The First Example of an Intermolecular Weak (Agostic) γ-Methyl–Metal Interaction: the Low Temperature Single Crystal *X*-Ray and Neutron Diffraction Structure of $(\mathrm{MgR_2})_\infty$ [R = $\mathrm{CH(SiMe_3)_2}$]†

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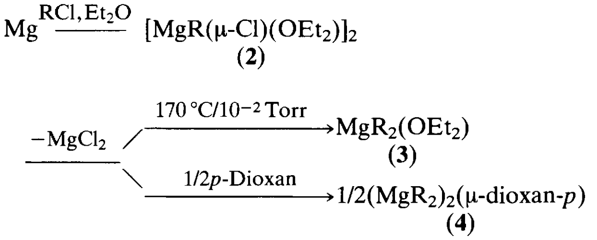
The crystalline homoleptic magnesium alkyl $(\mathrm{MgR_2})_\infty$ [R = $\mathrm{CH(SiMe_3)_2}$], derived from $\mathrm{Mg(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2}$ and 2LiR, is shown by low temperature *X*-ray (190 K) and neutron (15 K) diffraction to have the structure $[\mathrm{Mg\{CH(SiMe_3)[SiMe_2(\mu\text{-}Me)]\}R}]_\infty$, with the $\mathrm{MgC_2C'}$ unit coplanar (C′ refers to μ-$\mathrm{C'H_3}$ of a neighbouring $\mathrm{Mg'R_2}$ moiety), Mg–C 2.117(4) and 2.105(4) Å, short Mg′ ··· C [2.535(4) Å] and Mg′ ··· H [2.333(4), 2.414(5), and 2.516(4) Å] contacts, and the bridging methyl group adopting a pseudo trigonal bipyramidal arrangement [Mg ··· $\mathrm{C(H)_3}$–Si: Mg′ ··· C–Si 172.3(2)°, <H–C–H> 110.4°, and a longer {1.915(8) Å} C–Si bond than those {av. 1.877(6) Å} not involved in a Mg contact].

The homoleptic crystalline dialkylmagnesium compound $(\mathrm{MgR_2})_\infty$ [R = $\mathrm{CH(SiMe_3)_2}$] (**1**), obtained from $[\mathrm{Mg(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2}]_2$ (ref. 1) and LiR (ref. 2) in n-hexane, has novel and unique features. Its synthesis is noteworthy because (i) earlier experiments[3] using the conventional Grignard route led to crystalline $[\mathrm{MgR(\mu\text{-}Cl)(OEt_2)}]_2$ (**2**), $\mathrm{MgR_2(OEt_2)}$ (**3**), and $(\mathrm{MgR_2})_2(\mu\text{-dioxan-}p)$(**4**); and (ii)

$$\underset{(\mathbf{1})}{(\mathrm{MgR_2})_\infty[\mathrm{R} = \mathrm{CH(SiMe_3)_2}]}$$

the neutral *O*-centred coligand in (**2**) or (**3**) was tenaciously bound to magnesium, equation (1).



$$\mathrm{Mg} \xrightarrow{\mathrm{RCl,Et_2O}} \underset{(\mathbf{2})}{[\mathrm{MgR(\mu\text{-}Cl)(OEt_2)}]_2} \xrightarrow{-\mathrm{MgCl_2}} \begin{cases} \xrightarrow{170\,^\circ\mathrm{C}/10^{-2}\,\mathrm{Torr}} \underset{(\mathbf{3})}{\mathrm{MgR_2(OEt_2)}} \\ \xrightarrow{1/2p\text{-Dioxan}} \underset{(\mathbf{4})}{1/2(\mathrm{MgR_2})_2(\mu\text{-dioxan-}p)} \end{cases} \tag{1}$$

The colourless, hydrocarbon-soluble alkyl (**1**) has m.p. 38—40 °C, b.p. 72 °C/10^{-2} Torr. The FAB mass spectrum shows the monomeric parent ion (342 a.u.) as the highest *m*/*z* peak. The ^{1}H and ^{13}C NMR spectra‡ are consistent with a monomeric structure in $\mathrm{C_6D_6}$ solution, as is the molecular weight in $\mathrm{C_5H_{12}}$ (Signer method).

