm{THF})_2 \tag{2}$$

$$\mathrm{Me_2NH} + \mathrm{Et_2Mg} \xrightarrow[-\mathrm{EtH}]{\text{Ether}} [\mathrm{Me_2NMgEt}] \rightarrow 1/2(\mathrm{Me_2N})_2\mathrm{Mg} + 1/2\ \mathrm{Et_2Mg} \tag{3}$$

Centrosymmetric ring systems are common in amido(alkali metal) structural chemistry [11]. The amido(alkali earth metal) compound **1** also adopts this type of crystal structure, with alternating magnesium atoms and amido-nitrogen atoms [N(1), N(1′)] in a planar, four-membered ring (see Fig. 1). Chelation occurs through the tertiary-amine nitrogen atoms [N(2), N(2′)], which bind to the metal in a terminal manner. This arrangement generates two puckered five-membered ring systems ($\overline{\mathrm{N(1)C(8)C(9)N(2)Mg}}$ and its symmetry relation) which are fused *via* the central planar $\overline{\mathrm{MgN(1)Mg'N(1')}}$ ring. The structure of the aforementioned

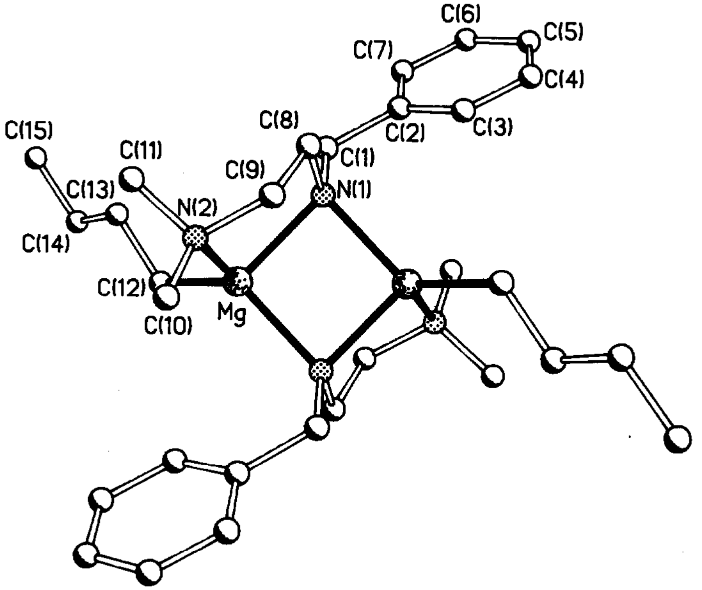

Fig. 1. Molecular structure of **1** showing the numbering scheme (hydrogen atoms are omitted for clarity).

$[Me(Me_2NCH_2CH_2)NMgMe]_2$ [8] contains the same fused tri-cyclic core; significantly, as in the case of **1**, the presence of a complexing ethereal solvent in the reaction mixture did not lead to complexation of the magnesium centres. The core dimensions of $[Me(Me_2NCH_2CH_2)NMgMe]_2$ are little different from those of **1**, *e.g.* (bridging) N–Mg 2.097(3)–2.118(3) Å *cf.* 2.113(2), 2.116(2) Å in **1**: (terminal) N–Mg 2.182(3), 2.190(3) Å *cf.* 2.200(2) Å; N(1)MgN(1′) 91.38(12)° *cf.* 92.4(1)°; MgNMg′ 88.62(12)° *cf.* 87.6(1)°; N(1)MgN(2) 83.36(13)° *cf.* 84.6(1)°. Overall, each magnesium atom and both types of nitrogen atom occupy local distorted tetrahedral environments. Four-coordination of the magnesium atoms in **1** is completed by a n-butyl group (C–Mg bond length, 2.135(2) Å *cf.* 2.100(4) and 2.104(4) for the (methyl) C–Mg bonds in the related structure), which like the benzyl group (or methyl group in the related structure) attached to the amido-nitrogen atom is directed away from the tri-cyclic core. A detailed examination of the bonding in **1** is unwarranted here since the related structure was previously subjected to such analysis. Table 1 gives a complete list of bond lengths and bond angles in **1**.

