

**“DIBUTYLMAGNESIUM”, A CONVENIENT REAGENT FOR THE
 SYNTHESIS OF USEFUL ORGANIC MAGNESIUM REAGENTS MgA_2
 INCLUDING CYCLOPENTADIENYLS, ARYLOXIDES, AND AMIDES.
 PREPARATION OF $Zr(C_5H_5)Cl_3$. X-RAY STRUCTURE OF
 $[Mg\{\mu-N(SiMe_3)C_6H_4N(SiMe_3)-o\}(OEt_2)]_2$ ***

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Summary

n-Heptane-soluble “di-butylmagnesium” (I) (a commercially available material, prepared by addition of $LiBu^s$ to $MgBu^uCl$, and subsequent addition of ca. 5% $MgOct_2^n$) has been found to be a useful starting material for obtaining numerous organic magnesium compounds. This is illustrated by its reaction with a number of protic compounds HA to give in good yields $Mg(C_5H_5)_2$, $Mg(C_5H_4Me)_2$, or the new compounds MgA_2 : IV ($A = C_5H_4SiMe_3$), V [$A = C_5H_3(SiMe_3)_2$], VII ($A = OC_6H_2Bu_2^{1-2,6-Me-4}$), and X [$A_2 = N(SiMe_3)C_6H_4N(SiMe_3)-o(OEt_2)$]. The value of such compounds MgA_2 as mild ligand transfer reagents is illustrated by the synthesis of $Zr(C_5H_3X_2)Cl_3$ ($X = H$ or $SiMe_3$). Compound X was isolated from OEt_2 solution as the crystalline dimer $(Et_2O)Mg\{N(SiMe_3)C_6H_4-N(SiMe_3)-o\}Mg\{N(SiMe_3)C_6H_4-N(SiMe_3)-o\}(OEt_2)$ with two $o-N(SiMe_3)C_6H_4-N(SiMe_3)$ ligands bridging two magnesium atoms and a terminal OEt_2 ligand completing a distorted tetrahedral environment around each Mg. Some key parameters are: $Mg-N_t$ 1.997(7), $Mg-N_b$ 2.083(8), $Mg-O$ 2.041(7) Å; $OMgN_t$ 112.1(3), $OMgN_b$ 119.7(3), and N_tMgN_b 118.5(3)°.

* No reprints available.

Introduction

Preparations of di-*n*-butyl- [1,2], di-*s*-butyl- [3,4], di-isobutyl- [3], and di-*t*-butylmagnesium [4] have all been reported. These usually involved direct alkylation of an activated form of MgCl_2 [2,4], or the reaction between a Grignard reagent and the corresponding alkylmagnesium reagent [5]. Direct reaction of a butyl halide with magnesium metal has also been used [1], as has the displacement of Schlenk equilibria [6], and the transfer of butyl ligands from di-butylmercury(II) to magnesium metal [7].

A limitation to the utility of these symmetrical di-butylmagnesium complexes is their poor alkane solubility, except for MgBu_2^s , which is a hydrocarbon-miscible liquid [8]. The presence of two different butyl groups, e.g. Bu^n and Bu^s , increases the solubility in aliphatic hydrocarbons of species such as MgBu^nBu^s , as does the addition of $\text{Mg}(\text{n-octyl})_2$. The 'dibutylmagnesium' reagent I used in this work was a commercially available material (Lithium Corporation of America); the *n*-heptane solution was prepared by the addition of *s*-butyllithium to *n*-butylmagnesium chloride, and subsequent addition of bis(*n*-octyl)magnesium (ca. 5%).

There appears to be a correlation between the hydrocarbon solubility of a dialkylmagnesium reagent MgR_2 and its reactivity, the more soluble reagents being the more reactive. Both features are probably attributable to the degree of molecular aggregation n of the dialkylmagnesium reagent $[\text{Mg}(\mu_2\text{-R})_2]_n$. The most active alkylating agent is likely to be the monomer. Hence for high values of n , not only is the nucleophilic cleavage of numerous $\mu_2\text{-R}^-$ bridges a necessary prelude to alkylation, but the low hydrocarbon solubility is associated with a polymeric structure of the magnesium dialkyl.

The "dibutylmagnesium" (I) is probably only weakly associated owing to the irregularity of its structure; and, as we shall show, I not only has good hydrocarbon solubility, so that it is employed as an *n*-heptane solution, but also has high reactivity towards protic substrates HA, which we consider to behave as *A*-centred nucleophiles.

An alternative strategy with a simple magnesium dialkyl $(\text{MgR}_2)_n$ has been to use a strong donor solvent such as $\text{P}(\text{O})(\text{NMe}_2)_3$ (HMPA) [9]. For example (i) $(\text{MgMe}_2)_n$ in diethyl ether appears to take ca. 5 d to react with an excess of cyclopentadiene to afford in 57% yield $\text{Mg}(\text{C}_5\text{H}_5)\text{Me}(\text{OEt}_2)$ [10]; or (ii) $(\text{MgEt}_2)_n$ reacts very slowly with fluorene ($\text{C}_{13}\text{H}_{10}$) in OEt_2 , but the metallation of the hydrocarbon to yield $\text{Mg}(\text{C}_{13}\text{H}_9)\text{Et}$ is promoted by addition of an equimolar portion of HMPA, the active reagent being considered to be the monomeric $\text{MgEt}_2(\text{HMPA})_2$ [9].

