DALTON
FULL PAPER

An unexpected transamination of bis[bis(trimethylsilyl)amido]zinc with dibenzylamine to form bis(dibenzylamido)zinc: structural studies by NMR spectroscopy, X-ray crystallography and theoretical calculations

David R. Armstrong,[a] Glenn C. Forbes,*[a] Robert E. Mulvey,*[a] William Clegg[b] and Duncan M. Tooke[b]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL. E-mail: r.e.mulvey@strath.ac.uk*
[b] *Department of Chemistry, University of Newcastle, Newcastle-Upon-Tyne, UK NE1 7RU*

Received 22nd November 2001, Accepted 5th February 2002
First published as an Advance Article on the web 26th March 2002

The transamination of bis[bis(trimethylsilyl)amido]zinc with two molar equivalents of dibenzylamine in benzene solution yields the dimeric, homoleptic, zinc bis(amide) $[\{(PhCH_2)_2N\}_2Zn]_2{\cdot}C_6H_6$ **1**. Characterisation of compound **1** has been performed by single-crystal X-ray diffraction, $^1H/^{13}C$ NMR spectroscopy, IR spectroscopy, melting point and elemental analysis. Variable concentration ^1H NMR spectroscopic studies have shown a dynamic monomer–dimer equilibrium in arene solution. Compound **1** is compared to the previously reported, isostructural magnesium analogue and other known zinc bis(amide) compounds. Theoretical calculations have been carried out at both SCF and DFT levels to probe the energetics involved in the transamination process.

Introduction

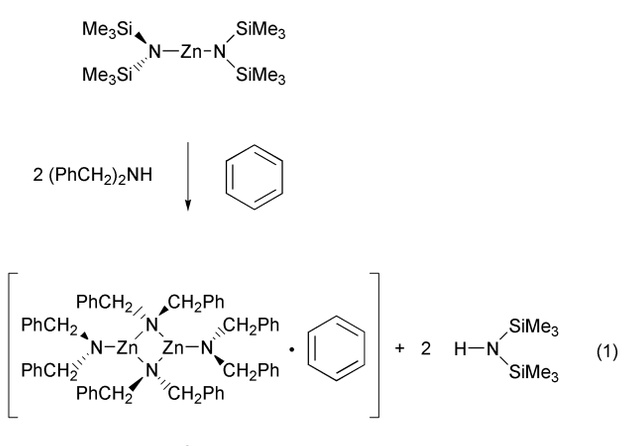
The beginning of organometallic chemistry is usually associated with the synthesis of diethylzinc[1] by Frankland in 1849, the intention of which was to prepare ethyl radicals from iodoethane and zinc powder. However, it took a significant amount of time thereafter until the α-halogenoester-derived zinc enolates pioneered by Reformatsky[2] became the first synthetically useful organometallic reagents at the turn of the 20th century. Subsequently, these were superseded by the more reactive and more easily prepared Grignard reagents.[3] Organozinc reagents received scant attention until recently with moderate interest in, for example, Simmons–Smith type cyclopropanations[4] and Reformatsky reactions.[5] However, due to their low reactivity, organozinc reagents are tolerant to many more functional groups compared with their lithium and magnesium counterparts and their synthetic utility is being re-examined. Among the most useful examples are the catalytic asymmetric addition to aldehydes[6] and the nickel- and palladium-catalysed cross-coupling reactions with organohalides.[7] Additionally, organozinc compounds of the form R_2Zn, $RZn(NR'_2)$ or $(R_2N)_2Zn$ also have potential applications as p-type dopants in the semiconductor/electronics industry.[8]

We are interested in the synergic effects brought about by the incorporation of compounds of the form $(R_2N)_2M$, where M = Zn or Mg, in the same molecular environment as alkali metal amides, $(R_2N)M$, where M = Li, Na or K. Our group has observed several examples of unprecedented synergism in these heterobimetallic systems to date.[9] Of most importance are the regioselective deprotonation of ferrocene[10] and of arene molecules in thermodynamically unfavourable positions.[11] Also of interest is the selective encapsulation of oxide or peroxide.[12] In our quest to extend this heterobimetallic work to new ligand systems, we have focussed on the dibenzylamido ligand, as previously this has been shown to display an interesting and versatile structural chemistry.[13]

Here we report the synthesis and characterisation of a new homoleptic zinc bis(amide) $[\{(PhCH_2)_2N\}_2Zn]_2{\cdot}C_6H_6$ **1**. This follows the structural characterisation of a number of zinc bis(amides) over the past ten years, including other dimers: $[(Ph_2N)_2Zn]_2$,[14] $[(Bu^i{}_2N)_2Zn]_2$,[15] $[\{[Ph(Me_3Si)]N\}_2Zn]_2$[16] and $[\{(Me_2SiCH_2CH_2Me_2Si)N\}_2Zn]_2$.[17] A comparison can also be made with the known isostructural magnesium derivative $[\{(PhCH_2)_2N\}_2Mg]_2$ which has been studied both in the solid state[18] and solution.[19] To the best of our knowledge, this allows the first direct structural comparison between dimeric zinc and magnesium bis(amides) in the solid state.

Results and discussion

The new homoleptic amide complex **1** was synthesised from what is seemingly a routine transamination *viz.* the reaction of bis[bis(trimethylsilyl)amido]zinc with dibenzylamine in benzene (eqn. (1)). Crystallisation at ambient temperature gave compound **1** as the only solid found to crystallise from solution. One benzene solvent molecule per dimer crystallises in the lattice.

