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THE STRUCTURE OF THE GRIGNARD REAGENT

IX. THE CRYSTAL STRUCTURE OF THE DIMERIC ETHYLMAGNESIUM BROMIDE/DIISOPROPYL ETHER COMPLEX

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Summary

The structure of the dimeric ethylmagnesium bromide/diisopropyl ether complex $[C_2H_5MgBr\cdot O(i\text{-}C_3H_7)_2]_2$ was studied with single crystal X-ray diffraction techniques. Crystals are monoclinic with spacegroup $P2_1/n$ and two dimers per unit cell of dimensions a 7.85(1), b 14.43(2), c 11,31(2) Å, β 100.3(1)° The structure was refined to a final R-value of 0.073. The magnesium is four coordinate; dimers are formed through bridging bromine atoms.

This result is briefly discussed in the context of factors governing complex formation of Grignard reagents.

Introduction

Our interest in the influence of solvents on the structure and physical properties of organomagnesium compounds has led us to study the behaviour of ethylmagnesium bromide in weakly basic solvents such as 1-ethoxy-2-methylbutane [1] and diisopropyl ether [2]. It has been reported that whereas diethylmagnesium exists in an equilibrium between dimers and tetramers in diisopropyl ether at concentrations as low as 40 mmol, ethylmagnesium bromide is dimeric over a large concentration range (0—40 mmol) [2]. This behaviour is unusual, as in general the Grignard compounds which possess the better bridging halogen group are more strongly associated than the symmetrical dialkylmagnesium compounds. In the complexes containing diisopropyl ether it was attributed to steric hindrance, which prevents two molecules of ether being involved in a

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monomeric complex. However, the possibility that in sterically hindered complexes the ethyl group might turn out to be a better bridging group than bromine could not be excluded. Therefore it seemed of interest to obtain information about the structure of such complexes.

Experimental

Single crystals were obtained by cooling a solution of ethylmagnesium bromide in diisopropyl ether [2]. A crystal with approximate dimensions 0.3 × 0.4 × 0.6 mm was sealed in a thin-walled pyrex glass capillary under vacuum. The space group is uniquely determined from systematic absences as $P2_1/n$. The cell parameters are a 7.85(1), b 14.43(2), c 11.31(2) Å, β 100.3(1)°. The calculated density on the basis of two dimers per unit cell is 1.24 g/cm^3. All atoms in the cell are in general positions: $\pm\ (x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$. The intensities of 1475 non-zero reflections, with $2\ \theta < 100°$, were collected with a Nonius three-circle automatic diffractometer, using Nickel-filtered Cu-K_α-radiation (λ(Cu-K_α 1.5418 Å). The ω-scan technique was used. The data were corrected for Lorentz and polarisation effects. No correction was applied for absorption (μ(Cu-K_α) 50 cm^{-1}).

Structure determination and refinement

The crystal structure was solved by a direct method [3]. An E-map, calculated for the solution with the highest value for the consistency criterium $\sum_{H,K} s_H s_K s_{H+K} \mid E_H E_K E_{H+K} \mid$, showed all non-hydrogen atoms. The structure was refined by blockdiagonal least squares to a final conventional R-value of 0.073. All reflections were treated with unit weight, except for two reflections which were omitted because of extinction.

The final values of the refined parameters are given in Table 1. Bond lengths and bond angles are given in Table 2 and Table 3, respectively. Scattering factors were taken from Cromer and Mann [4]. The applied corrections for the anoma-

TABLE 1

FINAL REFINED ATOMIC PARAMETERS FOR $[C_2H_5MgBr \cdot O(i\text{-}C_3H_7)_2]_2$ ($\beta_{ij} \cdot 10^4$) WITH STANDARD DEVIATIONS[a]

Atom	x/a[b]	y/b[b]	z/c[b]	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
Br(1)	0.3256(1)	0.4109(1)	0.4604(1)	329	77	122	—86	—1	64
Mg(2)	0.5011(4)	0.4806(2)	0.6549(2)	293	75	102	20	—11	107
O(3)	0.6756(7)	0.3800(4)	0.7111(5)	309	67	93	35	22	112
C(4)	0.7079(19)	0.2302(8)	0.6197(11)	639	91	183	60	—64	132
C(5)	0.7636(14)	0.3340(7)	0.6252(9)	411	101	126	75	—11	213
C(6)	0.9513(16)	0.3499(9)	0.6477(13)	376	134	275	24	—24	348
C(7)	0.7327(14)	0.3557(7)	0.8382(9)	429	82	119	—17	27	128
C(8)	0.5797(18)	0.3257(8)	0.8880(11)	597	105	176	—28	61	337
C(9)	0.8237(18)	0.4382(9)	0.9019(11)	528	127	166	—64	—41	—72
C(10)	0.3614(15)	0.5433(8)	0.7747(9)	399	129	132	153	—45	129
C(11)	0.2363(20)	0.6124(11)	0.7302(12)	579	182	201	246	—55	182

[a] The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$.

