

Low coordinate magnesium chemistry supported by a bulky β -diketiminate ligand

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A series of magnesium(II) alkyl, alkoxide, carboxylate, amide and halide complexes stabilised by the bulky β -diketiminate ligand, HC(C(Me)N-2,6- i -Pr₂C₆H₃)₂ (BDI), have been synthesised and structurally characterised. (BDI)H reacts with MgMe₂ in Et₂O to give the four-coordinate complex (BDI)MgCH₃(Et₂O), **1**, and in toluene to afford [(BDI)Mg(μ -CH₃)₂], **2**. Three coordinate complexes may be accessed by increasing the size of the alkyl ligand; hence, the reaction of (BDI)H with ^tBu₂Mg yields (BDI)Mg^tBu, **3**, while Li(BDI) reacts with ⁱPrMgCl to afford (BDI)MgⁱPr, **4**; a similar reaction with PhMgCl affords the diethyl ether adduct (BDI)MgPh(Et₂O), **5**. The etherates **1** and **5** may be converted into the base-free complexes, **2** and (BDI)MgPh, **6**, respectively, upon heating *in vacuo*. The direct reaction of (BDI)H with RMgX (X = Cl or Br) results in relatively inert halide-bridged dimers of formula [(BDI)Mg(μ -X)]₂, (X = Cl, **7**; X = Br, **8**). The alkylmagnesium derivatives react readily with alcohols, amines or carboxylic acids to yield alkoxide, amide and carboxylate complexes, respectively. For example, **4** reacts with ⁱPrOH (or O₂) to form [(BDI)Mg(μ -OⁱPr)]₂, **9**. Convenient one-pot synthetic procedures have been developed using commercially available Bu₂Mg. Treatment of Bu₂Mg with (BDI)H, followed by its reaction with MeOH, ^tBuOH, ⁱPr₂NH, (Me₃Si)₂NH, MeCO₂H or PhCO₂H affords [(BDI)Mg(μ -OMe)]₂, **10**, [(BDI)Mg(μ -O^tBu)]₂, **11**, (BDI)Mg(NⁱPr₂), **12**, (BDI)Mg(NTMS)₂, **13**, [(BDI)Mg(μ -O₂CMe)]₂, **14**, and [(BDI)Mg(μ -O₂CPh)]₂, **15**, respectively. The molecular structures of complexes **4–8** and **12–15** are reported.

Introduction

In recent years there has been great interest in the use of sterically demanding β -diketiminate ligands to stabilise unusual main group metal species, especially derivatives with low coordination numbers and/or low metal oxidation states.¹ In a preliminary report we described the synthesis of a series of low co-ordinate alkylmagnesium complexes stabilised by HC(C(Me)N-2,6- i -Pr₂C₆H₃)₂ (BDI).² In an independent study, closely related chemistry using a *tert*-butyl ketimino analogue of BDI was described by Bailey and co-workers.^{3,4}

Low coordinate (BDI)Mg compounds have found important applications as single-site initiators for controlled polymerisation: alkoxide derivatives have been shown to be highly active for the polymerisation of lactide,^{5,6} enolate species mediate the living polymerisation of methyl methacrylate to highly syndiotactic poly(methyl methacrylate),⁷ while the amide complex (BDI)Mg(NTMS)₂ has been employed to initiate the ring-opening polymerisation of a β -lactam derived from α -benzyl-L-aspartic acid.⁸

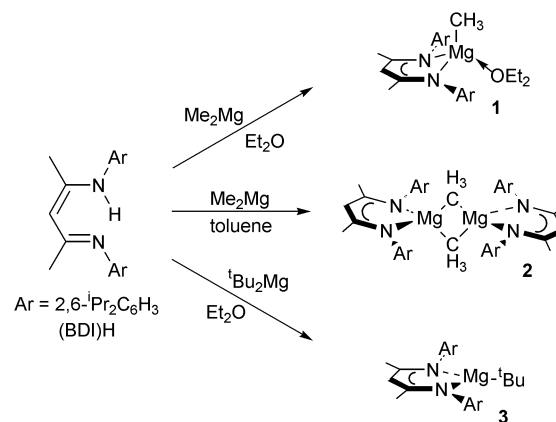
Here we report the synthesis and characterisation of a family of (BDI)Mg compounds containing alkyl, halide, alkoxide, amide and carboxylate ligands, and the use of commercially available dibutylmagnesium as a convenient precursor for 'one-pot' syntheses of some of these products.

Results and discussion

(i) Alkyl complexes

In an earlier report² we described how the alkyl derivatives **1–3** can be prepared from appropriate dialkylmagnesium precursors according to Scheme 1.

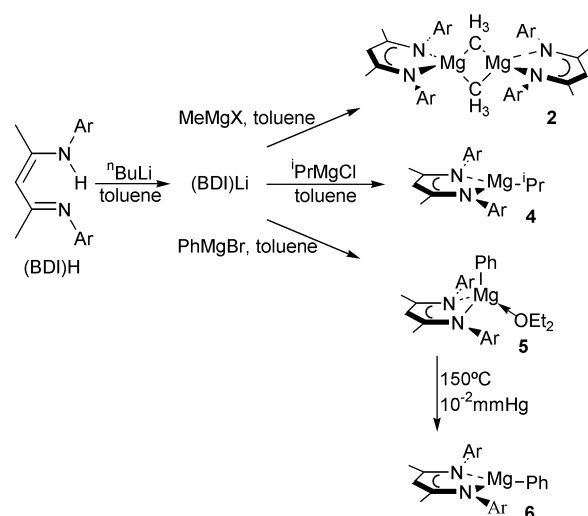
However, relatively few magnesium dialkyls are commercially available and their syntheses, although straightforward, can be laborious. We have therefore developed an alternative synthetic approach that employs more readily available Grignard reagents. *In situ* lithiation of (BDI)H and its subsequent treatment with RMgX affords the appropriate alkyl complexes in



Scheme 1

high yield (Scheme 2). For example, the methyl-bridged binuclear complex **2** is obtained in 57% yield upon treatment of Me₂Mg with (BDI)H, while the reaction of MeMgBr with (BDI)Li affords **2** in 84% isolated yield. Similarly, addition of an ethereal solution of ⁱPrMgCl to a toluene solution of (BDI)Li allows the base-free *iso*-propyl complex, **4**, to be isolated in > 90% yield. By analogy to the synthesis of **1**, when this reaction is performed in Et₂O, the product is the four-coordinate base adduct (BDI)MgⁱPr(Et₂O).⁹

X-Ray diffraction quality crystals of **4** were grown from toluene and the molecular structure is shown in Fig. 1; the complex exhibits a three-coordinate trigonal structure closely related to its *tert*-butyl analogue **3**.² The molecule displays non-crystallographic C₂ symmetry about a plane containing the magnesium centre, C(2) and C(30). The *iso*-propyl ligand exhibits mirror disorder (55 : 45) relative to the chelate ring plane; the parameters described in the following discussion refer to the major occupancy conformer. The geometry at magnesium, like that already observed for **3**, is essentially trigonal planar, the metal atom lying *ca.* 0.1 Å out of the plane of its substituents. The



Scheme 2

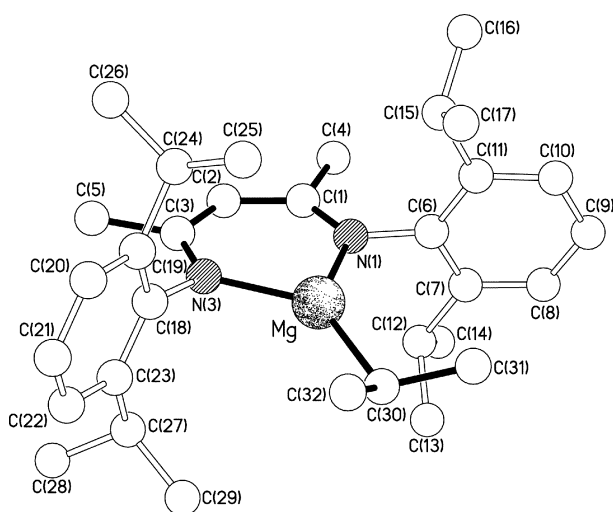


Fig. 1 The molecular structure of **4**. Selected bond lengths (Å) and angles (°): Mg–C(30) 2.120(4), Mg–C(30') 2.122(8), N(1)–Mg–C(30) 132.44(14), N(3)–Mg–C(30) 133.50(14), N(1)–Mg–C(30') 130.6(2), N(3)–Mg–C(30') 133.6(2).

chelate ring is non-planar having a small boat deformation with Mg and C(2) lying 0.084 and 0.027 Å respectively out of the plane of the remaining atoms (which are coplanar to within 0.003 Å). As a consequence of this ring folding Mg and C(2) lie 'below' the {N(1),C(1),C(3),N(3)} plane and C(4), C(5), C(6) and C(18) 'above'. Although this deformation is small it results in a significant difference in the separations of the pairs of *iso*-propyl groups that populate the 'upper' and 'lower' faces of the molecule and restrict the axial approaches to the metal centre; the C(15) ⋯ C(24) and C(12) ⋯ C(27) distances are 5.04 and 6.09 Å respectively. The 2,6-di-*iso*-propylphenyl rings are oriented essentially orthogonally to the chelate ring plane, a geometry that facilitates C–H ⋯ N(π) interactions¹⁰ between the *iso*-propyl methine hydrogen atoms and the chelate nitrogens (Fig. 2, Table 1). The pattern of bonding within the chelate ring does not differ significantly from that observed in **3**.² The crystals contain toluene solvent which is disordered and there are no intermolecular packing interactions of note.

Treatment of ethereal PhMgBr with *in situ* generated (BDI)Li in toluene affords (BDI)MgPh(Et₂O), **5**. Unlike complex **4**, the solvent remains bound to the magnesium centre. This may be a consequence of the phenyl group enhancing the electrophilicity of the magnesium centre or, alternatively, the metal centre may be more sterically accessible in the phenyl case. Crystals suitable for X-ray diffraction analysis were grown from a concentrated Et₂O solution.

