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Solvent induced disproportionation of alkyl(amido)magnesium species containing a (2-pyridyl)amido unit: synthetic, theoretical and NMR spectroscopic studies of bis(amido)magnesium compounds

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Abstract

Reaction of R(2-pyr)NH (where R = Me, Ph or 2-pyr) with 'Bu_2Mg' in an ether-free environment yields the corresponding alkyl(amido)magnesium derivative [{R(2-pyr)NMgBu}$_n$]. When polar solvent is added to these species only bis(amido)magnesium compounds separate from solution and not the expected solvated alkyl(amido) derivatives. Isolation of one such alkyl(amido) compound prior to reaction with donor solvent proves that the mixed anion species do indeed exist. However, when polar molecules are introduced a disproportionation reaction ensues, yielding the homoleptic compounds [{$R_2Mg \cdot (S)_x$}$_n$] and [{$(R_2N)_2Mg \cdot (S)_x$}$_n$], where S is THF, TMEDA or PMDETA. Theoretical calculations likewise show that the disproportionation reaction of model compounds closely related to our systems is strongly exothermic. A $^1H/^{13}C$ NMR spectroscopic study was used to assign the nature of the bis(amido) species in solution. From these analyses it was possible to propose that the solvated bis(amido) derivatives assume a common structural motif, that of a monomer ($n = 1$) with a *pseudo*-octahedral magnesium center.

Keywords: Magnesium; Amido; Ab initio MO calculations; Disproportionation

1. Introduction

Remarkably few studies, either synthetic or structural, have focused on bis(amido)magnesium compounds [{$(R_2N)_2Mg$}$_n$] in their own right [1]. This contrasts with the ever increasing number of publications concerning Grignard reagents [2] and to a lesser extent bis(organo)magnesium species [3]. The dearth of information on bis(amides) is even more surprising considering the vast utility of amides of lithium, magnesium's diagonal neighbor, [4] as reagents in organic synthesis [5]. Bases such as lithium diisopropylamide (LDA) [6] and lithium hexamethyldisilazide (LHMDS) [7] are commonly used as selective proton abstractors in organic transformations [5,8]. Also of note is the intriguing structural variety that is found for the lithium amides, which has led to intensive research over the past decade [9]. The little work that has been carried out on the corresponding amidomagnesium compounds has shown that they may have differing selectivities to their lithium counterparts, which is thought to be a consequence of their lower reactivity [10]. Also associated with the lower reactivity of these species is a higher thermal stability which allows reactions to be conducted at elevated temperatures without decomposition of the base [10]. Considering the obvious advantages that some magnesium amides may have over lithium amides, it is perhaps surprising that greater scrutiny has not been focused on the synthetic utility of these species. The limited investigations into the use of magnesium amides may in part be due to the reported difficulty in their preparation [11]. In particular alkyl(amido)magnesiums, [{$R(R_2N)Mg$}$_n$] do not always react with a secondary amine to give the corresponding bis(amido) derivative. We recently reported [12] that the reaction between the Grignard reagent ^{n}BuMgCl (in tetrahydrofuran solution) and the alkali metal amide Ph(2-pyr)NM (M = Li or Na) in 1 : 1 ratio yields exclusively the bis(amido) com-

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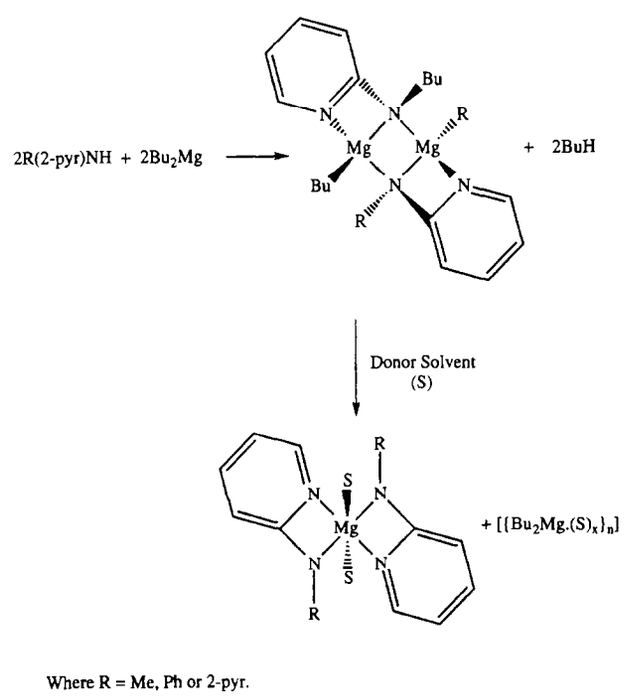
pound $[\{Ph(2\text{-pyr})N\}_2Mg \cdot (THF)_2]$ **1** (and the bis(alkyl) compound $[^nBu_2Mg \cdot (THF)_x]$) and not the expected alkyl(amido) derivative [Ph(2-pyr)NMg^{n}Bu] **2** (Eq. (1)). A comparative study was carried out on the alkali metal amide $PhCH_2NMCH_2CH_2NMe_2$ (derived from the polyamine *N'*-benzyl-*N*,*N*-dimethylethylenediamine) which was found to yield the expected alkyl(amido) compound $[\{PhCH_2(Me_2NCH_2CH_2)NMg^nBu\}_2]$ **3** on reaction with ^{n}BuMgCl (Eq. (2)). The crystal structures of **1** and **3** were elucidated.

$$2^nBuMgCl + 2Ph(2\text{-pyr})NM \xrightarrow{THF} [\{Ph(2\text{-pyr})N\}_2Mg \cdot (THF)_2] + [^nBu_2Mg \cdot (THF)_x] + 2MCl \quad (1)$$

$$2^nBuMgCl + 2PhCH_2NMCH_2CH_2NMe_2 \xrightarrow{THF} [\{PhCH_2(Me_2NCH_2CH_2)NMg^nBu\}_2] + 2MCl \quad (2)$$

