PREPARATION AND CRYSTAL STRUCTURE OF THE DICARBORANYL-MAGNESIUM BIS(DIOXANE) ADDUCT $Mg(2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10})_2 \cdot 2C_4H_8O_2$ *

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(Received December 4th, 1986)

Summary

The preparation of $Mg(2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10})_2 \cdot 2C_4H_8O_2$ from the carboranyl Grignard reagent RMgBr (R = the methyl-*ortho*-carboranyl residue, 2-Me-1,2-$C_2B_{10}H_{10}$) by a dioxane-induced disproportionation reaction is described. An X-ray crystallographic study of the product has revealed a monomeric molecular structure R_2MgL_2 (L = 1,4-dioxane, $C_4H_8O_2$) in which the carboranyl groups and dioxane ligands provide the central magnesium atom with a distorted tetrahedral coordination sphere of two carbon and two oxygen atoms, with bond lengths Mg–C 2.156(5) Å, Mg–O 2.038(8) Å and bond angles CMgC 123.5(4)°, OMgO 99.5(5)°, distortions from regular tetrahedral angles attributable to the relative bulk of the carboranyl ligands.

Introduction

This paper describes the use of the dioxane-induced disproportionation of a Grignard reagent ($2RMgBr \rightarrow R_2Mg + MgBr_2$) to provide the first known dicarboranylmagnesium compound R_2Mg (R = the icosahedral C-methyl-*ortho*-carboranyl group, 2-Me-1,2-$C_2B_{10}H_{10}$) in the form of a bis(dioxane) adduct.

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* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday. The subject matter of this short paper, combining main group organometallic chemistry with cluster chemistry, reflects the interests that KW was fortunate to develop under the guidance and encouragement of Professor Coates in Durham in the nineteen-sixties, interests that have remained a source of fascination for KW ever since.

$R_2Mg \cdot 2C_4H_8O_2$, whose crystal and molecular structure (see I and Fig. 1) is also reported.

(I)

(II)
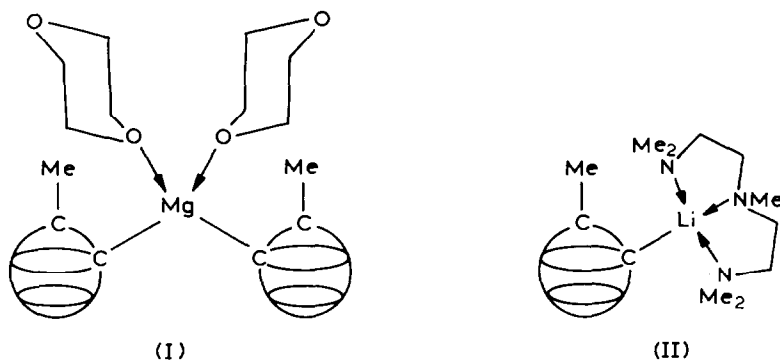
Although a wealth of structural information is now available on polyhedral boranes, carboranes and metalla derivatives thereof [1–6], no carborane with a Group II metal atom covalently bonded in an *exo* position to a skeletal boron or carbon atom has to our knowledge been structurally characterised. This is surprising in view of the use carboranyl Grignard reagents RMgX (R = a carboranyl group) have found as intermediates in the synthesis of functionally substituted carboranes [1–3,5]. Our own recent structural characterisation [7] of the lithiocarborane adduct $Li(2\text{-Me-}1,2\text{-}C_2B_{10}H_{10}) \cdot PMDETA$ (PMDETA = pentamethyldiethylenetriamine, $MeN(CH_2CH_2NMe_2)_2$), another intermediate through which C-substitution of methyl-*ortho*-carborane can be effected, has established structure II in which the 4-coordinate lithium atom is terminally attached by a bond of length 2.18 Å to the methyl-*ortho*-carborane residue, which was calculated to subtend a cone angle at the metal of 132–149°, depending on the methyl group orientation. Since lithium and magnesium atoms have similar covalent radii, it was therefore expected that the attachment of two methyl-*ortho*-carboranyl substituents to one magnesium atom might generate a metal atom so crowded as to limit its capacity to take up Lewis base molecules. Adoption of a polymeric structure $(R_2Mg)_n$ (III) of the type adopted by $(MgMe_2)_n$ [8]. $(MgEt_2)_n$ [9] and related dialkyls [10,11] with 4-coordinate metal atoms bridged by electron deficient 3-centre-2-electron (3c2e) MgCMg bonds, appeared unlikely on steric grounds, though a dimeric structure of type IV appeared possible for unsolvated dicarboranylmagnesium. This last type of structure

