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# BIFUNCTIONAL AND CYCLIC ORGANOMAGNESIUM COMPOUNDS

## III *. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE DIMER OF MAGNESIACYCLOHEXANE, 1,7-DIMAGNESIACYCLODODECANE

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## Summary

The structure of the dimer of magnesiacyclohexane, the 1,7-dimagnesiacyclododecane/tetrahydrofuran complex $[(CH_2)_5Mg]_2 \cdot 4THF$ (IV) has been determined by single X-ray diffraction techniques. Crystals are triclinic with spacegroup $P\bar{1}$ and one centrosymmetric dimer per unit cell of dimensions $a$ 8.85(2), $b$ 9.60(2), $c$ 9.63(2) Å, $\alpha$ 92.2(3), $\beta$ 93.2(3), $\gamma$ 112.7(3)°. The structure was refined to a final $R$-value of 0.094.

Dimer IV contains two tetracoordinated magnesium atoms in a twelve-membered ring. The conformation of IV is discussed in the context of other medium-sized ring structures. The strong tendency to form a twelve-membered ring is ascribed to the remarkably large C—Mg—C valence angle of 141.5°, which causes ring strain in monomeric magnesiacyclohexane and thus makes dimerization exothermic ($\Delta H = -11.5 \pm 0.8$ kcal mol$^{-1}$, $\Delta S = -25 \pm 3$ eu). The unfavourable entropy of association explains the absence of higher polymers in solutions.

## Introduction

In a previous paper in this series [2] we reported the synthesis of pure magnesiacyclohexane from the corresponding mercury compound by shaking with magnesium metal in tetrahydrofuran. Association measurements established the presence of monomeric magnesiacyclohexane (I); however, it was in equilib-

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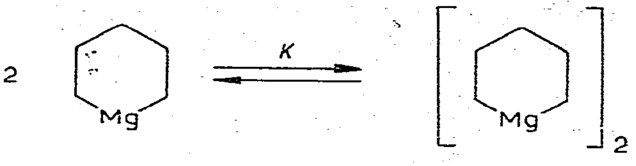
* For Part II see ref. 1.

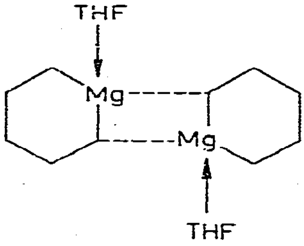
rium with its dimer (II). This equilibrium was to a remarkable extent in favour of the dimer: $K^{28.25} = 609 \pm 35$ l mol$^{-1}$; $K^{48.50} = 182 \pm 9$ l mol$^{-1}$; $\Delta H = -11.5 \pm 0.8$ kcal mol$^{-1}$; $\Delta S = -25 \pm 3$ eu [*].



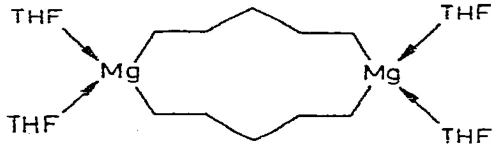
(I) (II)

Two interesting questions concerning II remained unanswered at that stage, namely what is the structure of II, and why does the polymerization of I stop at the level of the dimer?

In view of the strong preference of organometallic magnesium for the tetracoordinate state [4—15], two structures might have been considered for II, namely III, with alkyl bridges involved in three-center electron deficient bonding [4,6], which is more often encountered in boron- and in aluminium-organic compounds [16]; or IV, comprising a twelve-membered ring.



(III)



(IV)

A chemical distinction between III and IV would be possible, if one could determine the ratio THF: Mg, which should be 1 for III and 2 for IV. Unfortunately, this appraoch was not successful, as on thermolysis II released THF in a more or less continuous fashion.

It was therefore decided to determine the crystal structure of II.

## Experimental

A concentrated solution of "magnesiacyclohexane" in THF (formal concentration of I approximately 0.02 *M*) was sealed to the glass apparatus shown in Fig. 1.

