# Magnesium amido N-heterocyclic carbene complexes†

Polly L. Arnold,\*‡<sup>a</sup> Ian S. Edworthy,§<sup>a</sup> Christopher D. Carmichael,<sup>b</sup> Alexander J. Blake<sup>a</sup> and Claire Wilson¶<sup>a</sup>

Received 25th February 2008, Accepted 24th April 2008 First published as an Advance Article on the web 9th June 2008 DOI: 10.1039/b803253j

Magnesium dications bind strongly to a tridentate anionic dicarbene ligand L =

 $[N{CH_2CH_2(CNCHCHNMes)}_2]$  forming dinuclear and trinuclear Mg complexes with some particularly short Mg–C bonds. Treatment of the proligand H<sub>4</sub>LCl<sub>3</sub> with three equivalents of methyl magnesium chloride or benzyl magnesium chloride affords Mg<sub>3</sub>(HL)Cl<sub>6</sub> in high yield. A suspension of **1** in thf was heated to 80 °C for 2 h to afford Mg<sub>2</sub>(L)Cl<sub>3</sub>, consistent with the loss of one equivalent of MgCl<sub>2</sub>, and the deprotonation of the remaining acidic NH, lost as HCl gas. Treatment of Mg<sub>3</sub>(HL)Cl<sub>6</sub> with one equivalent of KC<sub>8</sub> results in deprotonation of the ligand amine NH to afford Mg<sub>3</sub>(L)Cl<sub>5</sub>; treatment with a second equivalent forms the radical anion of the complex, K[Mg<sub>3</sub>(L)Cl<sub>3</sub>], which decomposes upon storage, precluding its structural characterisation. The acidic NH proton of the ligand in Mg<sub>3</sub>(HL)Cl<sub>6</sub> can also be removed by deprotonation with Li{N(SiMe<sub>3</sub>)<sub>2</sub>}; additional equivalents of which also exchange the magnesium-bound chlorides for silylamido ligands, affording Mg<sub>2</sub>(L)Cl<sub>2</sub>N" and Mg<sub>2</sub>(L)Cl(N")<sub>2</sub>, which have both been characterised by single-crystal X-ray diffraction studies.

# Introduction

N-heterocyclic carbene (NHC) metal complexes are now widely used as homogeneous catalysts for organic transformations,<sup>1</sup> and recent years have witnessed an increasing demand for functionalised carbene-based ligands to tune the reactivity of more Lewis acidic metal catalysts.<sup>2</sup> For the more complex functionalised carbene ligands, the form containing the free carbene is often insufficiently kinetically inert to allow it to be isolated. The synthesis of the desired metal complex of many of these functionalised carbene ligands is then usually achieved by a transmetallation reaction that transfers the carbene ligand [NHC] from a metal salt adduct, [MNHC]X, M = group 1, 2, 13, Ag, X = halide.<sup>3</sup>

For the transfer of anionic functionalised carbene ligands to early d-block and f-block metal cations, and to avoid potential problems of 'ate' complex formation that are often encountered in the synthesis of such metal complexes from lithium salts, we have targeted the synthesis of magnesium carbene ligand adducts.

To date, only a handful of Group 2 NHC adducts have been reported, although the first magnesium–NHC adducts **A** and **B** (Chart 1), were reported by Arduengo *et al* in 1993.<sup>4</sup> The same workers reported the synthesis of the metallocene NHC complex





 $[Cp*_2Mg(C{N(Me)CMe}_2]$  in 1998 *via* a solvent displacement reaction, **C**, as well as metallocene NHC complexes of other group II elements (Ca, Sr, Ba).<sup>5</sup> In 2001, Schumann *et al* reported a

<sup>&</sup>quot;School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD

<sup>&</sup>lt;sup>b</sup>School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

<sup>†</sup> Electronic supplementary information (ESI) available: Details of the reaction of 1 with pyridine. CCDC reference numbers 679263 and 679264. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b803253j

<sup>&</sup>lt;sup>‡</sup> Present address: School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ. Email: Polly.Arnold@ed.ac.uk; Fax: +44 131 650 6453; Tel: +44 131 650 6453.

 $<sup>\</sup>S$  Present address: Onyx Scientific Limited, Silverbriar, Enterprise Park East, Sunderland, UK SR5 2TQ.

<sup>¶</sup> Present address: Rigaku Europe, Chaucer Business Park, Watery Lane, Sevenoaks, Kent, UK TN15 6QY.

similar set of metallocene complexes containing two magnesium complexes,  $\mathbf{D}$  and  $\mathbf{E}$ .<sup>6</sup>

Magnesium adducts of functionalised NHC ligands were first reported by us in 2004,  $\mathbf{F}$ ,<sup>1</sup> and more recently by Kawaguchi and Zhang,  $\mathbf{G}$ .<sup>7</sup>

Tridentate bis(pyrazolyl) ligands of the form NZN (Z = N, O, S), *e.g.* **H**, have recently been used as supporting ligands for metal-catalyzed polymerization processes in which Mg<sup>II</sup>,<sup>8</sup> and Zn<sup>II</sup> adducts function as highly controlled and well-defined initiators for the polymerization of lactide, while Cr<sup>II</sup>,<sup>9</sup> and Ni<sup>II</sup>,<sup>10</sup> complexes catalyse the selective dimerization or oligomerization of ethene. Magnesium adducts of tetradentate tris(pyrazolyl)borate carbene analogues HB(CNCHCHNBu<sup>1</sup>)<sub>3</sub>MgBr, I, have also been used as carbene transfer agents in transition-metal chemistry.<sup>11</sup> Here we report the synthesis and reactivity of a set of magnesium complexes of a tridentate, monoanionic dicarbene ligand [N{CH<sub>2</sub>CH<sub>2</sub>(CNCHCHNMes)}<sub>2</sub>], L.