Utilizing ^{1}H NMR spectroscopic and X-ray crystallographic evidence we proposed that **2** forms as an 'intermediate' in the reaction. Furthermore, we proposed that **2** is dimeric in solution, containing two four-coordinate magnesium centers with internal ligation from the nitrogen of the 2-pyridyl unit as is found in the known structure of $[\{Ph(2\text{-pyr})NMgNPh_2\}_2]$ [13]. Solvation of the metal center by THF molecules is possible in such a structure due to the 'flat', sterically undemanding nature of the Ph(2-pyr)N$^-$ unit in conjunction with the flexibility of the sp^2 N–Mg dative bond. This solvation induces a disproportionation reaction into the bis(amido) and bis(organo) derivatives, the driving force of which is the increase in coordination number of the metal, from four in the dimer **2** to six in the monomer **1** (Scheme 1). In comparison, the tetrahedral metal center in **3** is well protected towards attack from solvent molecules by the ligation of the NMe_2 unit which forms a rigid five-membered $MgNCH_2CH_2NMe_2$ ring (Fig. 1). In this case reaction ceases at the alkyl(amido) stage with no evidence of disproportionation. From these observations it seems that the nature of the 2-pyridyl amine ligand is paramount in the determination of the product from this apparently simple reaction.



Where R = Me, Ph or 2-pyr.

Scheme 1. General reaction pathway of the solvent induced disproportionation reaction of 2-pyridyl containing alkyl(amido)magnesium species; R = Me, Ph or 2-pyr and S = THF or a nitrogen atom from either TMEDA or PMDETA.

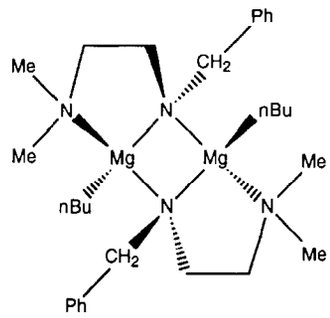


Fig. 1. Plan of the dimeric structure of $[\{PhCH_2(Me_2NCH_2CH_2)NMg^nBu\}_2]$.

We now outline further evidence for our proposed mechanism and also investigate the generality of this solvent induced disproportionation reaction. A $^1H/^{13}C$ NMR study was instigated for the compounds produced to assign the character of these species in solution and to correlate this with the known solid state structures. An *ab initio* theoretical investigation of model systems for the disproportionation reaction was undertaken to assess the relative stability of the compounds involved.

2. Results and discussion

2.1. Synthetic studies

Preparation of the alkyl(amido) 'intermediate' was carried out in an ether-free environment by reaction of 'Bu_2Mg' (in heptane) (purchased from Aldrich as a one molar solution in heptane, containing a 1 : 1 ratio of n-butyl to s-butyl units) with a secondary amine. These species were then subjected to attack by the donor solvents tetrahydrofuran (THF), N,N,N',N'-tetramethylethylenediamine (TMEDA), and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) to investigate if any solvation would take place and indeed if disproportionation would occur. In addition to the amine Ph(2-pyr)NH, two other 2-pyridyl containing amines, namely 2,2-dipyridylamine $[(2\text{-pyr})_2NH]$ and methyl-2-pyridylamine

[Me(2-pyr)NH], were studied for similar reaction. The aforementioned secondary amine $PhCH_2NHCH_2CH_2NMe_2$ was also the subject of similar reactions as a comparison to the 2-pyridyl containing amines. A series of compounds was isolated and these are listed in Table 1. On addition of donor solvent to the ether-free compounds only the bis(amido) derivatives were isolated. Plainly, addition of donor solvent to the alkyl(amido) species drives a disproportionation reaction similar to that described between ^nBuMgCl and Ph(2-pyr)NM in THF. As well as the bis(amides) **1** and **4–8** outlined in Table 1, we were able to obtain and characterize one ether-free alkyl(amido) 'intermediate'. Reaction of 'Bu_2Mg' and $(2\text{-pyr})_2NH$ in toluene yields a microcrystalline solid which was identified as a mixture of $[(2\text{-pyr})_2NMg^nBu]$ and $[(2\text{-pyr})_2NMg^sBu]$. From this finding it is clear that the compound at the alkyl(amido) stage is stable, *i.e.* there is no inherent instability associated with the mixed anion compounds that forces disproportionation. These results are fully in line with the proposed mechanism (Scheme 1). It is pertinent to note that reaction of $PhCH_2NHCH_2CH_2NMe_2$ with 'Bu_2Mg' yields the expected alkyl(amido) derivatives $[PhCH_2(Me_2NCH_2CH_2)NMg^nBu]$ and $[PhCH_2(Me_2NCH_2CH_2)NMg^sBu]$, which were then inert to attack by the polar solvents chosen. The mixture of isomers is a consequence of the reagent 'Bu_2Mg' consisting of a 1:1 blend of n-butyl to s-butyl units. Apparently a balance exists between thermodynamic and kinetic control of the reaction. Being the stronger base the s-butyl group would be expected to cleave from the metal before the n-butyl chain, but in reality a mixture of components is yielded. The average ratio (over five experiments) of n-butyl to s-butyl units was found to be approximately 1:3 for mixtures **9** and **10**. In these instances the reactions proceed under mainly kinetic control. A previous study by Raston, White and coworkers [14] revealed a similar result in which the reaction of 'Bu_2Mg' with $(Me_3Si)_2NH$ affords a crystalline form of $[\{(Me_3Si)_2NMg^sBu\}_2]$ in preference over the thermodynamically more favorable n-butyl derivative. Further investigation of the reactivity of 'Bu_2Mg' is currently in progress. In any event the metal centers in mixture **10** are protected from solvation by steric crowding. This is further evidence that it is the unique bonding mode of the 2-pyridyl ligand that is associated with the unexpected solvation reaction. The 2-pyridyl unit's relatively flat, sterically undemanding character, coupled with the sp^2 hybridized nature of the pyridyl N atom attached to Mg, may result in part of the metal surface being exposed to attack by solvent molecules. Another aspect of the flexibility of the ligand is that the pyridyl group and the second unit bound to the amido nitrogen (phenyl, pyridyl or methyl) can tilt out of each others way, which may allow space for donor solvent attack at the metal. The assumption that the alkyl(amido) 'intermediate' is dimeric appears reasonable from previous research results. Dimeric structures have been found in the solid state for alkyl(amido) compounds containing a chelating ligand, the classic example being $[\{Me(Me_2NCH_2CH_2)NMgMe\}_2]$ [15] which adopts a structure akin to that of **3**. Similar dimers are found for the non-chelating dinitrogen species $[\{(Me_3P)_3CoN{=}NMg^tBu\cdot(Et_2O)\}_2]$ [16], which utilizes two ether molecules for donation, and the aforementioned compound $[\{(Me_3Si)_2NMg^sBu\}_2]$ [14] which has the unusual coordination number of three at the metal. Monomeric structures may be produced only when the ligands present are large and bulky, as with the carbazole derivative $[(C_{28}H_{40}N)MgEt\cdot(THF)_2]$ [17], which to our knowledge is the only simple alkyl(amido)magnesium monomer to be crystallographically characterized. Dimeric alkyl(amido) compounds have also been observed as the predominant species in solution using both ebullioscopic [18] and proton NMR [19] experiments. In the light of these previous studies the most likely structure for the chelating alkyl(amido) 'intermediates' are dimers of the form $[\{R(2\text{-pyr})NMgBu\}_2]$ with each of the metal centers being coordinated by a pyridyl nitrogen leading to tetracoordination at the magnesiums.