Whereas a precedent exists for the crystal structure of **1**, that of **2** (Fig. 2) establishes a new structural type in magnesium amide chemistry. Bis(amido)magnesium compounds are relatively rare in any case, as mentioned in the Introduction, and those that have been crystallographically characterised hitherto contain four-coordinate, pseudo-tetrahedral magnesium. In the present case, in contrast, the metal atom is located at the centre of a distorted *octahedron*, a common arrangement in other types of magnesium compound. The monomeric structure is centrosymmetric, with magnesium bonded to pairs of amido-nitrogen, pyridyl-nitrogen, and (THF) oxygen atoms. This sixfold inner coordination shell resembles that in the mixed magnesium-molybdenum complex $\{(C_5H_5N)_4Mg[CpMo(CO)_3]_2\}$, in which the magnesium centre is surrounded by four pyridine nitrogen atoms and

Table 1

Bond lengths (Å) and angles (°) for 1

Mg-N(1)	2.113(2)	Mg-N(2)	2.200(2)
Mg-C(12)	2.135(2)	Mg-N(1′)	2.116(2)
N(1)-C(1)	1.457(2)	N(1)-C(8)	1.463(3)
N(2)-C(9)	1.502(3)	N(2)-C(10)	1.489(5)
N(2)-C(11)	1.443(6)	C(1)-C(2)	1.527(3)
C(2)-C(3)	1.381(3)	C(2)-C(7)	1.396(3)
C(3)-C(4)	1.401(3)	C(4)-C(5)	1.378(5)
C(5)-C(6)	1.371(6)	C(6)-C(7)	1.393(5)
C(8)-C(9)	1.507(4)	C(12)-C(13)	1.526(3)
C(13)-C(14)	1.523(3)	C(14)-C(15)	1.519(5)
N(1)-Mg-N(2)	84.6(1)	N(1)-Mg-C(12)	122.2(1)
N(2)-Mg-C(12)	118.2(1)	N(1)-Mg-N(1′)	92.4(1)
N(2)-Mg-N(1′)	111.4(1)	C(12)-Mg-N(1′)	120.4(1)
Mg-N(1)-C(1)	114.8(1)	Mg-N(1)-C(8)	107.9(1)
C(1)-N(1)-C(8)	110.9(2)	Mg-N(1)-Mg′	87.6(1)
C(1)-N(1)-Mg′	117.8(1)	C(8)-N(1)-Mg′	115.6(1)
Mg-N(2)-C(9)	100.8(1)	Mg-N(2)-C(10)	121.2(2)
C(9)-N(2)-C(10)	106.8(2)	Mg-N(2)-C(11)	107.5(2)
C(9)-N(2)-C(11)	110.0(2)	C(10)-N(2)-C(11)	109.9(3)
N(1)-C(1)-C(2)	117.6(2)	C(1)-C(2)-C(3)	122.5(2)
C(1)-C(2)-C(7)	118.4(2)	C(3)-C(2)-C(7)	119.1(2)
C(2)-C(3)-C(4)	120.5(2)	C(3)-C(4)-C(5)	119.8(3)
C(4)-C(5)-C(6)	120.1(3)	C(5)-C(6)-C(7)	120.5(3)
C(2)-C(7)-C(6)	120.0(3)	N(1)-C(8)-C(9)	111.6(2)
N(2)-C(9)-C(8)	111.8(2)	Mg-C(12)-C(13)	120.0(1)
C(12)-C(13)-C(14)	114.5(2)	C(13)-C(14)-C(15)	114.4(2)

Symmetry operation for primed atoms: $1-x$, $-y$, $1-z$.

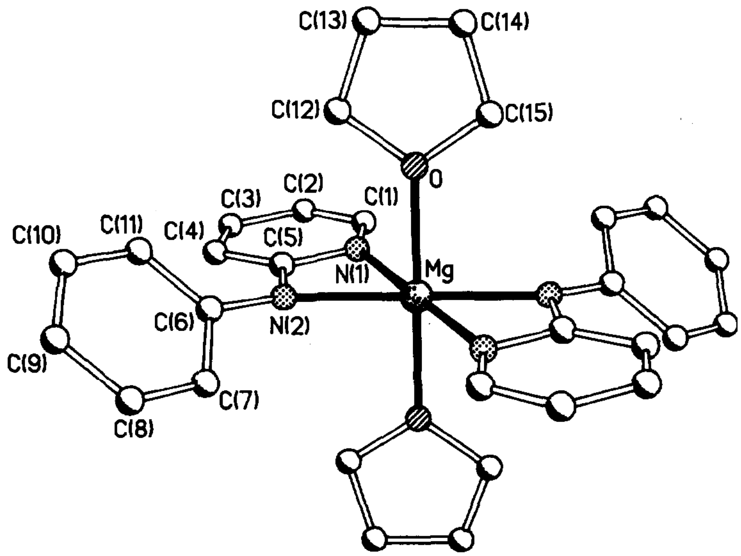

Fig. 2. Molecular structure of 2 showing the numbering scheme (hydrogen atoms are omitted for clarity).

