Monomeric magnesium 1-azaallyl and β-diketiminato complexes derived from the bis(trimethylsilyl)methyl ligand: The X-ray structure of the four-coordinate planar magnesium complex $[Mg\{N(R)C(Bu^t)C(H)R\}_2]$ and of $[Mg(\{N(R)C(Ph)\}_2CH)_2]$†

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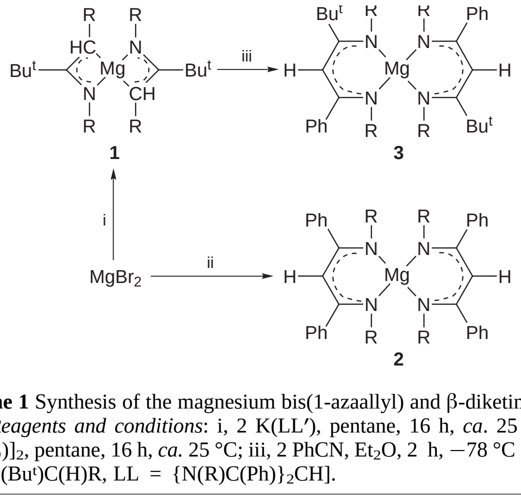
Reaction of $[K\{N(R)C(Bu^t)C(H)R\}]_n$ $\{[K(LL')]_n\}$ or $[Li(\{N(R)C(Ph)\}_2CH)]_2$ $\{\equiv [Li(LL)]_2\}$ with magnesium bromide yielded the monomeric, crystalline magnesium complexes $[Mg(LL')_2]$ 1 or $[Mg(LL)_2]$ 2, which have been structurally characterised; 1 has the magnesium atom in an unusual planar environment.

Monomeric magnesium complexes containing monoanionic bidentate ligands are rare. Four-coordinate examples have been based upon an alkyl-functionalised pyridyl or a 1,4-diazabutadiene ligand, $[Mg\{CR_2(C_5H_4N\text{-}2)\}_2]$[1] or $[Mg\{N(Bu^t)(CH)_2N(Bu^t)\}_2]$[2] (R = $SiMe_3$), while the benzamidinate ligand $[N(R)C(Ph)NR]^-$ has generated a range of solvated monomeric Mg complexes $[Mg\{N(R)C(Ph)NR\}_2L_n]$ (L = absent; L = PhCN, n = 1; or L = thf and n = 2).[3] Recent examples of main group metal β-diketiminates include $[Al\{N(p\text{-Tol})C(Me)C(H)C(Me)N(p\text{-Tol})\}Cl_2]$[4] ($p$-Tol = p-C_6H_4Me) and $[Ba_3\{N(R')C(Me)C(H)C(Me)NR'\}_3(NR_2)]$ (R = $SiMe_3$, R′ = C_6H_{11}).[5] The synthesis and reactions of some alkali metal α,ω-bis(trimethylsilyl)-1-azaallyl and α,β-diketiminates, including their role in preparing unusual transition metal and main group element complexes has been reviewed.[6] We now report the syntheses and structures of the magnesium bis(1-azaallyl) $[Mg(LL')_2]$ **1** (Scheme 1, step i) and bis(β-diketiminate) $[Mg(LL)_2]$ **2** (Scheme 1, step ii) and the subsequent reaction of **1** with PhCN to yield the asymmetric β-diketiminato complex $[Mg(LL'')_2]$ **3** (Scheme 1, step iii) [LL′ = $N(R)C(Bu^t)C(H)R$, LL = $N(R)C(Ph)C(H)C(Ph)NR$, LL″ = $N(R)C(Bu^t)C(H)C(Ph)NR$, R = $SiMe_3$].

The new, pale yellow, air-sensitive, readily hydrocarbon-soluble, crystalline solids **1**–**3** gave satisfactory elemental analyses, NMR spectroscopic‡ and X-ray (**1** and **2**)§ data.