The type of donor required to induce the disproportionation reaction may be varied from a relatively small molecule such as THF to a much bulkier, chelating group such as PMDETA. Consequently, it is reasonable to assume that complexation of the metal occurs with

Table 1
Products from reaction of 'Bu_2Mg' solution with amine and donor solvent

Amine	Donor solvent	Isolated product	Compound
Ph(2-pyr)NH	THF	$[\{Ph(2\text{-pyr})N\}_2Mg\cdot(THF)_2]$	**1**
Ph(2-pyr)NH	TMEDA	$[\{\{Ph(2\text{-pyr})N\}_2Mg\cdot(TMEDA)\}_n]$	**4**
Ph(2-pyr)NH	PMDETA	$[\{\{Ph(2\text{-pyr})N\}_2Mg\cdot(PMDETA)\}_n]$	**5**
$(2\text{-pyr})_2NH$	TMEDA	$[\{\{(2\text{-pyr})_2N\}_2Mg\cdot(TMEDA)\}_n]$	**6**
$(2\text{-pyr})_2NH$	PMDETA	$[\{\{(2\text{-pyr})_2N\}_2Mg\cdot(PMDETA)\}_n]$	**7**
Me(2-pyr)NH	TMEDA	$[\{\{Me(2\text{-pyr})N\}_2Mg\cdot(TMEDA)\}_n]$	**8**
$(2\text{-pyr})_2NH$	none	$[\{(2\text{-pyr})_2NMg^{n/s}Bu\}_n]$	**9**
$BzNHEtNMe_2$ [a]	THF/TMEDA or PMDETA	$[\{Bz(Me_2NEt)NMg^{n/s}Bu\}_n]$	**10**

[a] Abbreviation for $PhCH_2NHCH_2CH_2NMe_2$.

Table 2
^{1}H NMR chemical shift values for the 2-pyridyl groups of the amide ligands (deuterated solvent chosen, benzene or toluene, dependent on the compound's relative solubility)

Compound	Solvent	α	β	β'	γ
[{Ph(2-pyr)N}$_2$Mg · (THF)$_2$] **1**	C_6D_6	7.73	6.00	6.99	6.99
[{{Ph(2-pyr)N}$_2$Mg · (TMEDA)}n] **4**	C_6D_6	7.57	5.98	6.79	6.94
[{{Ph(2-pyr)N}$_2$Mg · (PMDETA)}$_n$] **5**	C_6D_6	7.67	5.98	6.80	6.89
[{{(2-pyr)$_2$N}$_2$Mg · (TMEDA)}$_n$] **6**	C_7D_8	7.95	6.11	6.88	6.98
[{{(2-pyr)$_2$N}$_2$Mg · (PMDETA)}$_n$] **7**	C_7D_8	7.92	6.12	6.88	7.09
[{{Me(2-pyr)N}$_2$Mg · (TMEDA)}$_n$] **8**	C_6D_6	7.53	5.92	6.12	7.19

ease in the alkyl(amido) compound. This is also supported by the fact that these reactions proceed under very mild conditions (ambient temperature) and that the products are obtained simply on cooling the resulting solutions. The generality of this reaction has been increased to cover two more 2-pyridyl containing amines, (2-pyr)$_2$NH and Me(2-pyr)NH. Although attempts were made at isolating all the species produced at both the alkyl(amido) stage and also after solvation with either THF, TMEDA or PMDETA, only those listed in Table 1 were fully isolated and identified. This was mainly due to the high hydrocarbon solubility of some of the species produced, which led to difficulty in their separation. Such high solubility is not surprising given their expected low oligomerisation or monomeric state. It is pertinent to note that reaction of PhCH$_2$NHCH$_2$CH$_2$NMe$_2$ with 'Bu$_2$Mg' yields the expected alkyl(amido) compound **10** regardless of which donor solvent is present. No further reaction can take place in this instance since the magnesium is protected from attack [12].

