Bis(neopentyl)-, Bis(trimethylsilylmethyl)- and Bis(2-methyl-2-phenylpropyl)-magnesium †

By **Richard A. Andersen** and **Geoffrey Wilkinson**,* Imperial College of Science and Technology, London SW7 2AY

The magnesium dialkyls $Mg(Me_3CCH_2)_2$, $Mg(Me_3SiCH_2)_2$, and $Mg(PhMe_2CCH_2)_2$ have been isolated as crystalline solids. The last two are insoluble in hydrocarbon solution and non-volatile whereas the former is the only known crystalline, volatile, benzene-soluble, trimeric dialkyl of magnesium. Low-temperature ^1H and ^{13}C-{^1H} n.m.r. spectra show that bridge–terminal exchange is rapid at −80 °C. The 2 :1 diethyl ether complexes of the first two compounds and 1 :1 *NNN'N'*-tetramethylethylenediamine complexes are also described.

SEVERAL pure, solvent-free dialkylmagnesiums are known[1] but the involatility and low solubility in hydrocarbons suggests that they are polymeric, as is dimethylmagnesium.[2] However, the dialkyls $Mg(n\text{-}C_5H_{11})_2$ [3] and $Mg(s\text{-}C_4H_9)_2$ [4] are soluble, and apparently

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† No reprints available.

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[2] E. Weiss, *J. Organometallic Chem.*, 1964, **2**, 314.

[3] W. H. Glaze and C. M. Sellman, *J. Organometallic Chem.*, 1966, **5**, 477.

[4] C. W. Kamienski and J. F. Eastham, *J. Org. Chem.*, 1969, **34**, 1116.

dimeric, in benzene. In view of the solubilities in hydrocarbons and the unusual structures of the manganese trimethylsilylmethyl, 2-methyl-2-phenylpropyl, and neopentyl dialkyls,[5] we have isolated the corresponding magnesium compounds in order to allow structural comparisons to be made,[6] and have studied their reactions with Lewis bases.

The dialkyls $Mg(Me_3SiCH_2)_2$, $Mg(Me_3CCH_2)_2$, and $Mg(PhMe_2CCH_2)_2$ are readily prepared by a slight modification [7] of the classic Schlenk disproportionation of a Grignard reagent with dioxan:

$$2RMgX + 2\text{dioxan} \longrightarrow R_2Mg + MgX_2\cdot 2\text{dioxan}$$

The R_2Mg is soluble in diethyl ether and the dioxan complex of MgX_2 insoluble.[8] Removal of dioxan (100—140 °C) under reduced pressure yields the base-free dialkyl contaminated with trace quantities of chloride.

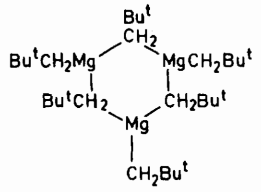
The trimethylsilylmethyl, $Mg(Me_3SiCH_2)_2$, and 2-methyl-2-phenylpropyl, $Mg(PhMe_2CCH_2)_2$, compounds are insoluble in hydrocarbon solvents, though soluble in diethyl ether giving solutions at least 1M, and are non-volatile and thermally stable to at least 200 °C. However, by contrast the neopentyl is freely soluble in benzene solution, in which it is trimeric, and it sublimes at 110 °C *in vacuo*.

There are two reasonable alternatives for the structure of this unique neopentyl. One is cyclic (I), based upon each magnesium atom being three-co-ordinate and being bonded to a terminal alkyl group and to two bridging alkyl groups by way of a three-centre two-electron bond. The other alternative is linear (II), with the central magnesium atom being four-co-ordinate while the other two magnesium atoms are only three-co-ordinate. The ^1H n.m.r. spectrum of $Mg(Me_3CCH_2)_2$ consists of only two resonances due to the t-butyl and methylene protons at room temperature, and, since lowering the temperature to −90 °C results only in line-broadening, is not diagnostic.