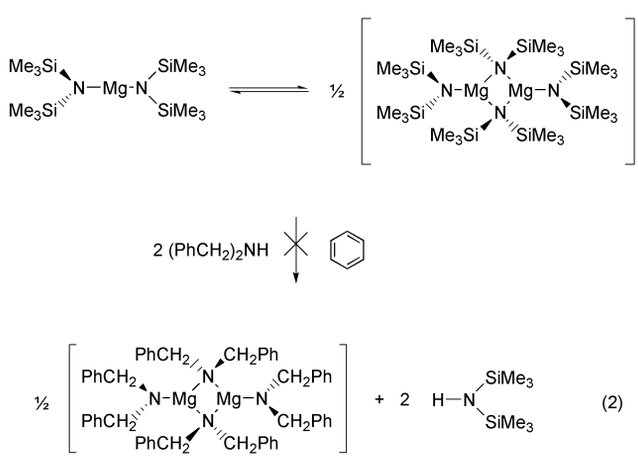


There is no precedent for this specific transamination in amido chemistry. Conventionally, one would normally expect

 DOI: 10.1039/b110696a

bis(trimethylsilyl)amine to displace a dibenzylamido unit from a metal centre (*e.g.* zinc), based purely on the relative thermodynamic acidities of the N*H* protons on each of the parent amines.[20] Here we find the opposite *i.e.* dibenzylamine displaces bis(trimethylsilyl)amide. A possible driving force for this transamination reaction is an increase in the coordination number at the zinc centre. Due to the inherent steric bulk of the trimethylsilyl-substituents, the coordinatively unsaturated zinc bis(amide) [{$(Me_3Si)_2N$}$_2$Zn] is monomeric[21] in the gas phase, although its solid state structure is yet to be determined. ^{1}H NMR spectroscopic evidence supports a monomeric structure in solution, since a singlet is observed at 0.20 ppm in C_6D_6 at 300 K, showing all silyl protons to be equivalent. The closely related compounds [{[Bu^t(Me_3Si)]N}$_2$Zn],[22] [{$(Ph_2MeSi)_2$N}$_2$Zn][23] and [$(Bu^t_2N)_2$Zn][15] are all similarly monomeric (in the solid state). Conversely, the less sterically demanding nature of the silylamido-ligand 2,2,5,5-tetramethyl-2,5-disila-1-aza-cyclopentanide (mean Si–N–Si angle 109° *cf.* 129° in [{$(Me_3Si)_2$N}$_2$Zn]), present in [{$(Me_2SiCH_2CH_2Me_2Si)N$}$_2$Zn]$_2$,[17] permits formation of a dimeric structure. The electronics of 2,2,5,5-tetramethyl-2,5-disila-1-aza-cyclopentanide are not too far removed from those of bis(trimethylsilyl)amide and therefore steric effects must play a greater role in determining the aggregation state of these zinc bis(amides) than electronic considerations. In compound **1**, transamination of the bis-(trimethylsilyl)amido-ligand by the less sterically demanding dibenzylamido-functionality leads to a higher aggregate and higher coordination saturation at the zinc centre.

In order to determine if a similar transamination process would occur on replacement of zinc by magnesium, two molar equivalents of dibenzylamine were added to a benzene solution containing one molar equivalent of [{$(Me_3Si)_2$N}$_2$Mg]$_2$[24] (eqn. (2)). Since [{$(Me_3Si)_2$N}$_2$Mg]$_2$ exists as a dimer–monomer



equilibrium in arene solution, in the aforementioned reaction transamination would afford no increase in coordination at the metal centre (for the dimer). Thus, it would not be expected that the transamination would take place. After heating the solution to reflux in benzene for two hours, an aliquot of the reaction solution was taken and the solvent was removed *in vacuo*. ^{1}H NMR spectral evidence of the residue in the benzyl region lacked the presence of dibenzylamide ligands, but showed a solitary singlet corresponding to the parent dibenzylamine. Thus, as expected, the transamination was unsuccessful and the 'product' from acidity considerations prevailed. In addition, during a similar control 'reaction' involving equimolar amounts of [{$(Me_3Si)_2$N}$_2$Li][25] and dibenzylamine, no transamination was observed.

Until now, we have only considered homoleptic amides. Although alkylzinc(amide) complexes are well known,[26] to the best of our knowledge, there are no heteroleptic zinc bis(amide) structures available for comparison. In an effort to form the as yet unknown heteroleptic complex [{$(PhCH_2)_2$NZnN-$(SiMe_3)_2$}$_x$], dibenzylamine was added to [{$(Me_3Si)_2$N}$_2$Zn] in a 1 : 1 stoichiometric ratio in benzene solution. However, no formation of the heteroleptic complex was observed and only the homoleptic compound **1** was produced. It can be inferred from this that the target heteroleptic molecule is unstable with respect to disproportionation. This can be accounted for by the steric bulk of bis(trimethylsilyl)amido units, which may preclude dimerisation in this case and, therefore, no concomitant increase in coordination number is realised.

Compound **1** has a similar melting point to its magnesium analogue (mp 172–173 °C for **1** *vs.* 175–177 °C for [{$(PhCH_2)_2$-N}$_2$Mg]$_2$). This is expected because melting points in compounds of this type are dictated by van der Waals interactions between the organic groups on the molecular periphery.