(III)

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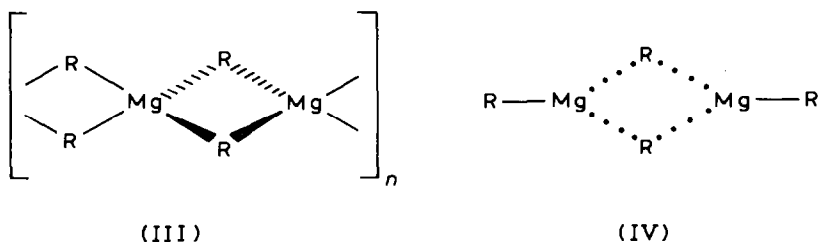
would generate an unprecedented environment for the metal-attached carbon atoms, which would be involved in skeletal bonding to five other atoms in the carborane residue, and to two metal atoms by means of a 3c2e bond. (Bonding of this type for
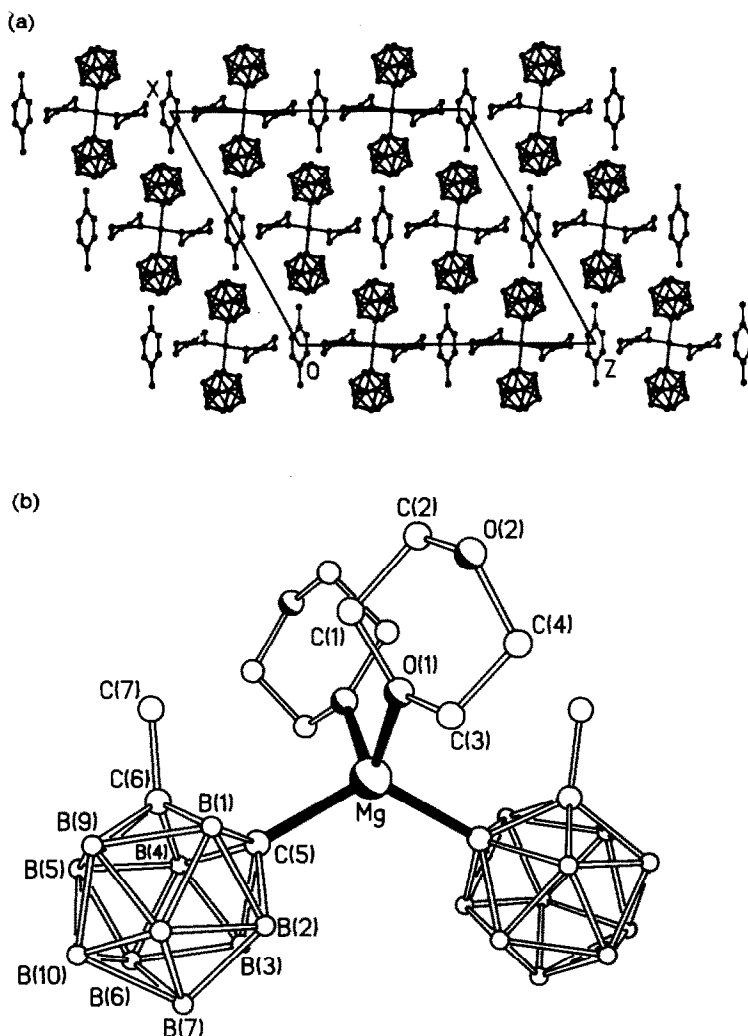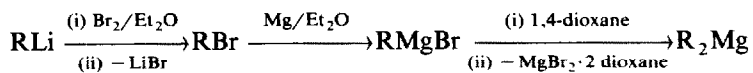
(a)

(b)

Fig. 1. (a) Packing of molecules of I in crystal; (b) skeletal atoms of molecule I.

carbon is not represented in a recent survey [12] of hypercoordinated carbon systems.) To explore such possibilities, we embarked on the present study.

Results and discussion

The dicarboranylmagnesium compound R_2Mg (I) ($R = 2\text{-Me-}1,2\text{-}C_2B_{10}H_{10}$) was prepared, as described in the Experimental section, by the following sequence of reactions, involving the disproportionation of the Grignard reagent RMgBr (the classical route [10,11,13] to diorganomagnesium compounds R_2Mg):

$$RLi \xrightarrow[\text{(ii) } -\text{LiBr}]{\text{(i) } Br_2/Et_2O} RBr \xrightarrow{Mg/Et_2O} RMgBr \xrightarrow[\text{(ii) } -\text{MgBr}_2 \cdot 2 \text{ dioxane}]{\text{(i) } 1,4\text{-dioxane}} R_2Mg$$

Separation of the product from the magnesium bromide-dioxane adduct was achieved by evaporation to dryness of the suspension obtained from the disproportionation reaction, and extraction of the residue with hot toluene, from which the dicarboranylmagnesium-dioxane adduct separated as colourless crystals that decomposed rapidly on exposure to moist air, suffering hydrolysis to methyl-*ortho*-carborane and magnesium hydroxide.