Di-alkylmagnesium compounds are widely used in industrial processes, particularly as components of catalyst systems for ethene polymerisation, and there are many examples in the recent patent literature [11]. Stoichiometric reactions of di-butylmagnesium reagents have been rather less well explored, although mixed metal complexes have been isolated by reaction with an alkali metal (to give, e.g., KMgBu_3 [8]) or its hydride (to give, e.g., KMgBu_2H [11]).

Dialkylmagnesium MgR_2 compounds have been reacted previously with various other protic substrates HA, including (a) $\text{HC}\equiv\text{CBu}^n$ to give $\text{Mg}(\text{CCBu}^n)_2$; (b) $\text{HCH}_2\text{PMe}_2\{=\text{NP}(\text{Me}_2)=\text{CH}_2\}$ to yield $\text{Mg}\{\text{CH}_2\text{P}(\text{Me}_2)\text{NP}(\text{Me}_2)\text{CH}_2\}_2$; (c) HC_6F_5 in THF to give $\text{Mg}(\text{C}_6\text{F}_5)_2$; (d) HOR' , HSR' , or HNR'_2 to afford $\text{Mg}(\text{A})\text{R}$ or MgA_2

[9]; and (e) HOAr to afford $\text{Mg}(\text{OAr})_2$ [12]. Many of these organic magnesium products have not been adequately characterised.

An objective of the present study was first to explore the potential of the commercially available "dibutylmagnesium" (I) as a reagent for the synthesis of organic magnesium compounds MgA_2 . We directed our attention to (a) dicyclopentadienyls ("magnesocenes") (b) bulky aryloxides, and (c) bulky arylamides. This selection was prompted by our interest in the ligand chemistry of species \bar{A} (including structures of their metal derivatives) such as $\bar{C}_5\text{H}_4\text{SiMe}_3$ (abbreviated as \bar{Cp}'), $\bar{C}_5\text{H}_3(\text{SiMe}_3)_2$ (abbreviated as \bar{Cp}'') [13], $\bar{\text{OC}}_6\text{H}_2\text{R}-4\text{-Bu}'_2-2,6$ (abbreviated as $\bar{\text{OAr}}^{\text{R}}$) [14], and $\bar{\text{N}}\text{HAr}^{\text{Bu}'}$ (i.e., $\bar{\text{N}}\text{HC}_6\text{H}_2\text{Bu}'_3-2,4,6$) [15]. Results on reactions of I with $\text{NH}_2\text{Ar}^{\text{Bu}'}$ are not yet to hand; but we report data on the $\text{I}/\text{HN}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N}(\text{SiMe}_3)\text{H}-o$ system. A second aim was to isolate pure crystalline compounds MgA_2 and to characterise them structurally; we provide here spectroscopic data for six such compounds and single crystal X-ray diffraction results for one of them. Finally, we examined the potential of compounds MgA_2 as ligand transfer agents, and report below on the use of MgCp_2 or MgCp''_2 to prepare monocyclopentadienylzirconium(IV) chlorides $\text{ZrCp}(\text{or Cp}'')\text{Cl}_3$. There are few convenient syntheses for the latter; many conventional (and more powerful) reagents, such as LiCp or TiCp , give the zirconocene(IV) chlorides [$\text{ZrCl}_2\text{Cp}_2(\text{or Cp}''_2)$] [16].

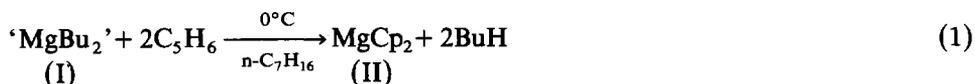
We draw attention to our previous use of a well characterised crystalline organomagnesium compound as a convenient source of the $\bar{\text{C}}\text{H}_2\text{C}_6\text{H}_4\bar{\text{C}}\text{H}_2-o$ ligand [17]. We have long advocated a preference for isolating pure crystalline organic derivatives of lithium [13,18] or magnesium [17] as ligand transfer reagents, in order (i) to facilitate control of stoichiometry in their reactions with metal halides, and (ii) to simplify the purification of the resulting products.

Results and discussion

Preparation of the cyclopentadienyls $\text{Mg}(\text{C}_5\text{H}_3\text{RR}')_2$

Two equivalents of mono-cyclopentadiene were reacted with 'MgBu₂', I, in n-heptane at 0°C to give bis(cyclopentadienyl)magnesium (II), in a 93% yield (eq. 1). One sublimation of the crude product, at ca. 80°C/10⁻³ Torr, gave an analytically pure sample (Table 1), which was recrystallised from n-hexane.

Previously reported routes to compound II have relied upon either a high tem-



perature reaction between cyclopentadiene and magnesium metal, or pyrolysis of cyclopentadienylmagnesium chloride or methyl; none of these provided MgCp_2 in particularly high yield; a yield of 60% was, however, obtained from a cyclopentadienyltrichlorotitanium(IV)-catalysed reaction [9].