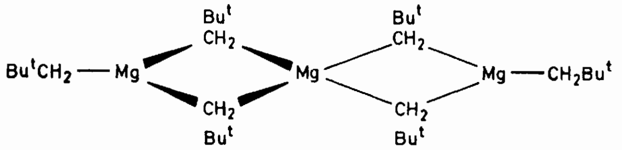
The ^{13}C-{^1H} n.m.r. spectrum in [$^2H_8$]toluene at room temperature consists of three resonances at δ 36.57, 33.03, and 30.75 (δ defined as p.p.m. to the high-frequency side of $SiMe_4$). The proton-coupled spectrum consists of a quartet (δ 36.57), a triplet (δ 33.03), and a singlet (δ 30.75) which are assigned to the methyl, methylene, and quaternary carbon atoms, respectively. Cooling the sample to −80 °C causes the resonances to broaden, an indication that bridge-terminal exchange is rapid at this temperature on both ^1H and ^{13}C n.m.r. time scales.

The marked difference between $Mg(Me_3CCH_2)_2$ and its silicon analogue is most reasonably ascribed to steric hindrance, silicon being larger than carbon, thus minimizing the steric congestion about the metal atom and allowing the latter to be four-co-ordinate while keeping the co-ordination number of the former less than four. This is supported by the observation that $Be(Me_3SiCH_2)_2$ is dimeric though $Be(Me_3CCH_2)_2$ exists in a monomer–dimer equilibrium in benzene solution.[9] The properties must also be compared to the corresponding manganese derivatives.[5] Thus the trimethylsilylmethyls are similar, $Mn(Me_3SiCH_2)_2$ being an infinite polymer in the solid, though it can be crystallized from boiling toluene and sublimes *in vacuo*. The neopentyls are also similar in being easily soluble in hydrocarbons, but in the solid state the manganese compound is a linear tetramer $[Mn(CH_2CMe_3)_2]_4$ rather than a trimer. The most marked difference is in the 2-methyl-2-phenylpropyls since the manganese compound is dimeric in the solid state with one carbon–carbon double bond of a bridging neophyl group interacting with a manganese atom and thereby increasing its co-ordination number. This difference might be due to the availability of *d*-orbitals in manganese.

We have crystallized 2 : 1 co-ordination complexes of $Mg(Me_3SiCH_2)_2(OEt_2)_2$ and $Mg(Me_3CCH_2)_2(OEt_2)_2$ by cooling an ethereal solution of the dialkyl to −70 °C. All three dialkyls yield monomeric, 1 : 1 complexes with the chelating diamine, *NNN'N'*-tetramethylethylenediamine (tmed).



(I)



(II)

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Limited, Middlesex, and by Pascher Microanalytical Laboratory, Bonn. The light petroleum used had b.p. 40—60 °C unless otherwise specified. Dioxan was distilled from sodium. Analytical and spectroscopic data are given in the Table. Proton n.m.r. spectra were measured on a Perkin-Elmer R-12 machine operating at 60 MHz. Carbon n.m.r. spectra were measured on a Varian XL-100 spectrometer in Fourier transform-mode at 25.14 MHz in C_6D_6 as internal lock and $SiMe_4$ as internal reference.

Bis(neopentyl)magnesium.—To Bu^tCH_2MgCl,[7] prepared from Bu^tCH_2Cl (46 g, 0.43 mol) and Mg (12 g, 0.50 g-atom) in diethyl ether (500 ml), dioxan (44 ml, 0.52 mol) was added slowly (1 h) with rapid stirring. The suspension was stirred for 12 h and then centrifuged; the supernatant liquid

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[6] *X*-Ray diffraction studies by Dr. M. B. Hursthouse, Queen Mary College, London, in progress.

[7] G. E. Coates and J. A. Heslop, *J. Chem. Soc.* (*A*), 1968, 514.

[8] W. Schlenk and W. Schlenk, *Chem. Ber.*, 1929, **62**, 920.

[9] G. E. Coates and B. R. Francis, *J. Chem. Soc.* (*A*), 1971, 1309.

was evaporated to dryness. The white solid was heated (110—130 °C) *in vacuo* (10^{-2} mmHg) for 24 h to remove traces of dioxan; yield was 54 g (65%). A sample sublimed (90—110 °C/10^{-2} mmHg) as colourless *prisms*.