The lipophilic benzyl groups in **1** shield the polar core, thus enforcing appreciable solubility of **1** in arene solvents. This enabled a detailed NMR spectroscopy study to be carried out. The ^{1}H NMR spectrum of **1** run in $C_6D_5CD_3$ at 300 K shows two sharp signals of equal integral in the benzylic region at 3.00 ppm and 4.07 ppm. The benzylic protons of the parent dibenzylamine appear at 3.55 ppm in the same solvent. An interesting point is the marked difference between the chemical shifts of the two resonances (1.07 ppm) in the spectrum of the metallated product **1**. A similar situation is observed in the ^{1}H NMR spectrum (also in $C_6D_5CD_3$) of the dimeric magnesium analogue [{$(PhCH_2)_2$N}$_2$Mg]$_2$.[19] These resonances can be assigned to bridging and terminal dibenzylamido units. Normally, the higher frequency signal should correspond to the proton with the greatest electron deficiency *viz.* the bridging group. Conversely, lower frequency resonance should relate to the amido function with the least electron deficiency *i.e.* the terminal group, but this is by no means always the case, as shown by Westerhausen.[24] He notes that in [{$(Me_3Si)_2$N}$_2$M]$_2$, where M = Mg, Ca or Sr, the location of signals corresponding to bridging and terminal amido groups follows a much more regular pattern for ^{13}C signals than ^{1}H signals. In the case of Mg, the signals for both the bridging Si(CH_3)$_3$ resonances (0.45 ppm) and the bridging Si(CH_3)$_3$ resonances (8.12 ppm) appear at a higher frequency than the respective terminal group resonances (0.38 ppm and 7.14 ppm, respectively). Conversely, in the derivatives with M = Ca or Sr, the positions of the ^{1}H bridging and terminal signals are reversed *i.e.* when M = Ca, the bridging resonance is at 0.21 ppm and the terminal resonance at 0.33 ppm; when M = Sr, the bridging and terminal resonances are 0.12 ppm and 0.33 ppm respectively. In both cases the order of the corresponding ^{13}C signals are the same as those in the Mg compound.

The ^{13}C NMR spectrum of **1** run in the same solvent at 300 K shows the presence of two distinct types of benzylic carbon at 53.5 ppm and 58.2 ppm. From a ^{1}H/^{13}C HMQC experiment, the (larger) peak at 58.2 ppm was shown to couple to both sets of benzylic protons. The peak at 53.5 ppm is assigned to the benzylic carbon of the monomer (see later). The majority of the phenyl-carbons appear as two sets of signals between 126.4 ppm and 130.1 ppm, which are obscured by solvent signals. However, the two distinct resonances at 141.0 ppm and 144.7 ppm are assigned to the *ipso*-carbons of the terminal and bridging dibenzylamido units, respectively. These data are consistent with the structure determined by X-ray diffraction. In addition, the ^{1}H NMR spectrum of **1** shows two relatively small but significant resonances at 3.56 ppm and 3.58 ppm. These signals are tentatively assigned to the benzyl protons of the two-coordinate monomeric complex [{$(PhCH_2)_2$N}$_2$Zn] **2**. The *ab initio* geometry optimised structure of the related monomer [{$(PhCH_2)_2$N}$_2$Mg][19] shows that one benzyl group from each amido-moiety is attracted to the metal centre, thus, rendering the CH_2 groups inequivalent. It is possible that the structure of **2** resembles this and similarly we would expect inequivalence between these CH_2 groups in this case. However, mitigating against this, it would be expected that the benzyl groups would

be undergoing a fast rotation process at ambient temperature and therefore they would show a time-averaged equivalency. An alternative possibility that the geminal benzyl hydrogen atoms are inequivalent (diastereotopic) should lead to a pair of doublets. While such is not observed here, this possibility cannot be completely ruled out, as they may be isochronous due to accidental equivalence. Cases of accidental equivalence for prochiral groups are common.[27] It is also known that the outer lines of two mutually coupled doublets can collapse into the baseline in cases (as here) where the coupling constant (^2J) approaches or is greater than the chemical shift difference ($\Delta\nu$, in Hz) between the distinct resonances.

Variable temperature NMR spectroscopic studies on compound **1** were also carried out (in $C_6D_5CD_3$), but these revealed little information. During a high temperature ^{1}H NMR spectroscopy study ranging from 300–373 K, the terminal and bridging benzyl proton resonances failed to coalesce. Since the corresponding resonances in $[\{(PhCH_2)_2N\}_2Mg]_2$ coalesce at 368 K, this reflects the greater strength of the Zn–N bond over the corresponding Mg–N bond in this system (*i.e.* the former bonds are more difficult to cleave). A low temperature ^{13}C NMR spectroscopy study was also undertaken in order to assess if the signal at 58.2 ppm would split to reveal resonances for both the terminal and bridging benzylic carbons. Unfortunately, loss of all benzylic carbon signals at subambient temperatures was observed, possibly due to precipitation of the analyte.

It appears that the dimeric structure of **1** fails to remain wholly intact in arene solution and a dynamic monomer–dimer equilibrium exists. This assignment of the peaks to the monomer **2** was confirmed by a variable concentration study (over the range 5–20 mg ml^{-1}) as can be seen from Fig. 1. This

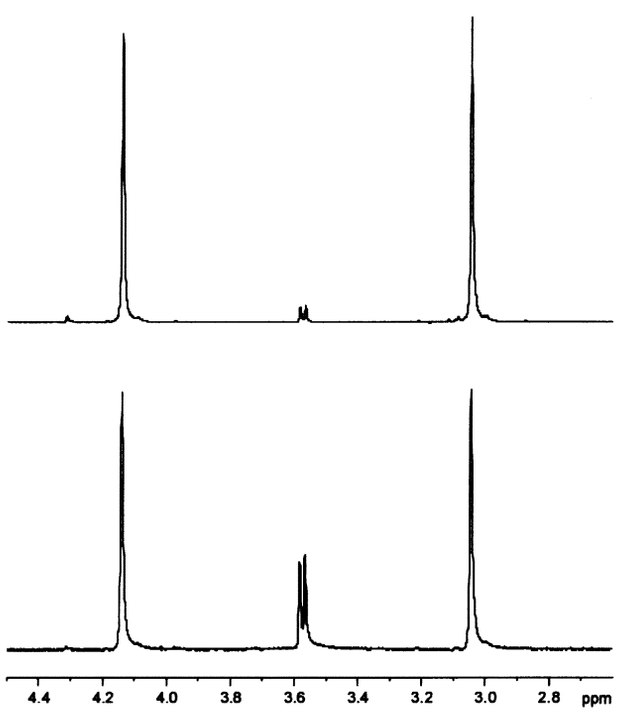


Fig. 1 Variable concentration [5 mg ml^{-1}(bottom)–20 mg ml^{-1}(top)] ^{1}H NMR spectra of **1** in C_6D_6, clearly showing the dynamic monomer–dimer equilibrium.

