

A monomeric three-coordinate magnesium bis(amide)

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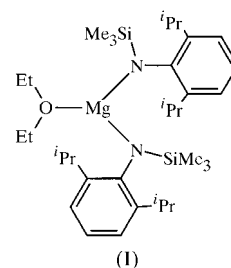
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The metallation reaction between dibutylmagnesium and 2,6-diisopropyl-*N*-(trimethylsilyl)aniline gives the unusual monomeric three-coordinate complex (diethyl ether- κO)bis[2,6-diisopropyl-*N*-(trimethylsilyl)anilido- κN]magnesium(II), [Mg-(C₁₅H₂₆NSi)₂(C₄H₁₀O)] or [Mg{(Me₃Si)(2,6-*i*Pr₂C₆H₃)N}₂(Et₂O)]. This low-coordinate species has a distorted trigonal-planar coordination environment, with an additional short Mg–C_{ipso} contact of 2.799 (2) Å.

Comment

Magnesium bis(amides) are typically isolated as tetrahedrally coordinated compounds of the type [MgL₂S₂], where *L* is an amide ligand and *S* a donating solvent, or as dimeric species of the type [LS_{*x*}Mg(μ-*L*)₂MgLS_{*x*}] (*x* = 0 or 1), where Mg is in either a trigonal-planar or a tetrahedral environment [for typical examples, see Sebestl *et al.* (1998) and Clegg *et al.* (1997)]. Lower coordination numbers are favoured by sterically demanding amide groups. Indeed, it has been shown that where *L* is (Me₃Si)₂N (hereafter HMDS) or (PhCH₂)₂N, monomers of the type MgL₂ are present in solution (Henderson *et al.*, 1997; Clegg *et al.*, 1997). In an attempt to isolate such coordinatively unsaturated species in the solid state, we turned to the sterically hindered amide [(Me₃Si)(2,6-*i*Pr₂C₆H₃)N], denoted *A*. This ligand is known to stabilize low coordination number complexes in *d*-block chemistry (Chao *et al.*, 1989; Kennepohl *et al.*, 1992), including ZnA₂ (Schumann *et al.*, 2000). This last example is of particular relevance, as many Mg and Zn amides are isostructural (Forbes *et al.*, 2000). To our knowledge, the use of this ligand in *s*-block chemistry has been limited to lithium chemistry, where it has allowed the structural characterization of the first non-solvated [Li(μ-*L*)₂Li] dimer (Kennepohl *et al.*, 1991) and of the unusual three-coordinate monomeric species [LiA(Et₂O)(C₅H₅N)] (Blake *et al.*, 1996). Reaction of [(Me₃Si)(2,6-*i*Pr₂C₆H₃)NH] with dibutylmagnesium produced a colourless material, which was identified as the title compound, (I), by single-crystal diffraction; the results are presented here.

The crystal structure of (I) consists of discrete monomers separated by at least the sum of the van der Waals radii. Unusually, the Mg atom is three-coordinate, bonding to two amide units and a diethyl ether molecule in a planar manner [Mg1 lies 0.042 (1) Å from the N1/N2/O1 plane]. Although this coordination geometry is common in dimeric (Clegg *et al.*, 1997) and polymeric (Andrews *et al.*, 2000) magnesium amide solid-state structures, a search of the Cambridge Structural Database (version 5.21; Allen & Kennard, 1993) revealed only



[Mg(HMDS)₂S], (II) (*S* = 2-picoline or 2,6-lutidine; Sebestl *et al.*, 1998), and the chelate [Mg⁺Bu{(N,N-(2,6-*i*Pr₂C₆H₃)NC-(Me)CHC(Me)N(2,6-*i*Pr₂C₆H₃))}] (Gibson *et al.*, 2000), with similar three-coordinate monomeric structures. An illustration of the coordinatively unsaturated nature of these species is that, unlike (I), (II) is not isolated in the presence of solvent. Indeed, dissolution of (II) in any suitable solvent gives only [Mg(HMDS)₂S₂] as an isolable product. Some relief from coordinative unsaturation is perhaps gained from the short Mg1...C4 interaction [2.799 (2) Å, compared with 2.399–2.443 Å for Mg–C distances in Mg–Cp (Cp is cyclopentadienyl); Lehmkuhl *et al.*, 1986]. This interaction is accompanied by a compression of the bond angle at N1 compared with that in the second *A* moiety [Mg1–N1–C4 109.37 (10)°, Mg1–N2–C19 116.07 (10)° and Mg1...C19 2.906 (2) Å]. A similar short contact was observed in [LiA(Et₂O)(C₅H₅N)] (Blake *et al.*, 1996).