Table 2

Bond lengths (Å) and angles (°) for **2**

Mg–N(1)	2.182(2)	Mg–N(2)	2.105(2)
Mg–O	2.212(2)	N(1)–C(1)	1.342(3)
N(1)–C(5)	1.368(2)	N(2)–C(5)	1.349(2)
N(2)–C(6)	1.395(2)	O–C(12)	1.442(3)
O–C(15)	1.420(4)	C(1)–C(2)	1.370(3)
C(2)–C(3)	1.396(3)	C(3)–C(4)	1.372(3)
C(4)–C(5)	1.421(3)	C(6)–C(7)	1.399(2)
C(6)–C(11)	1.403(3)	C(7)–C(8)	1.383(3)
C(8)–C(9)	1.388(3)	C(9)–C(10)	1.382(3)
C(10)–C(11)	1.388(3)	C(12)–C(13)	1.492(5)
C(13)–C(14)	1.451(6)	C(14)–C(15)	1.426(6)
N(1)–Mg–N(2)	63.0(1)	N(1)–Mg–O	90.5(1)
N(2)–Mg–O	89.9(1)	Mg–N(1)–C(1)	148.9(1)
Mg–N(1)–C(5)	91.0(1)	C(1)–N(1)–C(5)	119.9(2)
Mg–N(2)–C(5)	94.9(1)	Mg–N(2)–C(6)	140.6(1)
C(5)–N(2)–C(6)	123.6(1)	Mg–O–C(12)	124.4(1)
Mg–O–C(15)	125.6(2)	C(12)–O–C(15)	109.2(2)
N(1)–C(1)–C(2)	123.3(2)	C(1)–C(2)–C(3)	117.5(2)
C(2)–C(3)–C(4)	121.0(2)	C(3)–C(4)–C(5)	118.9(2)
N(1)–C(5)–N(2)	111.1(2)	N(1)–C(5)–C(4)	119.4(2)
N(2)–C(5)–C(4)	129.4(2)	N(2)–C(6)–C(7)	118.4(2)
N(2)–C(6)–C(11)	124.3(2)	C(7)–C(6)–C(11)	117.1(2)
C(6)–C(7)–C(8)	121.7(2)	C(7)–C(8)–C(9)	120.3(2)
C(8)–C(9)–C(10)	119.1(2)	C(9)–C(10)–C(11)	120.7(2)
C(6)–C(11)–C(10)	121.1(2)	O–C(12)–C(13)	106.3(2)
C(12)–C(13)–C(14)	105.4(3)	C(13)–C(14)–C(15)	108.4(3)
O–C(15)–C(14)	108.2(3)		

two carbonyl oxygen atoms [18]. Similar (pyridyl)N–Mg attachments are present in the carbon-magnesium compound $\{[2\text{-}(Me_3Si)_2\overline{C(C_5H_4N)]_2Mg}\}$, but in this case the bulky silyl substituents restrict the Mg centre to four-coordination [19]. In **2**, *transoid* positions are assumed by the phenyl(2-pyridyl)-amido anions and by the THF molecules, as required by the centre of symmetry. The magnesium atom interconnects two essentially planar, four-membered rings [$\overline{N(1)C(5)N(2)Mg}$ and its symmetry relation: the Mg atom lies 0.04 Å out of the N(1)C(5)N(2) plane] arising from the chelation provided by the amido anions. The dimensions of these four-membered rings signify that the metal has a slight preference for the amido-nitrogen atom, as indicated by the shorter bond length [2.105(2) Å *cf.* 2.182(2) Å for the (pyridyl)N–Mg attachment] and the larger C(5)N(2)Mg bond angle [94.9(1)° *cf.* 91.0(1)° for C(5)N(1)Mg]. Other known bis(amido)magnesium structures have consistently shorter (amido)N–Mg bonds [2.015(5), 2.027(5) Å in $\{[(Me_3Si)_2N]_2Mg \cdot (THF)_2\}$ [3] and 1.992(4), 2.004(4) Å in $\{[(Me_3Si)(8\text{-quinolyl})N]_2Mg\}$ [4]], and in the latter example also shorter (pyridyl)N–Mg distances [2.096(4) and 2.103(4) Å]. This diminution in bond length reflects the lower coordination state of the magnesium atoms, *i.e.* 4 *cf.* 6 in **2**. A similar pattern is discernible with the (THF)O–Mg bonds [length 2.212(2) Å in **2** *cf.* 2.086(5), 2.101(5) Å in the aforementioned bis(THF) complex]. Table 2 presents a complete list of bond lengths and bond angles in **2**.