Scheme 1 Synthesis of the magnesium bis(1-azaallyl) and β-diketiminates **1**–**3**. *Reagents and conditions*: i, 2 K(LL′), pentane, 16 h, *ca.* 25 °C; ii, $[Li(LL)]_2$, pentane, 16 h, *ca.* 25 °C; iii, 2 PhCN, Et_2O, 2 h, −78 °C [LL′ = $N(R)C(Bu^t)C(H)R$, LL = $\{N(R)C(Ph)\}_2CH$].

The X-ray molecular structures of crystalline **1** and **2** are shown in Figs. 1 and 2.§ Especially noteworthy is that the centrosymmetric **1** exhibits a very unusual planar coordination geometry around the magnesium centre (*cf.*[1] the distorted tetrahedral geometry in $[Mg\{CR_2(C_5H_4N\text{-}2)_2\}])$. The ligands in **1** are bonded in a *trans*-chelate fashion forming with the magnesium atom a chair skeletal conformation. The angle

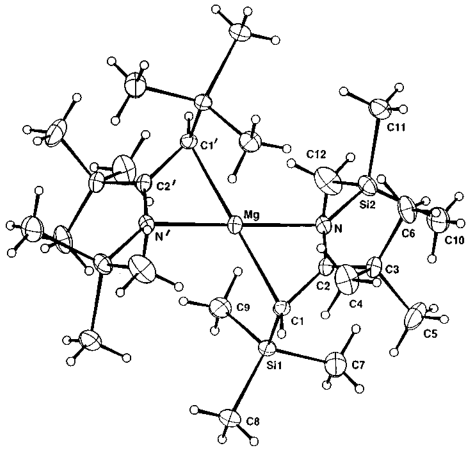


Fig. 1 Molecular structure of **1** with selected bond distances (Å) and angles (°): Mg–N 2.084(3), Mg–C(1) 2.284(4), Mg–C(2) 2.408(4), N–C(2) 1.347(5), C(1)–C(2) 1.405(6), C(2)–C(3) 1.546(6); N–Mg–N′ 180.0, C(1)–Mg–C(1)′ 180.0, N–Mg–C(1) 64.27(14), C(2)–N–Mg 86.3(2), N–Mg–C(1)′ 115.73(14), N–C(2)–C(1) 115.7(4), C(2)–N–Si(2) 140.7(3).

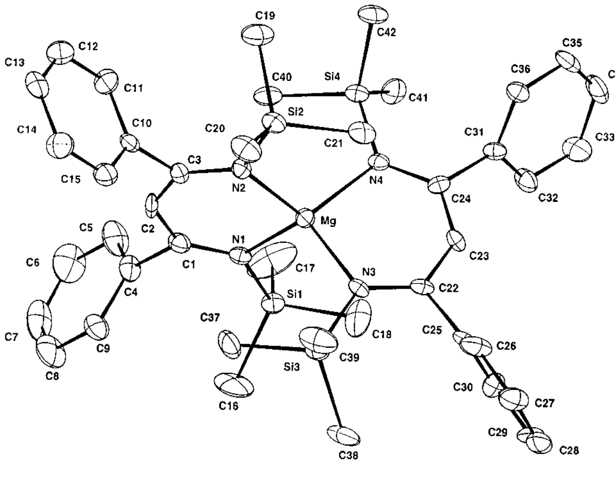


Fig. 2 Molecular structure of **2** with selected bond distances (Å) and angles (°): Mg–N(1) 2.096(8), Mg–N(2) 2.068(8), N(1)–C(1) 1.299(11), C(1)–C(2) 1.432(13), C(2)–C(3) 1.403(13), C(3)–N(2) 1.318(11), C(1)–C(4) 1.499(14); N(1)–Mg–N(2) 99.7(3), N(1)–Mg–N(3) 114.3(3), N(1)–Mg–N(4) 113.6(3), Mg–N(2)–C(3) 117.0(6), Mg–N(1)–C(1) 116.6(7), C(1)–C(2)–C(3) 131.5(9).