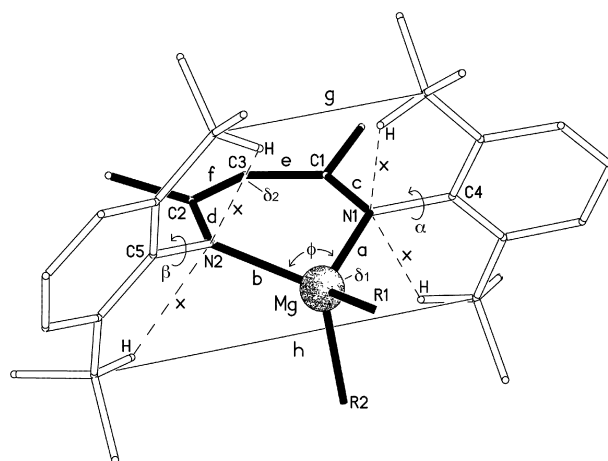


Fig. 2 Schematic representation of the (BDI)MgR¹R² complexes identifying the various molecular parameters presented in Table 1.

The structure (Fig. 3) has crystallographic mirror symmetry about a plane that includes Mg and C(2) and bisects the N(1)–Mg–N(1A) angle; the co-ordinated Et₂O group is symmetrically disordered either side of this plane. The geometry at magnesium can be considered as either distorted trigonal pyramidal with the metal atom lying 0.55 Å out of the {N(1),N(1A),C(16)} plane, or distorted tetrahedral (the deviations of the metal from the {N(1),C(16),O(20)} and {N(1),N(1A),O(20)} planes are 0.75 and 0.83 Å respectively). The chelate ring has a more pronounced (and very asymmetric) boat conformation than that in **4** with Mg and C(2) lying 0.383 and 0.093 Å respectively out of the plane of the remaining atoms. This increased folding results in a shortening of the separation of the 'uppermost' pair of *iso*-propyl groups such that the C(13) ⋯ C(13A) separation is reduced to 3.97 Å. The planes of the 2,6-di-*iso*-propylphenyl rings are oriented essentially orthogonally to the chelate ring plane (Table 1). The bonding within the β -diketiminato ligand is unchanged though the Mg–N(1) bond length is increased to 2.063(2) Å, a value comparable to that seen in the related structure of complex **1**.² An unusual feature of the present structure is a pronounced tilting of the plane of the phenyl ligand such that it is inclined by less than 6° to the {N(1),C(1),C(1A),N(1A)} plane. This geometry is accompanied by a pyramidalisation at C(16), which lies 0.14 Å out of the plane of its substituents, and a deviation of 0.64 Å of the magnesium atom from the phenyl ring plane. The only other example of a distortion of this type in a magnesium complex that we have identified is in the structure of *trans*-diphenyl-

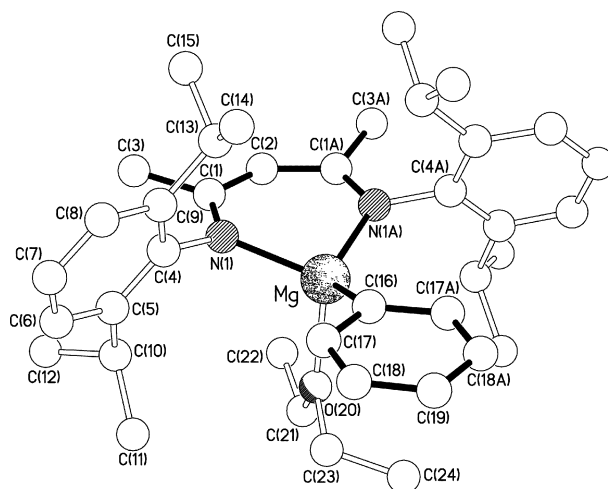


Fig. 3 The molecular structure of **5**. Selected bond lengths (Å) and angles (°): Mg–C(16) 2.139(3), Mg–O(20) 2.120(3), N(1)–Mg–O(20) 103.13(12), N(1A)–Mg–O(20) 116.97(12), N(1)–Mg–C(16) 122.32(7), O(20)–Mg–C(16) 97.59(12).

Table 1 Comparative geometric and conformational parameters for compounds **2–8**, **12–15** and related literature complexes

Ref.	R ¹	R ²	a ^a	b ^a	c ^a	d ^a	e ^a	f ^a	φ ^b	δ ₁ ^c	δ ₂ ^c	g ^d	h ^d	α ^e	β ^e	x ^f
Ref. 3	Me	—	2.014(2)	2.016(2)	1.335(2)	1.335(2)	1.406(3)	1.417(3)	95.68(7)	0.056	0.010	5.33	5.48	101	88	2.43–2.49
2 ²	Me	Me	2.091(2)	2.091(2)	1.333(3)	1.333(2)	1.397(3)	1.397(3)	91.30(6)	0.504	0.117	4.13	7.10	89	85	2.43–2.48
3a ^{g,2}	^t Bu	—	2.016(3)	2.016(3)	1.336(4)	1.326(4)	1.397(4)	1.405(4)	92.7(1)	0.027	0.008	5.33	5.71	85	91	2.43–2.45
3b ^{g,2}	^t Bu	—	2.024(3)	2.024(3)	1.334(4)	1.334(4)	1.390(4)	1.390(4)	92.4(2)	0.025	0.009	5.31	5.71	89	89	2.41–2.44
4	ⁱ Pr	—	2.017(2)	2.021(2)	1.330(3)	1.331(3)	1.406(3)	1.395(3)	93.38(8)	0.084	0.027	5.04	6.09	88	90	2.40–2.46
5	C ₆ H ₅	Et ₂ O	2.063(2)	2.063(2)	1.332(3)	1.332(3)	1.401(3)	1.401(3)	94.36(12)	0.383	0.093	3.97	7.29	83	83	2.46–2.49
6	C ₆ H ₅	—	1.999(1)	1.999(1)	1.330(2)	1.330(2)	1.404(2)	1.404(2)	93.99(8)	0.074	0.059	4.60	6.35	84	84	2.42–2.46
Ref. 6	O ⁱ Pr	O ⁱ Pr	2.114(3)	2.123(3)	1.337(4)	1.334(4)	1.398(5)	1.400(5)	91.3(1)	0.694	0.123	4.04	7.44	85	88	2.48–2.53
7a	Cl	Cl	2.031(2)	2.031(2)	1.339(2)	1.339(2)	1.397(2)	1.397(2)	94.38(9)	0.417	0.098	4.29	6.86	90	90	2.42–2.45
7b	Cl	Cl	2.032(2)	2.033(2)	1.337(4)	1.330(4)	1.392(4)	1.407(4)	95.59(9)	0.443	0.113	4.18	7.03	90	85	2.42–2.49
8	Br	Br	2.031(2)	2.028(2)	1.331(3)	1.332(3)	1.401(3)	1.406(3)	96.00(8)	0.439	0.095	4.22	7.01	90	85	2.43–2.49
12	N(ⁱ Pr) ₂	—	2.026(2)	2.034(2)	1.333(3)	1.333(3)	1.401(3)	1.405(3)	94.65(7)	0.526	0.101	4.01	7.24	95	81	2.42–2.50
13	N(TMS) ₂	—	2.013(2)	2.044(2)	1.337(2)	1.325(2)	1.397(3)	1.411(3)	95.11(6)	0.377	0.103	4.14	7.24	88	73	2.48–2.55
14	O ₂ CMe	O ₂ CMe	2.033(2)	2.040(2)	1.331(3)	1.327(3)	1.400(4)	1.405(3)	93.72(8)	0.540	0.094	4.09	6.96	89	88	2.39–2.50
15	O ₂ CPh	O ₂ CPh	2.029(2)	2.038(2)	1.335(3)	1.330(3)	1.408(4)	1.399(4)	93.60(8)	0.585	0.104	3.95	7.02	86	85	2.43–2.48
			2.038(2)	2.038(2)	1.328(2)	1.328(2)	1.405(2)	1.405(2)	95.42(9)	0.335	0.067	4.92	6.30	96	96	2.42–2.44

^a a–f are the bond lengths (Å) within the chelate ring. ^b φ is the chelate bite angle (°). ^c δ₁ and δ₂ are the deviations (Å) of Mg and C(3) respectively from the {N(1),C(1),C(2),N(2)} plane. ^d g and h are the separations (Å) of the 'upper' and 'lower' pairs of the *iso*-propyl carbon atoms. ^e α and β are the torsional rotations (°) about the N(1)–C(4) and N(2)–C(5) bonds respectively — a value of > 90° means that the 'upper' *iso*-propyl group is tilted away from the Mg centre. ^f x is the range of H...N distances (Å). ^g **3a** and **3b** are two different polymorphs of **3**.

bis(tetrahydrofuran)-magnesium,¹¹ though there the magnesium atom lies only 0.31 Å out of the ring plane. There are no noteworthy intermolecular interactions.

In the light of the apparent relationship between the size of the alkyl ligand and the nuclearity of the base-free β-diketiminato magnesium alkyls, we wondered whether the phenyl group would be sufficiently bulky to prevent formation of an alkyl-bridged structure of the type seen for **2**. Heating **5** at 150 °C for 2 h under reduced pressure (10⁻² mm Hg) afforded [(BDI)MgPh], **6**, in good yield. The most significant changes to the ¹H NMR spectrum (C₆D₆) are the shift of the *iso*-propyl septet from δ 3.36 for **5** to δ 3.20 for **6** and the BDI methine resonance, which is shifted from δ 4.89 to δ 4.97. Dimeric **2** can be obtained from **1** (and its THF analogue⁴) in a similar manner.