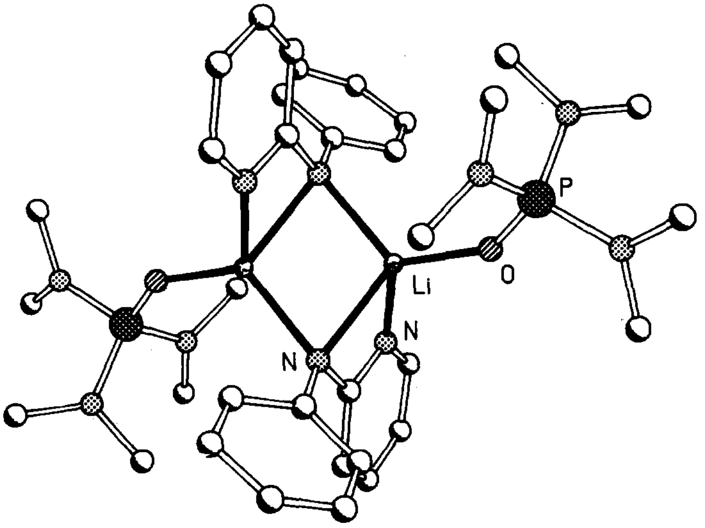

Fig. 3. Molecular structure of one of the structural isomers of the crystalline lithium amide [Ph(2-Pyr)NLi·HMPA]$_2$ [13]. The intermediate [Ph(2-Pyr)NMg^{n}Bu]$_2$ is likely to adopt the same basic structural arrangement.

A comparison of the structures of **1** and **2** reveals significant differences between their respective dinitrogen chelating units. Most obviously, the former offers the metal a four-atom N–C–C–N bridge, and the latter a three-atom N–C–N bridge. Five- and four-membered magnesacyclic rings, respectively, are thus formed as a consequence of chelation. Dimerisation in the case of **1** creates two such five-membered rings. A four-membered ring lies sandwiched between them to give a fused tricyclic core overall. It seems logical to assume that during the course of the reaction leading to **2** an intermediate akin to **1** is formed, having the empirical formula [Ph(2-Pyr)NMg^{n}Bu]$_n$. This intermediate would be expected to dimerise (*i.e.*, $n = 2$) in a manner matching that of **1**. Bearing in mind the smaller size of the bidentate Ph(2-Pyr)N$^-$ chelating unit, the fused, tricyclic core produced in this case would be made up entirely of four-membered rings: a central (amido N–Mg)$_2$ one with two $(\text{pyr}\overline{\text{N–C–amido N–M}}\text{g})$ end ones. There is indirect evidence to suggest that such an arrangement would be stable. Firstly, the structures of **1** and **2** contain one or the other ring type, testifying to their individual stabilities. Secondly, and more importantly, lithium chemistry provides a precedent in the dimeric species [Ph(2-Pyr)NLi · (HMPA)]$_2$ [13]. Its structure (Fig. 3) models that envisaged for the magnesium compound. Amido-nitrogen atoms bridge two lithium atoms in the central planar four-membered ring, which separates two other four-membered rings arising from the coordination of the pyridyl-nitrogen atoms. The distorted tetrahedral environment of the lithium atoms is completed by terminally-bound HMPA molecules. In the magnesium analogue this role would be filled by n-butyl groups (formally anions, rather than neutral molecules like HMPA, to satisfy the greater valency requirement of magnesium *cf.* lithium). Being less sterically demanding than HMPA, they could easily fit into the same coordination sites without affecting the basic structure. Also, substituting magnesium for lithium would not be expected to enlarge the dimensions of the structure significantly. Comparison of bond lengths in the lithium compound with those of a similar type in **2** [amido N–Li, 2.142 Å; amido N–Mg, 2.105(2) Å; pyridyl N–Li, 2.055 Å; pyridyl N–Mg 2.182(2) Å] supports this view. Since it has been demonstrated that such a structure would be stable, the questions arise of what causes it to disproportionate (see eq. 2) and why **1** does not undergo a similar reaction?