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† No reprints available.

between the planes NC(2)C(1) and MgNC(1)N′C(1)′ is *ca.* 46°; the Mg–C(2) distance of 2.408(4) Å is too long for a single bond but lies within the sum of the van der Waals radii. The Mg–N bond of 2.084(3) Å is longer than the terminal Mg–N bonds [1.975(7) Å] in the three-coordinate magnesium amide $[\mathrm{Mg}(\mu\text{-}\mathrm{NR}_2)(\mathrm{NR}_2)]_2$,[7] but shorter than in the related magnesium complex $[\overline{\mathrm{Mg}\{\mathrm{CR}_2(\mathrm{C}_5\mathrm{H}_4\mathrm{N}}\mathrm{)\text{-}2}\}_2]$ (2.13(1) Å).[1] The N–C and C–C bond lengths lie in between values for single and double bonds; therefore, a degree of π-delocalisation is assumed. 'Ideal' planar magnesium geometry exists in the (tetraphenylporphyrinato)magnesium bis(methyl benzoate) clathrate.[8] Porphyrins are so rigid, that they often form a nearly planar geometry about a metal;[8–10] however, the 1-azaallyl ligand is not rigid and therefore it is very surprising that **1** is planar. This unusual geometry has also been observed for the Group 2 metal compound, [*trans*-$\mathrm{Sr(NR_2)_2}$(μ-1,4-dioxane)], where the unexpected stereochemistry about the strontium atom was attributed to agostic intramolecular CH···Sr interactions [Sr···C 3.16(1) Å] with resultant widening of the Si–N–Si angles to 126.4°; the environment about the strontium atom was then best described as quasi-octahedral.[11] The polymeric dialkylmagnesium compound $[\mathrm{Mg(CHR_2)_2}]_\infty$ is stabilised by intermolecular interactions of 2.535(4) Å between each magnesium atom and a γ-methyl group of a neighbouring $\mathrm{Mg(CHR_2)_2}$.[12] In **1**, the closest possible intramolecular contacts (from a methyl group to the magnesium atom) are Mg···H 2.626(3) Å and Mg···C(9) 2.897(3) Å (within the limits of van der Waals forces); however, no significant lengthening of the C(9)–Si(1) bond or distortion of the geometry about the methyl group was observed. The large C(2)–N–Si(2) bond angle of 140.7(3)° in **1** may be due to steric repulsion between the $\mathrm{SiMe_3}$ and $\mathrm{Bu^t}$ groups as no distortion of the geometry about the Si atoms was observed.

Preliminary first principle AIMPRO (a local density functional, pseudo-potential code[13]) calculations on the whole, isolated molecule, support the planar structure, being 9 kJ $\mathrm{mol^{-1}}$ lower in energy than the tetrahedral structure.¶ Such a small energy difference is possibly beyond the accuracy of the code, but indicates the viability of the planar Mg structure. Further calculations will be reported in the full paper. Using the CAChe™ mechanics program, using an enhanced MM2 parametrised force field,[14] we found that the tetrahedral structure is disfavoured by virtue of interligand repulsion between an $\mathrm{SiMe_3}$ at the γ-C of one ligand and $\mathrm{SiMe_3}$ at N of the other.

Crystalline **2** is the first structurally authenticated example of a simple magnesium β-diketiminate [a macrocyclic bis(ketiminate) is known[15]]. In **2** the magnesium atom is in a distorted tetrahedral environment. The ligands bind η^2 to the magnesium atom through the nitrogen atoms with no observed interactions from the C(1), C(2) or C(3) atoms to the magnesium, as in the related Li complex.[5] Each $\overline{\mathrm{MgNCCCN}}$ skeleton is planar, as also is the case in the isoleptic transition metal $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$ or $\mathrm{Pd^{II}}$ compounds,[6,16] and in $\overline{\mathrm{Sn(LL)}}\mathrm{Cl}$. This differs from the situation found in the complexes $[\mathrm{Li(LL)}]_2$,[6] $[\overline{\mathrm{Sn(LL)}}\mathrm{Me_3}]$[6] or $[\overline{\mathrm{Al(LL)}}\mathrm{Me_2}]$[17] in which MLL is boat-shaped, $[\mathrm{LL}]^-$ having some η^5- character. It may be that the latter group of complexes favour the boat conformation not only because of their having strong Lewis acid metal sites, but also because the metal is coordinatively unsaturated. Calculations will be reported in the full paper.