A more detailed examination of the bis(amides) prepared reveals that a common structure may prevail. Each either contains one TMEDA or PMDETA unit or alternatively two THF molecules. Since internal ligation from the nitrogen of the 2-pyridyl ring is almost certain, as evidenced from the crystal structure of **1** [12], each metal center should contain (at least) tetracoordination from the two amide ligands. Donation of two nitrogens from the TMEDA or PMDETA will yield a structure similar to that of **1**, *i.e.* a monomer with a six-coordinate magnesium. Formation of the bis(THF) solvated *pseudo*-octahedral compound **1** takes place even if only one equivalent of donor is added, *i.e.* no solid monosolvated product is yielded. A strong preference must therefore exist for the formation of the six-coordinate magnesium center even though this implies that other metal centers must remain tetracoordinated in the alkyl(amido) dimer. The PMDETA ligand has the possibility of tricoordination. Also, in the case of the (2-pyr)$_2$N$^-$ containing compounds it is possible that further coordination may be achieved from the nitrogen of the second 2-pyridyl unit. In order to further investigate these questions a ^{1}H/^{13}C NMR study was undertaken. From these results it may be possible to provide information on the solution nature of these species and to consider if any comparisons and conclusions may be drawn with the known solid state structures.

2.2. NMR studies

Tables 2 and 3 lists the ^{1}H and ^{13}C NMR chemical shift values for the 2-pyridyl group of the bis(amides). As mentioned previously, an interesting feature of the compounds listed is the denticity of the donors used. THF is monodentate (binding through oxygen), TMEDA has the possibility to be didentate [20] (binding through nitrogen), while PMDETA has the possibility to be tridentate [21] (also binding through nitrogen). Remarkably similar chemical shift values for the anion are found for the TMEDA and PMDETA complexes of Ph(2-pyr)N$^-$, **4** and **5**, and also for those of (2-pyr)$_2$N$^-$, **6** and **7**. The averaged chemical shift difference for the ^{1}H and ^{13}C NMR spectra between **4** and **5** is only 0.03 ppm in both instances. A similar situation is found for **6** and **7** where the averaged ^{1}H chemical shift difference is 0.04 ppm and only 0.02 ppm for the ^{13}C spectra. Such similar chemical shift values in both the ^{1}H and ^{13}C NMR spectra is strong evidence for similar structures in solution [22]. This is reasonable to assume since

Table 3
^{13}C NMR chemical shift values for the 2-pyridyl groups of the amide ligands (run in the same deuterated solvents as listed in Table 2)

Compound	α	β	β'	γ	IPSO
[{Ph(2-pyr)N}$_2$Mg · (THF)$_2$] **1**	147.44	107.77	110.11	139.23	164.36
[{{Ph(2-pyr)N}$_2$Mg · (TMEDA)}$_n$] **4**]	146.62	106.79	107.21	138.70	167.20
[{{Ph(2-pyr)$_2$Mg · (PMDETA)}$_n$}] **5**	146.69	106.80	107.25	138.73	167.18
[{{(2-pyr)$_2$N}$_2$Mg · (TMEDA)}$_n$] **6**	146.80	111.90	112.40	137.97	163.55
[{{(2-pyr)$_2$N}$_2$Mg · (PMDETA)}$_n$] **7**	146.80	111.91	112.42	137.98	163.58
[{{Me(2-pyr)N}$_2$Mg · (TMEDA)}$_n$] **8**	146.68	103.49	103.54	138.62	169.73

the electronic environments of both sets of compounds appear to be almost identical. It is likely that the TMEDA ligand in **4**, **6** and **8** binds to the metal center in a didentate fashion resulting in a monomer similar to that of **1** with a magnesium coordination number of six. The probable structure for **5** and **7** is therefore a monomer with two nitrogen atoms bound to the metal leaving one nitrogen of the PMDETA hanging free. Such asymmetrical structures are known in the solid state for the PMDETA ligand [23], though it usually adopts a tridentate conformation [21]. It seems unlikely that coordination of all four pyridyl nitrogens in compounds **6** and **7** can take place in addition to the presence of the donor ligands TMEDA and PMDETA. Such a situation would create a coordination number of greater than six at the metal. Organomagnesium compounds are usually tetracoordinated in both the solid and solution states [24], though magnesium has a strong predilection for a coordination number of six in other types of compound, as recently noted in a structural review [25]. The bis(amido) compounds **1** and **4–8** reported here are probably six-coordinate and this makes them relatively rare examples of *pseudo*-octahedral organomagnesiums. With this in mind it would be extremely doubtful if enough space is available for more than six bonds to the metal in these species.

2.3. Theoretical studies

Calculations on a model system using $(NHCH{=}NH)^-$ as amide anion, methyl as the organic unit and water as donor solvent were conducted at the HF/6-31G* level using the Gaussian 94 program for the geometry optimizations [26]. The aza-allyl amide was chosen as a model since it has an sp^2 β nitrogen available for chelation, similar to the 2-pyridyl containing amines. Water was chosen as the simplest form of solvent, although in reality this would of course react to