#### **Results and discussion**

#### 1. $Mg^{II}$ adducts of HL and L

Treatment of a cold slurry of  $H_4LCl_3$ ,  $[H_2N{CH_2CH_2(CHN-CHCHNMes)}_2]Cl_3$  in thf with three equivalents of potassium hexamethyldisilazide results in the formation of a colourless precipitate and a yellow solution. A yellow solid, formulated as HL, can be isolated, but decomposes upon standing in the solid state to a brown–green solid.

However, treatment of  $H_4(L)Cl_3$  with three equivalents of methyl magnesium chloride in thf at 0 °C results in the immediate, visible evolution of gas from the colourless slurry; further stirring of the mixture for 6 h affords a red solution containing a colourless precipitate, eqn (1). Filtration of the mixture to isolate the filtrate, followed by washing with thf affords the magnesium compound  $Mg_3(HL)Cl_6$ ,  $[HN{CH_2CH_2(MgCNCHCHNMes)}_2]MgCl_6$  1 as a colourless powder in 71% yield. Treatment of  $H_4(L)Cl_3$  with three equivalents of benzyl magnesium chloride under analogous conditions yields the same product, again with 1 readily isolated as a colourless solid from a red thf solution.



The <sup>1</sup>H NMR spectrum of a  $d_5$ -pyridine solution of **1** confirms the removal of the two imidazolium protons and the ammonium proton. The remaining imidazole protons are observed at 7.11 and 6.57 ppm, shifted to lower frequency compared to the corresponding resonances in H<sub>4</sub>(L)Cl<sub>3</sub> (8.65 and 7.12 ppm). The amino proton could not be located in the <sup>1</sup>H NMR spectrum, but an NH absorption is present in the IR spectrum. The <sup>13</sup>C NMR spectrum displays a characteristic carbene resonance at high frequency, 194.0 ppm, compared to 138.2 ppm for the corresponding CH carbon chemical shift for H<sub>4</sub>(L)Cl<sub>3</sub>. This carbene resonance is almost identical to that in the dimesityl carbene in the Mg adduct **A** (194.8 ppm), which has a dimeric structure in solution, but somewhat surprisingly, approximately ten to fifteen ppm higher than the reported values for the other Mg–NHC complexes **B–G**. Single crystals suitable for an X-ray diffraction experiment have not been isolated, but by comparison with other S-block halide clusters, we suggest a possible structure in eqn (1), with two of the Mg cations more intimately bound to the ligand framework (see below). The only identifiable fragment in the mass spectrum (EI) of **1** is that of mesityl imidazole.

A suspension of 1 in thf was heated to 80 °C for 2 h, to afford a brown solution, which upon standing overnight changed to a strongly coloured dark purple solution (eqn (2)). Upon addition of toluene to the solution, a dark purple precipitate was obtained. The mixture was filtered and the solid washed with toluene. Elemental analysis of the purple solid 2 indicates that it has an empirical formula of Mg<sub>2</sub>(L)Cl<sub>3</sub>, consistent with the loss of one equivalent of MgCl<sub>2</sub>, and the deprotonation of the remaining acidic NH, which is lost as HCl gas during the reaction.

$$Mg_{3}(HL)Cl_{6} \xrightarrow{thf, 80^{\circ}C}_{2 hrs, - MgCl_{2}} \xrightarrow{N}_{N} \xrightarrow{Mes}_{N} \xrightarrow{Cl}_{Mg} \xrightarrow{Cl}_{N} \xrightarrow{Cl}_{N} \xrightarrow{Cl}_{N} \xrightarrow{Cl}_{N} \xrightarrow{N}_{N} \xrightarrow{N}_{N} \xrightarrow{(2)}_{Mg_{2}LCl_{3}} 2$$

$$(2)$$

The <sup>1</sup>H NMR spectrum of purple **2** in  $d_5$ -pyridine contains two resonances due to the imidazole protons at 6.87 and 6.80 ppm and four resonances due to the ligand ethyl groups at 4.76, 3.76, 3.51 and 3.27 ppm. The complex retains the intense purple colour in pyridine and thf solutions, in which it is soluble without decomposition. To our knowledge, compounds of this colour have precedence only in the chemistry of Grignard compounds with non-innocent  $\alpha$ -diimine organic compounds with low lying LUMOs. Diimine ligands such as bipyridine and phenanthroline have been known since the 1960s to form strongly coloured species based on [Mg( $\alpha$ -diimine)R] in which the ligand is reduced to a radical anion.<sup>12</sup> The complex [Mg{(2,6-Pr<sup>i</sup><sub>2</sub>Ph)BIAN}( $\mu$ -Me)]<sub>2</sub> (BIAN = bis(imino)acenaphthene) is a deep red colour, and has a well-resolved EPR spectrum at room temperature.<sup>13</sup>

This hints at a non-innocence of the carbene  $\pi$ -heterocycle in the same manner.

Fryzuk has also shown that sterically unhindered yttrium alkyls supported by a dianionic capping macrocycle,  $[Y[P_2N_2]CH_2SiMe_3]$  $([P_2N_2] = [PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh])$  form strongly coloured blue solutions in benzene. The colour derives from an intermolecular  $\sigma$ -bond metathesis arene CH activation reaction which occurs with loss of SiMe<sub>4</sub>. This results in the isolation of coupled biaryls which remain  $\pi$ -coordinated to the yttrium centres, forming  $\{Y[P_2N_2]\}_2(\mu,\eta^6,\eta^6-C_{12}H_{10})$ .<sup>14</sup>

However, upon exposure of the purple solid **2** to air, the solid changes colour to yellow and <sup>1</sup>H NMR spectroscopy indicates reprotonation of the ligand back to  $(H_3L)^{2+}$ ; this confirms the ligand in **2** does not undergo an aryl or heterocycle coupling, or a similar rearrangement upon heating. Unfortunately, we have been unable to grow crystals suitable for single-crystal structural analysis.