After high vacuum was achieved, the apparatus was sealed at A, the seal of B was broken and the solution transferred to C. Cooling of C to —80°C yielded

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[*] These new values fall within the limits of error given for the old values [2], but have a much smaller standard deviation. They were calculated from the experimental data of Table 1 in ref. 2 by computer optimalization of correction terms such as "initial rise", and of *K* itself (for details see ref. 3). The computer program also afforded a rigorous test and exclusion of other a priori possible equilibria comprising higher oligomers [3].

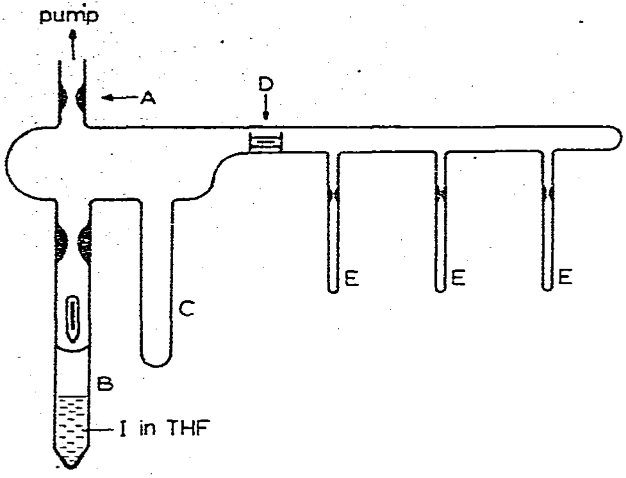

Fig. 1. Apparatus for obtaining and sealing crystals of "magnesiacyclohexane".

crystals of II: the mother liquor was decanted to B. By cooling B to 0°C the crystals were obtained dry enough to be transferrable. After sealing off B, they were stable at room temperature. By tilting the vessel, and with the aid of the glass sealed magnetic scratcher D, the crystals were transferred to thin-walled pyrex capillaries E, which were sealed off.

The crystals are triclinic. Statistical tests indicated the presence of a center of symmetry. The adopted spacegroup $P\bar{1}$ was confirmed by the successful structure determination. The cell parameters are $a$ 8.85(2), $b$ 9.60(2), $c$ 9.63(2) Å, $\alpha$ 92.2(3), $\beta$ 93.2(3), $\gamma$ 112.7(3)°. The density calculated on the basis of one dimer $[(CH_2)_5Mg]_2 \cdot 4THF$ per unit cell is 1.05 g cm$^{-3}$.

The intensities of 1022 reflections with $I > \sigma(I)$ and $\Theta < 23.5°$ were collected with a Nonius four circle automatic diffractometer (CAD-4) using Mo-$K_\alpha$-radiation. $\lambda = 0.71069$ Å. A graphite monochromator was used. The data were collected in the $\omega$-scan mode. Corrections were applied for Lorentz and polarisation effects.

## Structure determination and refinement

The crystal structure was solved by direct methods [17]. An $E$-map, calculated for the nontrivial solution with the highest value for the consistency criterium $\sum_{H,K} s_H s_K s_{H+K} |E_H E_K E_{H+K}|$, showed all ring atoms and part of the THF molecules. A subsequent difference Fourier synthesis showed the rest of the non-hydrogen atoms. As was shown in the subsequent refinement the temperature factors of the THF molecules are relatively high thus explaining the greater effort needed to locate their atoms.

The structure was refined by block-diagonal least-squares to a final $R$-value of 0.094 ($R_w = 0.089$) *.

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* The unweighted and weighted $R$ factors are defined as: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma|F_o|^2]^{1/2}$, respectively.