A similar procedure to that in eq. 1 was applied to methylcyclopentadiene, trimethylsilylcyclopentadiene, or $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$, to give the analogous products $\text{Mg}(\text{C}_5\text{H}_4\text{Me})_2$ (III) [19], MgCp'_2 (IV) or MgCp''_2 (V). Compound III was isolated as a pale yellow viscous oil which was not vacuum distillable and was extremely air-sensitive and pyrophoric. A sample of III submitted for elemental analysis reacted with the aluminium 'boat' being used, and thus no analytical data were

obtained. Complex IV was obtained as a colourless, viscous oil, and although still extremely air-sensitive was not pyrophoric; upon exposure to air it smouldered but did not ignite. In contrast, compound V was isolated as white crystals, very similar in air-sensitivity to MgCp_2 .

Details on colour, yields, m.p.'s and analyses for complexes II–V appear in Table 1, whilst NMR results are in Table 2. Mass spectra (EI, 70 V) were recorded for complexes II–IV, but only MgCp_2 displayed a parent ion (154 a.m.u.) or indeed any magnesium-containing ions.

The reactions of 'di-butylmagnesium' (I) with indene or fluorene were investigated. The expected products were $\text{Mg}(\text{C}_9\text{H}_7)_2$ or $\text{Mg}(\text{C}_{13}\text{H}_9)_2$, respectively, by analogy with the bis(cyclopentadienyl)magnesium preparations described above. Bis(indenyl)magnesium was obtained previously by pyrolysis of indenylmagnesium bromide or from C_9H_8 and MgH_2 [9].

The addition of two equivalents of indene to 'di-butylmagnesium' (I), at ca. 20°C gave a deep red-orange oil which was extremely moisture-sensitive. The oil had a good solubility in diethyl ether but was totally insoluble in petroleum ether; no crystalline products were obtained from the ethereal solution, either at low temperature or upon addition of petroleum ether. The ^1H NMR spectrum of the crude oily product suggested the presence of at least one Mg–Bu moiety, possibly indicating the formation of a species such as $\text{Mg}(\text{Bu})(\text{C}_9\text{H}_7)$.

Fluorene did not react with the 'di-butylmagnesium' reagent I at ambient temperature; however, when a mixture of the reactants in $n\text{-C}_6\text{H}_{14}/n\text{-C}_7\text{H}_{16}$ was refluxed, a pale yellow solid separated. The recrystallised product is tentatively identified as being $\text{Mg}(\text{C}_{13}\text{H}_9)_2$, but the NMR and mass spectra were not examined in detail.

Preparation of the aryloxide $[\text{Mg}(\text{OAr}^{\text{Me}})_2]_2$

The preparation of a solvated magnesium bis(aryloxide) $\text{Mg}(\text{OAr}^{\text{Me}})_2(\text{THF})_2$ (VI) ($\text{OAr}^{\text{Me}} = \text{OC}_6\text{H}_2\text{Me-4-Bu}^1_{2,6}$, THF = tetrahydrofuran) has been reported

TABLE 1

COLOURS, YIELDS, MELTING POINTS, AND ANALYSES FOR ORGANIC MAGNESIUM COMPOUNDS II–V, VII, AND X

Compound ^a	No.	Colour ^b	Yield (%)	M.p. ($\theta_c/^\circ\text{C}$)	Analysis (Found (calcd.) (%))	
					C	H
MgCp_2	II	White	93	(Subl. ca. 100°C/ 10 ⁻³ Torr)	77.5 (77.7)	6.70 (6.52)
$\text{Mg}(\text{C}_5\text{H}_4\text{Me})_2$	III	Pale yellow	80–85	<i>c</i>	–	–
MgCp'_2	IV	Yellow	88	<i>d</i>	–	–
MgCp''_2	V	White	58 ^e	80–83	57.2 (59.6)	9.19 (9.55)
$\text{Mg}(\text{OAr}^{\text{Me}})_2$	VII	White	62 ^e	–	–	–
Mg amide	X	White	52 ^e	190 (decomp.)	55.1 (55.4)	8.93 (8.72)

^a Abbreviations: Cp = C_5H_5 , Cp' = $\text{C}_5\text{H}_4(\text{SiMe}_3)$, Cp'' = $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$, $\text{OAr}^{\text{Me}} = \text{OC}_6\text{H}_2\text{Me-4-Bu}^1_{2,6}$, Mg amide = $[\text{Mg}\{\mu\text{-N}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N}(\text{SiMe}_3)\text{-o}\}(\text{OEt}_2)]_2$. ^b Complexes III and IV are probably colourless when pure. ^c Viscous, non-distillable, pyrophoric liquid. ^d Viscous, non-distillable liquid; reacts violently with air. ^e Yield after crystallisation; other yields are for crude products.

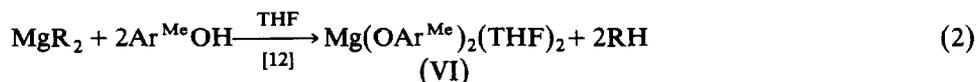
TABLE 2

^1H AND ^{13}C NMR CHEMICAL SHIFT DATA^a FOR THE COMPOUNDS $\text{Mg}(\text{C}_5\text{H}_3\text{RR}')_2$ [$\text{R} = \text{R}' = \text{H}$ (II); $\text{R} = \text{H}$, $\text{R}' = \text{Me}$ (III); $\text{R} = \text{H}$, $\text{R}' = \text{SiMe}_3$, (IV); or $\text{R} = \text{R}' = \text{SiMe}_3$ (V)]