It was also considered possible that the purple colour of complex **2** might originate from the formation of a radical anion-type ligand in which an extra electron resides on the NHC heterocycle. We have previously demonstrated the stability of the radical anion of the amino carbene  $HN(Bu^t)CH_2CH_2(CNCHCHNBu^t)$ , in which the

EPR spectrum shows the electron is coupled to the potassium reductant and the  $C_2H_2$  group in the backbone of the carbene heterocycle.<sup>15</sup>

An X-band EPR spectrum of 2 in fluid solution, recorded in the at room temperature, contains no resonances. An attempt to generate independently the radical anion of 1 by reduction was instead carried out.

#### 2. Reduction of Mg<sup>II</sup> adducts of HL and L

Treatment of 1 with one equivalent of potassium graphite at room temperature in thf yields an orange solution and a black solid. Filtration and removal of volatiles from the solution affords 3 as a yellow solid. However, elemental analysis confirmed that deprotonation of 1 had occurred instead of reduction, to afford 3 (eqn (3)), which contains formally a potassium amide group, in addition to the magnesium dichloride equivalents. The <sup>1</sup>H NMR spectrum of 3 in  $d_5$ -pyridine is almost identical to that of 1. Resonances due to the imidazole protons are observed at 7.09 and 6.59 ppm in the <sup>1</sup>H NMR spectrum. The <sup>13</sup>C NMR spectrum of 3 contains a resonance due to the carbene at 194.1 ppm, almost identical to 1, 194.0 ppm.

$$\mathbf{1} + \mathrm{KC}_{8} \xrightarrow{\mathrm{thf}, 48 \mathrm{h}} \mathrm{Mg}_{3}(\mathrm{KL})\mathrm{Cl}_{6} \mathbf{3}$$
(3)

It is, however, possible to reduce the amide **3** with a further equivalent of potassium graphite, eqn (4), at room temperature in thf. This yielded an orange solution and a black solid after 48 h. Filtration and removal of volatiles afforded an orange solid. The <sup>1</sup>H NMR spectrum of the orange solid in  $d_5$ -pyridine contains no resonances for **3**. The ES mass spectrum of a sample of the reduced species **3a** contained no peak for the molecular ion but contained peaks identifiable as  $[Mg_2Cl_3(L) + 2H]^+$  and  $[MesIm]^+$ , and although **3a** could be isolated as an orange solid, no satisfactory elemental analysis was obtained. The reduced species is unstable in solution and decomposes over the course of two days, possibly by attack on the  $\alpha$ -hydrogens of the ligand ethyl groups, with the resultant formation of free mesityl imidazole.



An X-band EPR spectrum of the solid in fluid solution, recorded in thf at room temperature is shown in Fig. 1. The 10-line spectrum is centred at a g value consistent with an organic radical. It is apparent that only one of the imidazole rings had been reduced.

The spectrum is simulated by incorporating hyperfine coupling of the electron to a potassium cation and to two identical nitrogen atoms and two identical hydrogen atoms, Fig. 1 upper. The parameters required for simulation are  $g_{iso} = 2.003$ ,  $A_{\rm K} = 6.750$  G,  $A_{\rm N} = 5.200$  G and  $A_{\rm H} = 5.000$  G. This indicates that the electron resides in the NHC  $\pi$ -system and is reminiscent of the potassium– pyrrole and potassium–permethylcyclopentadienide electrostatic  $\pi$ -bound fragments observed in reduced systems.<sup>2,3</sup> We have shown previously that the organic radical formed from the amino carbene HN(Bu<sup>1</sup>)CH<sub>2</sub>CH<sub>2</sub>(CNCHCHNBu<sup>1</sup>) exhibits a 14-line spectrum



**Fig. 1** X-Band EPR spectrum of **3a** thf solution, 300 K. Top: Simulated spectrum. Bottom: Experimental spectrum. Hyperfine coupling:  $A_{\rm K} = 6.750$  G,  $A_{\rm N} = 5.200$  G and  $A_{\rm H} = 5.000$  G.

with hyperfine coupling to potassium ( $A_{\rm K} = 3.07$  G), nitrogen ( $A_{\rm N} = 6.02$  G) and hydrogen ( $A_{\rm H} = 3.72$  G).

The lack of strong colour of solutions of **3a** provides further weight to the argument that the colour of **2** derives from a charge transfer between adjacent  $\pi$ -systems, rather than the presence of a  $\pi$ -centred radical system.

#### 3. Deprotonation of Mg<sup>II</sup> adducts of HL

Treatment of **1** with two equivalents of lithium hexamethyldisilazide, LiN", in the at room temperature yields a pink solution after 12 h. Removal of volatiles from the solution under reduced pressure yields crude **4** as a pink solid (Scheme 1). The pink solid was recrystallised from toluene at -30 °C to afford pure **4** as a colourless crystalline solid.



The <sup>1</sup>H NMR spectrum of **4** in C<sub>6</sub>D<sub>6</sub> contains four imidazole proton resonances observed at 6.09, 6.04, 5.97 and 5.43 ppm due to the lowered symmetry imparted by the amide and chloride ligands. The different chemical environments for the two magnesium centres also lead to the splitting of ligand ethyl group resonances into six multiplets between 5.35 and 2.98 ppm. The <sup>13</sup>C NMR spectrum contains two resonances assigned as the carbene carbon centres at 182.3 and 179.9 ppm.

Treatment of 1 with three equivalents of lithium hexamethyldisilazide in thf at room temperature yields a pink solution after 12 h. Removal of volatiles from the pink solution under reduced pressure afforded crude 5 as a pink solid. The material was recrystallised from toluene at -30 °C to afford pure 5 as a colourless crystalline solid.