[b] Standard deviation σ in parentheses.

TABLE 2

BOND LENGTHS (Å) FOR $[C_2H_5MgBr \cdot O(i\text{-}C_3H_7)_2]_2$[a]

No.	Atoms	Distance	No.	Atoms	Distance
1	Br(1)—Mg(2)	2.582(3)	7	O(3)—C(7)	1.470(12)
2	Br(1)—Mg(2)'	2.576(3)	8	C(7)—C(8)	1.479(17)
3	Mg(2)—O(3)	2.019(6)	9	C(7)—C(9)	1.504(17)
4	O(3)—C(5)	1.449(12)	10	Mg(2)—C(10)	2.094(11)
5	C(5)—C(6)	1.468(16)	11	C(10)—C(11)	1.427(19)
6	C(4)—C(5)	1.558(16)			

[a] The standard deviations of the last significant figures are in parentheses.

TABLE 3

BOND ANGLES (DEGREES) FOR $[C_2H_5MgBr \cdot O(i\text{-}C_3H_7)_2]_2$[a]

Atoms	Angle	Atoms	Angle
Br(1)—Mg(2)—Br(1)'	93. 2(1)	O(3)—C(5)—C(6)	113.3(9)
Mg(2)—Br(1)—Mg(2)'	86.8(1)	O(3)—C(5)—C(4)	107.6(8)
Br(1)—Mg(2)—O(3)	102.5(2)	C(5)—O(3)—C(7)	116.6(6)
Br(1)—Mg(2)—C(10)	117.3(3)	C(4)—C(5)—C(6)	115.0(9)
Br(1)'—Mg(2)—O(3)	101.9(2)	O(3)—C(7)—C(8)	108.4(9)
Br(1)'—Mg(2)—C(10)	116.7(3)	O(3)—C(7)—C(9)	108.4(8)
Mg(2)—O(3)—C(5)	119.7(5)	C(8)—C(7)—C(9)	113.4(9)
Mg(2)—O(3)—O(7)	123.4(5)		
Mg(2)—C(10)—C(11)	118.7(8)		
O(3)—Mg(2)—C(10)	120.7(3)		

[a] The standard deviations of the last significant figures are in parentheses.

TABLE 4

HYDROGEN ATOM POSITIONS FOR $[C_2H_5MgBr \cdot O(i\text{-}C_3H_7)_2]_2$ ($B = 9$ Å^2)

Atom	*x/a*	*y/b*	*z/c*
H(12)	0.7642	0.1921	0.5583
H(13)	0.7419	0.1996	0.7065
H(14)	0.5693	0.2248	0.5946
H(15)	1.0116	0.3147	0.5837
H(16)	0.9788	0.4209	0.6448
H(17)	1.0060	0.3239	0.7346
H(18)	0.7144	0.3615	0.5383
H(19)	0.8236	0.2988	0.8461
H(20)	0.6098	0.3069	0.9793
H(21)	0.4874	0.3820	0.8807
H(22)	0.5149	0.2692	0.8387
H(23)	0.8668	0.4246	0.9945
H(24)	0.9282	0.4596	0.8629
H(25)	0.7327	0.4947	0.8959
H(26)	0.4488	0.5697	0.8511
H(27)	0.2948	0.4905	0.8167
H(28)	0.7161	0.6405	0.7981
H(29)	0.3048	0.6693	0.6956
H(30)	0.1451	0.5872	0.6600

lous scattering of Br were $\Delta f'$ -0.96 and $\Delta f''$ $+1.46$. Hydrogen atoms were introduced at calculated positions, in agreement with a difference Fourier, but not refined (Table 4).

Discussion

The crystal structure of the ethylmagnesium bromide/diisopropyl ether complex consists of the packing of discrete dimers as shown in the stereoscopic pair (Fig. 1). The corresponding numbering of the atoms is shown in Fig. 2. The molecule lies on a crystallographic inversion centre.

The crystal structure of the complex shows a remarkable similarity to the structure of ethylmagnesium bromide crystallized from triethylamine [5], which is also dimeric, the bridging function being fulfilled by bromine; the mean magnesium bromine distance of 2.58 Å compares well with the value of 2.57 Å in the triethylamine complex. Furthermore, there is also only one molecule of solvent bound to each magnesium atom. This is in agreement with the general occurrence of tetracoordination in organometallic magnesium compounds, but it is surprising in so far as there is usually a large difference in complexing ability between diisopropyl ether and triethyl amine [6]. In particular, and in contrast to diisopropyl ether solutions [2], ethylmagnesium bromide is monomeric in triethylamine [7].