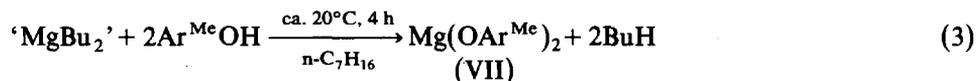
Compound	$\text{Mg}(\text{C}_5\text{H}_3\text{RR}')_2$		^1H		^{13}C	
	R	R'	$\text{C}_5\text{H}_3\text{RR}'$	$\text{C}_5\text{H}_3\text{RR}'$	$\text{C}_5\text{H}_3\text{RR}'$	$\text{C}_5\text{H}_3\text{RR}'$
II	H	H	5.89	—	107.69	—
III	H	Me	5.97	1.32	—	—
IV	H	SiMe_3	6.32	0.30	118.26 ^b	0.35
					114.72	
V	SiMe_3	SiMe_3	6.60	0.35	111.26	
					121.75	0.47
					121.51 ^b	
					118.47	

^a Chemical shifts (all singlets) are in ppm relative to the solvent peak (C_6D_6) at 7.27 ppm (^1H) or 128.00 ppm (^{13}C) except in the case of complex II where internal SiMe_4 was used. ^b Resonance assigned to the trimethylsilylated carbon atom(s), e.g., lowest intensity signal.

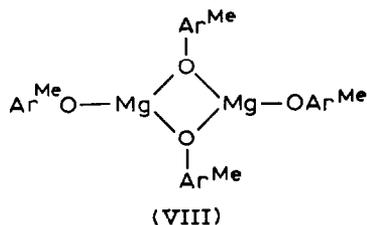
(eq. 2) ($\text{R} = \text{Me}$ or H) [12]; the monomeric nature of this compound was established by



ebullioscopy in THF. The homoleptic aryloxide $\text{Mg}(\text{OAr}^{\text{Me}})_2$ (VII) has now been prepared by an analogous procedure to that of eq. 2 (see eq. 3).



The crystalline compound VII, obtained in good yield (Table 1), was readily converted into the solvated adduct VI by dissolution in THF. Both ^1H and ^{13}C NMR spectra of a C_6D_6 solution of complex VII displayed resonances (in the



expected 1/1 integration ratio) at ambient temperature assignable to bridging and terminal aryloxide ligands (Table 3), and accordingly we propose that VII exists in benzene solution as the dimer VIII. When $\text{THF}-d_8$ was used as the NMR solvent, only resonances due to terminal aryloxide groups were observed (see Table 3), consistent with the monomeric structure VI.

The high solubility of complex VII in hydrocarbon solvents is unusual for a homoleptic magnesium aryloxide, which would normally be expected to be polymeric. However, the bulk of the aryloxide ligand (which is also known to confer lipophilicity on many of its metal complexes [14]) and the proposed dimeric structure VIII adequately account for the solubility.

TABLE 3

¹H AND ¹³C NMR CHEMICAL SHIFT DATA ^a FOR [Mg(OAr^{Me})₂]₂ (VII) IN C₆D₆ OR THF-*d*₈ (OAr^{Me} = OC₆H₂Me-4-Bu^{1,2,6})

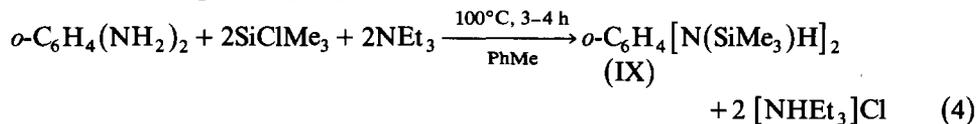
Solvent	¹ H (singlets)			Ref.
	For <i>o</i> -C ₄ H ₅ ¹	For <i>p</i> -CH ₃	Aromatic protons	
C ₆ D ₆	1.28	2.15	7.07	Int. SiMe ₄
THF- <i>d</i> ₈	1.63	2.30	6.82 } ^b 6.89 }	THF at 1.9 and 3.8
	1.64 } ^b	2.37		
	1.68 }			
	¹³ C			
	<i>o</i> -C(CH ₃) ₃	<i>o</i> -C(CH ₃) ₃	<i>p</i> -CH ₃	Aromatic carbon
C ₆ D ₆	34.45	36.02	21.46	158.33
	32.14	35.12	21.22	153.66
				138.25
				137.83
				129.94
				128.43
			125.88	
			123.15	

^a Chemical shifts are in ppm relative to the solvent peak (C₆D₆ = 7.27 ppm for ¹H NMR or 128.0 ppm for ¹³C NMR), unless otherwise stated. ^b These doublets are attributed to restricted rotation about the O-Ar bond.

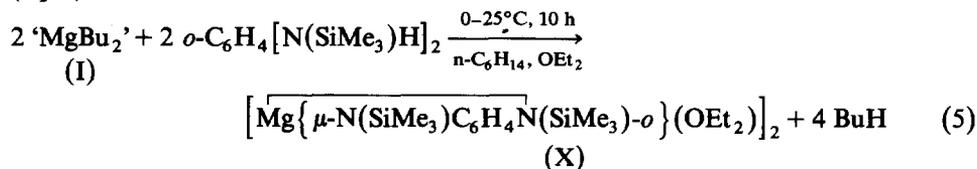
Aryloxide transfer reactions of compound VII have not yet been explored, but we predict that these will be useful for preparation of (i) those transition metal aryloxides where reduction is to be avoided (e.g., with [TiCl₄]), and to be superior in this respect to LiOAr^{Me}; or (ii) mono-aryloxides, e.g. ZrCl₃(OAr^{Me}).