was carried out in C_6D_6 as this afforded greater solubility of **1**. A six-fold increase in the monomer : dimer ratio is observed on dilution of the solution to 25% of its initial value. A comparable dynamic equilibrium is also observed for $[\{(PhCH_2)_2N\}_2Mg]_2$ in $C_6D_5CD_3$.[19]

The solid state structure of **1**, reveals a centrosymmetric dimer (Fig. 2). Selected bond angles and bond lengths are

Table 1 Selected bond lengths (Å) and angles (°) for $[\{(PhCH_2)_2N\}_2Zn]_2\cdot C_6H_6$ **1**

Zn(1)–N(1)	2.0083(13)	C(8)–C(9)	1.517(2)
Zn(1)–N(1′)	2.0620(12)	N(2)–C(15)	1.462(2)
Zn(1)–N(2)	1.8530(14)	N(2)–C(22)	1.453(2)
N(1)–C(1)	1.4895(19)	C(22)–C(23)	1.529(3)
C(1)–C(2)	1.508(2)	C(15)–C(16)	1.520(0)
N(1)–C(8)	1.4924(19)		
N(1)–Zn(1)–N(2)	141.95(6)	C(22)–N(2)–C(15)	112.81(13)
N(1)–Zn(1)–N(1′)	93.12(5)	C(1)–N(1)–C(8)	109.78(12)
N(1′)–Zn(1)–N(2)	124.87(6)	N(1)–C(1)–C(2)	109.38(12)
Zn(1)–N(1)–Zn(1′)	86.88(5)	N(1)–C(8)–C(9)	114.77(13)
C(1)–N(1)–Zn(1)	113.83(10)	C(22)–N(2)–Zn(1)	124.93(11)
C(1)–N(1)–Zn(1′)	113.68(9)	N(2)–C(22)–C(23)	115.94(14)
C(8)–N(1)–Zn(1)	118.39(10)	C(15)–N(2)–Zn(1)	122.14(11)
C(8)–N(1)–Zn(1′)	112.70(9)	N(2)–C(15)–C(16)	114.61(14)

Symmetry operations for equivalent atoms $-x+1, -y+1, -z+1$.

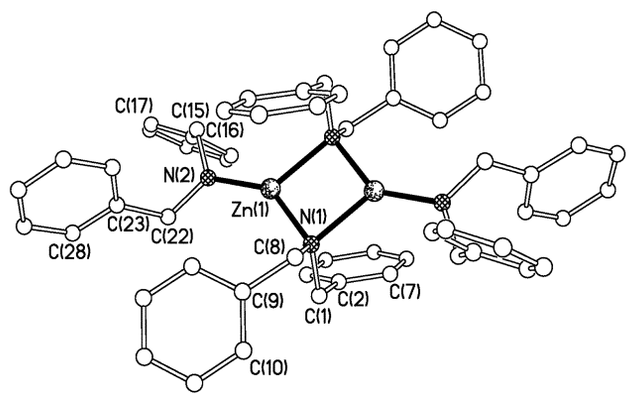


Fig. 2 The centrosymmetric dimeric molecule of **1** (without solvent or H atoms). Ring atoms are numbered sequentially.

shown in Table 1. As far as we are aware, this is the first structural characterisation of a dimeric zinc bis(amide) where a corresponding dimeric magnesium analogue is available for comparison. In compound **1**, the coordination arrangement is based on a rigorously planar $(ZnN)_2$ core (crystallographic inversion symmetry) and, unsurprisingly, the same structural motif is shared by other zinc bis(amides).[14–16] Each zinc bonds to three (two bridging and one terminal) dibenzylamido ligands and adopts a pseudo-trigonal planar geometry (mean N–Zn–N angle 119.98°). Likewise, the terminal nitrogen atoms occupy distorted trigonal planar environments, whilst the bridging nitrogens are pseudo-tetrahedral. Notably, the steric requirements of the dibenzylamido ligand prevent the zinc from expanding its coordination number from three to four as is common in zinc bis(dialkylamides)[28] and required for a chain like that observed in a $(ZnN)_2$ polymer. Steric congestion almost certainly precludes tetra-coordination at zinc to form a $(ZnN)_2$ polymer chain, which has previously been observed for magnesium in the lithium amidomagnesiate $[\{(PhCH_2)_2N\}_4MgLi_2]$.[18] Here, the formally two-coordinate Li centres in the heterobimetallic complex each draw two of the four bridging dibenzylamido ligands away from the central magnesium centre, thus reducing steric hindrance at the magnesium centre.