The disproportionation of [Ph(2-Pyr)NMg^{n}Bu]$_2$ can be attributed to the presence of THF in the reaction mixture. This view is given credence by the fact that two THF molecules ultimately complex to the metal centre in the isolated product. In this case complexation leads to an overall gain for the metal in terms of its coordination number. Initially all the magnesium centres would be four-coordinate and some probably remain so in [^{n}Bu$_2$Mg · (THF)$_x$] (with $x = 2$), but those in **2** are raised to six-coordinate. In theory attack by THF could have caused symmetrical cleavage of the dimeric arrangement rather than disproportionation. However, the monomeric structure produced in this case, [Ph(2-Pyr)NMg^{n}Bu · (THF)$_x$], would require three, as opposed to two, THF molecules (*i.e.*, $x = 3$) to render its magnesium centre similarly six-coordinate. This alternative situation would be entropically unfavourable. To initiate disproportionation the magnesium centres in the dimer must be sterically accessible to the approaching THF molecules. Herein lies the reason why the reactions involving the Ph(2-Pyr)N$^-$ and PhCH$_2$(Me$_2$NCH$_2$CH$_2$)N$^-$ chelating anions ultimately lead to different types of product. The dimeric structures of [Ph(2-Pyr)NMg^{n}Bu]$_2$ (predicted) and [PhCH$_2$(Me$_2$NCH$_2$CH$_2$)NMg^{n}Bu]$_2$ (known) exhibit similar gross features as outlined above, but where they do differ significantly is in the local stereochemistry about their respective internal nitrogen donor atoms. In the former structure these atoms are formally sp^2 hybridised in bonding to two carbon atoms as well as to one magnesium atom. Moreover they are located within planar pyridyl rings that are free to rotate, and such rotation need not necessarily disrupt the pyridyl N–Mg dative bonding. This leaves the magnesium atoms partially exposed and susceptible to attack by the sterically-undemanding THF ligands. Upon complexation the core-bonding concomitantly weakens as a prelude to disproportionation. In contrast, the internal nitrogen donor atoms in the latter structure [N(2), N(2′)] are formally sp^3-hybridised. Two methyl carbon atoms, one methylene carbon atom, and one magnesium atom surround them in a distorted tetrahedral shell. This extra branching imposes steric constraints that apparently keep the dinitrogen chelating units firmly clamped on to the metal atoms, while at the same time protecting them from attack by other molecules. This picture is consistent with the experimental observations that THF can neither complex with the magnesium centres within the dimer, nor break down the dimeric association. The results of the ^{1}H NMR spectroscopic studies, which are discussed below, fully support this interpretation.

Figure 4 shows with assignments the room temperature ^{1}H NMR spectrum of **1** recorded in benzene-d_6 solution. Assignments were verified by COSY 45 experiments. The spectrum clearly confirms the compact, highly rigid, nature of the structure. Its key feature is that every methylene proton and methyl group belonging to the chelating bridge, has its own individual signal. Those from the four CH$_2$CH$_2$ protons appear essentially as two doublets of triplets (dt, centred at 3.18 and 1.81 ppm; the latter resonance is partly obscured) and two triplets of

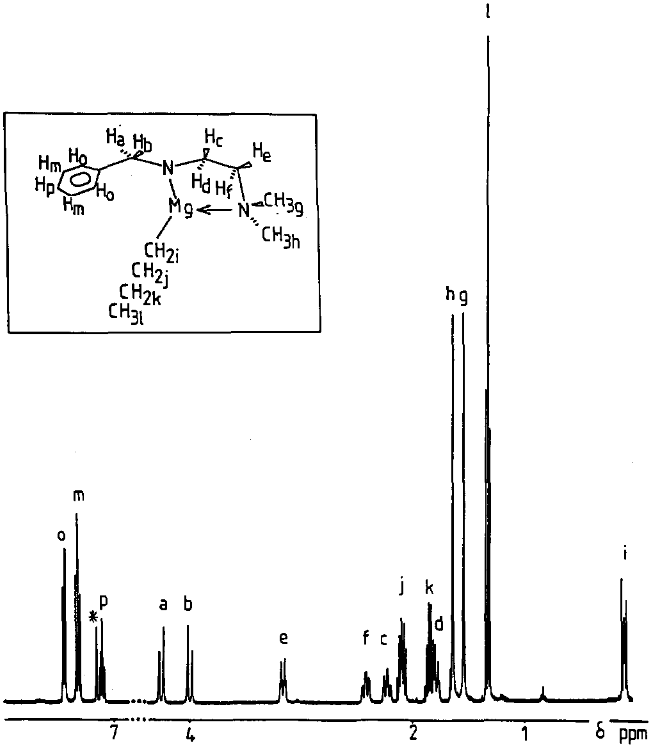

Fig. 4. ^1H NMR spectrum of **1** recorded in benzene-d_6 solution at 25°C, with assignments. The solvent peak is marked by an asterisk.