*Preparation of an *o*-phenylenediamidomagnesium compound derived from *o*-C₆H₄[N(SiMe₃)H]₂*

The parent *o*-phenylenediamine (IX) was prepared as shown in eq. 4 (an alternative, and probably superior, synthesis is described in ref. 20).

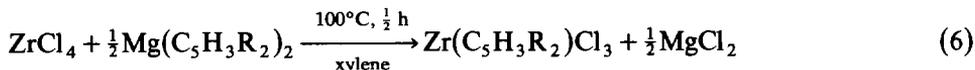


Treatment of the diamine IX with the magnesium reagent I in *n*-C₆H₁₄ at 0 to 25°C for 10 h, followed by addition of diethyl ether, and recrystallisation of the solvent-free residue from cold *n*-C₅H₁₂ afforded colourless crystals of the diethyl etherate of the dimeric white 2,5-diaza-1-magnesia-3,4-benzoindene (X) (see Table 1) (eq. 5).



Magnesium cyclopentadienyls as reagents

The use of pre-prepared crystalline magnesium compounds as ligand transfer reagents is here illustrated by the reactions of eq. 6 ($R = H$ or SiMe_3). The com-



plex $\text{ZrCp}''\text{Cl}_3$ [$\text{Cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_2$] (XI) is a new compound and was obtained by this simple procedure in good yield (ca. 80% of sublimed material). The related ZrCpCl_3 [16] was similarly prepared. Its X-ray structure has been published [27].

Compound XI is triboluminescent, probably a consequence of crystal packing forces.

X-Ray structure of $(\text{Et}_2\text{O})\text{Mg}\{\text{N}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N}(\text{SiMe}_3)-o\}\text{Mg}\{\text{N}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N}(\text{SiMe}_3)-o\}(\text{OEt}_2)$ (X)

The molecular structure is illustrated in Fig. 1. Bond lengths and angles (Table 4), mean planes (Table 5), and atomic coordinates (Table 6) are tabulated.

The crystal contains discrete dimers lying across crystallographic inversion centres. The bis-amido ligand $o\text{-}\bar{\text{N}}(\text{SiMe}_3)\text{C}_6\text{H}_4\bar{\text{N}}(\text{SiMe}_3)$ is chelating one Mg, with N(1) terminal and N(2) bridging to an adjacent Mg atom. The OEt_2 ligands complete a distorted tetrahedral coordination at the Mg atoms. The constraints of the fused 5.4.5 ring system result in the rather small N(1)–Mg–N(2) and N(2)–Mg–N(2)' angles of $87.8(3)$ and $93.9(3)^\circ$, respectively. The bridging N(2) atom has a tetrahedral bonding arrangement with a small Mg–N–Mg' angle of $86.1(3)^\circ$ within the four-membered ring, whilst N(1) is trigonally planar bonded to C(1), Mg, and Si(1); and the change in effective covalent radius between sp^2 and sp^3 hybridisation is reflected in the shorter Mg–N(1) bond of $1.997(7)$ Å compared to Mg–N(2) at

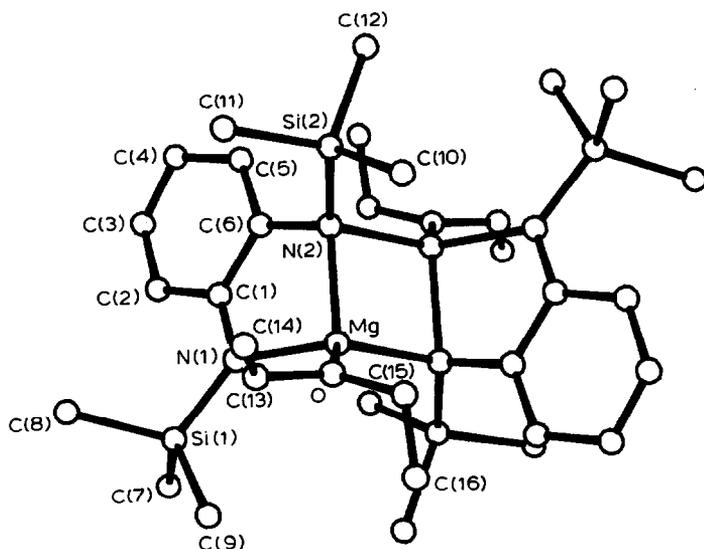


Fig. 1. Molecular structure of compound X.

2.082(7) Å. The latter Mg–N bond length is comparable to that of (i) tetrakis(*t*-butylamido)-tris-(hydridoaluminium)-tetrahydrofuran magnesium [21], 2.090(4) Å, and (ii) μ -6-nitrido-nonakis(μ -2-*t*-butylamido)hexamagnesium [22], 2.093(2) Å. In the five-membered chelate rings the N(1) and N(2) atoms are, as expected, co-planar with the aromatic ring, with the Mg atom completing the “flap” of an envelope conformation.