As yet, we have been unsuccessful in our attempts to obtain dicarboranylmagnesium, R_2Mg, in unsolvated form. Limiting the quantity of dioxane added to the minimum required for the disproportionation:

$$2RMgBr + 2C_4H_8O_2 \xrightarrow{\text{Et}_2O} MgBr_2 \cdot 2C_4H_8O_2 + R_2Mg$$
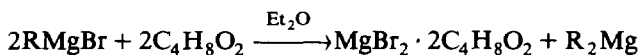
followed by evaporation of the ether suspension to dryness, the residue subsequently being extracted with toluene, afforded solutions containing carboranyl species, from which, however, only the dioxane adduct $MgR_2 \cdot 2$dioxane (I) or the parent carborane RH (presumably formed by hydrolysis) were recovered. Despite this failure to isolate unsolvated R_2Mg, we consider that the ease with which the carboranyl Grignard reagent RMgBr disproportionates into dicarboranylmagnesium (R_2Mg) and magnesium dihalide ($MgBr_2$) suggests that carboranyl-bridged dimagnesium species (the likely intermediates or transition states in such reactions) are readily accessible:
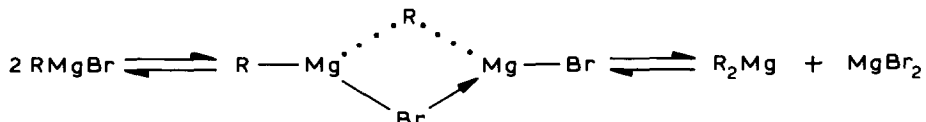
The solvate, $MgR_2 \cdot 2$dioxane (I), was subjected to an X-ray crystallographic study, which established the structure shown in Fig. 1. The packing of the individual molecules, accompanied by an equal number of toluene molecules occupying intermolecular sites remote from the metal atoms, is illustrated in Fig. 1(a); Fig. 1(b) shows the skeletal atoms of an individual molecule, $Mg(2\text{-Me-}1,2\text{-}C_2B_{10}H_{10})_2 \cdot 2C_4H_8O_2$, which has a 2-fold symmetry axis bisecting the OMgO and CMgC angles, which are 99.5(5) and 123.5(4)°, respectively. Atomic coordinates are given in Table 1. Selected bond distances and angles are given in Table 2.

The distorted tetrahedral geometry about the magnesium atom in I resembles that about the metal atom in the dicarboranyl(dimethyl)germanium compound $Ge(1,2\text{-}C_2B_{10}H_{11})_2Me_2$ [14]. In both compounds, the bulk of the carboranyl ligands causes their interligand CMgC bond angle to be greater than the tetrahedral angle (in the germanium compound [14] the carboranyl–Ge–carboranyl angle is 112.6(5)°). The crowding together of the dioxane ligands in I presumably results from the spatial requirements of the carboranyl groups.

The magnesium–carbon bond length of 2.156(5) Å in I is essentially identical to those in $Ph_2Mg(TMEDA)$ (2.167 Å) [15], in $Me_2Mg(TMEDA)$ (2.166 Å) [16], in $PhMgBr \cdot 2Et_2O$ (ca. 2.2 Å) [17], and in related compounds [11] indicating that all of these bonds are realistically regarded as 2-centre-2-electron (2c2e) Mg–C bonds. (The 3c2e MgCMg bonds in $(Me_2Mg)_n$ [8] and $(Et_2Mg)_n$ [9] by contrast are longer, with Mg–C distances ca. 2.25 Å). Some variation of these 2c2e Mg–C bond lengths with the coordination numbers of the carbon atoms might have been expected, but

TABLE 1

ATOMIC COORDINATES ($\times 10^4$)