doublets (td, centred at 2.46 and 2.24 ppm). These coupling patterns and their associated coupling constants are characteristic of a *gauche* conformation with two *trans vicinal* protons (H_c, H_f) and two staggered *vicinal* protons (H_d, H_e) in the $-NCH_2CH_2N-$ arrangement. Protons H_c and H_f have two major couplings (^2J(*geminal*) ~ 12 Hz, ^3J(*trans*) ~ 12 Hz) and one minor one (^3J(staggered) ~ 3 Hz) to give the td patterns. Protons H_d and H_e have one major coupling (^2J(*geminal*) ~ 12 Hz) and two minor ones (2 × ^3J(staggered) ~ 3 Hz) to give the dt patterns. Significantly, the chemical shift difference is substantially larger for the pair of dt signals (1.39 *cf.* 0.22 ppm for the td signals). The margin of the difference suggests that the electronic environment of one of these protons is strongly affected by the polarising power of the metal (in the case of free $PhCH_2(Me_2NCH_2CH_2)NH$ in toluene-d_8 solution the two methylene signals lie only 0.28 ppm apart). Distinct, well-separated, singlets (located at 1.68 and 1.57 ppm) are observed for the (amino)methyl groups. Thus the five-membered heterocyclic ring generated by chelation must be in a locked conformation with its substituents in fixed orientations, for the protons of each type to be anisochronous. The benzylic-CH_2 protons are also chemically inequivalent, appearing as mutually-coupled doublets (centred at 4.24 and 3.99 ppm). At this temperature (298 K) the aromatic rings to which they are attached are freely rotating (the *ortho*, *meta*, and *para* resonances are centred at 7.45, 7.32 and 7.11 ppm, respectively). The butyl groups terminally bound to the metal are positioned *exo* to the tricyclic core, and so give rise to just four separate multiplets (centred at 0.14, 2.12, 1.87 and 1.35 ppm for the α-, β-, γ-CH_2, and CH_3, respectively). An essentially identical spectrum is obtained in toluene-d_8 solution at the same temperature. This solution was also examined at higher temperatures. Remarkably, even at 350 K the signals due to the ring protons retain their individuality (though not surprisingly resolution is lower), indicating that the rigidity of the structure is maintained.

Complex **2** also dissolves in benzene-d_6 solution, permitting recording of a ^1H NMR spectrum (at 298 K). Evidence that the THF molecules remain intact on the metal (and, by implication, that the discrete octahedral arrangement in the crystal is retained in solution) comes from a comparison of the chemical shifts of the distinct methylene multiplets (centred at 3.52 and 1.14 ppm) with those of free THF under the same conditions (3.54 and 1.48 ppm). Signals due to the pyridyl protons were assigned by selectively decoupling each in turn and by running NOE experiments. These appear in order of decreasing chemical shift in the sequence α-H (7.73), β'-H/γ-H (overlapping at 6.99), and β-H (6.00 ppm). The free amine exhibits a similar sequence (*i.e.*, at 8.19, 6.56/7.00 and 6.35 ppm, respectively) but metallation moves the α-H and β-H signals to lower frequency (by 0.46 and 0.35 ppm, respectively), the β'-H signal to higher frequency (by 0.43 ppm), and the γ-H signal hardly at all. Free rotation of the phenyl rings about the *ipso* C–amido N bonds results in the appearance of one signal each for the *ortho*-H's, the *meta*-H's, and the *para*-H: the first two coincide at 7.32 ppm with the third distinct at 6.94 ppm, *cf.* 7.25, 7.13 and 6.88 ppm, respectively, for free Ph(2-Pyr)NH.

In conclusion, it has been established that mono(amido)- or bis(amido)-magnesium products can be formed by reaction of ^{n}BuMgCl with one molar proportion of a dinitrogen functionalised amide in the presence of THF. Which type is produced is largely dictated by the stereochemical characteristics of the chelating dinitrogen unit. Further work in the short term will be aimed at isolating the intermediate to **2**, $[Ph(2\text{-}Pyr)NMg^nBu]_n$, in the absence of THF. Attempts to achieve this by treating $(^nBu_2Mg)_n$ in hydrocarbon solution with a molar equivalent of the amine Ph(2-Pyr)NH have so far not given solid products. However, 1:2 mixtures on addition of THF again yield crystals of **2**. In the long term, a series of chelating amides will be explored, with a view to developing a general strategy for synthesising bis(amido)magnesium compounds.

Experimental

Syntheses

$[PhCH_2(Me_2NCH_2CH_2)NMg^nBu]_2$ 1. n-Butyllithium (10 mmol) in hexane was added to a chilled hexane solution of dried N'-benzyl-N, N-dimethylethylenediamine (10 mmol) in a Schlenk tube under dry oxygen-free argon. Vigorous gas evolution took place as a red solid was formed in the deep-red liquid. Addition of a solution of n-butylmagnesium chloride (10 mmol in THF), caused immediate dissolution of the solid. Stirring of the homogeneous solution formed, led to deposition of lithium chloride, which was filtered off from the deep red solution. Upon standing at ambient temperature for 24 h, the solution afforded small pale yellow crystals, which were filtered off, washed with chilled hexane, and dried under vacuum. Yield of first batch (without recourse to refrigeration) 58%; m.p. 141–143°C. (Found: C, 69.6, H, 10.5; Mg, 8.9. $C_{30}H_{52}N_4Mg_2$ calc.: C, 69.7; H,

10.1; Mg, 9.4; N, 10.8%). A similar procedure, but starting from n-butylsodium rather than from n-butyllithium, afforded crystalline **1** in a 52% yield.