X-Ray quality crystals of **6** were obtained by slow-cooling of a warm heptane solution; the structure is shown in Fig. 4. The complex is indeed three co-ordinate with the phenyl ligand essentially coplanar with the β-diketiminato backbone; the magnesium atom here lies only 0.02 Å out of the phenyl ring plane. The complex has crystallographic C_s symmetry about a plane that includes Mg, C(2), C(16) and C(19). The geometry at magnesium is distorted trigonal planar with the metal atom lying only 0.04 Å out of the plane of its substituents. The chelate ring still exhibits a small boat deformation with Mg and C(2) lying 0.074 and 0.059 Å respectively out of the {N(1),N(1A),C(1),C(1A)} plane. The metal co-ordination distances are unexceptional and these, together with other geometric parameters, are summarised in Table 1. The only packing feature of note is an approximately orthogonal (*ca.* 82°) approach of C(2)–H of one molecule to the centroid of the phenyl ligand of another, though the H...ring-centroid distance of 3.15 Å is a little long for any significant C–H...π interaction.

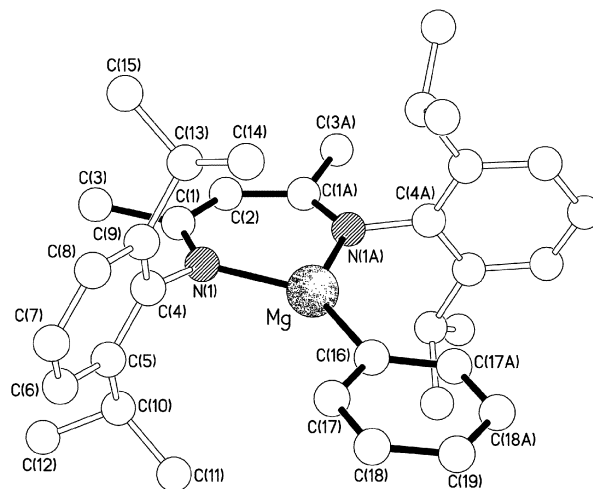


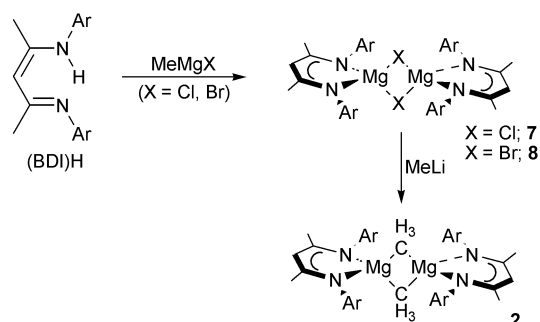
Fig. 4 The molecular structure of **6**. Selected bond lengths (Å) and angles (°): Mg–C(16) 2.095(3), N(1)–Mg–C(16) 132.94(4).

(ii) Halide derivatives

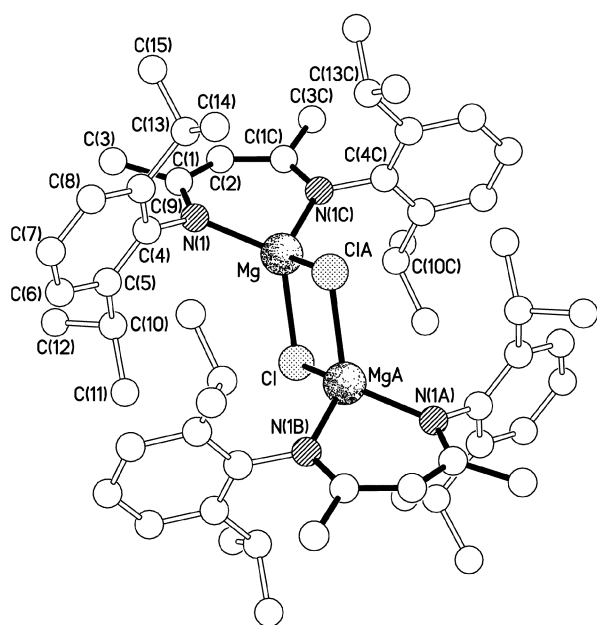
The synthesis of monomeric solvated magnesium halides has previously been reported by Roesky *et al.*⁹ The reaction of (BDI)Li·Et₂O with MgI₂ in Et₂O results in the formation of (BDI)MgI(Et₂O). In addition, Holland and co-workers have shown that (BDI)H reacts with MeMgCl in THF to give (BDI)MgCl(THF).¹² We have found that the base-free halide products **7** and **8** can be obtained *via* reactions of (BDI)H with ethereal solutions of MeMgX (X = Cl, Br) in toluene (Scheme 3). Both compounds are white, free-flowing powders, which are only sparingly soluble in hydrocarbon solvents. The halide complexes may therefore be purified by washing the crude reaction product with hydrocarbon solvents such as pentane or toluene.

Table 2 Selected bond lengths (Å) and angles (°) for **7b** and **8**

	7b [X = Cl]	8 [X = Br]	7b [X = Cl]	8 [X = Br]
Mg–X	2.3815(11)	2.5282(7)	Mg–XA	2.3952(11)
Mg ⋯ MgA	3.392(2)	3.5253(13)		2.5498(7)
N(6)–Mg–X	118.70(8)	118.36(6)	N(2)–Mg–X	119.01(8)
N(6)–Mg–XA	119.06(8)	117.72(6)	N(2)–Mg–XA	117.19(7)
X–Mg–XA	89.51(4)	92.07(2)	Mg–X–MgA	90.49(4)
				87.93(2)

**Scheme 3**

As expected the structures of complexes **7** and **8** are very similar, adopting bridged dimeric structures analogous to that seen previously for $[(\text{BDI})\text{Mg}(\mu\text{-CH}_3)]_2$. Two different crystalline forms of compound **7** were analysed; one, **7a**, is an *n*-heptane solvate, whereas the other, **7b**, was grown from hot benzene and is solvent free. Both crystallise in centred monoclinic space groups, but surprisingly the solvated form has the smaller unit cell and higher molecular symmetry. Complex **7a** has crystallographic C_{2h} symmetry with the 2-fold axis passing through the centre of, and perpendicular to, the plane of the Mg_2Cl_2 ring (Fig. 5), whereas **7b** has only inversion symmetry at this ring centre. Overall, differences between the two forms are small, each exhibiting boat deformations of their chelate rings and consequent large differences in the separations of their pairs of *iso*-propyl groups 'above' and 'below' the chelate ring planes (Table 1). The most noticeable difference between the two forms is the intranuclear $\text{Mg} \cdots \text{Mg}$ separation which is 3.434(2) Å in **7a** and 3.392(2) Å in **7b**. As was observed in the

**Fig. 5** The molecular structure of the C_{2h} -symmetric dimer complex **7a**. Selected bond lengths (Å) and angles (°): Mg–Cl 2.4091(10), Mg–ClA 2.3926(10), Mg ⋯ MgA 3.434(2), N(1)–Mg–ClA 119.32(5), N(1)–Mg–Cl 118.84(5), Cl–Mg–ClA 88.68(3), Mg–Cl–MgA 91.32(3).

related CH_3 -bridged dimer,² the conformations of the molecules are again stabilised by intramolecular $\text{C-H} \cdots \pi$ interactions between one of the hydrogen atoms of each of the four 'inwardly' directed methyl groups of the *iso*-propyl substituents and their proximal phenyl rings; the $\text{H} \cdots$ ring-centroid distances are in the range 2.93–3.08 Å.

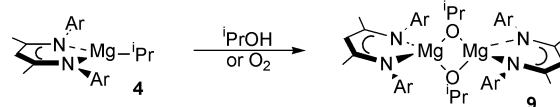
Diffraction quality crystals of **8** were obtained by slow cooling of a hot toluene solution. The bromide-bridged dimer is isomorphous with **7b** and has a $\text{Mg} \cdots \text{Mg}$ separation of 3.525(1) Å. Again, as was seen in **7a** and **7b**, there is a small but significant asymmetry in the metal–halide bond lengths, 2.5282(7) and 2.5498(7) Å (Table 2). The Br–Mg–Br angle of 97.07(2)° is as expected increased relative to Cl–Mg–Cl [88.68(3)°] as a consequence of the larger van der Waals radius of Br *cf.* Cl. None of these three complexes are involved in any noteworthy inter-dimer packing interactions.

In non-coordinating solvents we believe that the dimeric structures of **7** and **8** are retained. The solution state ^1H spectrum of **7** in benzene- d_6 reveals that rotation about the N–aryl bonds is hindered such that two ^1Pr septets and four doublets are observed. A similar effect is also seen in the ^{13}C spectra with twice as many signals seen for the ^1Pr substituents than in any of the hydrocarbonyl complexes **1–6** discussed above and is unlikely to arise from a mononuclear three-coordinate complex. The analogous zinc complex, $(\text{BDI})\text{ZnCl}$,¹³ which gives rise to two doublets and one septet for the ^1Pr groups in its ^1H NMR spectrum, is believed to be monomeric on the basis of cryoscopic measurements.^{14,15} The bromide complex **8** exhibits such poor solubility that we have only been able to acquire its NMR spectrum at 60 °C. At this temperature rotation about the N– C_{ipso} bond appears to be less restricted, with only one set of *iso*-propyl signals observed in both ^1H and ^{13}C spectra.

We had envisaged that the halide complexes may serve as useful precursors to a variety of derivatives *via* simple metathesis chemistry. However, over a range of different conditions, all attempts to convert **7** and **8** into alkoxide and amide complexes *via* their reactions with LiOR and LiNR_2 reagents led to intractable product mixtures. To date, the only success we have encountered in these types of reactions has been the conversion of **7** to **2** *via* its treatment with MeLi.