The Zn–N bridging distances in **1** have a mean value of 2.035 Å and these are not significantly different from the corresponding bridging distances in $[(Ph_2N)_2Zn]_2$[14] and $[(Bu^i{}_2N)_2Zn]_2$[15] which are 2.033 Å and 2.028 Å, respectively. However, the sterically demanding nature of the silylamido ligands in $[\{[Ph(Me_3Si)]N\}_2Zn]_2$[16] results in a marginally larger mean Zn–N bridging distance of 2.052 Å. The mean Zn–N bridging distance in **1** is also significantly larger than the terminal bond distance (1.853 Å), implying that the terminal amido ligands bind more strongly to the zinc centres. This is entirely expected, considering the number of metal centres that the amido ligand

spans in each case. The d-electrons in zinc (*i.e.* Zn^{2+}) do not favour the formation of π-complexes. In line with this, there are no short contacts between the metal centres and phenyl-substituents of the bridging dibenzylamido ligands. The closest centroid [of ring C(2)–C(7)] to the zinc centre Zn(1) is 3.843 Å and the nearest ring atom is C(2), at a distance of 3.146 Å. However, short contacts between the benzyl groups of dibenzylamido ligands and metal centres, in particular lithium, have been observed previously.[13] Comparing **1** to dimeric $[Ph_2Zn]_2$,[29] it can be seen that much shorter (Ph)C–Zn contacts are present in the bis(alkyl)zinc compound, whereby the phenyl groups bridge the two zinc centres asymmetrically, giving two short, 2.006(5) and 2.016(3) Å, and two long, 2.364(5) and 2.442(4) Å, Zn–C bridging distances.

Electrostatic (and steric) repulsion between the amido units (and between the two zinc atoms) causes the endocyclic N–Zn–N bond angle to mildly contract in comparison to the Zn–N–Zn bond angle [*i.e.* 86.88(5)° for N–Zn–N *cf.* 93.12(5)° for Zn–N–Zn]. The following zinc bis(amides) also share these characteristics: $[(Ph_2N)_2Zn]_2$,[14] $[(Bu^i{}_2N)_2Zn]_2$,[15] $[\{[Ph(Me_3Si)]_2N\}_2Zn]_2$[16] and $[\{(Me_2SiCH_2CH_2Me_2Si)N\}_2Zn]_2$[17] with corresponding N–Zn–N and Zn–N–Zn bond angles: [88.14(7)° *vs.* 91.86(7)°], [86.63(9)° *vs.* 93.37(9)°], [88.74(7)° *vs.* 91.26(7)°] and [88.05(8)° *vs.* 91.92(9)°] respectively.

When we compare zinc and magnesium, they are found to have covalent radii of 1.20 Å and 1.45 Å, respectively.[30] In addition, zinc has a higher electronegativity in comparison to magnesium: the Pauling values are 1.65 and 1.31, respectively.[31] These data suggest that Zn–N bonds are stronger and more covalent than Mg–N bonds. The Zn–N bridging and terminal bond distances are found to be in fairly close agreement to the analogous Mg–N bond distances (*i.e.* mean distances: Mg–N bridging 2.088 Å, Mg–N terminal 1.935 Å in $[\{(PhCH_2)_2N\}_2Mg]_2$ *cf.* Zn–N bridging 2.035 Å, Zn–N terminal 1.853 Å in **1**). These systematic variations are attributed to the higher electronegativity of zinc over magnesium.

Other comparisons between zinc and magnesium bis(amides) are restricted to isomorphous compounds in the monomeric state. Similar differences in bond distances can be seen in the vapour phase structures of $[\{(Me_3Si)_2N\}_2Zn]$[21] and $[\{(Me_3Si)_2N\}_2Mg]$[32] which have M–N bond distances of 1.824 Å and 1.935 Å, respectively and in the solid state structures of $[\{(Ph_2MeSi)_2N\}_2Zn]$[23] and $[\{(Ph_2MeSi)_2N\}_2Mg]$[33] which have mean M–N bond distances of 1.852 Å and 1.968 Å, respectively. In order to shed light on the energetics involved in the transamination procedure and to compare the structural data obtained from the X-ray diffraction study, model compounds were subjected to geometry optimisation calculations[34] carried out at the SCF level using the 6-31G* basis set.[35] These optimised geometries were in turn subjected to single point DFT[36] energy calculations using the B3LYP method[37] and the 6-31G* basis set. All of the reaction components in eqn. (3) and (4)

$$[\{(Me_3Si)_2N\}_2Zn] + 2\,(PhCH_2)_2NH \longrightarrow [\{(PhCH_2)_2N\}_2Zn] + 2\,(Me_3Si)_2NH\ \Delta E_f = +7.4\ (+10.8)\ \text{kcal mol}^{-1} \quad (3)$$

$$[\{(Me_3Si)_2N\}_2Zn] + 2\,(PhCH_2)NH \longrightarrow 1/2[\{(PhCH_2)_2N\}_2Zn]_2 + 2\,(Me_3Si)_2NH\ \Delta E_f = -1.9\ (+4.1)\ \text{kcal mol}^{-1} \quad (4)$$

were independently optimised in this way and their total energies computed (Table 2) thus allowing the energy of formation (ΔE_f in kcal mol^{-1}) of each model reaction to be calculated (DFT values are shown along with SCF values).

Eqn. (3), which disregards the aggregation of the bis(dibenzylamido)zinc product and treats it as a monomer, reveals that the reaction is significantly endothermic at both levels of theory. However, when the more experimentally realistic dimeric structure is considered (eqn. (4)), the reaction becomes exothermic (using DFT data), albeit only moderately so. This clearly suggests that the ability of bis(dibenzylamido)zinc to dimerise is a key factor in the transamination process (note that for two monomers to generate a dimer, the energy released in the formation of new bonds must outweigh the loss of translational entropy). Table 3 compares the principal dimensions of the model $[\{(Me_3Si)_2N\}_2Zn]$ monomer with that of its magnesium congener $[\{(Me_3Si)_2N\}_2Mg]$. Most significantly, this reveals that the Zn–N bond length (1.855 Å) is decidedly shorter (and, by implication, stronger) than the corresponding Mg–N bond (length, 1.914 Å).

This size diminution (0.086 Å) which has its origin in the greater covalency of zinc–organoelement bonds *versus* their magnesium counterparts (see above) proves that the steric demands of the bulky silylamide ligand have a greater influence on zinc than magnesium. This is consistent with the fact that in the crystalline state $[\{(Me_3Si)_2N\}_2Mg]$ is dimeric whereas the zinc counterpart remains a monomer (in the hypothetical zinc dimer the amide ligands would approach each other more closely than they do in the magnesium case). Table 4 lists the principal dimensions of the model dimer $[\{(Ph_2CH_2)_2N\}_2Zn]_2$.