The <sup>1</sup>H NMR spectrum of **5** in C<sub>6</sub>D<sub>6</sub> contains only two imidazole CH proton resonances, at 6.07 and 5.96 ppm, confirming the symmetry of the two halves of the ligand L in this complex. The <sup>1</sup>H NMR spectrum of solutions of **5** also contains a relatively high frequency resonance for one CH<sub>2</sub> of the ligand ethyl groups at 5.48 ppm; the other resonances for the ligand ethyl groups are at more conventional frequencies, resonating at 3.7, 3.3 and 3.2 ppm. The <sup>13</sup>C NMR spectrum now again contains a single resonance for the two carbene carbon atoms at 182.3 ppm, comparable to literature values for Mg–NHC complexes.<sup>5</sup>

Although a number of complexes with bridging trimethylsilylamides are known,<sup>16</sup> the addition of an excess of lithium hexamethyldisilazide to solutions of **1** still affords only **5** as the product.

#### 4. Single-crystal structures of Mg<sub>2</sub>(L)X<sub>3</sub> complexes

Single crystals suitable for X-ray structure analysis were grown for both 4 and 5 by slow cooling of a saturated toluene solution of each complex to -30 °C.

4.1 X-Ray crystal structure of  $Mg_2(L)Cl_2N''$  4. The molecular structure of 4 is shown in Fig. 2. Both magnesium cations, Mg(1) and Mg(2), are four coordinate with a distorted tetrahedral geometry. Selected distances and angles are collated in Table 1. One chloride ligand bridges both magnesium atoms as does the central ligand amide nitrogen. The remaining coordination sites are filled by one NHC and one chloride for Mg(2) and one NHC and one silylamide for Mg(1), which accounts for asymmetry of the ligand environment observed in the NMR spectra. The general  $M_2$ -bridging coordination geometry of the ligand L is reminiscent of the structures formed by the amido-bis(pyrazolyl) ligand complexes reported by Carpentier and co-workers for

 Table 1
 Selected distances and angles for complexes 4 and 5



Fig. 2 Displacement ellipsoid plot of the molecular structure of 4 (50% probability). Lattice solvent and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Mg1–C2 2.180(2), Mg2–C22 2.153(2), Mg1–N40 2.115(2), Mg2–N40 2.093(2), Mg1–C11 2.5299(8); C2–Mg1–N01 125.81(8), C22–Mg2–Cl2 111.65(6).

 $[Mg(H)(Cl)]_2$  although the smaller substituents of H allow for two ligands to bridge the bimetallic core in those systems.<sup>8</sup>

X-Ray crystallography reveals a large difference in the bond lengths to the bridging chloride, Cl(1), 2.5299(8) Å from Mg(1) and 2.3767(8) Å from Mg(2). The terminal magnesium-chloride bond is shortest at 2.2939(8) Å, and lies at the shorter end of the range of terminal Mg-Cl distances. Asymmetric magnesium-chloride bond lengths for a  $Mg_2(\mu$ -Cl)<sub>2</sub> unit have been shown previously in a zirconium-magnesium complex with a tridentate diamido ligand.<sup>17</sup> The difference between the bridging magnesium-amide bonds to N40 in 4 is much smaller, with the bond lengths of 2.115(2) Å for Mg(1)–N(40) and 2.093(2) Å for Mg(2)–N(40). Also the Mg-NHC bond lengths differ; 2.180(2) Å for Mg(1)-C(2) and 2.153(2) Å for Mg(2)–C(22). Both of these are shorter than any previously reported literature values for Mg-NHC bond lengths, which fall in the range 2.194–2.279 Å, indicating that this ligand binds strongly to magnesium. The average Mg-C  $\sigma$ -bond length (data from the CSD, sample size 751)<sup>18</sup> is 2.181(2) Å, with fewer than ten complexes exhibiting Mg-C distances shorter than 2.1 Å.

	4		5
Mg(1)–C(2)	2.180(2)	Mg(1)–C(32)	2.199(2)
Mg(2)-C(22)	2.153(2)	Mg(2)-C(12)	2.193(2)
Mg(1) - N(40)	2.115(2)	Mg(1)-N(1)	2.116(2)
Mg(2) - N(40)	2.093(2)	Mg(2) - N(1)	2.123(2)
Mg(1)-Cl(1)	2.5299(8)	Mg(1)-Cl(1)	2.4392(9)
Mg(2)-Cl(1)	2.3767(9)	Mg(2)-Cl(1)	2.4384(9)
Mg(2)-Cl(2)	2.2939(8)	Mg(2) - N(01)	2.006(2)
Mg(1) - N(01)	1.999(2)	N(11) - C(12)	1.358(3)
N(1) - C(2)	1.354(2)	N(13) - C(12)	1.360(3)
N(3) - C(2)	1.361(2)	N(31) - C(32)	1.357(3)
N(21)-C(22)	1.357(2)	N(33) - C(32)	1.364(3)
N(23)-C(22)	1.360(2)		
Mg(1)-N(40)-Mg(2)	96.93(7)	Mg(1)-N(1)-Mg(2)	97.17(8)
Mg(1)-Cl(1)-Mg(2)	79.79(3)	Mg(1)-Cl(1)-Mg(2)	81.34(3)
N(1)-C(2)-N(3)	103.78(17)	N(11)-C(12)-N(13)	103.18(18)
N(21)-C(22)-N(23)	103.87(17)	N(31) - C(32) - N(33)	103.3(2)
C(2)-Mg(1)-N(01)	125.81(8)	C(12)-Mg(2)-N(01)	124.97(8)
C(22) - Mg(2) - Cl(2)	111.65(6)		

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There is a large range of angles around each magnesium centre, 120.8–93.6° for Mg(2) and 125.8–88.8° for Mg(1), comparable to the distortion in the structure seen for **F**, the previous example of functionalised-NHC magnesium adduct reported by our group.<sup>1</sup> The low coordination number, combined with the steric demands of the ligands makes it impossible to suggest if there is a secondary interaction between the  $\pi$ -donor amido or chloride ligand, and the formally empty carbenic carbon  $\pi^*$ , an interaction that is suggested to enhance the stability of some d<sup>0</sup> metal complexes.<sup>19</sup>

**4.2** X-Ray crystal structure of  $Mg_2(L)Cl(N'')_2$  5. The molecular structure of 5 is shown in Fig. 3. Both magnesium cations, Mg(1) and Mg(2), are four coordinate with distorted tetrahedral geometry. Selected distances and angles are collated in Table 1. One chloride ligand bridges both magnesium atoms as does the central amide of L. The remaining coordination sites are filled by one NHC and one silylamide for both magnesium centres, which accounts for the single ligand environment observed in the NMR spectra.