(iii) Alkoxide, carboxylate and amide complexes

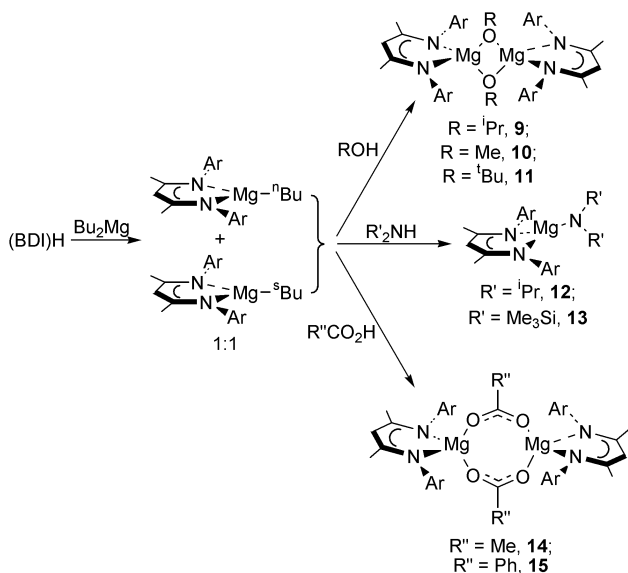
The alkyl complexes were found to be useful precursors for the synthesis of alkoxide, amide and carboxylate derivatives. For example, addition of one equivalent of $^i\text{PrOH}$ to **4** results in clean formation of the *iso*-propoxide bridged dimer, $[(\text{BDI})\text{Mg}(\mu\text{-O}^i\text{Pr})]_2$, **9**,⁶ with the elimination of alkane (Scheme 4). Complex **9** can also be accessed by stirring a solution of **4** under a dioxygen atmosphere. However, we have found that the dioxygen reaction is not clean, possibly a consequence of the formation of peroxide by-products, and recrystallisation from hot toluene is required to afford analytically pure **9** in quite low

**Scheme 4**

yields (typically <30%). The crystal structure of **9** has been reported previously by Coates and co-workers,⁶ and was shown to be a bridged dimer similar to the corresponding zinc complex, [(BDI)Zn(μ -OⁱPr)]₂.¹⁶

The ready reaction of dialkylmagnesium compounds with protic reagents led us to explore the use of commercially available dibutylmagnesium as a convenient precursor. Bu₂Mg (Aldrich Chemical Co) is an equimolar mixture of *n*-butyl and *sec*-butyl species,¹⁷ and its reaction with (BDI)H results in formation of both (BDI)Mg(ⁿBu) and (BDI)Mg(^sBu). A ¹H NMR spectrum of the product mixture reveals multiplet resonances at δ -0.22 and δ +0.21 attributable to the α -CH₂ unit of the ⁿBu ligand and the α -CH group of the ^sBu unit respectively in an approximate 2 : 1 ratio, implying that the ratio of the two butyl species is *ca.* 1 : 1. Other signals confirm the presence of these two products in approximately equal concentrations; for example, two similar intensity singlets at δ 4.93 and δ 4.87 due to the methine hydrogens of the BDI ligand. During the course of this study, the structure of [(BDI)Mg(ⁿBu)]₂ was described by Roesky and co-workers, and shown to be an alkyl-bridged dimagnesium species analogous to **2** in the solid state.¹⁸

In 'one-pot' procedures, Bu₂Mg was treated first with (BDI)H, followed by an alcohol, secondary amine or carboxylic acid to give the corresponding alkoxide, amide and carboxylate products (Scheme 5). On steric grounds, and by analogy to the solid state structure of **9**, the methoxide derivative, **10**, is formulated as the dimeric species [(BDI)Mg(μ -OMe)]₂. Its ¹H NMR spectrum reveals two ligand-based ¹Pr doublets and one septet; however, these resonances are broadened suggesting that rotation about the N-C_{ipso} bond is hindered, consistent with a dimeric solution structure. The ¹H NMR spectrum of the *tert*-butoxide derivative **11** shows four ¹Pr doublets and two septet resonances clearly indicating a dimeric species, which contrasts with the monomeric (solid state) structure for the analogous zinc complex.¹⁹ We ascribe the increased tendency of Mg (relative to Zn) to form 4-coordinate dimeric structures to its greater electrophilicity.²⁰ Thus, while a binuclear structure is found for **2**, its zinc analogue, (BDI)ZnMe, is mononuclear,¹⁵ as is the propagating species in the (BDI)Zn(OR)-initiated ring-opening polymerisation of lactide.¹⁹



Scheme 5

Magnesium amides may also be prepared from Bu₂Mg by analogous one-pot protocols. For example, the reaction of (BDI)Mg(ⁿBu) with ¹Pr₂NH or (Me₃Si)₂NH affords the mononuclear complexes, (BDI)Mg(NR₂), R = ¹Pr, **12**, Me₃Si, **13**, in >60% yield after recrystallisation. X-Ray quality crystals of **12** and **13** were obtained from heptane and their structures are

illustrated in Figs. 6 and 7 respectively. As expected, the structures are closely related and so only the details of **12** are discussed, with the parameters for **13** given in parentheses. Both complexes are monomeric having distorted trigonal planar geometries for their magnesium centres with the metal atom lying 0.038 (0.021 Å) out of the N₃ plane. The chelate ring has a similar boat conformation to that seen in the other complexes, with Mg and C(2) lying 0.526 (0.377) and 0.101 (0.103 Å) respectively out of the {N(1),C(1),C(3),N(3)} plane. It should be noted however, that in these two structures this plane is not as 'flat' as in the chelate rings discussed above, there being deviations from planarity of 0.024 and 0.050 Å in **12** and **13**, respectively. These distortions are accompanied by quite large departures from C_s symmetry within the molecules as a whole. This absence of molecular symmetry is particularly pronounced in **12** where the N(1)–C(1) ⋯ C(3)–N(3) torsion angle is *ca.* 9° and the rotations about the N(1)–C(6) and N(3)–C(18) bonds are in the opposite sense such that the C(15) *iso*-propyl group is directed 'back' towards C(2) whereas its counterpart, C(24), is tilted towards the metal atom. Data for other structures containing a trigonal MgN₃ core are sparse and we have found no comparable examples containing an N(ⁱPr)₂ ligand. In **13** the Mg–N(30) bond length of 1.961(2) Å is within the range observed for other trigonal Mg–NSiMe₃ containing complexes.²¹ Neither structure has any intermolecular packing interactions of note.

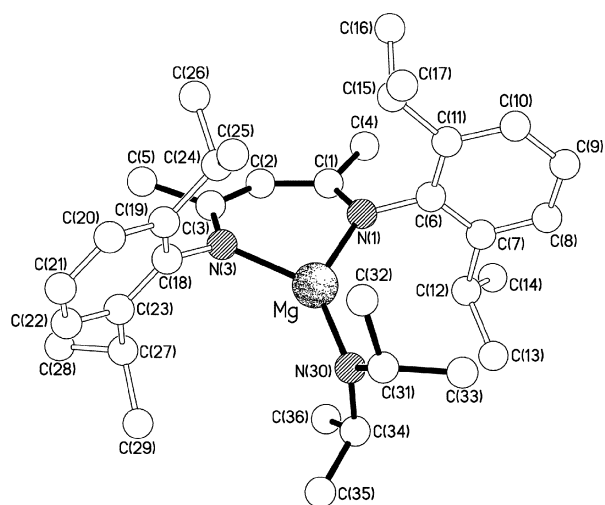


Fig. 6 The molecular structure of **12**. Selected bond lengths (Å) and angles (°): Mg–N(30) 1.938(2), N(30)–Mg–N(1) 130.67(8), N(30)–Mg–N(3) 134.56(8).

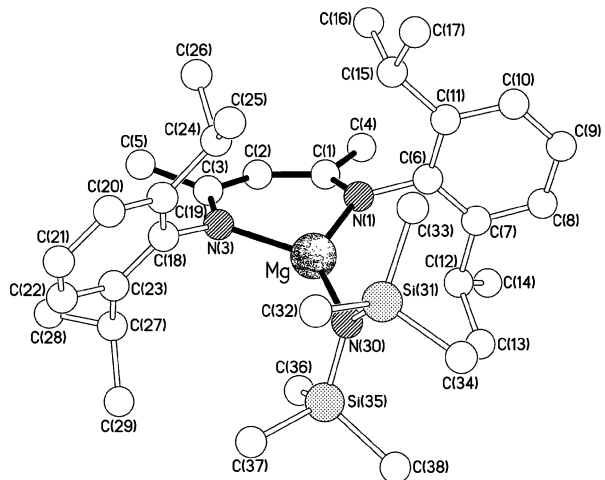


Fig. 7 The molecular structure of **13**. Selected bond lengths (Å) and angles (°): Mg–N(30) 1.961(2), N(30)–Mg–N(1) 133.57(7), N(30)–Mg–N(3) 131.28(7).

We have also successfully prepared and structurally characterised two magnesium carboxylates, synthesised *via* the reaction of Bu_2Mg with (BDI)H, and subsequent addition of a carboxylic acid. Acetic acid affords the bridged acetate dimer $[(\text{BDI})\text{Mg}(\mu\text{-O}_2\text{CMe})_2]_2$, **14**, whereas benzoic acid gives the benzoate complex, $[(\text{BDI})\text{Mg}(\mu\text{-O}_2\text{CPh})_2]_2$, **15**.

The structures of complexes **14** and **15** share obvious similarities (Figs. 8 and 9 respectively). Both are dimeric and feature bridging carboxylate ligands, giving rise to essentially planar eight-membered central cores analogous to that observed previously for $[(\text{BDI})\text{Zn}(\mu\text{-O}_2\text{CMe})_2]_2$.^{13,22} The magnesium atoms both exhibit distorted tetrahedral co-ordination geometries (Tables 3 and 4) and the chelate rings have distinctly asymmetric boat-like conformations (Table 1). Although at first glance complex **14** appears to have molecular C_{2h} symmetry, closer inspection shows the central $\text{Mg}_2\text{O}_4\text{C}_2$ core to be slightly puckered; there is an absence of even a crystallographic inversion centre. The magnesium atoms lie 0.128 and 0.071 Å 'above' the plane of the four oxygen atoms (which

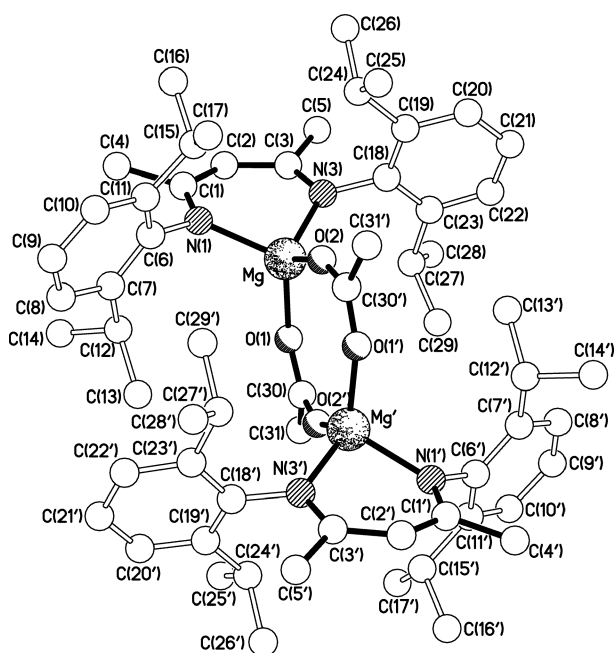


Fig. 8 The molecular structure of **14**.