Observing the data presented in Table 4, we are able to compare how well the model $[\{(Ph_2CH_2)_2N\}_2Zn]_2$ reflects the structure of experimentally observed compound **1**. It can be seen that the bond lengths and bond angles in both sets of data are in close agreement. The mean Zn–N bridging and terminal distances for the model compound vary by less than 2.2% from the experimentally observed structural data. The endocyclic Zn–N–Zn and N–Zn–N bond angles observed in the model compound differ by less than 0.5% from those found in compound **1**.

Table 2 Calculated energies (Hartrees) of the model compounds at the SCF and DFT levels

Model compound	Total Energy E (E_h) SCF	DFT
$[\{(Me_3Si)_2N\}_2Zn]$	−3517.725140	−3525.857144
$[\{(PhCH_2)_2N\}_2Zn]$	−2963.027849	−2972.480531
$[\{(PhCH_2)_2N\}_2Zn]_2$	−5926.077823	−5944.990648
$[\{(Me_3Si)_2N\}_2Mg]$	−1939.844353	−1946.835584
$(PhCH_2)_2NH$	−593.336109	−597.265016
$(Me_3Si)_2NH$	−870.67181	−873.947456

Table 3 Comparison of bond lengths (Å) and bond angles (°) in the model $[\{(Me_3Si)_2N\}_2Zn]$ with those of the magnesium congener $[\{(Me_3Si)_2N\}_2Mg]$

	$[\{(Me_3Si)_2N\}_2Zn]$	$[\{(Me_3Si)_2N\}_2Mg]$
M–N	1.855	1.914
N–Si	1.731	1.720
Si–C	1.893–1.902	1.894–1.908
M–N–M	180.0	179.9
M–N–Si	116.3	115.5
Si–N–Si	127.5	129.1

Table 4 Comparison of the dimensions in the model compound $[\{(PhCH_2)_2N\}_2Zn]_2$ with those in the crystal structure of **1**

	Model $[\{(PhCH_2)_2N\}_2Zn]_2$	Compound **1**
$Zn–N_{br}$	2.063	2.035
$Zn–N_t$	1.893	1.853
Zn–N–Zn	86.5	86.9
N–Zn–N	93.5	93.1

br = bridging, t = terminal.

In conclusion, we have shown that $[\{(PhCH_2)_2N\}_2Zn]_2{\cdot}C_6H_6$ **1** can be synthesised from an unconventional transamination of $[\{(Me_3Si)_2N\}_2Zn]$ with dibenzylamine in benzene. Crystalline **1** is dimeric in the solid state as shown by X-ray structural analysis, but forms a dynamic monomer–dimer equilibrium in arene solution, as established by a variable ^{1}H NMR concentration study. Compound **1** has also been shown to be isostructural to other zinc bis(amides) and its magnesium derivative $[\{(PhCH_2)_2N\}_2Mg]_2$.

Experimental

General procedures

All reactions were carried out using standard Schlenk techniques[38] with products stored in an argon-filled glove box. Bis[bis(trimethylsilyl)amido]zinc was synthesised according to Bürger's method[39] and characterised by its ^{1}H NMR spectrum. Dibenzylamine was distilled from CaH_2 and stored over molecular sieves. Benzene was freshly distilled from Na/benzophenone, rigorously degassed and stored over molecular sieves prior to use. Compound **1** has been characterised by single-crystal X-ray crystallography, NMR and IR spectroscopy, melting point and elemental analysis.

Physical measurements

^{1}H and ^{13}C NMR spectral data were recorded on a Bruker DPX 400 MHz spectrometer operating at 400.13MHz for ^{1}H and 100.62 MHz for ^{13}C. ^{1}H and ^{13}C chemical shifts are given relative to external $SiMe_4$. C, H and N analyses were performed using a Perkin-Elmer 2400 elemental analyser. The IR spectra were obtained from Nujol mulls between NaCl plates using a Nicolet Avatar 360 FT-IR spectrometer. Melting point studies were carried out in sealed capillaries using an electrothermal melting point apparatus and are uncorrected.