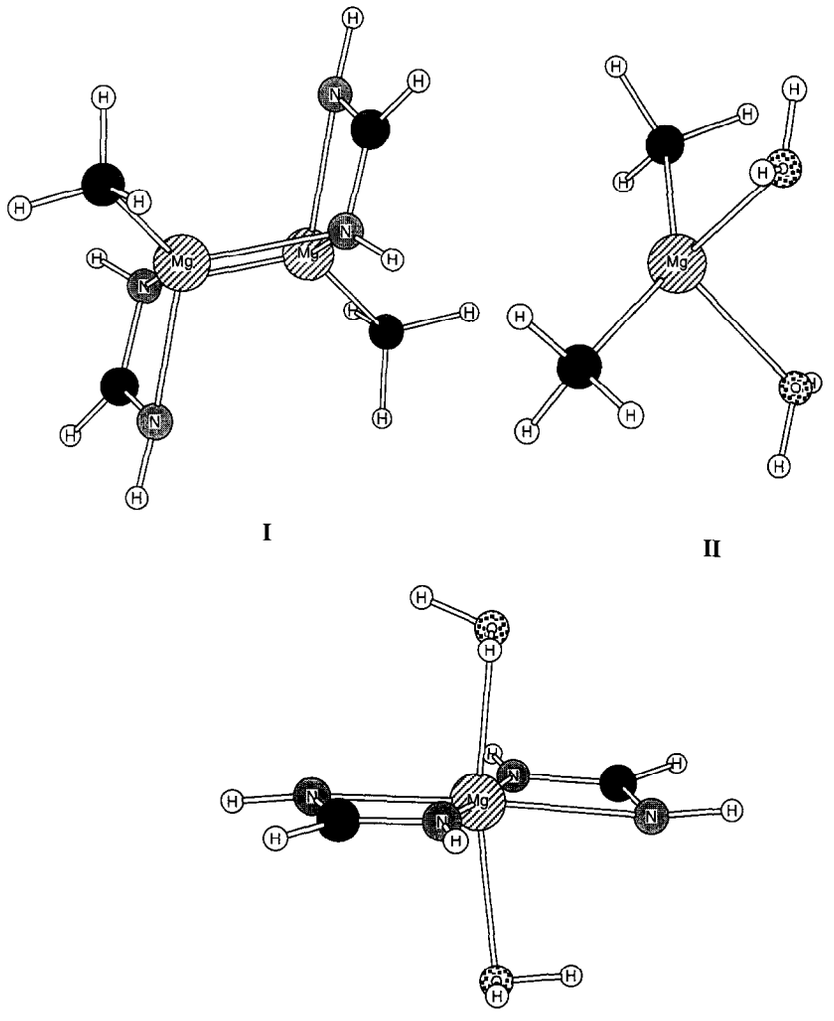


Fig. 2. Geometry optimized structures I–III.

form $Mg(OH)_2$. Formation of monomeric dialkylmagnesium appears to be reasonable from previous NMR evidence [27]. The geometry optimized structures of the components involved are shown in Fig. 2 [28]. The energy of the disproportionation reaction was calculated according to Eq. (3) and found to be exothermic by -21.8 kcal mol^{-1}.

$$[\{NH{=}CHN(H)MgMe\}_2] + 4H_2O \rightarrow [\{NH{=}CHN(H)\}_2Mg \cdot (H_2O)_2] + [Me_2Mg \cdot (H_2O)_2] \quad (3)$$

All the structures outlined in Fig. 2 have features comparable with known structures. The step-like alkyl(amido) dimer **I** is similar to the silylamido dianion $[\{SiMe_2(^tBuN)_2Mg \cdot (THF)\}_2]$ [29]. A common structural theme for dialkylmagnesium compounds is a tetracoordinate monomer such as **II** [30]. Lastly, we know from our own crystal structure evidence that the octahedral bis(amido) derivatives such as **III** are stable [12]. The exothermicity of Eq. (3) supports the experimental observations for the disproportionation reaction.

3. Conclusions

In summary, we have given further evidence that the addition of donor solvent to an alkyl(amido)magnesium compound containing a 2-pyridyl amine unit causes a disproportionation reaction which yields the respective bis(amido) and bis(organo)magnesium compounds. It appears that it is the 'flat', flexible character of the ligands in the 'intermediate' alkyl(amido) compound which allows solvation and encourages subsequent cleavage of the compound. We reiterate that the driving force for alkyl(amido) cleavage lies in the effective increase in coordination number at the metal center. The reactions studied so far in this series show that the type of donor solvent used and the nature of the second organic group of the amine do not affect the outcome of the reaction, *i.e.* disproportionation proceeds regardless of which donor solvent is chosen or which R group is on the amine along with the 2-pyridyl unit.

4. Experimental

4.1. Syntheses

All syntheses were conducted in Schlenk type glassware under a blanket of argon gas. The metallated compounds isolated were all found to be highly air and moisture sensitive and were handled in an argon filled glove box fitted with a recirculating column.

Preparation of all of the bis(amides) was carried out in a similar manner. Dibutylmagnesium (purchased from Aldrich as a one molar solution in heptane, containing a 1:1 ratio of n-butyl to s-butyl units) (10 mmol) was added dropwise to a stirred solution of amine (Ph(2-pyr)NH, $(2\text{-pyr})_2NH$ or Me(2-pyr)NH) (10 mmol) in 10 ml of toluene. After gas evolution ceased, a clear yellow solution remained. Donor solvent (THF, TMEDA or PMDETA) (10 mmol) was added to the stirred solutions showing no visible change. Conditions for the precipitation of solid material varied between reactions and are outlined individually. The solids were filtered from solution, washed with hexane (2×2 ml) and dried under vacuum. Yields reported represent the first batch of solid material produced.

$[\{Ph(2\text{-pyr})N\}_2Mg \cdot (THF)_2]$ **1**. Pale yellow crystals were formed after one day at ambient temperature. Analyses of these crystals have been reported previously [12].

$[\{Ph(2\text{-pyr})N\}_2Mg \cdot (TMEDA)]$ **4**. On standing at -4°C for two days a small amount of yellow microcrystalline solid was deposited from solution. Yield (based on consumption of amine) 6%; m.p. 209–212°C. Anal. Found: C, 72.2; H, 7.1; N, 16.9; Mg, 4.7. $C_{28}H_{34}N_6Mg$ Calc.: C, 70.2; H, 7.1; N, 17.6; Mg, 5.1%.