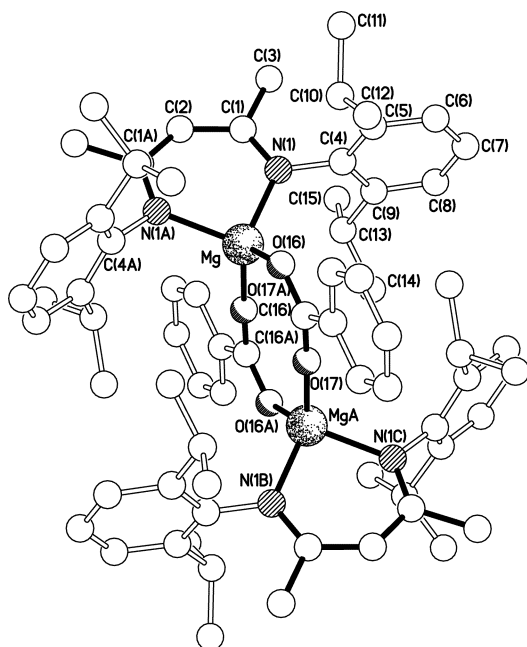


Fig. 9 The structure of the C_{2h} -symmetric dimer complex **15**.

Table 3 Selected bond lengths (Å) and angles (°) for **14**

Mg–O(1)	1.941(2)	Mg–O(2)	1.918(2)
O(1)–C(30)	1.247(3)	O(2)–C(30')	1.253(3)
C(30)–C(31)	1.495(4)	Mg'–O(1')	1.932(2)
Mg'–O(2')	1.913(2)	O(1')–C(30')	1.246(3)
O(2')–C(30)	1.244(3)	C(30')–C(31')	1.502(4)
O(2)–Mg–O(1)	112.83(9)	O(2)–Mg–N(3)	112.52(9)
O(1)–Mg–N(3)	110.24(9)	O(2)–Mg–N(1)	113.75(9)
O(1)–Mg–N(1)	112.33(9)	C(30)–O(1)–Mg	147.5(2)
O(2')–C(30)–O(1)	124.8(2)	C(30')–O(2)–Mg	153.4(2)
O(2')–Mg'–N(3')	114.58(9)	O(2')–Mg'–O(1')	112.29(9)
O(2')–Mg'–N(1')	111.15(9)	O(1')–Mg'–N(3')	111.82(9)
O(1')–Mg'–N(1')	112.10(10)	C(30)–O(2')–Mg'	153.5(2)
C(30')–O(1')–Mg'	148.7(2)	O(1')–C(30')–O(2)	124.8(3)

Table 4 Selected bond lengths (Å) and angles (°) for **15**

Mg–O(16)	1.958(2)	Mg–O(17A)	1.918(2)
O(16)–C(16)	1.254(3)	C(16)–O(17)	1.253(3)
C(16)–C(23)	1.494(3)		
O(17A)–Mg–O(16)	113.74(9)	O(17A)–Mg–N(1A)	109.02(6)
O(16)–Mg–N(1A)	114.06(6)	O(17A)–Mg–N(1)	109.02(6)
O(16)–Mg–N(1)	114.06(6)	O(17)–C(16)–O(16)	123.1(2)
C(16)–O(16)–Mg	127.4(2)	C(16)–O(17)–MgA	175.8(2)

are coplanar to within 0.031 Å) whilst the two carbon atoms lie respectively 0.120 and 0.022 Å 'below' this plane. There is a marked asymmetry in the Mg–O bond lengths at each metal centre of *ca.* 0.02 Å (*i.e.* 10σ). Asymmetric Mg–O distances in acetate bridges have also been observed in, for example, the structures of (μ-aqua)-bis(μ-acetato-*O,O'*)-acetoxy-bis(imidazol-3-yl)-magnesium, (μ-aqua)-bis(μ-acetato-*O,O'*)-acetoxy-bis(benzimidazol-3-yl)-magnesium and (μ-aqua)-bis(μ-2-furancarboxylato-*O,O'*)-bis(2-furancarboxylato-*O*)-tetra-aqua-di-magnesium.²³

In contrast, the solid state structure of **15** has crystallographic C_{2h} symmetry with a planar $\text{Mg}_2\text{O}_4\text{C}_2$ ring, the C_2 axis passing through its centre and perpendicular to the ring plane. Furthermore the angles at the carboxylate oxygen atoms, which in **14** are in the narrow range 147.5(2)–153.5(2)°, here in **15** are distinctly asymmetric with that at O(16) being 127.4(2)° whilst that at O(17) approaches linearity at 175.8(2)°. Though the Mg–O bond lengths differ by 0.040 Å, their distances overall suggest that, as in **14**, delocalisation over the carboxylate unit still occurs. Neither structure has any noteworthy packing interactions.

Experimental

All manipulations were carried out under a nitrogen atmosphere using Schlenk vacuum-line techniques and glove boxes. NMR spectra were recorded on a Bruker AC250 and a DRX 400 spectrometer in sealed tubes, and were referenced relative to residual solvent resonances. Data quoted was recorded at 293 K unless otherwise stated. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Germany, or by Stephen Boyer at the University of North London.

The β-diketimine ligand, **1**,²⁴ Me_2Mg ²⁵ and ${}^t\text{BuMg}_2$ ²⁶ were prepared as described in the literature. All reaction solvents were dried by prolonged reflux over appropriate drying agents and were degassed immediately prior to use. Unless otherwise stated commercially available chemicals were purchased from Aldrich Chemical Co. ${}^i\text{Pr}_2\text{NH}$, TMS_2NH , ${}^i\text{PrOH}$, MeOH, ${}^t\text{BuOH}$ and MeCO_2H were dried, distilled and degassed immediately prior to use. PhCO_2H was recrystallised from benzene and dried *in vacuo*.

$[(\text{BDI})\text{MgMe}(\text{OEt}_2)]_2$, **1**: Me_2Mg (0.120 g, 2.21×10^{-3} mol) was dissolved in Et_2O (25 cm^3) and to this stirred solution was added dropwise a 30 cm^3 Et_2O solution of (BDI)H (0.837 g, 2.00×10^{-3} mol). The reaction was stirred for 1 h at room

temperature and was then filtered. The filtrate was warmed and then concentrated until crystallisation commenced. Complex **1** was isolated by filtration and dried *in vacuo* (0.49 g); concentration of the filtrate led to a second crop of crystals, which was isolated in a similar manner (0.23 g). Total yield 61%.

^1H NMR (C_6D_6): δ 7.12 (m, 6H, *m-H*, *p-H*), 4.87 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.31 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 3.29 (q, 4H, $^3J_{\text{HH}} = 7.0$ Hz, OCH_2), 1.64 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.23 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.88 (t, 6H, $^3J_{\text{HH}} = 7.0$ Hz, OCH_2CH_3), -1.10 (s, 3H, MgCH_3). ^{13}C NMR (C_6D_6): δ 168.79 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 145.25 (C_{ipso}), 142.43 (C_{ortho}), 125.50 (C_{para}), 123.96 (C_{meta}), 95.00 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 65.66 (OCH_2CH_3), 28.30 ($\text{ArCH}(\text{CH}_3)_2$), 25.02 ($\text{ArCH}(\text{CH}_3)_2$), 24.15 ($\text{ArCH}(\text{CH}_3)_2$), 24.07 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 14.96 (OCH_2CH_3), -17.38 (MgCH_3). Calculated elemental analysis for $\text{C}_{34}\text{H}_{54}\text{N}_2\text{OMg}$: C 76.89, H 10.25, N 5.27%. Found C 77.00, H 10.30, N 5.32%.

$[(\text{BDI})\text{Mg}(\mu\text{-Me})_2$, **2**: *Route (a)*. To a stirred solution of Me_2Mg (0.143 g, 2.63×10^{-3} mol) in toluene (60 cm^3) was added a 30 cm^3 toluene solution of (BDI)H (1.00 g, 2.39×10^{-3} mol). The resulting suspension was stirred for 12 h, then heated until a clear solution formed. This solution was filtered and the filtrate warmed, then concentrated until crystals started to form. The solution was heated to redissolve the crystals and then left to stand. The product (0.53 g) was isolated by filtration and dried *in vacuo*. A second crop (0.09 g) was obtained by further concentration of the filtrate. Yield 57%.

Route (b). $^n\text{BuLi}$ (4.8 cm^3 , 2.5 M in heptane, Acros Chemicals, 1.20×10^{-2} mol) was added dropwise to a 60 cm^3 toluene solution of (BDI)H (5.02 g, 1.20×10^{-2} mol) at -78°C . The reaction was allowed to reach room temperature and was stirred for a further 1 h. Methylmagnesium bromide (4.0 cm^3 , 3.0 M in Et_2O , 1.20×10^{-2} mol) was added dropwise over 5 min to the rapidly stirred solution chilled in a 0°C ice bath. The reaction was stirred at ambient temperature for 18 h, then filtered and reduced under vacuum to yield a pale yellow powder which was washed with 10 cm^3 pentane (4.62 g, 84%).

Route (c). (BDI)Mg $\text{CH}_3(\text{Et}_2\text{O})$ was heated to 150°C under a dynamic vacuum (10^{-2} mm Hg) for 30 min. A ^1H NMR spectrum confirmed that the coordinated Et_2O had been removed to afford complex **2** with a small quantity (*ca.* 5%) of an unidentified contaminant present.