# Fig. 3 Displacement ellipsoid plot of the molecular structure of 5 (50% probability). Lattice solvent and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Mg1–N02 2.0096(18), Mg1–N1 2.116(2), Mg1–C32 2.199(2), Mg1–C11 2.4392(8), Mg2–N01 2.007(2), Mg2–N1 2.122(2), Mg2–C12 2.193(2), Mg2–C11 2.4382(8); N11–C12–N13 103.18(19), Mg2–C11–Mg1 81.34(3), Mg1–N1–Mg2 97.17(8), N1–Mg2–C11 90.65(5), C12–Mg2–C11 100.40(6), N01–Mg2–C12 124.97(8).

In contrast to the structure of **4**, the bridging chloride– magnesium bonds are now symmetrical in **5**; as are the Mg–NHC bond lengths; these are within the reported literature values for Mg–NHC bond lengths and longer than in **4**. As in **4** there is a large range of angles around each magnesium centre in **5**, 125.0– 90.7° for Mg(2) and 127.4–90.8° for Mg(1) and with smallest angle between bridging chloride, magnesium centre and bridging amide, comparable to **4**.

The magnesium–amide bonds for the central ligand amide in **5** are 2.116(2) Å for Mg(1)–N(1) and 2.122(3) Å for Mg(2)–N(1); both are longer than the Mg–amide bonds for the magnesium–NHC adduct **F** reported by our group, but in the normal range of magnesium amide bonds.<sup>20</sup>

# **Concluding remarks**

Attempts to isolate the free carbene, HL, from the protonated proligand have been unsuccessful due to the thermal lability of the ligand. However, treatment of the proligand  $H_4(L)Cl_3$  with

methylmagnesium chloride leads to the formation of a magnesium chloride adduct,  $Mg_3(HL)Cl_6$  1, which has been characterised by multinuclear NMR spectroscopy, EI mass spectrometry and elemental analysis.

Reduction chemistry has been carried out on 1, with the unexpected result of deprotonation of the amine in 1 and the formation of a potassium salt,  $Mg_3(KL)Cl_6$  3, which can subsequently be reduced to form an organic radical, in which the electron is centred predominantly on the back of the carbene ring.

Upon heating a solution of 1 in thf a purple-coloured compound is isolated which was characterised as  $Mg_2(L)Cl_3$ , 2, again as a result of the elimination of the acidic NH ligand proton, and loss of one of the incorporated equivalents of  $MgCl_2$  from the salt 1. The reaction of 1 with two or three equivalents of lithium hexamethyldisilazide leads to the formation of  $Mg_2(L)Cl_2N''$  4 and  $Mg_2(L)Cl(N'')_2$  5, both of which have been structurally characterised. The first equivalent of lithium amide is used in each case to deprotonate the ligand NH group once more. All of the Mg–C distances determined in the molecular structures of 4 and 5 are particularly short; compound 4 contains the shortest magnesium–carbene bond reported to date.

The robustness of the  $Mg_2L$  core in these complexes, and the ready functionalisation of the remaining anionic ligands of the two metals suggests that adducts of these complexes may be useful in Lewis acid catalysis, or coordination polymerisation initiation applications in the future. They may also serve as transmetallation sources of the ligand for metals that are capable of binding the NHC groups more strongly than the Mg cations.

# Experimental

### General experimental details

All manipulations of oxygen- or moisture-sensitive materials used standard Schlenk techniques (rotary pump for vacuum 10<sup>-4</sup> mbar) or a glove box (Mbraun Unilab or Mbraun Labstar) under dry dinitrogen. NMR spectra were recorded on a Bruker DPX 300 spectrometer, operating frequency 300 MHz (1H), 75 MHz (<sup>13</sup>C{<sup>1</sup>H}), 116 MHz (<sup>7</sup>Li), 121.5 Hz (<sup>31</sup>P{<sup>1</sup>H}) and 282.4 MHz (<sup>19</sup>F), variable temperature unit set to 300 K unless otherwise stated. Chemical shifts are reported in parts per million, and referenced internally to residual solvent proton resonance, and externally to TMS. FTIR spectra (4000–400 cm<sup>-1</sup>) were recorded as nujol mull on a JASCO 460 PLUS spectrophotometer. Mass spectra (EI, ES) were run by Mr. A. Hollingworth and Mr. G. Coxhill on a VG autospec instrument at the University of Nottingham. Elemental analyses were determined by S. Boyer at London Metropolitan University. EPR spectra were recorded on a Bruker X-band ESP 300E spectrometer with microwave frequencies calibrated with a Bruker ER035M NMR gaussmeter. EPR spectra were simulated using WINEPR SimFonia Version 1.25 (Bruker). All solvents used were either degassed and purified by passage through activated alumina towers prior to use, or were freshly distilled from the appropriate drying reagent under dinitrogen, and thoroughly degassed prior to use: DME and pyridine from potassium; dichloromethane from CaH<sub>2</sub>. NMR spectroscopic grade  $d_6$ -benzene and  $d_5$ -pyridine were dried over potassium metal, thoroughly degassed by the freeze-thaw method and transferred under reduced pressure before use. The synthesis



of  $[H_4L]Cl_3$  has been previously described.<sup>21</sup> MesIm = mesityl imidazole,  $C_3N_2H_2(C_6H_2Me_3-2,4,6)$ .