$[\{Ph(2\text{-pyr})N\}_2Mg \cdot (PMDETA)]$ **5**. Large orange crystals were obtained after 4 h at ambient temperature. Yield 68%; m.p. 123°C. Anal. Found: C, 69.5; H, 8.1; N, 17.7; Mg, 4.5. $C_{31}H_{41}N_7Mg$ Calc.: C, 69.5; H, 7.5; N, 18.3; Mg, 4.5%.

$[\{(2\text{-pyr})_2N\}_2Mg \cdot (TMEDA)]$ **6**. On stirring the solution at ambient temperature for 1 h a yellow solid was precipitated from solution. Yield 52%; m.p. 136–138°C. Anal. Found: C, 65.0; H, 6.2; N, 22.1; Mg, 4.9. $C_{26}H_{32}N_8Mg$ Calc.: C, 65.0; H, 6.7; N, 23.3; Mg, 5.0%.

$[\{(2\text{-pyr})_2N\}_2Mg \cdot (PMDETA)]$ **7**. On standing for 12 h at -4°C a deep yellow solid was gleaned from solution. Yield 36%; m.p. 82–84°C. Anal. Found: C, 68.1; H, 7.4; N, 21.8; Mg, 4.4. $C_{29}H_{39}N_9Mg$ Calc.: C, 64.8; H, 7.2; N, 23.4; Mg, 4.5%.

$[\{Me(2\text{-pyr})N\}_2Mg \cdot (TMEDA)]$ **8**. After one day at -20°C a pale yellow solid was deposited from solution. Yield 83%; m.p. 115–117°C. Anal. Found: C, 61.5; H, 8.3; N, 23.5; Mg, 6.8. $C_{18}H_{30}N_6Mg$ Calc.: C, 61.0; H, 8.5; N, 23.7; Mg, 6.8%.

$[(2\text{-pyr})_2NMg^{n/s}Bu]$ **9**. The reaction was conducted as outlined above with the exception that no donor solvent was added to the solution. This solution yielded a bright yellow microcrystalline material on standing at ambient temperature for 12 h. Yield 34%; decomposed above 160°C. Anal. Found: C, 66.8; H, 7.0; N, 16.3; Mg, 9.7. $C_{14}H_{17}N_3Mg$ Calc.: C, 66.8; H, 6.8; N, 16.7; Mg, 9.7%.

$[PhCH_2(Me_2NCH_2CH_2)NMg^{n/s}Bu]$ **10**. A solution of dibutylmagnesium (10 mmol) in 10 ml of pentane was stirred while the amine *N'*-benzyl-*N*,*N*-dimethyl-

ethylenediamine (10 mmol) was added. Gas evolution was observed and the solution changed color from pale yellow to pale pink. On standing the resulting solution for 12 h at −4°C small pink needles were obtained. Yield 9%; m.p. of mixture 94–96°C. Anal. Found: C, 69.7; H, 10.4; N, 11.1; Mg, 10.0. $C_{15}H_{26}N_2Mg$ Calc.: C, 69.7; H, 10.1; N, 10.8; Mg, 9.4%.

4.1.1. IR spectra (Perkin-Elmer 457 grating spectrometer; cm^{-1}; Nujol mulls)

4: 2920s, 2875s, 1604s, 1585s, 1538m, 1465s, 1434s, 1380s, 1300s, 1285m, 1239m, 1171m, 1150s, 1063m, 1038m, 1010m, 998s, 951m, 849m, 834m, 819m, 800m, 762s, 754s, 737s, 700s, 660m, 642m, 592w, 581m, 513m, 480w, 444w, 428m, 419w, 295w.

5: 2925s, 2850s, 1602s, 1538s, 1537m, 1467s, 1440s, 1387s, 1311m, 1299s, 1290w, 1261w, 1238m, 1173m, 1153m, 1108w, 1025m, 997m, 989m, 945w, 901w, 860w, 835w, 820w, 808w, 762w, 739m, 705m, 700m, 660w, 623w, 530m, 394w.

6: 2921s, 2859s, 1590s, 1552m, 1465s, 1431s, 1380s, 1300s, 1286s, 1255w, 1168w, 1142m, 1025w, 1000m, 996w, 950w, 910m, 866m, 825w, 798m, 785m, 774m, 731m, 690w, 550w, 429w.

7: 2925s, 2859s, 1590s, 1552s, 1470s, 1430s, 1377s, 1305s, 1284m, 1248m, 1144s, 1105w, 1050m, 998s, 985m, 950m, 911m, 863m, 830w, 799w, 775s, 745w, 735s, 688w, 640w, 625w, 549m, 530w, 428m.

8: 2922s, 2854s, 1751w, 1600s, 1535w, 1491s, 1460s, 1404m, 1370m, 1300m, 1255w, 1154m, 1073w, 1031w, 979w, 950w, 803w, 760m, 731m, 699w, 639w.

9: 2930s, 2855s, 1464s, 1378m, 1346m, 1302w, 1288w, 1276w, 1252w, 1189w, 1168w, 1110m, 1074w, 1026m, 953w, 937m, 847m, 778m, 729m, 700m, 664m, 500w, 541w.

10: 2920s, 2845s, 2785m, 1607s, 1598s, 1556m, 1470s, 1434s, 1380m, 1360s, 1305m, 1288m, 1249w, 1153m, 1106w, 1064w, 1014m, 982w, 902w, 873w, 808w, 839m, 778s, 750m, 739m, 666w, 626m, 542w, 495m, 480m, 420w.

4.1.2. ^1H NMR spectra (Bruker AMX 400 MHz, 300 K)

4: Ph (*p*H, 2H, m, ∂6.94; *o*H, 4H, d, ∂7.23; *m*H, 4H, t, 7.30) Pyr (βH, 2H, m, ∂5.98; β'H, 2H, m, ∂6.79; γH, 2H, m, ∂6.94; αH, 2H, m, ∂7.57) TMEDA (CH_2, 4H, s, ∂1.70; CH_3, 12H, s, ∂1.92) in C_6D_6.