^1H NMR (C_6D_6): δ 7.05 (m, 6H, *m-H*, *p-H*), 4.87 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.13 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.58 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.15 (br, d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.10 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), -1.17 (s, 3H, MgCH_3). ^{13}C NMR (C_6D_6): δ 169.39 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 143.97 (C_{ipso}), 142.03 (C_{ortho}), 125.97 (C_{para}), 124.01 (C_{meta}), 95.42 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 28.49 ($\text{ArCH}(\text{CH}_3)_2$), 24.66 ($\text{ArCH}(\text{CH}_3)_2$), 23.74 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 23.48 ($\text{ArCH}(\text{CH}_3)_2$), -18.6 (detected only by coupling to the methyl protons, MgCH_3). Calculated elemental analysis for $\text{C}_{60}\text{H}_{88}\text{N}_4\text{Mg}_2$: C 78.85, H 9.70, N 6.13%. Found C 78.96, H 9.81, N 6.12%.

(BDI)Mg ^tBu , **3**: A solution of Mg^tBu_2 (4.0 cm^3 , 1.10 M in Et_2O , 4.4×10^{-3} mol) was diluted in 25 cm^3 toluene and then cooled to *ca.* -30°C . To this stirred solution was added dropwise a solution of (BDI)H (1.67 g, 4.00×10^{-3} mol) in toluene (30 cm^3). The reaction was allowed to warm to room temperature and after stirring for 1 h it was heated to 45°C briefly to ensure complete reaction. The solution was filtered and the filtrate warmed and concentrated to form a saturated solution which was left to crystallise. The product (0.82 g) was isolated by filtration and dried under vacuum; concentration of the filtrate led to a second crop of crystals (0.44 g) which was isolated similarly. Yield 63%.

^1H NMR (C_6D_6): δ 7.10 (m, 6H, *m-H*, *p-H*), 4.92 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.10 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.67 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.28 (br, d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.13 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.90 (s,

3H, $\text{MgC}(\text{CH}_3)_3$). ^{13}C NMR (C_6D_6): δ 169.30 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 144.37 (C_{ipso}), 141.59 (C_{ortho}), 125.97 (C_{para}), 124.11 (C_{meta}), 95.23 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 34.60 ($\text{MgC}(\text{CH}_3)_3$), 28.94 ($\text{ArCH}(\text{CH}_3)_2$), 24.20 ($\text{ArCH}(\text{CH}_3)_2$), 23.67 ($\text{ArCH}(\text{CH}_3)_2$), 23.50 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), -17.66 ($\text{MgC}(\text{CH}_3)_3$). Calculated elemental analysis for $\text{C}_{33}\text{H}_{50}\text{N}_2\text{Mg}$: C 79.42, H 10.10, N 5.61%. Found C 79.13, H 9.72, N 5.47%.

$[(\text{BDI})\text{Mg}^t\text{Pr}]$, **4**: $^n\text{BuLi}$ (6.7 cm^3 , 2.5 M in heptane, 1.68×10^{-2} mol) was added dropwise to a 50 cm^3 toluene solution of (BDI)H (6.880 g, 1.64×10^{-2} mol) at room temperature to furnish a bright yellow solution. After stirring for 90 min $^t\text{PrMgCl}$ (8.4 cm^3 , 2.0 M in Et_2O diluted into 20 cm^3 toluene, 1.68×10^{-2} mol) was added dropwise at 0°C . The reaction was stirred for 18 h at ambient temperature, then filtered and pumped dry to yield a slightly sticky solid. This was washed with 10 cm^3 cold (-78°C) pentane and dried *in vacuo* to afford 7.732 g of a cream coloured powder (97%). Crystals suitable for an X-ray diffraction study were obtained from a saturated toluene solution.

^1H NMR (C_6D_6): δ 7.10 (m, 6H, *m-H*, *p-H*), 4.92 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.13 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.67 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.26 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.86 (d, 6H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{MgCH}(\text{CH}_3)_2$), 0.13 (sept, 1H, $^3J_{\text{HH}} = 6.3$ Hz, $\text{MgCH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 168.84 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 143.63 (C_{ipso}), 141.41 (C_{ortho}), 125.71 (C_{para}), 123.80 (C_{meta}), 94.89 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 28.39 ($\text{ArCH}(\text{CH}_3)_2$), 24.10 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 24.02 ($\text{MgCH}(\text{CH}_3)_2$), 23.15 ($\text{ArCH}(\text{CH}_3)_2$), 9.22 ($\text{MgCH}(\text{CH}_3)_2$). Calculated elemental analysis for $\text{C}_{32}\text{H}_{48}\text{N}_2\text{Mg}$: C 79.24, H 9.97, N 5.78%. Found C 79.31, H 9.94, N 5.68%.

$[(\text{BDI})\text{MgPh}(\text{Et}_2\text{O})]$, **5**: The lithium salt of the (BDI) ligand was generated by the addition of $^n\text{BuLi}$ (2.1 cm^3 , 2.5 M in heptane, 5.25×10^{-3} mol) to a 50 cm^3 toluene solution of (BDI)H (2.12 g, 5.06×10^{-3} mol) at -78°C . The mixture was warmed to room temperature and stirred for 1 h. It was then chilled back to 0°C and PhMgCl (1.67 cm^3 , 3.0 M in Et_2O , 5.01×10^{-3} mol) was added dropwise over 5 min. The solution was stirred for 18 h whilst warming to room temperature before being filtered and reduced under vacuum to yield a pale yellow powder (2.22 g, 3.74×10^{-3} mol, 74%). Diffraction quality crystals were obtained by slow cooling of a saturated Et_2O solution.

^1H NMR (C_6D_6): δ 7.34 (br, m, 2H, $\text{MgAr } o\text{-H}$), 7.16 (m, 9H, $\text{MgAr } m\text{-H}$, $\text{MgAr } p\text{-H}$, $\text{NAr } m\text{-H}$, $\text{NAr } p\text{-H}$), 4.89 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.39 (q, 4H, $^3J_{\text{HH}} = 7.0$ Hz, OCH_2), 3.36 (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, CHMe_2), 1.70 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.20 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.13 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.70 (t, 6H, $^3J_{\text{HH}} = 7.0$ Hz, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 169.01 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 165.22 (MgC_{ipso}), 145.68 (NC_{ipso}), 142.66 (NC_{ortho}), 140.75 ($\text{MgC}_{\text{ortho}}$), 126.33 (MgC_{meta}), 125.52 (NC_{para}), 125.29 (MgC_{para}), 124.10 (NC_{meta}), 94.89 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 65.66 (OCH_2CH_3), 28.30 ($\text{ArCH}(\text{CH}_3)_2$), 24.96 ($\text{ArCH}(\text{CH}_3)_2$), 24.41 ($\text{ArCH}(\text{CH}_3)_2$), 24.15 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 13.68 (OCH_2CH_3). Calculated elemental analysis for $\text{C}_{39}\text{H}_{56}\text{N}_2\text{OMg}$: C 78.97, H 9.52, N 4.72%. Found C 79.10, H 9.52, N 4.82%.

$[(\text{BDI})\text{MgPh}]$, **6**: Complex **5** (1.204 g, 2.03×10^{-3} mol) was heated to 150°C under a dynamic vacuum for 8 h to afford a cream coloured solid (0.819 g, 1.58×10^{-3} mol, 78%). Diffraction quality crystals were grown from heptane.

^1H NMR (C_6D_6): δ 7.18 (m, 6H, $\text{NAr } m\text{-H}$, $\text{NAr } p\text{-H}$), 7.05 (m, 3H, $\text{MgAr } m\text{-H}$, $\text{MgAr } p\text{-H}$), 6.84 (m, 2H, $\text{MgAr } o\text{-H}$), 4.96 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.20 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.70 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.20 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 169.39 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 143.26 (NC_{ipso}), 141.75 (NC_{ortho}), 140.65 ($\text{MgC}_{\text{ortho}}$), 126.65 (MgC_{meta}), 126.30 (MgC_{para}), 126.00 (NC_{para}), 124.08 (NC_{meta}), 95.06 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 28.40 ($\text{ArCH}(\text{CH}_3)_2$), 24.63 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 23.05 ($\text{ArCH}(\text{CH}_3)_2$); MgC_{ipso} resonance not

observed. Calculated elemental analysis for $C_{35}H_{46}N_2Mg$: C 80.99, H 8.93, N 5.40%. Found C 81.14, H 9.05, N 5.50%.

[(BDI)MgCl]₂, **7**: (BDI)H (1.06 g, 2.53×10^{-3} mol) was dissolved in 50 cm³ toluene and chilled to 0 °C. MeMgCl (0.85 cm³, 2.55×10^{-3} mol, 3.0 M in THF) was then added dropwise over 5 min with stirring. The solution was slowly allowed to warm to room temperature over 18 h. The solvent was then removed *in vacuo* to yield a sticky white product. Trituration with cold pentane (5 × 50 cm³) yielded a free-flowing white powder (0.84 g, 8.80×10^{-4} mol, 70%).

¹H NMR (C₆D₆): δ 7.11 (m, 6H, *m-H*, *p-H*), 4.77 (s, 1H, HC{C(CH₃)NAr}₂), 3.28 (sept, 2H, ³J_{HH} = 6.8 Hz, CHMe₂), 2.89 (sept, 2H, ³J_{HH} = 6.8 Hz, CHMe₂), 1.42 (s, 6H, HC{C(CH₃)NAr}₂), 1.26 (d, 6H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.03 (d, 6H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.02 (d, 6H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 0.95 (d, 6H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂). ¹³C NMR (C₆D₆): δ 170.28 (HC{C(CH₃)NAr}₂), 144.45 (C_{ipso}), 142.76 (C_{ortho}), 142.64 (C_{ortho}), 125.96 (C_{para}), 125.83 (C_{para}), 124.24 (C_{meta}), 123.56 (C_{meta}), 95.56 (HC{C(CH₃)NAr}₂), 28.60 (ArCH(CH₃)₂), 28.25 (ArCH(CH₃)₂), 24.87 (ArCH(CH₃)₂), 24.70 (ArCH(CH₃)₂), 24.45 (ArCH(CH₃)₂), 24.32 (HC{C(CH₃)NAr}₂), 23.42 (ArCH(CH₃)₂). Calculated elemental analysis for C₅₈H₈₂N₄Mg₂Cl₂: C 72.96, H 8.66, N 5.87%. Found C 72.68, H 8.56, N 5.74%.