#### Synthetic procedures

Synthesis of HL. To a suspension of H<sub>4</sub>LCl<sub>3</sub> (1.00 g, 1.8 mmol) in thf (20 cm<sup>3</sup>) at -30 °C was added potassium hexamethyldisilazide (1.09 g, 5.4 mmol). The resulting mixture was stirred at -30 °C for 4 h to afford a yellow solution and white precipitate. The solution was filtered through a bed of Celite and volatiles were removed under reduced pressure at low temperature (> -10 °C) to afford a yellow solid of HL. Solutions and solid samples of HL decomposed over time to give a green–brown solid. <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  7.07 (s, 2H, CH), 6.86 (s, 6H, CH + Ar), 4.47 (t, 4H, <sup>3</sup>J = 6.2 Hz, CH<sub>2</sub>), 3.22 (t, 4H, <sup>3</sup>J = 6.2 Hz, CH<sub>2</sub>), 2.21 (s, 6H, *p*-CH<sub>3</sub>), 2.07 (s, 12H, *o*-CH<sub>3</sub>).

Synthesis of Mg<sub>3</sub>(HL)Cl<sub>6</sub> 1. To a Schlenk containing a cooled  $(0 \degree C)$  suspension of H<sub>4</sub>(L)Cl<sub>3</sub> (4.73 g, 8.58 mmol) in thf (30 cm<sup>3</sup>) was added methylmagnesium chloride (3 M solution in thf, 8.6 cm<sup>3</sup>, 25.75 mmol), dropwise over 10 minutes. The mixture was stirred at 0 °C for 4 h. During this time, the solution became red in colour and gas evolution was observed. The red solution was stirred at 0 °C for a further 16 h. During this time, a colourless precipitate formed, which was filtered and washed with thf  $(2 \times 20 \text{ cm}^3)$  to afford 1 as a colourless, solid, bis (thf) solvate, HL·3MgCl<sub>2</sub>·2thf (5.30 g, 70.9%). <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N): δ 7.11 (d, 2H,  ${}^{3}J = 1.2$  Hz, CH), 6.57 (d, 2H,  ${}^{3}J = 1.2$  Hz, CH), 6.24 (s, 4H, Ar), 4.62 (br, 4H, CH<sub>2</sub>), 3.60 (t, 8H, thf), 3.27 (br, 4H, CH<sub>2</sub>), 2.08 (s, 12H, o-CH<sub>3</sub>), 2.03 (s, 6H, p-CH<sub>3</sub>) and 1.56 (q, 8H, thf);  $^{13}C{^{1}H}$  NMR (C<sub>5</sub>D<sub>5</sub>N): 194.0 (N*C*N), 137.4, 137.1, 128.8 (all Ar), 121.7 (CH), 120.2 (CH), 67.8 (thf), 51.1 (CH<sub>2</sub>), 50.0 (CH<sub>2</sub>), 25.8 (thf), 20.8 (p-CH<sub>3</sub>) and 18.6 (o-CH<sub>3</sub>). IR (Nujol): 3274 (w), 3156 (w), 3115 (m), 3087 (m), 1608 (m), 1560 (m), 1480 (s), 1405 (m), 1098 (m), 1028 (s), 935 (w), 867 (m), 806 (w), 749 (m), 682 (w), 581 (w), 424 (m). MS (EI): m/z = 186 ([MesIm]<sup>+</sup>, 100%),  $159 ([MesIm - 2CH_3 + H]^+, 64\%), 144 ([PhIm]^+, 47\%).$  Anal. for  $C_{36}H_{51}Cl_6Mg_3N_5O_2$  [found (calc.)]: C, 49.54 (49.62); H, 5.99 (5.90); N, 8.08 (8.04%).

**Reaction of 1 with thf, 2.** A suspension of **1** (0.39 g, 0.45 mmol) in thf (10 cm<sup>3</sup>) was heated at 70 °C for 16 h yielding a purple solution. Removal of volatiles from the solution under reduced pressure afforded a dark purple solid of Mg<sub>2</sub>(L)Cl<sub>3</sub>, **2** <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  7.28 (s, 2H, Ar), 6.87 (s, 2H, CH), 6.80 (s, 2H, CH), 6.78 (s, 2H, Ar), 4.76 (br, 2H, CH<sub>2</sub>), 3.78 (br, 2H, CH<sub>2</sub>), 3.51 (br, 2H, CH<sub>2</sub>), 3.27 (br, 2H, CH<sub>2</sub>), 2.20 (s, 12H, *o*-CH<sub>3</sub>), 2.03 (s, 6H, *p*-CH<sub>3</sub>). Anal. for C<sub>28</sub>H<sub>34</sub>Cl<sub>3</sub>Mg<sub>2</sub>N<sub>5</sub> [found (calc.)]: C, 56.31 (56.47); H, 5.75 (5.75); N, 11.64 (11.76%).