A metal coordination geometry rather similar to that in the title complex X has been observed previously for bis[dimethylaminoethyl(methyl)amino]di(methylmagnesium) [23], which also contains a *trans*-5.4.5-fused ring system, although both terminal and bridging N atoms are tetrahedrally bonded; the average dimensions are

TABLE 4

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) FOR $[\overline{\text{Mg}}\{\mu\text{-N}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N}(\text{SiMe}_3)\}\text{-}(\text{OEt}_2)_2]_2$ (X) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES^a

<i>Bond lengths</i>			
Mg–O	2.041(7)	Mg–N(1)	1.997(7)
Mg–N(2)	2.082(7)	Mg–N(2)'	2.085(7)
Si(1)–N(1)	1.714(7)	Si(1)–C(7)	1.853(10)
Si(1)–C(8)	1.865(10)	Si(1)–C(9)	1.847(11)
Si(2)–N(2)	1.778(7)	Si(2)–C(10)	1.819(12)
Si(2)–C(11)	1.840(10)	Si(2)–C(12)	1.867(10)
O–C(13)	1.408(13)	O–C(15)	1.472(15)
N(1)–C(1)	1.371(11)	N(2)–C(6)	1.472(11)
C(1)–C(2)	1.399(12)	C(1)–C(6)	1.418(12)
C(2)–C(3)	1.358(13)	C(3)–C(4)	1.339(13)
C(4)–C(5)	1.381(12)	C(5)–C(6)	1.345(12)
C(13)–C(14)	1.26(2)	C(15)–C(16)	1.33(2)
<i>Bond angles</i>			
O–Mg–N(1)	112.1(3)	O–Mg–N(2)	119.7(3)
O–Mg–N(2)'	119.4(3)	N(1)–Mg–N(2)	87.8(3)
N(1)–Mg–N(2)'	118.5(3)	N(2)–Mg–N(2)'	93.9(3)
N(1)–Si(1)–C(7)	115.9(4)	N(1)–Si(1)–C(8)	110.8(4)
N(1)–Si(1)–C(9)	110.3(4)	C(7)–Si(1)–C(8)	107.1(5)
C(7)–Si(1)–C(9)	106.9(5)	C(8)–Si(1)–C(9)	105.2(5)
N(2)–Si(2)–C(10)	109.1(4)	N(2)–Si(2)–C(11)	110.0(4)
N(2)–Si(2)–C(12)	116.1(4)	C(10)–Si(2)–C(11)	109.6(5)
C(10)–Si(2)–C(12)	104.6(5)	C(11)–Si(2)–C(12)	107.2(5)
Mg–O–C(13)	120.7(8)	Mg–O–C(15)	123.7(6)
C(13)–O–C(15)	115.6(9)	Mg–N(1)–Si(1)	129.8(4)
Mg–N(1)–C(1)	107.8(6)	Si(1)–N(1)–C(1)	122.4(7)
Mg–N(2)–Mg'	86.1(3)	Mg–N(2)–Si(2)	119.8(4)
Mg–N(2)–C(6)	104.1(5)	Mg'–N(2)–Si(2)	117.4(3)
Mg'–N(2)–C(6)	113.9(5)	Si(2)–N(2)–C(6)	112.6(6)
N(1)–C(1)–C(2)	125(1)	N(1)–C(1)–C(6)	121.5(9)
C(2)–C(1)–C(6)	113.4(9)	C(1)–C(2)–C(3)	124.1(9)
C(2)–C(3)–C(4)	121(1)	C(3)–C(4)–C(5)	116(1)
C(4)–C(5)–C(6)	124.0(9)	N(2)–C(6)–C(1)	117.7(9)
N(2)–C(6)–C(5)	121.8(9)	C(1)–C(6)–C(5)	120.5(9)
O–C(13)–C(14)	130(2)	O–C(15)–C(16)	120(2)

^a Atoms marked ' are related by symmetry operation $1 - x, -y, 1 - z$.

TABLE 5

DEVIATIONS (Å) OF ATOMS FOR COMPOUND X FROM VARIOUS MEAN PLANES. ATOMS MARKED* WERE NOT USED IN THE CALCULATION OF THE PLANE (Angles (°) between planes: a-b 41, a-c 37, a-d 33, b-c 4, b-d 12, c-d 11)

- (a) Mg, Mg', N(2), N(2)
 (b) C(1) 0.00, C(2) 0.02, C(3) -0.04, C(4) 0.03, C(5) -0.01, C(6) -0.01; N(1)* 0.11, N(2)* -0.11
 (c) Mg 0.00, N(2) 0.00, C(6) 0.00, C(1) 0.00; N(1)* 0.17
 (d) Mg, C(1), Si(1); N(1)* -0.01

Mg-N (bridging) 2.104(3), Mg-N (terminal) 2.196(3) Å, and N-Mg-N' 91.5(1)°.

Experimental

Starting materials

The 'di-butylmagnesium' (I) (a gift from I.C.I. PLC) was a commercially available n-heptane solution (from Lithium Corporation of America).

Trimethylsilylcyclopentadiene (Cp'H) [24] and bis(trimethylsilyl)cyclopentadiene (Cp''H) [25] were prepared by the literature procedures, and *N,N'*-bis(trimethylsilyl)-*o*-phenylenediamine according to eq. 4 (cf., ref. 20). 2,6-Di-*t*-butyl-4-methylphenol was purchased from Aldrich, and purified before use by drying its solution in n-hexane over basic alumina, and then removing the solvent.