Single crystals of (**1**) were grown from an n-$\mathrm{C_5H_{12}}$ solution at −30 °C. An ambient temperature *X*-ray study indicated a polymeric array, with unprecedented *intermolecular* interaction between the magnesium atoms and a γ-methyl group of a neighbouring $\mathrm{MgR_2}$ unit. Accordingly, low temperature data were collected both by *X*-ray (190 K) and neutron (15 K) diffraction.§ The structure, with selected geometrical parameters (neutron data), is illustrated in Figure 1. The

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† No reprints available.

‡ *Selected NMR data* for (**1**) in $\mathrm{C_6D_6}$ at 305 K: ^{1}H (80 MHz) δ −1.57 (s, 2H), 0.16 (s, 36H); ^{13}C (90 MHz) δ 5.64 (CH) [$^1J(^{13}\mathrm{C}\text{–}^1\mathrm{H})$ 100.8 Hz], 5.27 ($\mathrm{CH_3}$) [$^1J(^{13}\mathrm{C}\text{–}^1\mathrm{H})$ 117.2 Hz, $^3J(^{13}\mathrm{C}\text{–}^1\mathrm{H})$ 2.18 Hz].

§ *Crystal data* for (**1**) (neutron data at 15 K): $\mathrm{C_{14}H_{38}MgSi_4}$, M = 343.1, monoclinic, space group $P2_1$ (No. 4), a = 9.502(1), b = 10.435(1), c = 12.323(2) Å, β = 112.484(6)°, U = 1129 Å^3, Z = 2, D_c (298 K) 0.97 g cm^{-3}, λ = 1.3168 Å (Ge^{115} monochromatic thermal neutrons), T 15 K (Displex cryorefrigerator), μ 3.25 cm^{-1}; crystal size 0.1 × 0.1 × 0.4 cm^3. Of the 5143 intensities recorded on D19 equipped with a position-sensitive detector, 2389 were unique, and 2276 absorption corrected intensities were used to refine the starting model obtained from low temperature (190 K) *X*-ray diffraction.[17] All atoms were given anisotropic displacement parameters and refinement converged at R (R') 0.056 (0.047). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