[(BDI)MgBr]₂, **8**: This complex was prepared in an analogous manner to the procedure described for complex **7**. Using 1.05 g (BDI)H (2.51×10^{-3} mol), **8** was obtained as a free-flowing white powder (1.07 g, 82% yield).

¹H NMR (C₆D₆, 333 K): δ 7.11 (m, 6H, *m-H*, *p-H*), 4.74 (s, 1H, HC{C(CH₃)NAr}₂), 3.16 (sept, 4H, ³J_{HH} = 6.8 Hz, CHMe₂), 1.48 (s, 6H, HC{C(CH₃)NAr}₂), 1.13 (d, 12H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 0.97 (d, 12, ³J_{HH} = 6.9 Hz, CH(CH₃)₂). ¹³C NMR (C₆D₆, 333K): δ 170.36 (HC{C(CH₃)NAr}₂), 144.39 (C_{ipso}), 143.00 (C_{ortho}), 126.10 (C_{para}), 124.26 (C_{meta}), 95.58 (HC{C(CH₃)NAr}₂), 28.38 (ArCH(CH₃)₂), 25.23 (ArCH(CH₃)₂), 24.80 (ArCH(CH₃)₂), 24.31 (HC{C(CH₃)NAr}₂). Calculated elemental analysis for C₅₈H₈₂N₄Br₂Mg₂: C 66.74, H 7.92, N 5.37%. Found C 66.84, H 8.02, N 5.44%.

[(BDI)Mg(OⁱPr)]₂, **9**: *Route (a)*. ⁱPrOH (0.195 cm³, 2.55×10^{-3} mol) was added dropwise over 60 s to a stirred solution of complex **4** (1.237 g, 2.55×10^{-3} mol) in toluene (30 cm³) at -78 °C. The reaction was then allowed to warm to room temperature and was stirred for 14 h, during which time a white precipitate formed. The solvent was concentrated *in vacuo* to 5 cm³ and the supernatant solution was filtered off. The residue was then washed with 15 cm³ pentane to afford a white, free-flowing powder (1.011 g, 79%).

Route (b). A Schlenk tube containing [(BDI)Mg(ⁱPr)]₂, **4**, (0.604 g, 1.25×10^{-3} mol) dissolved in toluene (15 cm³) under a dinitrogen atmosphere was evacuated and an atmosphere of dioxygen was then introduced. The evacuation/refill cycle was repeated a total of three times. Almost immediately the solution turned cloudy, with more precipitate forming during the time-scale of the reaction. After 30 min stirring at room temperature the solution was filtered to afford a white solid which was recrystallised from toluene. Yield: 0.168 g, 27%.

Characterising data was found to be in agreement with literature values.¹⁶

In situ generation of [(BDI)MgⁿBu]: In a typical reaction, 2.0 cm³ dibutylmagnesium (1.0 M in heptane, 2.0×10^{-3} mol), was slowly added to a stirred solution of (BDI)H (0.837 g, 2.00×10^{-3} mol) in toluene (35 cm³) cooled to -30 °C. The resulting solution was allowed to warm to room temperature and then warmed to 50 °C for *ca.* 30 min. The solution was then treated with a second reagent as described below for the generation of complexes **10–15**.

[(BDI)Mg(OMe)]₂, **10**: A stirred solution of [(BDI)MgⁿBu] (2.0×10^{-3} mol), formed as above, was diluted with toluene (30 cm³) and then cooled to -30 °C. Dropwise addition of MeOH (81 μl, 2.0×10^{-3} mol) afforded a white suspension

which was allowed to warm to ambient temperature and left to stir overnight. The reaction mixture was then warmed to 50 °C and filtered whilst hot. The filtrate was kept warm and evaporated to give a saturated solution, which was set aside to crystallise. The dimeric product co-crystallised with 1 equivalent of toluene (0.55 g, 53%).

¹H NMR (C₆D₆): δ 7.2–6.9 (m, 17H, *m-H*, *p-H* and C₆H₅Me), 4.73 [s, 2H, HC{C(CH₃)NAr}₂], 3.44 (s, 6H, OCH₃), 3.17 (br sept, 8H, ³J_{HH} = 6.8 Hz, CHMe₂), 2.10 (s, 3H, CH₃Ph), 1.45 (s, 12H, HC{C(CH₃)NAr}₂), 1.15 (d, 12H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 0.88 [br, 12H, CH(CH₃)₂]. ¹³C NMR (C₆D₆): δ 169.65 (HC{C(CH₃)NAr}₂), 147.29 (C_{ipso}), 142.61 (C_{ortho}), 137.85 (PhMe C_o), 129.29 (PhMe C_{ortho}), 128.51 (PhMe C_{meta}), 125.56 (PhMe C_{para}), 125.65 (C_{para}), 123.91 (C_{meta}), 95.38 (HC{C(CH₃)NAr}₂), 51.27 (OCH₃), 28.35 (ArCHMe₂), methyl resonances at 24.88, 24.46, 23.76 [CH(CH₃)₂, CH(CCH₃)₂], 21.36 (CH₃Ph). Calculated elemental analysis for C₆₇H₉₆Mg₂N₄O₂: C 77.52, H 9.32, N 5.40%. Found C 77.6, H 9.3, N 5.3%.

[(BDI)Mg(O^tBu)]₂, **11**: A 20 cm³ toluene solution of ^tBuOH (191 μl, 2.0×10^{-3} mol) was added dropwise to a solution of [(BDI)MgⁿBu] (2.0×10^{-3} mol) chilled to -30 °C. The resulting suspension was allowed to warm to ambient temperature and stirred overnight. The suspension was warmed to 50 °C to give a solution, which was then filtered hot. The resultant filtrate was concentrated to give a saturated solution, which was set aside to crystallise. The product was collected as small white needles (0.74 g, 72%).

¹H NMR (C₆D₆): δ 7.2–6.9 (m, 6H, *m-H*, *p-H*), 4.83 (s, 1H, HC{C(CH₃)NAr}₂), 3.55 (sept, 2H, ³J_{HH} = 6.8 Hz, CHMe₂), 3.22 (sept, 2H, ³J_{HH} = 6.8 Hz, CHMe₂), 1.55 (s, 6H, HC{C(CH₃)NAr}₂), 1.42 (d, 6H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 1.21 (s, 9H, OC(CH₃)₃), 1.14 [(d, 6H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 1.10 (d, 6H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 0.65 (d, 6H, ³J_{HH} = 6.8 Hz, CH(CH₃)₂). ¹³C NMR (C₆D₆): δ 169.73 (HC{C(CH₃)NAr}₂), 148.65 (C_{ipso}), 142.61 (C_{ortho}), 125.35 (C_{para}), 123.46 (C_{meta}), 96.01 (HC{C(CH₃)NAr}₂), 66.21 (OC(CH₃)₃), 35.17 (OC(CH₃)₃), 29.56, 28.61, 27.67, 27.26, 26.54, 26.22, 25.10, 23.65 (CHMe₂, CH(CH₃)₂, CH(CMe₂)). Calculated elemental analysis for C₆₆H₁₀₀Mg₂N₄O₂: C 76.95, H 9.78, N 5.44%. Found C 76.5, H 9.5, N 5.0%.

[(BDI)MgNPr₂]₂, **12**: A stirred toluene solution of 2.0×10^{-3} mol [(BDI)MgⁿBu] was cooled to -30 °C and treated dropwise with ⁱPr₂NH (290 μl, 2.1×10^{-3} mol). The resulting solution was allowed to warm to ambient temperature, and then stirred at 60 °C for 15 min. The volatile components were then removed *in vacuo* and the residue was extracted into pentane (35 ml). Cooling of this pentane solution to -30 °C afforded crystals of **12** (0.67 g, 62%).

¹H NMR (C₆D₆): δ 7.12 (m, 6H, *m-H*, *p-H*), 4.84 (s, 1H, HC{C(CH₃)NAr}₂), 3.23 (sept, 4H, ³J_{HH} = 6.7 Hz, CHMe₂), 3.07 (sept, 2H, ³J_{HH} = 6.1 Hz, NCH(CH₃)₂), 1.66 (s, 6H, HC{C(CH₃)NAr}₂), 1.34 (d, 12H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 1.17 (d, 12H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 0.87 (d, 12H, ³J_{HH} = 6.1 Hz, NCH(CH₃)₂). ¹³C NMR (C₆D₆): δ 170.10 (HC{C(CH₃)NAr}₂), 144.55 (C_{ipso}), 142.33 (C_{ortho}), 125.87 (C_{para}), 124.15 (C_{meta}), 95.42 (HC{C(CH₃)NAr}₂), 47.30 (NCH(CH₃)₂), 28.85 (ArCH(CH₃)₂), 26.39 (ArCH(CH₃)₂), 24.69 (ArCH(CH₃)₂), 24.66 (ArCH(CH₃)₂), 24.30 (HC{C(CH₃)NAr}₂). Calculated elemental analysis for C₃₅H₅₅N₃Mg: C 77.54, H 10.23, N 7.75%. Found C 77.56, H 10.28, N 7.68%.

[(BDI)MgN(SiMe₃)₂]₂, **13**: (Me₃Si)₂NH (530 μl, 2.5×10^{-3} mol) was added to a stirred toluene solution of 2.0×10^{-3} mol [(BDI)MgⁿBu] at ambient temperature. The reaction was then heated at 90 °C for 60 h. The solution was evaporated to dryness and the residue was dried under high vacuum. The solid thus obtained was dissolved in heptane (35 cm³) with warming to obtain complete dissolution. This solution was then concentrated to *ca.* 20 cm³ and was filtered whilst hot. The product was

obtained as colourless crystals (0.51 g), which were isolated by filtration. Concentration of the filtrate led to isolation of a second crystalline fraction (0.32 g). Overall yield: 69%.