TABLE 6

FRACTIONAL ATOMIC COORDINATES FOR COMPOUND X WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
<i>Non-hydrogen atoms ($\times 10^4$)</i>			
Mg	5520(3)	-225(3)	4401(2)
Si(1)	4855(3)	-1714(3)	3308(2)
Si(2)	4342(4)	1612(2)	4386(2)
O	6741(7)	213(6)	3864(4)
N(1)	4578(8)	-914(6)	3842(5)
N(2)	4273(8)	545(6)	4597(5)
C(1)	3595(11)	-634(9)	3943(7)
C(2)	2708(10)	-1011(9)	3689(7)
C(3)	1741(12)	-711(10)	3775(8)
C(4)	1580(11)	31(10)	4054(8)
C(5)	2432(11)	419(9)	4322(8)
C(6)	3398(10)	125(9)	4257(7)
C(7)	4384(15)	-2748(9)	3568(9)
C(8)	4324(13)	-1508(10)	2456(8)
C(9)	6259(13)	-1805(10)	3188(9)
C(10)	5641(14)	1984(10)	4544(8)
C(11)	4020(12)	1759(11)	3497(7)
C(12)	3496(14)	2319(9)	4879(8)
C(13)	6667(16)	321(15)	3166(9)
C(14)	7029(25)	881(21)	2797(11)
C(15)	7727(15)	458(15)	4166(9)
C(16)	8552(17)	-18(20)	4091(14)

Preparation of bis(η -cyclopentadienyl)magnesium (II)

Freshly 'cracked' cyclopentadiene (17.45 g, 264.0 mmol) was added at 0°C during 45 min to a stirred solution of 'di-butylmagnesium' (I) (200.0 cm³ of a 0.66 mol dm⁻³ n-heptane solution, 132 mmol); a white microcrystalline precipitate was formed. The temperature was raised to ca. 20°C and the reaction mixture was stirred for a further 2 h. Removal of volatiles in vacuo gave the product (19.0 g, 93%) as a white, free flowing, microcrystalline solid. Sublimation of the crude product at ca. 100°C/10⁻³ Torr gave the analytical sample of the title compound II.

Further reactions of 'di-butylmagnesium'

(a) With methylcyclopentadiene

Methylcyclopentadiene (2.64 g, 33.0 mmol) was added at 0°C to a solution of 'di-butylmagnesium' (I) (25 cm³ of a 0.66 mol dm⁻³ n-heptane solution, 16.5 mmol); the solution became 'cloudy' but no obvious precipitate was observed. The solution was warmed to ca. 20°C and left for 2 h; then the volatiles were removed in vacuo to give a pale yellow oil (ca. 2.5 g, 80–85%). The oil was extremely sensitive to air/moisture and was pyrophoric. Attempts to distil the product Mg(C₅H₄Me)₂ (III), using a short path distillation apparatus under high vacuum failed, thermal decomposition being observed.

(b) With trimethylsilylcyclopentadiene

The procedure was performed as described for the preparation of Mg(C₅H₅)₂ (II) starting from freshly distilled trimethylsilylcyclopentadiene (4.56 g, 33.0 mmol) and 'di-butylmagnesium' (I) (25 cm³ of a 0.66 mol dm⁻³ n-heptane solution, 16.5 mmol). The yellow solution was stirred for a further 15 h at ca. 20°C. Removal of volatiles in vacuo gave the yellow viscous MgCp₂ (IV) (4.34 g, 88%). Short path vacuum distillation produced an 'off-white' viscous liquid.

Preparation of bis{bis(trimethylsilyl)cyclopentadienyl}magnesium (V)

An n-heptane solution of 'di-butylmagnesium' (I) (12.87 cm³ of a 0.66 mol dm⁻³ solution, 8.5 mmol) was added dropwise at 20°C to a solution of bis(trimethylsilyl)cyclopentadiene (3.20 g, 17.0 mmol) in n-hexane (ca. 30 cm³). After stirring for a further 15 h at ca. 20°C the volatiles were removed in vacuo to give an oily white solid. The residue was extracted into n-hexane (ca. 50 cm³), and the suspension was filtered through Celite. The filtrate was concentrated to ca. 20 cm³ in vacuo. Cooling of the filtrate at -30°C gave crystals of the title product V (2.17 g, 58%), which were very air-sensitive and smouldered in air.

Preparation of bis(fluorenyl)magnesium

'Di-butylmagnesium' (I) (20.0 cm³ of a 0.66 mol dm⁻³ n-heptane solution, 13.2 mmol) was added from a syringe to an n-hexane suspension (ca. 30 cm³) of fluorene (4.39 g, 26.4 mmol) at ca. 20°C. There was no visible reaction and the mixture was heated to reflux. At ca. 60°C a clear yellow solution was formed and, after reflux (1 h), a pale yellow solid slowly began to precipitate. Refluxing was maintained for a further 2 h before removal of volatiles in vacuo. Extraction of the residue into diethyl ether (ca. 50 cm³), filtration through Celite, concentration of the yellow

filtrate in vacuo, and cooling to -30°C gave crude bis(fluorenyl)magnesium (2.42 g, 52%) as pale yellow crystals. Analysis: Found: C, 87.7; H, 5.99. $\text{C}_{26}\text{H}_{18}\text{Mg}$ calcd.: C, 88.0; H, 5.11%. The crystals were collected by decantation and washed with petroleum ether then dried in vacuo, m.p. $110\text{--}113^{\circ}\text{C}$.