Synthesis of Mg<sub>3</sub>(KL)Cl<sub>6</sub> 3. A Schlenk was charged with 1 (540 mg, 0.62 mmol) and KC<sub>8</sub> (84 mg, 0.62 mmol). To this was added thf (15 ml) and the resultant mixture was stirred at room temperature for 48 h. After this time the solution had become orange and the solid black. The mixture was filtered and volatiles were removed under reduced pressure to afford **3** as a light brown solid (0.45 g, 94.8%). <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  7.09 (d, 2H, <sup>3</sup>*J* = 1.4 Hz, C*H*), 6.59 (d, 2H, <sup>3</sup>*J* = 1.4 Hz, C*H*), 6.26 (s, 4H, Ar), 4.64 (br, 4H, C*H*<sub>2</sub>), 3.29 (br, 4H, C*H*<sub>2</sub>), 2.10 (s, 12H, *o*-C*H*<sub>3</sub>) and 2.01 (s, 6H, *p*-C*H*<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  194.1 (NCN), 137.4, 137.1, 129.3, 128.8 (all Ar), 121.6 (CH), 120.3 (CH), 51.1

(CH<sub>2</sub>), 50.0 (CH<sub>2</sub>), 20.8 (*p*-CH<sub>3</sub>) and 18.6 (*o*-CH<sub>3</sub>). IR (Nujol): 3122 (m), 3098 (m), 1609 (w), 1547 (w), 1489 (s), 1404 (m), 1236 (w), 1101 (m), 1029 (s), 937 (m), 853 (s), 803 (w), 671 (m), 580 (m). MS (EI): m/z = 586 ([M - 3CH<sub>3</sub> - MgKCl<sub>2</sub>]<sup>+</sup>, 34%), 305 ([Mg<sub>3</sub>Cl<sub>2</sub>(L)K - CH<sub>2</sub>]<sup>2+</sup>, 94%), 280 ([MgCl<sub>2</sub>(MesIm)]<sup>+</sup>, 34%), 197 (100%), 186 ([MesIm + H]<sup>+</sup>, 58%), 159 ([MesIm - 2CH<sub>3</sub> + H]<sup>+</sup>, 47%). Anal. for C<sub>28</sub>H<sub>34</sub>Cl<sub>6</sub>KMg<sub>3</sub>N<sub>5</sub> [found (calc.)]: C, 44.31 (43.94); H, 4.53 (4.48); N, 8.94 (9.15%).

Reduction of 3, 3a. A Schlenk was charged with 3 (100 mg, 0.13 mmol) and  $KC_8$  (18 mg, 0.13 mmol). To this was added thf (10 cm<sup>3</sup>) and the resulting mixture was stirred at room temperature for 48 h. After this time a yellow solution and black solid was afforded. The solution was filtered and the solid was washed with thf  $(2 \times 5 \text{ cm}^3)$  and the washings added to the yellow solution. Removal of the volatiles from the yellow solution under reduced pressure afforded an orange solid 3a. EPR spectrum of orange solid (X-band, modulation amplitude 1.0 G): fluid thf, referenced to dpph, simulated with  $g_{iso} = 2.00300$ . Spectral features simulated according to a hyperfine coupling to potassium, two nitrogens and two hydrogens, resolved as  $A_{\rm K} = 6.750$  G,  $A_{\rm N} = 5.200$  G and  $A_{\rm H} =$ 5.000 G, line width 3.20 G. MS (EI): m/z = 502 (8%), 428 ([H<sub>2</sub>L - $CH_3$ ]<sup>+</sup>, 17%), 354 (45%), 280 ([MgCl<sub>2</sub>(L)K - CH<sub>3</sub> + H]<sup>2+</sup>, 55%),  $186 ([MesIm]^+, 100\%), 159 ([MesIm - 2CH_3 + H]^+, 80\%), 144$  $([MesIm - 3CH_3 + H]^+, 60\%).$ 

Synthesis of Mg<sub>2</sub>(L)Cl<sub>2</sub>N", 4. To a suspension of 1 (0.50 g, 0.57 mmol) in thf (10 cm<sup>3</sup>) at room temperature was added a solution of lithium hexamethyldisilazide (0.19 g, 1.15 mmol) in thf (10 cm<sup>3</sup>). The resultant mixture was stirred for 48 h to yield a colourless solution. Removal of volatiles from the solution under reduced pressure afforded a colourless solid. The product was extracted with toluene  $(2 \times 10 \text{ cm}^3)$  to afford 4 as a colourless powder (0.26 g, 64.3%). Single crystals of 4 suitable for X-ray analysis were obtained by cooling a saturated toluene solution to -30 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.78 (s, 3H, Ar), 6.58 (s, 1H, Ar), 6.09 (d, 1H,  ${}^{3}J = 1.5$  Hz, CH), 6.04 (d, 1H,  ${}^{3}J = 1.5$  Hz, CH), 5.96 (d, 1H,  ${}^{3}J = 1.6$  Hz, CH), 5.82 (d, 1H,  ${}^{3}J = 1.6$  Hz, CH), 5.32 (br, 1H, CH<sub>2</sub>), 5.00 (m, 1H, CH<sub>2</sub>), 3.61 (2 m, 2H, CH<sub>2</sub>), 3.27 (m, 1H, CH<sub>2</sub>), 3.14 (m, 2H, CH<sub>2</sub>), 2.98 (m, 1H, CH<sub>2</sub>), 2.13 (s, 3H, CH<sub>3</sub>), 2.11 (s, 3H, CH<sub>3</sub>), 2.07 (s, 6H, CH<sub>3</sub>), 1.97 (s, 3H, CH<sub>3</sub>), 1.88 (s, 3H, CH<sub>3</sub>), 0.15 (s, 18H, N(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>);  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>): δ 182.3 (NCN), 179.9 (NCN), 139.1, 138.8, 136.2, 135.9, 135.7, 135.6, 134.9, 133.9, 130.0, 129.4 (All Ar), 122.4, 122.0, 121.0, 120.6 (CH), 56.0, 55.0, 52.7, 52.4 (All CH<sub>2</sub>), 21.0, 20.8, 18.5, 18.1, 17.9, 17.8 (All CH<sub>3</sub>), 6.0 (N(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>). IR (Nujol): 3398 (w, br), 3145 (w), 3124 (w), 3107 (w), 1653 (w), 1609 (w), 1488 (m), 1404 (w), 1245 (w), 934 (w), 850 (m), 737 (m), 582 (w). Anal. for C<sub>34</sub>H<sub>52</sub>Cl<sub>2</sub>Mg<sub>2</sub>N<sub>6</sub>Si<sub>2</sub> [found (calc.)]: C, 56.87 (56.68); H, 6.91 (7.27); N, 12.10 (11.66%).