Bis(neopentyl)magnesium–Diethyl Ether (1/1).—A sample of the dialkyl was dissolved in diethyl ether at −70 °C, and the solution was allowed to warm to room temperature. After being stirred for 30 min the solution was concentrated to *ca.* 3 ml, cooled to −70 °C, and the colourless *prisms* collected at −70 °C. These were dried *in vacuo* to leave a semisolid mass. The ^{1}H n.m.r. spectrum contained resonances at 0.13 (s) ($\mathit{Me}_3\mathrm{CCH_2Mg}$), and 1.47 p.p.m. ($\mathrm{Me_3C}\mathit{CH}_2\mathrm{Mg}$) relative to the centre resonance of the methyl triplet of diethyl ether.

Analyses and physical properties of magnesium dialkyls

		Found (%)				Calculated (%)				
Compound	M.p. (θ_c/°C)	C	H	N	*M* [a](Wt. %)	C	H	N	*M*	^{1}H n.m.r.[b]
$[\mathrm{Mg(Bu^tCH_2)_2}]_3$	111—113	72.5	12.8		424 (1.20) 461 (1.31) 454 (1.84)	72.3	13.3		498	$\mathit{Me}_3\mathrm{CCH_2}$, 8.70s (9); $\mathrm{Me_3C}\mathit{CH}_2$, 9.60s (2)
$\mathrm{Mg(Bu^tCH_2)_2(OEt_2)_2}$		68.8	13.3			68.8	13.3			$\mathrm{MeC}\mathit{H}_2\mathrm{O}$, 6.54q (4); $\mathit{Me}_3\mathrm{CCH_2}$, 8.55s (9); $\mathit{Me}\mathrm{CH_2O}$, 9.03t (6); $\mathrm{Me_3C}\mathit{CH}_2$, 9.70s (2)
$\mathrm{Mg(Bu^tCH_2)_2(tmed)}$	114—116	67.8	13.5	9.38	274 (1.16)	68.0	13.4	9.92	282	$\mathit{Me}_2\mathrm{NCH_2}$, 8.03s (6); $\mathrm{Me_2NC}\mathit{H}_2$, 8.26s (2); $\mathit{Me}_3\mathrm{CCH_2}$, 8.41s (9); $\mathrm{Me_3C}\mathit{CH}_2$, 9.93s (2)
$\mathrm{Mg(Me_3SiCH_2)_2}$	200—205	48.0	10.8			48.4	11.1			
$\mathrm{Mg(Me_3SiCH_2)_2(OEt_2)_2}$	102—105	56.1	11.4			56.7	11.2			$\mathit{Me}\mathrm{CH_2O}$, 6.40q (4); $\mathrm{MeC}\mathit{H}_2\mathrm{O}$, 9.00t (6); $\mathit{Me}_3\mathrm{SiCH_2}$, 9.60s (9); $\mathrm{Me_3Si}\mathit{CH}_2$, 11.2s (2)
$\mathrm{Mg(Me_3SiCH_2)_2(tmed)}$	93—95	52.6	12.2	8.49	319 (1.21)	53.4	12.1	8.92	314	$\mathit{Me}_2\mathrm{NCH_2}$, 8.04s (6); $\mathrm{Me_2NC}\mathit{H}_2$, 8.30s (2); $\mathit{Me}_3\mathrm{SICH_2}$, 9.49s (9); $\mathrm{Me_3Si}\mathit{CH}_2$, 11.4s (2)
$\mathrm{Mg(PhMe_2CCH_2)_2}$	143—147	82.7	8.36			82.7	8.95			
$\mathrm{Mg(PhMe_2CCH_2)_2(tmed)}$	103—105	75.4	10.3	6.42	378 (1.29)	76.8	10.3	6.90	406	*o*-H, 2.70m (2); *m,p*-H, 3.20m (3); $\mathit{Me}_2\mathrm{NCH_2}$,[c] 8.68s (6); $\mathrm{Ph}\mathit{Me}_2\mathrm{CCH_2}$,[c] 8.92s (6); $\mathrm{Me_2NC}\mathit{H}_2$, 8.94s (2); $\mathrm{PhMe_2C}\mathit{CH}_2$, 10.8s (2)

[a] Cryoscopically in benzene under nitrogen. [b] Measured at 60 MHz using benzene as standard (τ 2.73) and as solvent except for the last compound which was dissolved in C_6D_6 and referenced to internal $SiMe_4$. [c] These assignments might be reversed.