Atom	x	y	z
Mg	5000	2114(4)	2500
O(1)	4856(4)	3529(7)	3136(3)
O(2)	4900(7)	5536(11)	4114(6)
C(1)	4402(8)	4822(12)	2935(7)
C(2)	4820(10)	5977(12)	3480(10)
C(3)	4936(7)	3091(10)	3798(5)
C(4)	5321(8)	4184(17)	4316(7)
C(5)	3921(3)	1017(7)	1953(3)
C(6)	3071	1734	1404
C(7)	3084	3310	1234
B(1)	3238	1352	2197
B(2)	3721	−271	2399
B(3)	3867	−743	1712
B(4)	3472	596	1095
B(5)	2473	590	792
B(6)	2968	−1021	984
B(7)	3129	−1570	1807
B(8)	2729	−248	2111
B(9)	2327	1061	1479
B(10)	2270	−728	1239
C(8)	4677	1231	5116
C(9)	5468	1069	5443
C(10)	5792	−162	5327
C(11)	6643	−336	5679

no significant differences have been detected. The magnesium–oxygen bond length in I (2.038(8) Å) lies within the range of values (2.01–2.06 Å) normally found for other ether complexes of organomagnesium compounds [11,17–21].

The orientations of the carboranyl-methyl substituents in I, as far as possible away from the other carboranyl group and between the dioxane ligands, are clearly

TABLE 2

UNCONSTRAINED BOND LENGTHS (Å) AND ANGLES (°)

Mg–O(1)	2.038(8)	Mg–C(5)	2.156(5)
O(1)–C(1)	1.443(13)	O(1)–C(3)	1.446(15)
O(2)–C(2)	1.389(27)	O(2)–C(4)	1.459(18)
C(1)–C(2)	1.529(18)	C(3)–C(4)	1.447(17)
O(1)–Mg–C(5)	105.2(3)	O(1)–Mg–O(1′)	99.5(5)
C(5)–Mg–O(1′)	110.5(2)	C(5)–Mg–C(5′)	123.5(4)
Mg–O(1)–C(1)	126.9(7)	Mg–O(1)–C(3)	121.7(6)
C(1)–O(1)–C(3)	107.3(10)	C(2)–O(2)–C(4)	109.6(14)
O(1)–C(1)–C(2)	108.5(9)	O(2)–C(2)–C(1)	109.9(12)
O(1)–C(3)–C(4)	111.0(10)	O(2)–C(4)–C(3)	110.7(9)
Mg–C(5)–C(6)	127.5(2)	Mg–C(5)–B(1)	117.9(2)
Mg–C(5)–B(2)	116.9(2)	Mg–C(5)–B(3)	121.7(2)
Mg–C(5)–B(4)	125.8(2)		

those that minimise nonbonding repulsions between ligands. The CMgC angle of 123.5(4)°, though larger than the regular tetrahedral angle, is nevertheless smaller than might have been expected from our earlier calculation [17] of carboranyl group cone angles, from which a CMgC angle of ca. 132° would have been expected. Close examination of the carboranyl group orientations in I shows that these ligands mesh together, allowing significantly closer approach than would be possible if their respective B–H groups were aligned opposite each other.

Experimental

Preparation of 1-bromo-2-methyl-1,2-dicarba-closo-dodecaborane, $C_2B_{10}H_{10}MeBr$

A diethyl ether/hexane solution of 1-lithio-2-methyl-*ortho*-carborane, $LiC_2B_{10}H_{10}Me$, was slowly added to a stirred solution of bromine in diethyl ether at $0°C$. The resulting solution was shaken with an equal volume of dilute aqueous sodium thiosulphate, the ether layer separated, and was then dried over anhydrous magnesium sulphate. Removal of the ether by pumping afforded a white solid, which after purification by sublimation at $80°C$ and 0.004 mmHg was identified as 1-bromo-2-methyl-1,2-dicarba-closo-dodecaborane $C_2B_{10}H_{10}BrMe$, m.p. $222°C$ (lit. $220-221°C$) [22] (Found: C, 15.3; H, 5.7; B, 45.5; Br, 34.5. $C_3H_{13}B_{10}Br$ calcd.: C, 15.2; H, 5.5; B, 45.6; Br, 33.7%).

Preparation of the bis(2-methyl-1,2-dicarba-closo-dodecaboranyl)magnesium · bis-(dioxane) adduct (I)