Synthesis of Mg<sub>2</sub>(L)ClN"<sub>2</sub>, **5**. To a suspension of **1** (0.40 g, 0.46 mmol) in thf (10 cm<sup>3</sup>) at room temperature was added a solution of lithium hexamethyldisilazide (0.31 g, 1.84 mmol) in thf (5 cm<sup>3</sup>). The resultant mixture was stirred overnight to yield a pale pink solution. Removal of volatiles from the solution under reduced pressure afforded an off-white solid. The product was extracted with toluene giving **5** as a colourless solid (0.37 g, 76.8%). Single crystals of **5** suitable for X-ray analysis were obtained by cooling a saturated toluene solution to -30 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):

#### Table 2 Experimental crystallographic data

	4	5
Crystal data		
Chemical formula	$C_{34}H_{52}Cl_2Mg_2N_6Si_2.C_7H_8$	$C_{40}H_{70}ClMg_2N_7Si_4\cdot 2C_7H_8$
$M_{\rm r}$	812.65	1029.73
Cell setting	Monoclinic	Orthorhombic
Space group	$P2_{1}/c$	Pbca
T/Κ	150(2)	150(2)
a/Å	16.2204(12)	20.303(2)
b/Å	9.3907(7)	15.0642(11)
c/Å	31 198(2)	39.978(3)
$\beta/^{\circ}$	100 191(2)	59.976(5)
$V/Å^3$	4677 1(10)	12227(2)
7	4	8
$D / Mg m^{-3}$	1 154	1 119
Radiation type	Mo-Ka	Mo-Ka
$\mu/\text{mm}^{-1}$	0.25	0.20
Crystal form	Tablet	Cuboid
Colour	Colourless	Colourless
Crystal size/mm	$0.30 \times 0.23 \times 0.10$	$0.75 \times 0.62 \times 0.60$
Data collection		
Data collection method	$\omega$	(0)
Absorption correction	Multi-scan (based on symmetry-related measurements)	
$T_{\min}$	0.815	0.600
	0.932	0.769
No. measured, indep., observed reflections	34501, 10661, 7424	54860, 11314, 8741
Criterion for observation	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.044	0.047
$\theta_{\rm max}^{\rm max}/^{\circ}$	27.5	26.45
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.048, 0.122, 0.94	0.047, 0.124, 1.04
No. reflections	10661	11314
No. parameters	482	672
Weighting scheme <sup>a</sup>	$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 8.0274P]$
$(\Delta/\sigma)_{\rm max}$	0.001	0.006
$\Delta ho_{ m max},\Delta ho_{ m min}$ / e Å $^{-3}$	0.60, -0.37	0.52, -0.40
$^{a}P = (F_{o}^{2} + 2F_{c}^{2})/3.$		

δ 6.27 (d, 4H, <sup>3</sup>*J* = 8.0 Hz, Ar), 6.07 (d, 2H, <sup>3</sup>*J* = 1.7 Hz, C*H*), 5.96 (s, 2H, <sup>3</sup>*J* = 1.7 Hz, C*H*), 5.47 (m, 2H, C*H*<sub>2</sub>), 3.65 (m, 2H, C*H*<sub>2</sub>), 3.31 (m, 2H, C*H*<sub>2</sub>), 3.17 (m, 2H, C*H*<sub>2</sub>), 2.20 (s, 6H, C*H*<sub>3</sub>), 2.10 (s, 6H, C*H*<sub>3</sub>), 1.93 (s, 6H, C*H*<sub>3</sub>), 0.24 (s, 18H, N(Si(C*H*<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 0.16 (s, 18H, N(Si(C*H*<sub>3</sub>)<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 182.3 (NCN), 138.9, 136.2, 134.2, 130.2, 129.1 (All Ar), 122.2 (CH), 121.0 (CH), 54.5 (CH<sub>2</sub>), 53.0 (CH<sub>2</sub>), 20.9 (CH<sub>3</sub>), 18.4 (CH<sub>3</sub>), 18.1 (CH<sub>3</sub>), 6.4 (N(Si(C*H*<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 6.0 (N(Si(C*H*<sub>3</sub>)<sub>3</sub>)<sub>2</sub>). Anal. for C<sub>40</sub>H<sub>70</sub>ClMg<sub>2</sub>N<sub>7</sub>Si<sub>4</sub> [found (calc.)]: C, 56.67 (56.83); H, 8.28 (8.35); N, 11.42 (11.60%).

# Crystallographic details

Single-crystal diffraction data were collected using graphite monochromated Mo-K $\alpha$  X-radiation on either a Bruker SMART APEX (for 4) or a Bruker SMART1000 (for 5) CCD area detector diffractometer equipped with an Oxford Cryosystems Cryostream cooling device.<sup>22</sup> Details of the individual data collections, solutions and refinements are given in Table 2.

CCDC reference numbers 679263 and 679264.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b803253j

Structures were solved by direct methods using SHELXS97.<sup>23</sup> All structures were refined by full-matrix least-squares against  $F^2$  using SHELXL97, and all fully occupied non-H atoms refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were geometrically placed and included as part of a riding model, except for methyl hydrogen atoms which were located from difference Fourier maps and included as part of a rigid rotor. Two molecules of toluene were each modeled as disordered over two half-occupied sites, with isotropic adps and distance restraints applied.

# Acknowledgements

We thank Professor Martin Schröder of the University of Nottingham for helpful discussions. We also thank the Alexander von Humboldt Foundation, the Royal Society, the EPSRC and the Universities of Edinburgh and Nottingham for funding.

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