5: Ph (*p*H, 2H, ∂6.97; *o*H, 4H, ∂7.21; *m*H, 4H, ∂7.27) Pyr (βH, 2H, m, ∂5.98; β'H, 2H, m, ∂6.80; γH, 2H, m, ∂6.89; αH, 2H, m, ∂7.67) PMDETA (CH_3, 12H, s, ∂1.92; CH_2, 4H, m, ∂1.98; CH_3, 3H, s, ∂2.09; CH_2, 4H, m, 4H, ∂2.39) in C_6D_6.

6: Pyr (βH, 4H, m, ∂6.11; β'H, 4H, m, ∂6.88; γH, 4H, m, ∂6.98; αH, 4H, m, ∂7.95) TMEDA (CH_3, 12H, s, ∂2.10; CH_2, 4H, s, ∂2.32) in toluene-d_8.

7: Pyr (βH, 4H, m, ∂6.12; β'H, 4H, m, ∂6.88; γH, 4H, m, ∂7.09; αH, 4H, m, ∂7.92) PMDETA (CH_3, 12H, s, ∂2.12; CH_3, 3H, s, ∂2.18; CH_2, 4H, t, ∂2.34; CH_2, 4H, t, ∂2.46) in toluene-d_8.

8: Me (∂2.80, s) Pyr (βH, 4H, m, ∂5.92; β'H, 4H, m, ∂6.12; γH, 4H, m, ∂7.19; αH, 4H, m, ∂7.53) in C_6D_6.

9: Pyr (β_aH, 1H, m, ∂6.11; β_bH, 1H, m, ∂6.25; β'_aH, 1H, m, ∂6.71; β'_bH/γ_aH, 1H/1H, m, ∂6.80; γ_bH/α_aH, 1H/1H, m, ∂7.00; α_bH, 1H, m, ∂7.75) $^{n/s}$Bu (series of overlapping multiplets ∂0.18–∂2.23, with characteristic CH_2–Mg triplet of ^{n}Bu at ∂0.51 and CH_3CH–Mg doublet at ∂1.53) in toluene-d_8.

10: the ^{1}H NMR spectrum of this compound was very complex owing to the high degree of secondary splitting leading to overlapping signals, compounded by the fact that two components ^{n}Bu and ^{s}Bu were present (characteristic CH_2–Mg triplet of ^{n}Bu at ∂0.15 and CH multiplet of ^{s}Bu at ∂0.37) in C_6D_6.

4.1.3. ^{13}C NMR spectra

1: Ph (*p*C, 121.38 ppm; *o*C, 122.65 ppm; *m*C, 129.80 ppm; *i*C, 148.69 ppm) Pyr (βC, 107.77 ppm; β'C, 110.11; γC, 139.23 ppm; αC, 147.55 ppm; *i*C, 164.36 ppm) THF (CH_2, 25.90 ppm; OCH_2, 68.68 ppm) in C_6D_6.

4: Ph (*p*C, 120.61 ppm; *o*C, 124.25 ppm; *m*C, 129.75 ppm; *i*C, 152.73 ppm) Pyr (βC, 106.79 ppm; β'C, 107.21; γC, 138.70 ppm; αC, 146.62 ppm; *i*C, 167.20 ppm) TMEDA (CH_3, 46.65 ppm; CH_2, 56.76 ppm) in C_6D_6.

5: Ph (*p*C, 120.62 ppm; *o*C, 124.30 ppm; *m*C, 129.76 ppm; *i*C, 152.67 ppm) Pyr (βC, 106.80 ppm; β'C, 107.25; γC, 138.73 ppm; αC, 146.69 ppm; *i*C, 167.18 ppm) PMDETA (CH_3, 42.28 ppm; CH_3, 46.30 ppm; CH_2, 57.50 ppm) in C_6D_6.

6: Pyr (βC, 111.90 ppm; βC, 111.40; γC, 137.97 ppm; αC, 146.80 ppm; *i*C, 163.55 ppm) TMEDA (CH_3, 45.97 ppm; CH_2, 58.41 ppm) in toluene-d_8.

7: Pyr (βC, 111.91 ppm; β'C, 112.42; γC, 137.98 ppm; αC, 146.80 ppm; *i*C, 163.58 ppm) PMDETA (CH_3, 43.12 ppm; CH_3, 45.99 ppm; CH_2, 56.97 ppm; CH_2, 58.39 ppm) in toluene-d_8.

8: Me (34.49 ppm) Pyr (βC, 103.49 ppm; β'C, 103.54; γC, 138.62 ppm; αC, 146.68 ppm; *i*C, 169.73 ppm) TMEDA (CH_3, 46.33 ppm; CH_2, 58.80 ppm) in C_6D_6.

^{13}C NMR spectra of **9** and **10** were of little diagnostic value due to numerous overlapping peaks arising from the mixture of compounds.

Assignment of the spectra was aided by the use of *J*mod, COSY 45 and C–H correlation experiments.

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References and notes

[1] M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1980; M. Veith, *Adv. Organomet. Chem., 31* (1990) 269; A.G. Pinkus, *Coord. Chem. Rev., 25* (1978) 173; A.W. Duff, P.B. Hitchcock, M.F. Lappert, R.G. Taylor and J.A. Segal, *J. Organomet. Chem., 293* (1985) 271; for a review of the early work on alkyl(amido)magnesiums see B.J. Wakefield, *Adv. Inorg. Chem. Radiochem., 11* (1968) 341.