Reaction of indene with 'di-butylmagnesium'

'Di-butylmagnesium' (I) (29.3 cm^3 of a 0.66 mol dm^{-3} n-heptane solution, 19.4 mmol) was added to freshly distilled indene (4.5 g, 38.7 mmol) at ca. 0°C . The solution immediately became yellow-orange, and darkened slightly upon warming to ca. 20°C . After 1 h at ca. 20°C the volatiles were removed in vacuo to give a deep red-orange oil which was immiscible with petroleum ether. Extraction with diethyl ether (ca. 40 cm^3) and filtration through Celite gave a red filtrate. Repeated concentration in vacuo and cooling of the filtrate to -30°C did not give crystals; addition of petroleum ether to the filtrate produced only a red-orange oil.

*Preparation of bis(2,6-di-*t*-butyl-4-methylphenoxo)magnesium (VII)*

A solution of 2,6-di-*t*-butyl-4-methylphenol (5.0 g, 22.7 mmol) in n-hexane (ca. 70 cm^3) was added to an n-heptane solution of 'di-butylmagnesium' (I) (17.2 cm^3 of a 0.66 mol dm^{-3} solution, 11.35 mmol). After stirring for 4 h at ca. 20°C the volatiles were removed in vacuo to leave a viscous oil. Extraction into petroleum ether (ca. 50 cm^3) and filtration through Celite gave a clear, colourless filtrate which was concentrated in vacuo to ca. 20 cm^3 and cooled to -30°C . The title product VII (1.63 g, 62%) was obtained as white crystals, collected by decantation, and dried in vacuo.

Preparation of the magnesium amide $[\overline{\text{Mg}\{\mu\text{-N}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{N}(\text{SiMe}_3)\text{-o}\}}(\text{OEt}_2)]_2$ (X)

A solution of the diamine IX (6.2 g, 25 mmol) in n-hexane (50 cm^3) was added dropwise to a solution of 'di-butylmagnesium' (I) (42 cm^3 of a 0.66 mol dm^{-3} n-heptane solution, 27.7 mmol) in n-hexane (50 cm^3) at 0°C ; then the mixture was slowly warmed to 25°C . After stirring for 5 h at 25°C the hexane was evaporated off in vacuo and replaced by OEt_2 (100 cm^3). The mixture was filtered, concentrated, and cooled to give the title compound X (4.5 g, 52%) as colourless crystals which were washed with cold (-30°C) pentane ($2 \times 10\text{ cm}^3$); ^1H NMR spectrum in (CD_2Cl_2): δ (ppm): 6.50 (multiplet, aromatic H's), 3.75 (quartet, CH_2Me), 1.20 (triplet, CH_2CH_3) and 0.20 (singlet SiMe_3).

Preparation of {bis(trimethylsilyl)cyclopentadienyl}trichlorozirconium(IV) (XI)

Freshly sublimed zirconium tetrachloride (8.00 g, 34.2 mmol) was placed in *o*-xylene (ca. 50 cm^3) and heated to 100°C . Bis((trimethylsilyl)cyclopentadienyl)-magnesium (9.20 g, 17.1 mmol) was added as an *o*-xylene solution (ca. 30 cm^3) during 1 h. The reaction mixture adopted a chocolate brown colour and was maintained at 100°C for a further $\frac{1}{2}$ h, before removal of volatiles in vacuo. The brown residue was transferred to a sublimation tube and sublimed (ca. 100°C at 10^{-3} Torr) to give the title product XI (10.71 g, 77%). Analysis: Found: C, 32.5; H, 5.12. $\text{C}_{11}\text{H}_{21}\text{Cl}_3\text{Si}_2\text{Zr}$ calcd.: C, 32.5; H, 5.20%. Some of the crude product was resublimed to give the analytical sample, m.p. $84\text{--}94^{\circ}\text{C}$ (decomp.).

Crystal data for compound X. $C_{32}H_{64}Mg_2N_4O_2Si_4$, $M = 697.9$, orthorhombic, space group *Pbca*, a 12.996(3), b 16.165(5), c 19.975(1) Å, U 4195.5 Å³, $Z = 4$, D_c 1.11 g cm⁻³. Monochromated Mo- K_α radiation, λ 0.71069 Å, μ 2.0 cm⁻¹.

Structure determination for compound X

A crystal ca. $0.3 \times 0.3 \times 0.3$ mm, sealed in a Lindemann glass capillary under argon, was mounted on an Enraf-Nonius CAD4 diffractometer. Unique data with $2 < \theta < 22^\circ$ were measured by an ω - 2θ scan with a maximum scan time of 60 s. No absorption correction was applied. 1086 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma^2(F) = [\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

The structure was solved by direct methods using the MULTAN [26] program. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least-squares. Hydrogen atoms were placed at calculated positions (C-H 1.08 Å) and held fixed with a common B_{iso} of 6.0 Å². Refinement converged at $R = 0.100$, $R' = 0.100$, with a weighting scheme of $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless. All calculations were done on a PDP11/34 computer using the Enraf-Nonius SDP program package. Tables of temperature factors, H atom coordinates, and structure factors are available from one of the authors (P.B.H.) on request.

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