Preparation of $[\{(PhCH_2)_2N\}_2Zn]_2{\cdot}C_6H_6$ 1

To a solution containing bis[bis(trimethylsilyl)amido]zinc (10 mmol, 3.86 g) and benzene (10 ml) was added dibenzylamine (20 mmol, 3.80 ml) at ambient temperature. The resultant clear, deep red solution was stirred for 18 hours, by which time a colourless solid had precipitated. Recrystallisation of the solid from benzene yielded cube-shaped crystals of **1** (5.8 mmol, 2.90 g). Yield 58%. mp 172–173 °C (Found: C, 73.9; H, 6.3; N, 5.7%. Calculated for $C_{56}H_{56}N_4Zn_2{\cdot}C_6H_6$: C, 74.9; H, 6.4; N 5.6%). IR (cm^{-1}) 2725s, 2674s, 1350m, 1342m, 1319w, 1298w, 1131w, 1053m, 1005w, 953m, 760m, 750m, 741m, 725m, 701m. ^{1}H NMR (δ) in C_6D_6 (5 mg ml^{-1}): 3.04 (4H, s, $PhCH_2$ dimer), 3.56 (1.2H, s, $PhCH_2$ monomer), 3.58 (1.2H, s, $PhCH_2$ monomer), 4.14 (4H, s, $PhCH_2$ dimer), 6.96–7.52 (26H, series of multiplets, Ph). ^{1}H NMR (δ) in C_6D_6 (20 mg ml^{-1}): 3.04 (4H, s, $PhCH_2$ dimer), 3.56 (0.2H, s, $PhCH_2$ monomer), 3.58 (0.2H, s, $PhCH_2$ monomer), 4.14 (4H, s, $PhCH_2$ dimer), 7.01–7.52 (21H, series of multiplets, Ph). ^{13}C NMR (δ) in C_6D_6 (20 mg ml^{-1}): 58.6 ($PhCH_2$), 126.9–130.4 (series of overlapping signals, Ph), 141.4 (*ipso*-C terminal), 145.1 (*ipso*-C bridging). C_6H_6 solvent of crystallisation obscured by overlapping phenyl signals and deuterated solvent. ^{1}H NMR (δ) in $C_6D_5CD_3$: 3.00 (4H, s, $PhCH_2$ dimer), 3.54 (0.4H, s, $PhCH_2$ monomer), 3.56 (0.4H, s, $PhCH_2$ monomer), 4.07 (4H, s, $PhCH_2$ dimer), 6.98–7.46 (29H, series of multiplets, Ph). ^{13}C NMR (δ) in $C_6D_5CD_3$: 53.5 ($PhCH_2$, monomer), 58.2 ($PhCH_2$, dimer), 126.4–130.1 (series of overlapping signals, Ph), 141.0 (*ipso*-C terminal), 144.7 (*ipso*-C bridging). C_6H_6 solvent of crystallisation obscured by overlapping phenyl signals and deuterated solvent.

X-Ray crystallography

Crystal data for **1**: $C_{56}H_{56}N_4Zn_2{\cdot}C_6H_6$, M = 993.9, triclinic, space group $P\bar{1}$, a = 10.1530(7), b = 12.1247(8), c = 12.6655(9) Å, α = 67.811(2), β = 73.637(2), γ = 65.482(2)°, U = 1298.97(15) Å^3, Z = 1, D_c = 1.271 g cm^{-3}, μ = 0.97 mm^{-1} (Mo-Kα, λ = 0.71073 Å), T = 160 K; 10926 measured reflections, 5747 unique (R_{int} = 0.017, θ < 28.2°, semi-empirical absorption correction); R (F, $F^2 > 2\sigma$) = 0.029, R_w (F^2, all data) = 0.075, goodness of fit = 1.05 for 307 refined parameters, final difference map extremes +0.87 and −0.26 e Å^{-3}. Hydrogen atoms were constrained. The unit cell contains one dimeric molecule of the complex and one molecule of benzene, both lying on inversion centres. There is no disorder. Programs used were standard Bruker SMART (data collection), SAINT (integration) and SHELXTL (structure determination),[40] together with local programs.

CCDC reference number 175760.

See http://www.rsc.org/suppdata/dt/b1/b110696a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We gratefully acknowledge the financial support of the EPSRC (through grant award no. GR/M78113 and for equipment funding to W.C.). Our thanks are also extended to Dr K. W. Henderson for helpful discussions.

References

1 (*a*) E. Frankland, *Ann. Chem Pharm.*, 1849, **71**, 171; (*b*) for an excellent review of Frankland's work, see D. Seyferth, *Organometallics*, 2001, **20**, 2940.
2 S. N. Reformatsky, *Ber. Dtsch. Chem. Ges.*, 1887, **20**, 1210.
3 H. Richey, Jr, *Grignard Reagents: New Developments*, Wiley, Chichester, 2000.
4 (*a*) K.-P. Zeller and H. Gugel, in *Houben-Weyl, Methoden der Organischen Chemie*, ed. M. Regitz, G. T. Verlag, Stuttgart, 1989, vol. E 19b, p. 195; (*b*) J. Furukawa and N. Kawabata, *Adv. Organomet. Chem.*, 1974, **12**, 83; (*c*) H. E. Simmons, T. L. Cairns, S. A. Vladuchick and C. M. Hoines, *Org. React.*, 1973, 201.
5 (*a*) A. Fürstner, *Synthesis*, 1989, 571; (*b*) M. W. Rathke, *Org. React.*, 1975, **22**, 423; (*c*) M. Gaudemar, *Organomet. Chem. Rev., Sect. A*, 1972, **8**, 183; (*d*) P. L. Shriner, *Org. React*, 1942, **1**, 1.
6 (*a*) R. Noyori and M. Kitamura, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 49; (*b*) H. Takahashi, T. Kawakita, M. Ohno, M. Yoshioka and S. Kobayashi, *Tetrahedron*, 1992, **48**, 5691; (*c*) D. Seebach, A. K. Beck, B. Schmidt and Y. M. Wang, *Tetrahedron*, 1994, **50**, 4364; (*d*) L. Schwink, S. Vettel and P. Knochel, *Organometallics*, 1993, **14**, 5000; (*e*) L. Pu and H.-B Yu, *Chem Rev.*, 2001, **101**, 3.
7 (*a*) M. Kobayashi and E. Negishi, *J. Org. Chem.*, 1980, **45**, 5223; (*b*) E. Negishi, V. Bagheri, S. Chatterjee, F.-T Luo, J. A. Miller and A. T. Stoll, *Tetrahedron Lett.*, 1983, **24**, 5181; (*c*) R. A. Grey, *J. Org. Chem.*, 1984, **49**, 2288; (*d*) R. Rossi, F. Bellina, A. Carpita and R. Gori, *Synlett.*, 1995, 344; (*e*) E. Negishi, A. O. King and N. Okukado, *J. Org. Chem.*, 1977, **42**, 1821; (*f*) E. Negishi, H. Matsushitu, M. Kobayashi and C. L. Rand, *Tetrahedron Lett.*, 1983, **24**, 3824.
8 (*a*) M. A. Malik, P. O'Brien, M. Montevalli and A. C. Jones, *Inorg. Chem.*, 1997, **36**, 5076; (*b*) M. A. Malik and P. O'Brien, *Polyhedron*, 1997, **16**, 3593; (*c*) W. S. Rees, Jr, O. Just, H. Schumann and R. Weimann, *Polyhedron*, 1998, **17**, 101.
9 R. E. Mulvey, *Chem. Commun.*, 2001, 1049.
10 W. Clegg, K. W. Henderson, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings and D. M. Tooke, *Angew. Chem., Int. Ed.*, 2001, **40**, 3902.
11 (*a*) P. C. Andrews, A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts and R. B. Rowlings, *Angew. Chem., Int. Ed.*, 2000, **11**, 2036; (*b*) D. R. Armstrong, A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *Angew. Chem., Int. Ed.*, 1999, **38**, 131.
12 G. C. Forbes, A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, W. Clegg, S. T. Liddle and C. C. Wilson, *Chem. Commun.*, 2000, 1759.
13 (*a*) P. C. Andrews, D. R. Armstrong, R. E. Mulvey and D. Reed, *J. Am. Chem. Soc.*, 1988, **110**, 5235; (*b*) D. R. Armstrong, R. E. Mulvey, G. T. Walker, D. Barr, R. Snaith, W. Clegg and D. Reed, *J. Chem. Soc., Dalton. Trans.*, 1988, 617; (*c*) D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 285, 287.
14 M. A. Putzer, A. Dashti-Mommertz, B. Neumuller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1998, **624**, 263.