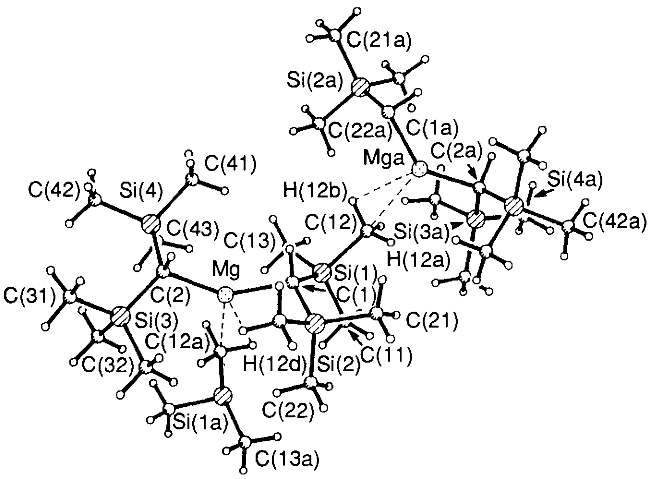


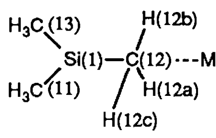
Figure 1. Molecular structure and atom numbering scheme for $(MgR_2)_\infty$ [$R = CH(SiMe_3)_2$] (**1**). Selected bond distances (Å) and angles (°) not indicated in the text (from neutron data at 15 K): C(1)–Mg–C(2) 140.0(2), C(1)–Mg ··· C(12′) 108.4(2), C(2)–Mg ··· C(12′) 111.6(2), C(1)–Si(1) 1.836(6), C(2)–Si(2) 1.862(5); C(2)–Si(3) 1.842(7), C(2)–Si(4) 1.857(5), Si(1)–C(1)–Si(2) 120.2(2); Si(3)–C(2)–Si(4) 120.7(3), Mg–C(1)–H(1) 97.8(4), Mg–C(2)–H(2) 98.2, C(1)–H(1) 1.107(9); C(2)–H(2) 1.111(9); mean (Me)C–Si–C(Me) 107.3°, mean Si–C(Me) 1.884 Å [all, excluding C(12) values].

Atom (M′) is related to atom (M) by the symmetry operator (2_1).

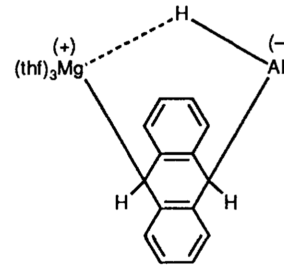
co-ordination geometry at Mg for (**1**) is compared with that established for a number of other magnesium alkyls in Table 1.

In order to discuss the nature of the intermolecular weak ('agostic') interactions, reference is made to the fragment (**5**), using the atom labelling scheme of Figure 1. The following features (i)—(v) are apparent. (i) The intermolecular C(12) ··· Mg′ distance of 2.535(4) Å is much shorter than the sum of the van der Waals radii (3.4 Å), although significantly longer than the Mg–C(1) and Mg–C(2) bond lengths [2.117(4) and 2.105(4) Å]. (ii) The Si–C(12) ··· Mg′ angle of 172.3(2)° indicates an almost linear arrangement. (iii) The Si–C(12) bond [1.915(8) Å] is longer than the Si–C(11) and Si–C(13) bonds [1.876(6) and 1.879(5) Å, respectively]. (iv) The intermolecular Mg′ ··· H contacts of 2.333(4), 2.414(5), and 2.516(4) Å are shorter than the sum of the van der Waals radii (2.9 Å), but only marginally shorter than the intramolecular Mg ··· H contacts to the H atoms on C(1) and C(2) [2.519 and 2.516 Å] and much longer than the value found by *X*-ray diffraction in the supposedly zwitterionic (**6**), Mg ··· H 1.96(3) Å.[4] (v) The H–C(12)–H angles are opened out (av. 110.5°) compared to the other H–C–H angles (107.1°) with a concomitant decrease in the Si–C(12)–H angles to 108.5°.

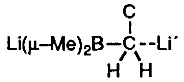
Lithium-to-β-Me *intermolecular* interactions have been recognised in crystalline $[Li(\mu\text{-}Me)_2BMe_2]_\infty$ (ambient temperature neutron diffraction) to contain the fragment (**7**): Li′ ··· C 2.359(11) [comparable to the Mg′ ··· C(12) distance in (**1**) allowing for the difference in covalent radii: Li 1.34, Mg 1.45 Å], Li–$CH_3(\mu)$ 2.207(9), B–C(···) 1.640(6), B–$CH_3(\mu)$ 1.654(4), <H ··· Li′> 2.228(10) Å; B–C ··· Li′ 176.3(4), <H–C–H> 108.0(4)°.[5] Lithium-to-α-methyl intermolecular interactions have been discussed as contributing to the structure of crystalline $[\{Li(\mu_3\text{-}Me)\}_4]_\infty$, (powder *X*-ray diffraction) but the intra- [2.31(5) Å] and inter- [2.36(5) Å] molecular Li ··· CH_3 contacts (ambient temperature *X*-ray diffraction) were comparable.[6] The presence of CHLi′ three-centre bonds, *cf.* (**8**), in these and related compounds (believed to be due to the Lewis acidity of the lithium centre[5]) has been discussed in terms of molecular orbital index calculations.[7] The crystal structure of KCD_3 by low temperature neutron diffraction on the powder revealed each CD_3 co-ordinated to six K, with three K^+ ions having shorter K ··· C contacts than the three others.[8]



(5)

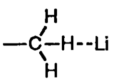


(6) thf = tetrahydrofuran



$$Li(\mu\text{-}Me)_2B{-}\underset{H\ \ H}{\overset{C}{C}}{--}Li'$$

(7)



$${-}\underset{H}{\overset{H}{C}}{-}H{--}Li$$

(8)

Table 1. Comparative selected structural data for some crystalline magnesium alkyls.

