Selective crystallization of di-*sec*-butylmagnesium. *N*,*N*,*N'*,*N'*-tetramethylethylenediamine from solutions containing mixtures of normal-butyl and secondary-butyl isomers

Nicholas D.R. Barnett [a], William Clegg [b], Robert E. Mulvey [a,*], Paul A. O'Neil [b], David Reed [c]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK*
[b] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK*
[c] *Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, UK*

Abstract

Found to crystallise selectively from treatment of commercial $^sBu(^nBu)Mg$ solutions with *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), the complex ($^sBu_2Mg \cdot$ TMEDA) is mononuclear in the crystal state and undergoes a solvation–desolvation equilibrium in arene solution. The crystal structure is noteworthy for the large C–Mg–C bond angle of 133.6(2)°, attributable to the branched nature of the alkyl substituents. This angular distortion is thought to encourage the partial loss of TMEDA from Mg centres in solution.

Keywords: Magnesium; sec Butyl; Crystal structure; Nuclear magnetic resonance; Organomagnesium

1. Introduction

The commercial availability of "dibutylmagnesium" (DBM) has significantly increased opportunities for synthesizing new magnesium organic derivatives as it can facilitate easily and efficiently magnesium–hydrogen transfer reactions with a variety of organic substrates bearing acidic hydrogen atoms. First utilized a decade ago [1], DBM has most recently been reported to be a valuable starting material for the synthesis of magnesium heteroleptic bis(amides) [2]. In industry, it serves as a raw material for the production of catalysts and catalyst supports used in stereospecific polymerizations of α-olefins [3]. Developed by FMC [4], DBM is not a precise stoichiometric compound but rather a solution mixture consisting formally of Mg atoms, approximately equal amounts of ^sBu and ^nBu groups, and a small percentage of ^nOct groups to aid solubility in acyclic hydrocarbons (commercial solutions come in *n*-heptane). This property, which circumvents the need

for ethereal solvents, gives DBM a distinct advantage over conventional Grignard reagents. DBM is easily prepared by the two-step method [4] outlined in Scheme 1. No definite structural information is available on DBM, although it is assumed to be oligomeric with pairs of Mg atoms linked by μ_2-bonding ^nBu chains, while bulkier ^sBu branches occupy the more open terminal sites (Fig. 1). As reported here, attempts to secure bona fide structural data have led to a surprising discovery; the addition of stoichiometric amounts of the diamine *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) ($Me_2NCH_2CH_2NMe_2$) causes preferential crystallization of the complex ($^sBu_2Mg \cdot$ TMEDA) (1), i.e. "^sBu groups" are selectively extracted from solution, leaving "^nBu groups" behind. The crystal structure of 1 reveals a distorted tetrahedral mononuclear arrangement with a large C–Mg–C bond angle, that exerts strain on the (bidentate) TMEDA–Mg linkage. Consequently, dissolution of 1 in benzene-d_6 sets up a solvation–desolvation equilibrium, the TMEDA-free component of which is presumably dimeric [($^sBu_2Mg)_2$].
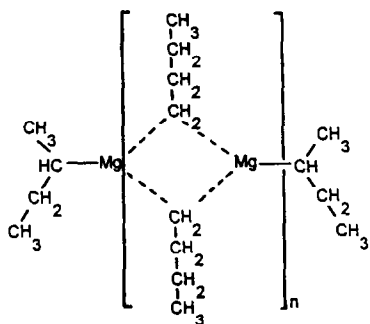
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* Corresponding author.

Fig. 1. One suspected oligomeric structure of DBM. For the stoichiometry shown, $n = 1$.

2. Results and discussion

The best method for preparing X-ray quality crystals of 1 with a high yield (greater than 90%) was to treat a heptane solution of DBM (10 mmol) with the minimum amount of TMEDA necessary to complex all the $^sBu_2Mg$ present (i.e. 2.5 mmol). This method would leave "pure" $^nBu_2Mg$ in solution. The known solvated analog $[(^nBu_2Mg \cdot TMEDA)_n]$, reputed to be a liquid at ambient temperature [5], would be generated in addition to 1 in cases where DBM:TMEDA ratios fall below 1:0.25 (maximum yield would be reached at 1:1). These findings can be summed up by the following equilibrium (ignoring ^nOct groups):

$$2^nBu(^sBu)Mg \xrightleftharpoons{\hspace{1cm}} {}^nBu_2Mg + {}^sBu_2Mg \qquad (1)$$