The environment of atom N1 is less planar than that of N2 [the deviations from planarity are 0.119 (2) and 0.037 (2) Å,

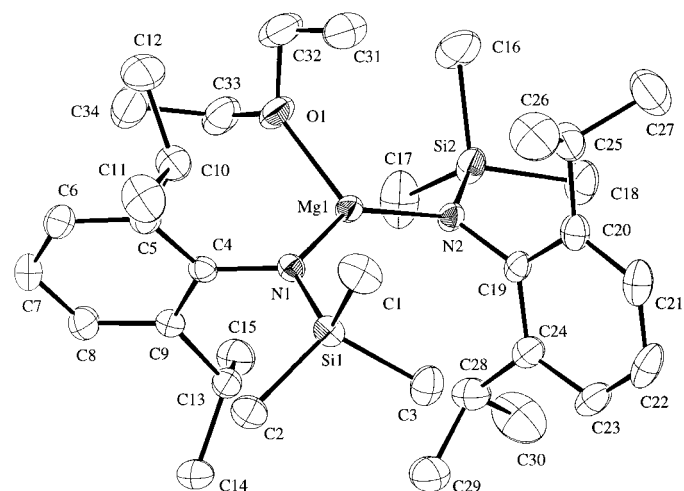


Figure 1

The molecular view of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

respectively]. The Mg–N bond lengths are similar to each other (Table 1), and to those found in (II) and in the non-bridging bonds of [(HMDS)Mg(μ -HMDS)₂Mg(HMDS)] (Westerhausen & Schwarz, 1992). They are, however, approximately 0.05–0.06 Å shorter than the typical distances observed in the tetrahedral species [Mg(HMDS)₂S₂] (Sebestl *et al.*, 1998; Forbes *et al.*, 2001). The N1–Mg1–N2 angle of 140.69 (6)° shows considerable widening to accommodate the two A ligands. The planes of the two aryl rings and of the ether ligand lie approximately perpendicular to the N1/N2/O1 plane [85.92 (5), 88.83 (5) and 83.35 (7)° for the angles to the planes defined by C4–C9, C19–C24 and O1/C32/C33, respectively] so as to minimize steric interactions. Similarly, the two aryl rings are mutually *anti* with respect to the coordination plane, and the improper torsion angle C4–N1–N2–C19 is –150.1 (3)°.

Experimental

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk tube techniques. 2,6-Diisopropyl-*N*-(trimethylsilyl)aniline was synthesized as an ether-containing yellow liquid according to the method of Chao *et al.* (1989). This amine (6 mmol) was then added to a 0.875 M solution of dibutylmagnesium (3 mmol) in heptane at 273 K. After heating the solution at reflux for 2 h, the volatile portions were removed under vacuum to leave (I) as a colourless solid (0.6 mmol, 20% yield), together with an unidentified orange oil. Crystals of (I) suitable for study by single-crystal diffraction were obtained from hexane solution.

Crystal data

[Mg(C ₁₅ H ₂₆ NSi) ₂ (C ₄ H ₁₀ O)]	$D_x = 1.044 \text{ Mg m}^{-3}$
$M_r = 595.35$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 12.359 (2) \text{ \AA}$	$\theta = 15.7\text{--}18.5^\circ$
$b = 18.443 (3) \text{ \AA}$	$\mu = 0.14 \text{ mm}^{-1}$
$c = 16.984 (2) \text{ \AA}$	$T = 123 (2) \text{ K}$
$\beta = 101.900 (14)^\circ$	Plate, colourless
$V = 3788.1 (10) \text{ \AA}^3$	$0.55 \times 0.30 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7S diffractometer	$h = 0 \rightarrow 16$
$\omega/2\theta$ scans	$k = 0 \rightarrow 23$
9082 measured reflections	$l = -22 \rightarrow 21$
8689 independent reflections	3 standard reflections
5523 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.023$	intensity decay: 0.9%
$\theta_{\text{max}} = 27.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.9303P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
8689 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
377 parameters	
H-atom parameters constrained	

All H atoms were placed in calculated positions and refined as riding, with C–H = 0.95–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR* (Altomare *et al.*, 1994); program(s) used to refine structure:

Table 1

Selected geometric parameters (Å, °).

Mg1–N1	1.9761 (14)	Mg1–O1	2.0361 (13)
Mg1–N2	1.9789 (14)		
N1–Mg1–N2	140.69 (6)	Si1–N1–Mg1	131.15 (8)
N1–Mg1–O1	109.54 (6)	C19–N2–Si2	116.59 (10)
N2–Mg1–O1	109.63 (6)	C19–N2–Mg1	116.07 (10)
C4–N1–Si1	117.98 (10)	Si2–N2–Mg1	127.20 (8)
C4–N1–Mg1	109.37 (10)		
N1–Mg1–O1–C32	87.27 (14)	O1–Mg1–N1–C4	36.30 (12)
N2–Mg1–O1–C32	–96.17 (14)	N1–Mg1–N2–C19	–20.50 (17)
N2–Mg1–N1–C4	–138.58 (11)	O1–Mg1–N2–C19	164.61 (11)

SHELXL97 (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1003). Services for accessing these data are described at the back of the journal.

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