[2] W.E. Lindsell, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 1, Pergamon Press, Oxford, 1982, Chapter 4; C.H. Heathcock, in B.M. Trost and I. Flemming (eds.), *Comprehensive Organic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1991, Chapter 1.6.

[3] J.J. Eisch and R. Sanchez, *J. Organomet. Chem., 296* (1985) C27; P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, P. Van Der Sluis and A.L. Spek, *J. Organomet. Chem., 393* (1990) 315.

[4] N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984; A.G. Massey, *Main Group Chemistry*, Ellis Horwood, Chichester, 1990.

[5] B.J. Wakefield, *Organolithium Methods*, Academic Press, London, 1988.

[6] D.A. Whiting, *Aldrichim. Acta, 19* (1986) 31; N.D.R. Barnett, R.E. Mulvey, W. Clegg and P.A. O'Neil, *J. Am. Chem. Soc., 113* (1991) 8187.

[7] R.D. Rodgers, J.L. Atwood and R. Grüning, *J. Organomet. Chem., 157* (1978) 229.

[8] D.A. Evans, in J.D. Morrison (ed.), in *Asymmetric Synthesis*, Vol. 3, Academic Press, New York, 1984, p. 1.

[9] R.E. Mulvey, *Chem. Soc. Rev., 20* (1991) 167; K. Gregory, P.v.R. Schleyer and R. Snaith, *Adv. Inorg. Chem., 31* (1991) 47; E. Weiss, *Angew. Chem., 105* (1993) 1565; *Angew. Chem., Int. Ed. Engl., 32* (1993) 1501; P.G. Williard, in B.M. Frost and I. Flemming (eds.), *Comprehensive Organic Synthesis*, Vol. 1, Pergamon Press, Oxford, 1991, Chapter 1.

[10] P.E. Eaton, C.H. Lee and Y. Xiong, *J. Am. Chem. Soc., 111* (1989) 8016; P.E. Eaton, Y. Xiong and J.P. Zhou, *J. Org. Chem., 57* (1992) 4277; N.A. Van Draanen, S. Arseniyadis, M.T. Crimmins and C.H. Heathcock, *J. Org. Chem., 56* (1991) 2499.

[11] G. Dozzi, G. Del Piero, M. Cesari and S. Cucinella, *J. Organomet. Chem., 190* (1980) 229.

[12] K.W. Henderson, R.E. Mulvey, P.A. O'Neil and W. Clegg, *J. Organomet. Chem., 439* (1992) 237.

[13] K.W. Henderson, R.E. Mulvey, P.A. O'Neil and W. Clegg, *Polyhedron, 20* (1993) 2535.

[14] L.M. Engelhardt, B.S. Jolly, P.C. Junk, C.L. Raston, B.W. Skelton and A.H. White, *Aust. J. Chem., 39* (1986) 1337.

[15] V.R. Magnuson and G.D. Stucky, *Inorg. Chem.*, 8 (1969) 1427.

[16] H.F. Klein, H. Konig, S. Koppert, K. Ellrich and J. Riede, *Organometallics, 6* (1987) 1341.

[17] N. Kuhn, M. Schulten, R. Boese and D. Blaser, *J. Organomet. Chem., 1* (1991) 421.

[18] E.C. Ashby, Li-Chung Chao and H.M. Neumann, *J. Am. Chem. Soc., 95* (1973) 5186.

[19] G.E. Coats and D. Ridley, *J. Chem. Soc. A*, (1967) 56.

[20] M.A. Nichols and P.G. Williard, *J. Am. Chem. Soc., 115* (1993) 1568; N.D.R. Barnett, R.E. Mulvey, W. Clegg and P.A. O'Neil, *J. Am. Chem. Soc., 115* (1993) 1573.

[21] P.C. Andrews, R.E. Mulvey, W. Clegg and D. Reed, *J. Organomet. Chem., 368* (1990) 287.

[22] L.M. Jackman, L.M. Scarmoutzous, B.D. Smith and P.G. Williard, *J. Am. Chem. Soc., 110* (1988) 6058; J.S. DePue and D.B. Collum, *J. Am. Chem. Soc., 110* (1988) 5518; A.S. Galiano-Roth, E.M. Michaelides and D.B. Collum, *J. Am. Chem. Soc., 110* (1988) 2658; N. Kallman and D.B. Collum, *J. Am. Chem. Soc., 109* (1987) 7466.

[23] P.C. Andrews, R.E. Mulvey and W. Clegg, *Angew. Chem., 102* (1990) 1480, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1440.

[24] P.R. Markies, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets and A.L. Spek, *Adv. Organomet. Chem., 32* (1991) 147.

[25] C.E. Holloway and M. Melink, *J. Organomet. Chem., 465* (1994) 1.

[26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Repogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkely, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, *Gaussian 94 (Revision A.1)*, Gaussian Inc., Pittsburgh, PA, 1995.

[27] G.E. Parris and E.C. Ashby, *J. Am. Chem. Soc., 93* (1971) 1206; E.C. Ashby, F.W. Walker and H.M. Neumann, *Chem. Commun.*, (1970) 330.

[28] Absolute energies (Hartrees) of the optimized structures **I** −775.56711; H_2O −76.01075; **II** −648.77935 and **III** −430.86551.

[29] M. Veith, W. Frank, F. Tollner and H. Lange, *J. Organomet. Chem., 326* (1987) 315.

[30] D. Thoennes and E. Weiss, *Chem. Ber., 111* (1978) 3381; T. Greiser, J. Kopf, D. Thoennes and E. Weiss, *J. Organomet. Chem., 191* (1980) 1; H. Viebrock and E. Weiss, *J. Organomet. Chem., 464* (1994) 121; J. Toney and G.D. Stucky, *J. Organomet. Chem., 22* (1970) 241; P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, P. van der Sluis and A.L. Spek, *J. Organomet. Chem., 393* (1990) 315.