$$\downarrow \text{TMEDA}$$

$$1$$
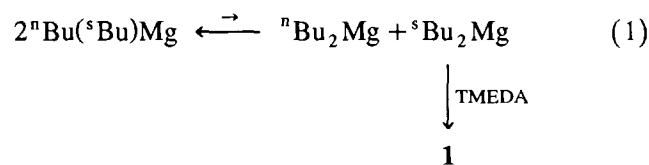
The crystallographic characterization of 1 (Fig. 2) allows comparison with closely related diorganomagnesium · TMEDA monomeric structures, $R_2Mg \cdot TMEDA$ (where R = Ph [6], Et [7] or Me [7]). Compared with the C–Mg–C bond angles in these structures (119.4°, 128.3° (mean) and 130.0° respectively), the even larger value found for 1 (133.6°) confirms that the ^sBu ligand is the most sterically demanding in the vicinity of the metal atom. There is a concomitant diminution in the N–Mg–N bond angles (82.5°, 82.4°, 81.5° and 81.0° respectively), but the differences are not so marked. A trend is also discernible in N–Mg bond distances, reflecting a gradual pushing away of the chelating TMEDA ligand from the metal centre (respective mean values, 2.202, 2.237, 2.242 and 2.252 Å), although again differences are small. Similarly, C–Mg bond distances vary little,
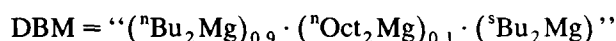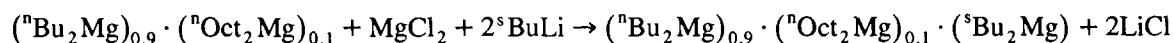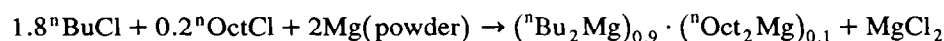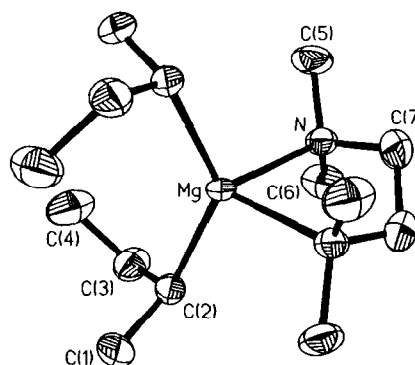

Fig. 2. Thermal ellipsoid plot (40% probability) of the molecular structure of 1 without hydrogen atoms. Key dimensions: Mg–C(2), 2.181(3) Å; Mg–N, 2.252(3) Å; C(2)–Mg–C(2a), 133.6(2)°; N–Mg–N(a), 81.0(2)°; C(2)–Mg–N, 108.72(12)°; C(2a)–Mg–N, 106.20(12)°. Symmetry operator (C_2 rotation) for equivalent atoms denoted by a: $-x, y, -z + \frac{3}{2}$.

although the longest are found in 1 (respective mean values, 2.167, 2.150, 2.166 and 2.181 Å). All the bond distances and bond angles in 1 are listed in Table 1; Table 2 gives atomic coordinates.

In the wider context of organomagnesium chemistry, the monomeric distorted-tetrahedral configuration of 1 and its associated features (large C–Mg–C bond angle and small N–Mg–N bond angle; in general, a large C–Mg–X bond angle and a small L–Mg–L bond angle (X = anion; L = solvent ligand), e.g. as in Grignard complexes RMgX.2L) are commonplace. Interestingly, the angular distortion cannot be due exclusively to steric restrictions imposed by the formation of chelate bridges. Structures containing two monodentate ligands L show the same effect. Even with bulky ligands, as in $[Me_2Mg.2(Quinuclidine)]$, a large C–Mg–C bond angle is maintained (129°; cf. N–Mg–N, 108°) [8]. Hybridization arguments can be invoked to help to explain this phenomenon. Regarding such complexes as strong, covalently bonded R_2Mg fragments solvated by N-donor molecules, then the inherent linear sp hybridization of the C–Mg–C unit is only partially disturbed by the weaker coordination of the Lewis base, i.e. in effect the monomeric R_2Mg unit "remembers" what its geometry was prior to undergoing solvation. An excellent review describing X-ray structural analyses of organomagnesium compounds [9] has discussed this topic in considerable detail.