15 H. Schumann, J. Gottfriedsen and F. Girgsdies, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1881.
16 H. Schumann, J. Gottfriedsen, S. Dechert and F. Girgsdies, *Z. Anorg. Allg. Chem.*, 2000, **626**, 747.
17 O. Just, D. A. Gaul and W. S. Rees, Jr, *Polyhedron*, 2001, **20**, 815.
18 W. Clegg, K. W. Henderson, R. E. Mulvey and P. A. O'Neil, *J. Chem Soc., Chem. Commun.*, 1994, 769.
19 W. Clegg, F. J. Craig, K. W. Henderson, A. R. Kennedy, R. E. Mulvey, P. A. O'Neil and D. Reed, *Inorg. Chem.*, 1997, **36**, 6238.
20 (*a*) R. R. Fraser, T. S. Mansour and S. Savard, *J. Org. Chem.*, 1985, **50**, 3232; (*b*) J. J. Christensen, R. M. Izatt, D. P. Wrathall and L. D. Hansen, *J. Chem. Soc. A*, 1969, 1212; (*c*) J. J. P. Furlong, E. S. Lewkowitcz and N. S. Nudelman, *J. Chem. Soc, Perkin Trans. 2*, 1990, 1461 and references therein.
21 K. Haaland, K. Hedberg and P. P. Power, *Inorg. Chem.*, 1984, **23**, 1972.
22 W. S. Rees, Jr, D. M. Green and W. Hesse, *Polyhedron*, 1992, **11**, 1697.
23 P. P. Power, K. Ruhlandt-Senge and S. C. Shoner, *Inorg. Chem.*, 1991, **30**, 5013.
24 M. Westerhausen, *Inorg. Chem.*, 1991, **30**, 96.
25 R. D. Rogers, J. L. Atwood and R. Grüning, *J. Organomet. Chem*, 1978, **157**, 229.
26 (*a*) M. M. Olmstead, W. J. Grigsby, D. R. Chacon, T. Hascall and P. P. Power, *Inorg. Chim. Acta*, 1996, **251**, 273; (*b*) L. M. Engelhardt, G. E. Jacobsen, W. C. Patalinghug, B. W. Skelton, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton. Trans.*, 1989, 2859; (*c*) M. A. Malik, P. O'Brien, M. Motavalli and A. C. Jones, *Inorg. Chem.*, 1997, **36**, 5076; (*d*) N. A. Bell, H. M. M. Shearer and C. B. Spencer, *Acta Crystallogr., Sect. C*, 1983, **39**, 1182; (*e*) M. Westerhausen, T. Bollwein, A. Pfitzner, T. Nilges and H. Deiseroth, *Inorg. Chim. Acta*, 2001, **312**, 239; (*f*) M. Westerhausen, T. Bollwein, N. Makropoulos, T. M. Rotter, T. Habereder, M. Suter and H. Nöth, *Eur. J. Inorg. Chem.*, 2001, 851.
27 W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.
28 M. F. Lappert, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1980, pp. 545–566.
29 P. R. Markies, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets and A. L. Spek, *Organometallics*, 1990, **9**, 2243.
30 (*a*) J. E. Huheey, E. A. Keiter and R. C. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper-Collins, New York, 4th edn., 1993, p. 292; (*b*) M. C. Ball and A. H. Norbury, *Physical Data for Inorganic Chemists*, Longman, London, 1974, pp. 139–144.
31 A. L. Allred, *J. Inorg. Nucl. Chem.*, 1961, **17**, 1.
32 M. Westerhausen and W. Schwartz, *Z. Anorg. Allg. Chem.*, 1992, **609**, 39.
33 R. A. Bartlett, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1994, **33**, 4800.
34 Gaussian 98, Revision A. 9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
35 (*a*) K. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (*b*) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; (*c*) J. D. Dill and J. A. Pople, *J. Chem. Phys.*, 1975, **62**, 292; (*d*) V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223.
36 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133.
37 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
38 D. F. Shriver and M. A. Drezdon, *Manipulation of Air-Sensitive Compounds*, Wiley, New York, 2nd edn., 1986.
39 H. Bürger, W. Sawodny and U. Wannagat, *J. Organomet. Chem.*, 1965, **13**, 3.
40 SMART, SAINT and SADABS, Siemens Analytical X-Ray Systems, Inc., Madison, WI, 1996; G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.