Compound	Mg–C/Å	ΣCMgC/°	CN of Mg	Ref.
$(MgR_2)_\infty$ (**1**)	2.105(4) 2.117(4) 2.535(4)	351.2[a]	3[a]	This work
$[MgR(\mu\text{-}Cl)(OEt_2]_2$ (**2**)	2.131(8)	—	4	3
$MgR_2(OEt_2)$ (**3**)	2.17(1)	(360)[b]	3	3
$(MgR_2)_2(\mu\text{-dioxan-}p)$ (**4**)	2.118(5)	(360)[b]	3	3
$[MgNp_3]^-$ [d]	2.22(1)	(360)[b]	3	14
{$MgNp_2$ (gas)	2.126(5)	180	2	15 }[c]
$Mg[C(SiMe_3)_3]_2$	2.16(2)	180	2	16

[a] On the basis of the unit $Mg'(R_2)_2(\cdots CH_3)$. [b] This is the sum of CMgC + 2CMgO angles. [c] Electron diffraction data. [d] Np = CH_2Bu^t.

Similarly, the *intramolecular* interaction often found between an aliphatic C–H bond and a transition metal M has been described in terms of a three-centre, two-electron bond encompassing the C ··· H ··· M atoms, so that M achieves a more effective closed-shell configuration than in the absence of such an agostic effect.[9]

As for $(MgR_2)_\infty$ (**1**), the *weak intermolecular* γ-methyl-magnesium association is attributed to an intermolecular (agostic) Mg′ ··· CH_3 interaction. This could be primarily between Mg′ and the C(12)–H(12b) bond, although the other two Mg′ ··· H interactions with the methyl group are not much longer. However, the C(12)–H bonds (av. 1.088 Å) do not differ significantly in length from the average methyl C–H bond length of 1.087 Å and show no signs of the lengthening to *ca.* 1.17 Å usually (*X*-ray) found[9] for C–H bonds involved in agostic interactions.

An alternative explanation is that the agostic interaction is due to a linear three-centre, two-electron bond involving the Si(1), C(12), and Mg′ atoms, with incipient five co-ordinate trigonal bipyramidal geometry at C(12). This should give a lengthening of the Si(1)–C(12) bond, a distortion towards sp^2 bonding for the CH_3 group with increased H–C–H angles and decreased Si–C–H angles, and a slight decrease in the C–H bond lengths. This seems to be more in accord with the observed geometry. Furthermore, the geometrical similarity of the fragments (**5**) and (**7**) points to the possibility that in the latter an important contributor to the agostic interaction is a linear three-centre, two-electron bond involving B, C, and Li′.

The co-ordination number (CN) of 4 for magnesium in organomagnesium compounds is common [*e.g.*, in $(MgMe_2)_\infty$] and CNs of 5 or 6 are well documented,[10] while instances of CN = 3 are rare. An early proposal for such a CN in solution, based on molecular weight measurements, was made for $(MgR'_2)_n$ [R′ = CH(Me)Et[11] or CH_2Bu^t (≡Np)[12]]. Published *X*-ray data for 3-CN magnesium appear to be restricted to the natural zeolite offretite[13] and the anion of $[MgNp(crypt)][MgNp_3]$;[14] to these can now be added compounds (**1**) (neglecting possible H ··· Mg′ interactions), (**3**), and (**4**). In each of these, the metal is in a planar, very approximately trigonal environment.

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