Bis(neopentyl)magnesium–NNN′N′-*Tetramethylethylenediamine* (1/1).—A sample of the dialkyl was dissolved in toluene and excess of tmed was added. The solution was stirred (30 min) and then evaporated to dryness; the resulting white solid crystallized from toluene (−20 °C) as colourless *prisms*.

Bis(trimethylsilylmethyl)magnesium.—To $\mathrm{Me_3SiCH_2MgCl}$,[10] prepared from $\mathrm{Me_3SiCH_2Cl}$ (62 g, 0.50 mol) and magnesium (13 g, 0.54 mol) in diethyl ether (500 ml), dioxan (45 ml, 0.52 mol) was slowly added (1 h) with rapid stirring. The suspension was stirred for 15 h, centrifuged, and the supernatant liquid evaporated to dryness under reduced pressure. The white *solid* was heated (120—140 °C) *in vacuo* (10^{-2} mmHg) for 24 h; yield was 80 g (79%). The ^{1}H n.m.r. spectrum of a diethyl ether solution contained resonances at 1.30 (s) ($\mathit{Me}_3\mathrm{SiCH_2Mg}$) and 2.95 p.p.m. (s) ($\mathrm{Me_3Si}\mathit{CH}_2\mathrm{Mg}$) to high field of the methyl triplet of diethyl ether.

Bis(trimethylsilylmethyl)magnesium–Diethyl Ether (1/1).—A sample of the dialkyl was dissolved in diethyl ether (−70 °C) and warmed to room temperature (30 min). After concentration to *ca.* 3 ml, and cooling (−70 °C), the colourless *prisms* were collected and dried *in vacuo* at room temperature for 30 min.

Bis(trimethylsilylmethyl)magnesium–NNN′N′-*Tetramethylethylenediamine* (1/1).—To a sample of the diethyl ether complex in Et_2O was added an excess of tmed; the solution was stirred (15 min) and then evaporated to dryness. The resulting white solid crystallized from light petroleum (−20 °C) as colourless *needles*.

Bis(2-methyl-2-phenylpropyl)magnesium.—To $\mathrm{PhMe_2CCH_2MgCl}$,[11] prepared from $\mathrm{PhMe_2CCH_2Cl}$ (84 g, 0.50 mol) and magnesium (13 g, 0.54 g-atom) in diethyl ether (500 ml), was slowly added (1 h) with rapid stirring dioxan (45 ml, 0.52 mol). The suspension was stirred (16 h), centrifuged, and the supernatant liquid was evaporated to dryness. The white *solid* was heated (110—115 °C) *in vacuo* (10^{-2} mmHg) for 24 h; yield was 84 g (60%). The ^{1}H n.m.r. spectrum of a diethyl ether solution contained resonances at −6.16 (m) $\mathit{Ph}\mathrm{Me_2CCH_2Mg}$, −0.33 p.p.m. (s) ($\mathrm{Ph}\mathit{Me}_2\mathrm{CCH_2Mg}$), and +0.98 p.p.m. (s) ($\mathrm{PhMe_2C}\mathit{CH}_2\mathrm{Me}$) relative to the centre resonance of the methyl triplet of diethyl ether.

Bis(2-methyl-2-phenylpropyl)magnesium–NNN′N′-*Tetramethylethylenediamine* (1/1).—To a sample of the dialkyl in diethyl ether was added an excess of tmed. The solution was stirred (30 min) and evaporated to dryness. The *complex* crystallized as colourless *needles* from light petroleum–toluene (6 : 1).

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