A solution of 1-bromo-2-methyl-*ortho*-carborane, $C_2B_{10}H_{10}BrMe$ (1.81 g, 7.63 mmol) in 20 cm³ Et_2O was slowly added to magnesium turnings (0.35 g, 10.29 mmol) in 10 cm³ of refluxing diethyl ether. A small crystal of iodine was added to initiate the reaction. After all the bromocarborane solution had been added, the solution was boiled for 3 h and then filtered to remove unreacted magnesium. Addition of 1,4-dioxane (5 cm³) caused precipitation of a white solid. The solution was stirred overnight and evaporated to dryness under vacuum. The resulting solid was extracted with 15 cm³ of hot toluene, and colourless crystals separated from the filtered solution on cooling. These were identified as the bis(dioxane) adduct I crystallising with an equimolar proportion of toluene as $Mg(2-Me-1,2-C_2B_{10}H_{10})_2-(C_4H_8O_2)_2 \cdot MePh$, m.p. $180-185°C$ (dec.) (1.5 g, ca. 50% yield). (Found: C, 40.0; H, 10.3; B, 33.2; Mg, 3.8. $C_{21}H_{50}B_{20}MgO_4$ calcd.: C, 41.5; H, 8.3; B, 35.6; Mg, 4.0%) ν_{max} (Nujol mull): 2565(s,br), 1299(m), 1264(m), 1223(w), 1131(s), 1096(w), 1047(s), 1017(w,sh), 972(w), 937(w,br), 895(m), 878(s), 846(w), 823(m), 793(w), 773(w), 763(s), 697(w), 670(w), 654(w), 621(m), 573(w), 503(w), 467(w), 458(w) cm⁻¹. The compound was extremely air sensitive, its infrared spectrum developing absorptions characteristic of OH and carboranyl C–H groups immediately on exposure to moist air. Its mass spectrum showed characteristic dioxane and methyl-carboranyl parent and fragment peaks.

Attempts to prepare unsolvated bis(methyl-*ortho*-carboranyl)magnesium, $Mg(2-Me-1,2-C_2B_{10}H_{10})_2$, by similar reactions to the above, but using one mmol dioxane per mmol of the Grignard reagent, afforded toluene solutions from which only small quantities of I and of methyl-*ortho*-carborane, $C_2B_{10}H_{11}Me$, were recovered.

X-ray crystallography

$C_{21}H_{50}B_{20}MgO_4$, $M_r = 607.1$, monoclinic, $C2/c$, a 19.890(4), b 9.304(2), c 21.997(5) Å, β 118.29(2)°, V 3584.5 Å^3, $Z = 4$, D_{calc} 1.125 g cm^{-3}, $F(000) = 1280$, μ 0.07 mm^{-1} for Mo-K_α radiation (λ 0.71069 Å). Crystal size 0.3 × 0.4 × 0.4 mm. Stoe-Siemens AED diffractometer. Cell parameters were refined from 2θ values (20–25°) of 23 reflections. Data were collected in a ω/θ scan mode by a profile-fitting procedure [23]: $2\theta_{max}$ 42°, no significant variation in three standard reflections. The crystal was twinned; reflections with $l = 7n$ were badly affected by overlap and were rejected, 4812 reflections were measured (no absorption correction), giving 1713 unique data, 1032 with $F > 4\sigma(F)$ (merging $R = 0.027$).

The structure was solved by direct methods and refined by blocked-cascade least squares on F, with $\omega^{-1} = \sigma^2(F) + 0.00252F^2$. The twinning and high degree of thermal motion made a satisfactory resolution of individual boron atoms impossible, so the whole carborane ligand was constrained as a rigid group with the geometry observed in its lithium complex [7]. Toluene molecules are two-fold disordered over centres of symmetry and were constrained as rigid hexagons (C–C 1.395 Å) with two half-occupancy methyl groups (C–Me 1.500 Å, no H atoms). Dioxane atoms were refined freely. All non-H atoms were assigned anisotropic thermal parameters, H atoms were assigned $U(H) = 1.2U_{eq}(C)$ or $1.2U_{eq}(B)$ and made to ride on the C or B atoms (C–H 0.96 Å, H–C–H 109.5°) [24]. Final values of R and R' ($= (\Sigma w\Delta^2/\Sigma wF_0^2)^{\frac{1}{2}}$) were 0.127 on 0.153. A final difference synthesis showed no major features, but there were indications of a possible disorder of different rotational positions of the carborane ligands.

Conclusions

The classical route to diorganomagnesium compounds R_2Mg [10,11,13], using the dioxane-induced disproportionation of a Grignard reagent RMgBr, has been shown to be applicable to the synthesis of a dicarboranylmagnesium compound, $Mg(2\text{-Me-}1,2\text{-}C_2B_{10}H_{10})_2$, isolated in the form of its bis(1,4-dioxane) adduct which crystallised from toluene with an equimolar proportion of lattice toluene. An X-ray crystallographic study of the adduct has shown it to contain a distorted tetrahedral arrangement of carboranyl groups and dioxane ligands about the metal atom, attached by normal length Mg–C and Mg–O 2c2e bonds. The angle subtended by the carboranyl ligands at the metal atom, 123.5(4)°, indicates that a previous assessment of the cone angle subtended by a methyl-*ortho*-carboranyl ligand overestimated the spatial requirements of this ligand by ca. 8°.

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46

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