^1H NMR (C_6D_6): δ 7.13 (br m, 6H, *m-H*, *p-H*), 4.81 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.21 (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.63 (s, 6H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.37 (d, 12H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, 12H, $^3J_{\text{HH}} = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.21 (t, 18H, $^2J_{\text{SiH}} = 3.1$ Hz, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR: δ 170.76 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 144.53 (C_{ipso}), 142.20 (C_{ortho}), 126.06 (C_{para}), 124.30 (C_{meta}), 95.62 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 29.02 ($\text{ArCH}(\text{CH}_3)_2$), 24.88 ($\text{ArCH}(\text{CH}_3)_2$), 24.71 ($\text{ArCH}(\text{CH}_3)_2$), 24.61 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 5.37 ($\text{Si}(\text{CH}_3)_3$). Calculated elemental analysis for $\text{C}_{35}\text{H}_{59}\text{MgN}_3\text{Si}_2$: C 69.79, H 9.87, N 6.98%. Found: C 69.6, H 10.0, N 7.0%.

$[(\text{BDI})\text{Mg}(\mu\text{-O}_2\text{CMe})_2]_2$, **14**: A stirred toluene solution of 2×10^{-3} mol $[(\text{BDI})\text{Mg}^{\text{n}6}\text{Bu}]$ generated as described above, was diluted with an additional 40 cm^3 toluene and to this was slowly added, *via* syringe, glacial acetic acid (115 μl , 1.8×10^{-3} mol). The resulting solution was heated at 70 $^\circ\text{C}$ for 30 min and was then filtered hot. The filtrate was then concentrated to give a saturated solution and this was left to crystallise. The crystalline product (0.32 g) was isolated by filtration and was pumped dry. Concentration of the liquor led to isolation of a small second crop. Total yield 0.36 g (36%).

^1H NMR (C_6D_6): δ 7.23–7.05 (m, 12H, *m-H*, *p-H*), 4.74 (s, 2H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.28 (sept, 8H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.61 (s, 12H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.21 (d, 24H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.88 (d, 24H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 178.89 (O_2CMe), 168.54 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 145.01 (C_{ipso}), 142.60 (C_{ortho}), 125.14 (C_{para}), 123.87 (C_{meta}), 94.32 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 27.96 ($\text{ArCH}(\text{CH}_3)_2$), 24.73 (O_2CCH_3), 24.69 ($\text{ArCH}(\text{CH}_3)_2$), 24.47 ($\text{ArCH}(\text{CH}_3)_2$), 23.83 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$). Calculated elemental analysis for $\text{C}_{62}\text{H}_{88}\text{Mg}_2\text{N}_4\text{O}_4$: C 74.32, H 8.85, N 5.59%. Found: C 73.9, H 8.8, N 5.8%.

$[(\text{BDI})\text{Mg}(\mu\text{-O}_2\text{CPh})_2]_2$, **15**: A 20 cm^3 toluene solution of benzoic acid (0.244 g, 2.0×10^{-3} mol) was slowly added to a solution of 2×10^{-3} mol $[(\text{BDI})\text{Mg}^{\text{n}6}\text{Bu}]$ (toluene). The resulting solution was stirred at ambient temperature for 1 h and was then warmed briefly to 100 $^\circ\text{C}$. It was then concentrated to 15 cm^3 and treated with heptane (45 cm^3). The resulting solution was concentrated, and was then warmed and further concentrated to form a saturated solution from which large crystals were obtained on standing at ambient temperature. The product (0.44 g) was isolated by filtration and was dried *in vacuo*. Concentration of the filtrate and cooling led to second and third crystalline product fractions providing a total yield of 0.59 g (48%). Analysis confirms that the dimer co-crystallises with one molecule of heptane, *i.e.* **15**· C_7H_{16} .

^1H NMR (C_6D_6): δ 8.30 (m, 4H, $\text{O}_2\text{CPh } o\text{-H}$), 7.2–7.0 (m, 18H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$ *m-H*, *p-H*, $\text{O}_2\text{CPh } m\text{-H}$, *p-H*), 4.92 (s, 2H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.37 (br, 8H, $\text{CH}(\text{CH}_3)_2$), 1.66 (s, 12H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.66 (br s, 10H, $\text{Me}(\text{CH}_2)_3\text{Me}$), 1.09 (br m, 24H, $\text{CH}(\text{CH}_3)_2$), 0.89 (t, 6H, $^3J_{\text{HH}} = 6.6$ Hz, $n\text{-CH}_3(\text{CH}_2)_5\text{CH}_3$), 0.65 (v br m, 24H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 173.14 (O_2CPh), 169.09 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 145.28 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2\text{C}_{\text{ipso}}$), 142.56 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2\text{C}_{\text{ortho}}$), 133.93 ($\text{O}_2\text{CPh } \text{C}_{\text{ipso}}$), 132.64 ($\text{O}_2\text{CPh } \text{C}_{\text{ortho}}$), 130.90 ($\text{O}_2\text{CPh } \text{C}_{\text{para}}$), 128.02 ($\text{O}_2\text{CPh } \text{C}_{\text{meta}}$), 125.18 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2\text{C}_{\text{para}}$), 123.88 (br, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2\text{C}_{\text{meta}}$), 93.75 ($\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 32.23 ($\text{CH}_2\text{CH}_2\text{Me}$ of $n\text{-C}_7\text{H}_{16}$), 29.41 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ of C_7H_{16}), 28.16 (br, $\text{ArCH}(\text{CH}_3)_2$), 24.29 ($\text{ArCH}(\text{CH}_3)_2$), 24.07 ($\text{ArCH}(\text{CH}_3)_2$), 23.06 (CH_2Me of $n\text{-C}_7\text{H}_{16}$), 14.32 (CH_3 of $n\text{-C}_7\text{H}_{16}$). Calculated elemental analysis for $\text{C}_{79}\text{H}_{108}\text{Mg}_2\text{N}_4\text{O}_4$: C 77.37, H 8.88, N 4.57%. Found: C 77.1, H 8.6, N 4.9%.

Crystal data, data collection and refinement parameters for compounds **4–8** and **12–15** are given in Table 5.

CCDC reference numbers 207267–207276.

See <http://www.rsc.org/suppdata/dt/b3/b303550f/> for crystallographic data in CIF or other electronic format.

Table 5 Crystal data, data collection and refinement parameters for compounds **4–8** and **12–15**^a

	4	7a	7b	8	12	13	14	15
Formula	$\text{C}_{33}\text{H}_{48}\text{N}_2\text{Mg}\cdot\text{C}_7\text{H}_{16}$	$\text{C}_{38}\text{H}_{82}\text{N}_4\text{Cl}_2\text{Mg}_2\cdot 2\text{C}_7\text{H}_{16}$	$\text{C}_{38}\text{H}_{82}\text{N}_4\text{Br}_2\text{Mg}_2$	$\text{C}_{38}\text{H}_{82}\text{N}_4\text{Cl}_2\text{Mg}_2$	$\text{C}_{35}\text{H}_{59}\text{N}_3\text{Si}_2\text{Mg}$	$\text{C}_{62}\text{H}_{88}\text{N}_4\text{O}_4\text{Mg}_2$	$\text{C}_{72}\text{H}_{92}\text{N}_4\text{O}_4\text{Mg}_2\cdot\text{C}_7\text{H}_{16}$	
Formula weight	577.2	1155.2	954.8	1043.7	542.1	1002.0	1226.3	
Temperature/K	193	183	173	173	183	183	183	
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$I2/m$ (no. 12)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$Cmca$ (no. 64)	
<i>a</i> /Å	9.910(1)	12.218(1)	22.889(3)	22.984(1)	10.702(1)	17.316(2)	17.758(1)	
<i>b</i> /Å	20.430(2)	17.954(1)	14.957(1)	15.063(1)	11.173(1)	15.188(1)	19.444(1)	
<i>c</i> /Å	18.414(2)	16.420(1)	16.349(1)	16.464(1)	15.478(1)	23.294(3)	21.618(2)	
<i>a</i> / $^\circ$	90.83(1)	97.65(1)	90.27(1)	90.50(1)	88.89(1)	90.15(1)	—	—
β / $^\circ$	—	—	—	—	78.70(1)	101.73(1)	—	—
γ / $^\circ$	—	—	—	—	70.35(2)	—	—	—
<i>V</i> /Å ³	3727.7(6)	3569.8(3)	5597.2(8)	5699.5(4)	1707.02(8)	3766.5(6)	7464.4(8)	
<i>Z</i>	4	2 ^c	4 ^d	4 ^d	2	4	4 ^c	
μ/mm^{-1}	0.590	1.29	1.55	2.30	0.622	0.717	0.659	
Unique reflections measured	5522	3082	4157	4228	5058	8890	3221	
Unique reflections observed, $ F_o > 4\sigma(F_o)$	4226	2560	3617	3661	4216	4786	2670	
R_1 , wR_2 ^e	0.056, 0.144	0.047, 0.117	0.065, 0.177	0.032, 0.074	0.047, 0.116	0.040, 0.104	0.052, 0.126	0.052, 0.137

^a Details in common: graphite monochromated Cu-K α radiation, refinement based on F^2 . ^b The complex has crystallographically C_s symmetry. ^c The complex has crystallographically C_{2h} symmetry. ^d The complex has crystallographically C_1 symmetry. ^e $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2) + (aP)^2 + bP]\}^{1/2}$.

Summary and acknowledgements

The bulky β -diketiminate ligand, $\text{HC}(\text{C}(\text{Me})\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2$, has been shown to stabilise a variety of magnesium complexes containing alkyl, halide, alkoxide, amide and carboxylate co-ligands. X-Ray crystal structure determinations show that the magnesium centres adopt either three coordinate trigonal planar or four-coordinate distorted tetrahedral geometries. The use of some of these complexes for initiating the controlled polymerisation of cyclic esters and methyl methacrylate will be reported elsewhere.

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