The two ligands in **2** are almost orthogonal to one another. The N–C and C–C bond lengths lie in between those for single and double N–C and C–C bonds. This, combined with the coplanarity of each ring, shows that there is a degree of π-delocalisation. The four Mg–N bond lengths in **2** are identical within estimated standard deviations and are similar to values reported for $[\overline{\mathrm{Mg}\{\mathrm{N(Bu^t)(CH)_2N}}\mathrm{(Bu^t)}\}_2]$.[2] The monomeric nature of **2** is presumably due to the $\mathrm{SiMe_3}$ ligands preventing further attack at the metal centre, demonstrated by the relatively air-stable nature of **2**, as well as its surprising inertness to reaction with small donor molecules (*e.g.* PhCN), metal halides or even protic species.

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Notes and references

‡ Selected spectroscopic data [^{1}H at 300 MHz and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ at 62.9 MHz in $\mathrm{C_6D_6}$ (**1**–**3**)]. **1**: ^{1}H δ 0.29 ($\mathrm{SiMe_3}$, s), 0.33 ($\mathrm{SiMe_3}$, s), 1.19 ($\mathrm{Bu^t}$, s) and 3.40 (CH, s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ δ 74.8 (CH) and 207.5 (C(2)). **2**: ^{1}H δ 0.32 ($\mathrm{SiMe_3}$, s) and 5.23 (CH, s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ δ 3.8 ($\mathrm{SiMe_3}$) and 107.7 (CH). **3**: ^{1}H δ 0.31 ($\mathrm{SiMe_3}$, s), 0.73 ($\mathrm{SiMe_3}$, s), 0.97 ($\mathrm{Bu^t}$, s) and 5.52 (CH, s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ δ 104.6 (CH).

§ *Crystal data* for **1** and **2**: data for each of **1** and **2** were collected at 173(2) K on an Enraf-Nonius CAD4 diffractometer in the ω-2θ mode in the range $2 < \theta < 25°$ (**1**) or 23° (**2**). The structures were refined by full-matrix least squares on all F^2 (SHELXL 93).

1: $\mathrm{C_{24}H_{56}MgN_2Si_4}$, M = 509.4, orthorhombic space group *Pbca*, a = 10.929(2), b = 17.815(4), c = 16.857(6) Å, U = 3282(2) Å^3, Z = 4, D_c = 1.03 g cm^{-3}, μ(Mo-Kα) = 0.21 mm^{-1}. Final residuals were R_1 = 0.064, for the 1729 with $I > 2\sigma(I)$ and wR_2 = 0.183 for all 2875 reflections.

2: $\mathrm{C_{42}H_{58}MgN_4Si_4{\cdot}C_5H_{12}}$, M = 827.74, monoclinic space group $P2_1/c$ (no.14), a = 12.078(4), b = 35.114(8), c = 12.123(3) Å, β = 104.25(2)°, U = 4983(2) Å^3, Z = 4, D_c = 1.10 g cm^{-3} μ(Mo-Kα) = 0.17 mm^{-1}. Final residuals were R_1 = 0.094, for the 2971 with $I > 2\sigma(I)$, and wR_2 = 0.290 for all 6923 reflections. CCDC 182/1320.

¶ AIMPRO is a density functional code using non-conserving pseudopotentials, a wave function basis of atom-centred s,p Gaussians and a charge density fitted to s Gaussians. Three independent Gaussian exponents were used for H (for which the bare Coulomb potential was used), four for C and five each for N, Si and Mg. Geometry optimisation was by conjugate gradient and the local density approximation was employed.

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