Evidently, in solution the solvating power of triethylamine overcomes the energy barrier caused by steric hindrance when two molecules of solvent are complexed, whereas the weakly basic diisopropyl ether seems to be able to form only one oxygen—magnesium coordinative bond, even in the presence of a large excess of the solvent. Once having filled the coordination number 4 of magnesium, diisopropyl ether is apparently unable to compete with the bromine bridges which results in the dimeric state of ethylmagnesium bromide over the concentration range measured.

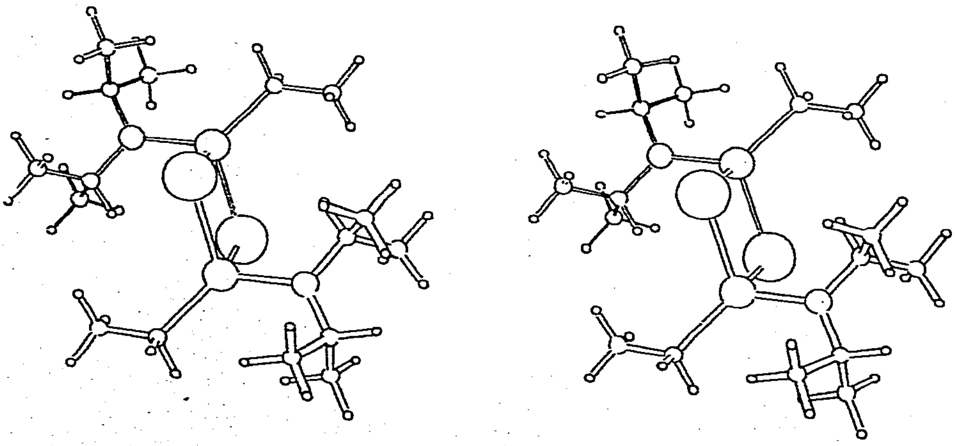

Fig. 1. Stereoscopic pair of the dimeric ethylmagnesium bromide/diisopropyl ether complex $[C_2H_5MgBr\cdot O(i\text{-}C_3H_7)_2]_2$.

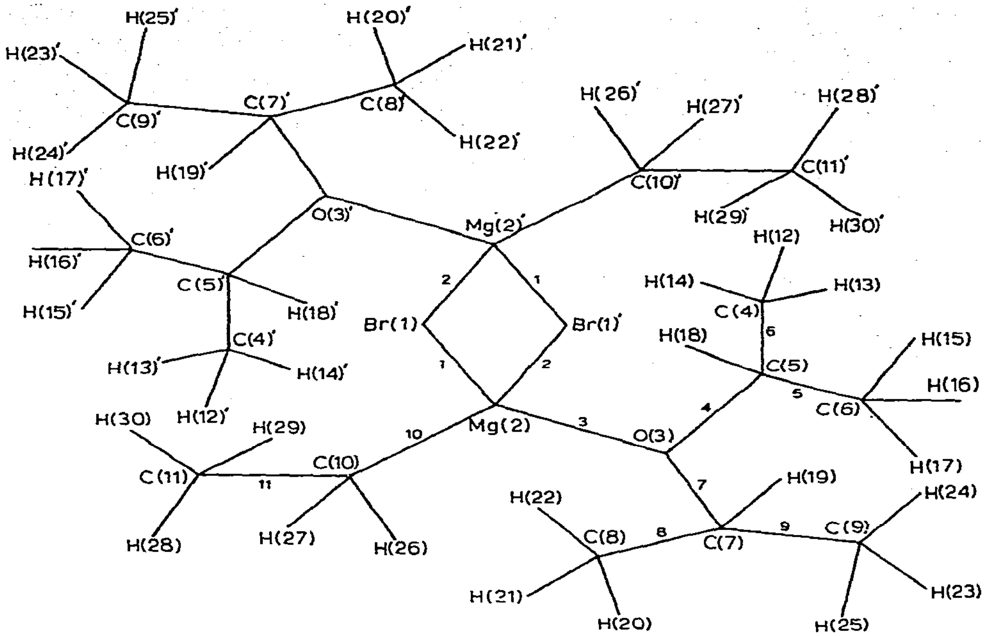

Fig. 2. Numbering of atoms of $[C_2H_5MgBr \cdot O(i\text{-}C_3H_7)_2]_2$.

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