The tight fit of the TMEDA ligand within the monomeric structure of 1 leads to a partial breakdown of the complex in benzene-d_6 solution, as seen in the ^1H

$$1.8^nBuCl + 0.2^nOctCl + 2Mg(powder) \rightarrow (^nBu_2Mg)_{0.9} \cdot (^nOct_2Mg)_{0.1} + MgCl_2$$

$$(^nBu_2Mg)_{0.9} \cdot (^nOct_2Mg)_{0.1} + MgCl_2 + 2^sBuLi \rightarrow (^nBu_2Mg)_{0.9} \cdot (^nOct_2Mg)_{0.1} \cdot (^sBu_2Mg) + 2LiCl$$

$$DBM = \text{``}(^nBu_2Mg)_{0.9} \cdot (^nOct_2Mg)_{0.1} \cdot (^sBu_2Mg)\text{''}$$

Scheme 1.

Table 1
Bond lengths (Å) and angles (°) for 1

Bond lengths

Mg–C(2)	2.181(3)	Mg–N	2.252(3)
C(1)–C(2)	1.546(6)	C(2)–C(3)	1.526(5)
C(3)–C(4)	1.509(6)	N–C(6)	1.462(5)
N–C(7)	1.470(5)	N–C(5)	1.481(5)
C(7)–C(7a)	1.505(9)		

Bond angles

C(2)–Mg–C(2a)	133.6(2)	C(2)–Mg–N	108.72(12)
C(2a)–Mg–N	106.20(12)	N(a)–Mg–N	81.0(2)
C(3)–C(2)–C(1)	109.5(3)	C(3)–C(2)–Mg	115.5(2)
C(1)–C(2)–Mg	114.4(2)	C(4)–C(3)–C(2)	113.1(3)
C(6)–N–C(7)	112.8(4)	C(6)–N–C(5)	108.3(3)
C(7)–N–C(5)	107.4(3)	C(6)–N–Mg	111.7(2)
C(7)–N–Mg	104.9(2)	C(5)–N–Mg	111.7(2)
N–C(7)–C(7a)	111.2(3)		

Symmetry transformations used to generate equivalent atoms as indicated by a: $-x, y, -z + \frac{3}{2}$.

NMR spectrum (Fig. 3). Free TMEDA characteristically appears as two singlet resonances (Me at 2.13 ppm; CH_2CH_2 at 2.36 ppm). In contrast, the solvated variety appear as more complex, second-order resonance patterns (centred at 1.82 and 1.53 ppm respectively), suggesting non-equivalent Me groups and non-equivalent CH_2CH_2 protons consistent with a metal-bound ligand in a fixed stereochemistry. From the integration values, the bound-TMEDA : free-TMEDA ratio is approximately 2 : 1. The free- and bound-TMEDA molecules exchange and this process can be monitored by saturation transfer, e.g. irradiation of the "free" Me signal causes a reduction in intensity of the "bound" Me signal. It follows that there should be two distinct solution species containing ^sBu groups: 1 and a TMEDA-free derivative. Given that an authentic sample of $[(^sBu_2Mg)_n]$ has previously been reported to be dimeric ($n = 2$) in cyclopentane (measured by osmometry) [10], the latter species is presumably the dimer. However, only one set of ^sBu signals (CH, 0.05 ppm; CH_3, 1.44 ppm; CH_3CH, 1.75 ppm; CH_2, 2.17 ppm; assignments verified by decoupling experiments) was observed in the spectrum. One possible explanation for

Table 2
Atomic coordinates for 1

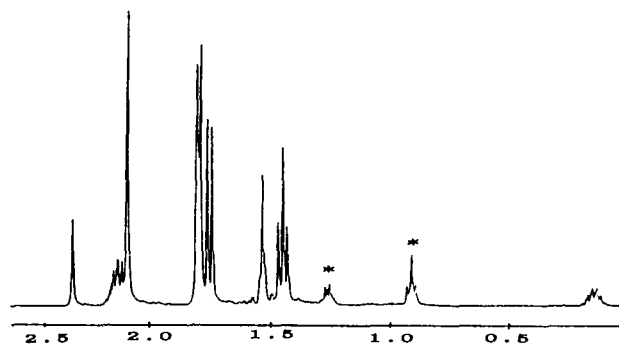| Atom	x (×10⁴)	y (×10⁴)	z (×10⁴)
Mg	0	1306(2)	7500
C(1)	1561(3)	−528(4)	9902(4)
C(2)	1525(3)	390(4)	8980(3)
C(3)	2035(3)	−420(4)	8574(4)
C(4)	1355(4)	−1588(6)	7660(4)
N	209(2)	3131(3)	6661(2)
C(5)	−443(3)	2955(5)	5314(3)
C(6)	1296(3)	3281(5)	7207(4)
C(7)	−180(4)	4387(4)	6862(4)