$\{[Ph(2\text{-}Pyr)N]_2Mg\cdot(THF)_2\}$ **2**. To dried phenyl(2-pyridyl)amine (10 mmol) in a Schlenk tube under dry oxygen-free argon was added a chilled solution of n-butyllithium (10 mmol in hexane), causing vigorous gas evolution and the appearance of a brownish solid. On addition of n-butylmagnesium chloride (10 mmol in THF solution) the brownish solid dissolved, but a second solid separated from solution. This white solid (lithium chloride) was collected by filtration and washed with hot toluene, and the washings were added to the orange filtrate. When the orange solution was kept at ambient temperature for twenty-four hours yellow crystals separated, and these were filtered off, washed with chilled hexane, dried under vacuum, and identified as **2**. Yield of first batch (without recourse to refrigeration) 41%; m.p. 124–126°C. (Found: C, 71.0; H, 6.5; Mg, 4.6. $C_{30}H_{34}MgN_4O_2$ calc.: C, 71.1; H, 6.8; Mg, 4.8; N, 11.0; O, 6.3%). A similar procedure but starting from n-butylsodium afforded crystalline **2** in a 46% yield.

Both **1** and **2** are moisture and oxygen sensitive, but appear to be stable indefinitely in their absence.

IR spectra

1: 2910s, 2855s, 1465s, 1380s, 1345w, 1290w, 1270w, 1180w, 1150w, 1115m, 1095w, 1075w, 1025s, 935m, 900w, 845m, 780m, 730s, 700m, 665w. **2**: 2915s, 2875s, 1580m, 1490m, 1460s, 1380m, 1330w, 1295w, 1150w, 1070w, 1040w, 1020m, 1000w, 765w, 750w, 700m, 665w (cm^{-1}; nujol mulls). Spectra were recorded on a Philips PU9714 infrared spectrophotometer.

^1H NMR spectra (400 MHz, 298 K)

1: (For key see Fig. 4) ^{n}Bu(CH_{2i}, 2H, m, δ 0.14 ppm; CH_{3l}, 3H, t, δ 1.35 ppm; CH_{2k}, 2H, m, δ 1.87 ppm; CH_{2j}, 2H, m, δ 2.12 ppm) Me_2N(CH_{3g}, 3H, s, δ 1.57 ppm; CH_{3h}, 3H, s, δ 1.68 ppm) CH_2CH_2 (H_d, 1H, dt, δ 1.81 ppm; H_c, 1H, td, δ 2.24 ppm; H_f, 1H, td, δ 2.46 ppm; H_e, 1H, dt, δ 3.18 ppm) PhCH_2 (H_b, 1H, d, δ 3.99 ppm; H_a, 1H, d, δ 4.24 ppm) Ph (*p*H, 1H, t, δ 7.11 ppm; *m*H, 2H, t, δ 7.32 ppm; *o*H, 2H, d, δ 7.45 ppm). **2**: THF (CH_2, 8H, m, δ 1.14 ppm; CH_2O, 8H, m, δ 3.52 ppm) Pyr (β-H, 2H, m, δ 6.00 ppm; γ-H/β'H, 2H/2H, m, δ 6.99 ppm; α-H, 2H, m, δ 7.73 ppm) Ph(*p*H, 2H, m, δ 6.94 ppm; *m*H, 4H, m, δ 7.32 ppm; *o*H, 4H, m, δ 7.32 ppm). Spectra were recorded on a Bruker AMX400 spectrometer. Chemical shifts are quoted relative to $SiMe_4$. The solvent employed was benzene-d_6 and solutions were prepared in a glove-box and tubes subsequently sealed under argon gas.

X-Ray crystallographic study

Crystal data for **1**: $C_{30}H_{52}Mg_2N_4$, $M = 517.4$, monoclinic, $P2_1/n$, $a = 10.293(3)$, $b = 7.962(2)$, $c = 20.017(5)$ Å, $\beta = 101.20(2)°$, $V = 1609.3$ Å^3, $Z = 2$, $D_c = 1.068$ g cm^{-3}, $F(000) = 568$, $\lambda = 1.54184$ Å (Cu-K_α radiation), $\mu = 0.81$ mm^{-1}. Cell parameters were refined from 2θ values (25–40°) of 32 reflections centred at $\pm\omega$ at 240 K on a Stoe-Siemens diffractometer. Data were collected by an on-line profile fitting procedure [20] with ω/θ scans; $2\theta_{max}$ 130°. No corrections were required for standard reflection intensity decay or absorption. 5524 measured data yielded 2708 unique reflections, of which 2336 had $F > 4\sigma_c(F)$ (σ_c based on counting statistics only); $R_{int} = 0.019$.