Fig. 3. ^{1}H NMR spectrum (360 MHz) of 1 recorded in benzene-d_6 at 298 K. Signals associated with unidentified impurities are denoted by an asterisk.

this is that the chemical shifts of the ligated and non-ligated $^sBu_2Mg$ species may be too close and therefore be indistinguishable on the NMR time scale. Assuming that the latter species is the dimer then the bridging and terminal ^sBu groups are also likely to be in rapid equilibrium. It should be noted that, while no ^nBu groups could be detected in NMR spectra of solutions of product 1, two complex multiplets (at 0.87 and 1.23 ppm), small in integral terms but ever present, cannot as yet be assigned. These protic impurities presumably originate from commercial DBM.

3. Experimental details

3.1. Synthesis

Mixing of DBM heptane solutions (purchased from the Aldrich Chemical Co.) with TMEDA was carried out in Schlenk tubes under protective argon blankets. Formation of 1, usually precipitating in microcrystalline form, occurred independent of the DBM : TMEDA stoichiometry (1 : 1, 1 : 2, 1 : 3, 1 : 4 and 2 : 1 molar equivalents were examined). In order to obtain single crystals suitable for X-ray diffraction study, a DBM (10 mmol)–TMEDA (2.5 mmol) mixture in heptane (5 ml) had to be diluted with a large volume of hexane (20 ml) and stored in a refrigerator at −4°C for 3 weeks. Based on TMEDA consumption, the yield of the air-sensitive colourless product exceeded 90%.

Anal. Found: C, 65.9; H, 13.2; Mg, 9.4; N, 10.5. 1 ($C_{14}H_{34}MgN_2$) Calc.: C, 66.1; H, 13.4; Mg, 9.5; N, 11.0%.

3.2. ^{1}H NMR spectrum (360 MHz; 298 K)

1: $^sBu(CH, 2H, m, \delta = 0.05$ ppm; CH_3CH$_2$, 6H, t, $\delta = 1.44$ ppm; CH_3, 6H, d, $\delta = 1.75$ ppm; CH_2, 4H, m, $\delta = 2.17$ ppm); TMEDA (CH_2CH_2, 4H, bound, m, $\delta = 1.53$ ppm, free, s, $\delta = 2.36$ ppm; CH_3, 12H, bound, m, $\delta = 1.82$ ppm, free, s, $\delta = 2.13$ ppm). This was

recorded on a Bruker WH 360 MHz spectrometer. Assignments were verified by homonuclear decoupling experiments. Chemical shifts are quoted relative to SiMe$_4$ at $\delta = 0.00$ ppm. The solvent employed was benzene-d_6.

3.3. X-ray crystallographic studies

Crystal data for 1: C$_{14}$H$_{34}$MgN$_2$; $M = 254.7$; monoclinic; space group, $C2/c$; $a = 16.953$ (7), $b = 9.387(4)$ and $c = 14.365(6)$ Å; $\beta = 130.83(2)°$; $V = 1729.7(13)$ Å^3; $Z = 4$; $D_c = 0.978$ g cm^{-3}; $\mu = 0.089$ mm^{-1} for Mo Kα radiation ($\lambda = 0.71073$ Å); $F(000) = 576$; $T = 200$ K. Unit-cell parameters were refined from 2θ values (20–25°) of 32 reflections measured at $\pm\omega$ on a Stoe–Siemens diffractometer fitted with an Oxford Cryostream cooler [10]. Intensities were measured with ω–θ scans, from a crystal of size $0.77 \times 0.63 \times 0.27$ mm. No significant variation was observed in the intensities of five standard reflections monitored at regular intervals; no corrections were necessary for absorption or extinction.

The structure was determined by direct methods [11] and refined on F^2 by full-matrix least-squares methods [11] from 1142 unique reflections ($2\theta_{max} = 45°$), with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.1273P)^2 + 1.526P$, where $P = (F_o^2 + 2F_c^2)/3$. Isotropic hydrogen atoms were refined with a riding model; all other atoms were assigned anisotropic displacement parameters. At convergence, with all shift to estimated standard deviation ratios less than 0.001, $R' = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1929$ for all data, conventional $R = 0.0632$ on F values of 829 reflections hav-

ing $F_o^2 > 2\sigma(F_o^2)$, and goodness of fit of 1.063 on F^2 for 82 refined parameters. All features in a final difference synthesis were within ± 0.5 electrons Å^{-3}.

Tables of anisotropic displacement parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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