Table 3

Atomic coordinates for **1**

Atom	x	y	z
Mg	0.36768(5)	0.04457(7)	0.51086(3)
N(1)	0.5211(1)	−0.1091(2)	0.56387(7)
N(2)	0.2610(2)	−0.1936(2)	0.4860(1)
C(1)	0.5727(2)	−0.0581(3)	0.6339(1)
C(2)	0.7124(2)	−0.1152(3)	0.66626(9)
C(3)	0.7880(2)	−0.2155(3)	0.6324(1)
C(4)	0.9187(2)	−0.2560(4)	0.6626(1)
C(5)	0.9720(3)	−0.1962(5)	0.7266(2)
C(6)	0.8969(4)	−0.0994(5)	0.7612(2)
C(7)	0.7670(3)	−0.0578(3)	0.7316(1)
C(8)	0.4721(2)	−0.2820(3)	0.5611(1)
C(9)	0.3743(3)	−0.3159(3)	0.4961(2)
C(10)	0.1812(4)	−0.2255(5)	0.4168(2)
C(11)	0.1808(4)	−0.2210(4)	0.5366(3)
C(12)	0.2760(2)	0.2355(2)	0.5606(1)
C(13)	0.2246(2)	0.1944(2)	0.6253(1)
C(14)	0.1765(2)	0.3460(3)	0.6601(1)
C(15)	0.1236(4)	0.3046(5)	0.7239(2)

The structure was solved by direct methods and refined by blocked-cascade refinement [21] on F, with a weighting scheme $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 19 + 24G - 6G^2 - 47H + 29H^2 - 20GH$ ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$) [22]. Anisotropic thermal parameters were refined for non-hydrogen atoms; H atoms were constrained to give C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring angle

Table 4

Atomic coordinates for **2**

Atom	x	y	z
Mg	0.5	0	0
N(1)	0.52285(9)	0.1076(1)	0.1261(2)
N(2)	0.43572(8)	0.01048(9)	0.1803(1)
O	0.59029(9)	−0.0706(1)	0.1092(1)
C(1)	0.5596(1)	0.1798(1)	0.1434(2)
C(2)	0.5454(1)	0.2316(1)	0.2500(3)
C(3)	0.4888(1)	0.2077(1)	0.3432(2)
C(4)	0.4500(1)	0.1343(1)	0.3294(2)
C(5)	0.46818(9)	0.0826(1)	0.2178(2)
C(6)	0.38687(9)	−0.0357(1)	0.2635(2)
C(7)	0.3269(1)	−0.0809(1)	0.2034(2)
C(8)	0.2792(1)	−0.1322(1)	0.2782(2)
C(9)	0.2903(1)	−0.1404(1)	0.4166(2)
C(10)	0.3502(1)	−0.0979(1)	0.4779(2)
C(11)	0.3978(1)	−0.0458(1)	0.4032(2)
C(12)	0.5948(2)	−0.0776(2)	0.2543(2)
C(13)	0.6671(2)	−0.1251(3)	0.2839(4)
C(14)	0.7103(2)	−0.1263(4)	0.1579(5)
C(15)	0.6590(2)	−0.1037(3)	0.0509(4)

external bisectors, $U(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$; extinction parameter $x = 1.0(3) \times 10^{-5}$, $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$. Final $R = 0.072$, $wR = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2} = 0.070$, S = 1.45 for 173 parameters, largest shift/esd = 0.07, largest features in a final difference map 0.91, −0.52 e $\mathrm{Å}^3$.

Crystal data for **2**: $C_{30}H_{34}MgN_4O_2$, $M = 506.9$, orthorhombic, *Pccn*, $a = 17.202(6)$, $b = 16.231(3)$, $c = 9.888(2)$ Å, $V = 2760.8$ $\mathrm{Å}^3$, $Z = 4$, $D_c = 1.219$ g cm^{-3}, $F(000) = 1080$, $\lambda = 0.71073$ Å (Mo-K_α radiation), $\mu = 0.092$ mm^{-1}. Data collection, solution and refinement as for **1** with 20–25° range for cell determination, $2\theta_{max}$ 50°, 16881 measured, 2443 unique, 2139 with $F > 4\sigma_c(F)$, $R_{int} = 0.028$. Weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 4 + 23\mathrm{G} - 7\mathrm{H} + 4\mathrm{H}^2 - 39\mathrm{GH}$, extinction parameter $x = 3.8(12) \times 10^{-7}$. $R = 0.053$, $\omega R = 0.035$, $S = 1.03$ for 170 parameters, largest shift/esd = 0.02, largest features in a final difference map 0.38, −0.31 e $\mathrm{Å}^{-3}$.

Tables 3 and 4 give the refined atomic coordinates for **1** and **2** respectively. Lists of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre. A list of structure factors is available from the authors.

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