TABLE 1

FINAL REFINED ATOMIC COORDINATES FOR $[(CH_2)_5Mg]_2 \cdot 4THF$ [a]

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Mg(1) | 0.6007(4) | 0.7762(4) | 0.3570(4) |
| O(2) | 0.7653(8) | 0.7579(8) | 0.2173(8) |
| O(3) | 0.6462(10) | 0.9986(7) | 0.3014(7) |
| C(4) | 0.3659(13) | 0.6428(13) | 0.2505(11) |
| C(5) | 0.2199(13) | 0.5418(12) | 0.3200(12) |
| C(6) | 0.2473(15) | 0.4311(13) | 0.4128(13) |
| C(7) | 0.2690(17) | 0.3022(14) | 0.3492(12) |
| C(8) | 0.2727(14) | 0.1764(11) | 0.4408(11) |
| C(9) | 0.7395(17) | 0.6456(15) | 0.1119(15) |
| C(10) | 0.8930(19) | 0.6592(19) | 0.0708(16) |
| C(11) | 1.0141(16) | 0.8037(18) | 0.1276(16) |
| C(12) | 0.9328(15) | 0.8417(19) | 0.2286(18) |
| C(13) | 0.5939(19) | 1.0366(15) | 0.1730(14) |
| C(14) | 0.6573(21) | 1.1992(14) | 0.1705(13) |
| C(15) | 0.7301(16) | 1.2587(13) | 0.3073(13) |
| C(16) | 0.7283(16) | 1.1338(13) | 0.3895(13) |
| H(17) | 0.654(8) | 0.552(8) | 0.150(7) |
| H(18) | 0.926(8) | 0.586(8) | 0.118(7) |
| H(19) | 1.136(8) | 0.807(8) | 0.135(7) |
| H(20) | 0.984(8) | 0.835(8) | 0.318(7) |
| H(21) | 0.620(8) | 0.977(8) | 0.084(7) |
| H(22) | 0.744(8) | 1.229(8) | 0.113(7) |
| H(23) | 0.853(8) | 1.360(8) | 0.310(7) |
| H(24) | 0.841(8) | 1.143(8) | 0.432(7) |
| H(25) | 0.336(8) | 0.703(8) | 0.200(7) |
| H(26) | 0.397(8) | 0.589(8) | 0.181(7) |
| H(27) | 0.182(8) | 0.602(8) | 0.371(7) |
| H(28) | 0.115(8) | 0.480(8) | 0.251(7) |
| H(29) | 0.348(8) | 0.499(8) | 0.478(7) |
| H(30) | 0.130(8) | 0.340(8) | 0.456(7) |
| H(31) | 0.197(8) | 0.256(8) | 0.253(7) |
| H(32) | 0.378(8) | 0.355(8) | 0.307(7) |
| H(33) | 0.158(8) | 0.123(8) | 0.447(7) |
| H(34) | 0.328(8) | 0.114(8) | 0.372(7) |
| H(35) | 0.656(8) | 0.647(8) | 0.028(7) |
| H(36) | 0.889(8) | 0.635(8) | −0.037(7) |
| H(37) | 1.002(8) | 0.858(8) | 0.030(7) |
| H(38) | 0.950(8) | 0.949(8) | 0.233(7) |
| H(39) | 0.456(8) | 0.978(8) | 0.154(7) |
| H(40) | 0.573(8) | 1.236(8) | 0.137(7) |
| H(41) | 0.658(8) | 1.303(8) | 0.347(7) |
| H(42) | 0.664(8) | 1.123(8) | 0.479(7) |

[a] Values in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

The hydrogen atoms were introduced on calculated positions (H—C—H = 109°, and C—H = 1.05 Å, B (iso) = 4.5 Å$^2$) in agreement with a difference Fourier synthesis calculated at this stage. Only their positions were refined. The final refined parameters are given in Tables 1 and 2 *. Scattering factors were taken from ref. 18 except for hydrogen for which those of ref. 19 were used.

All observed reflections were treated with unit weight. A final difference

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* Tables of structure factors may be obtained from the authors.

(continued on p. 337)

TABLE 2

FINAL ANISOTROPIC TEMPERATURE FACTORS (× 10000) FOR THE NONHYDROGEN ATOMS IN $[(CH_2)_5Mg]_2 \cdot 4THF$ [a]

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $2\beta_{12}$ | $2\beta_{23}$ | $2\beta_{13}$ |
|---|---|---|---|---|---|---|
| Mg(1) | 193(6) | 127(5) | 132(4) | 95(9) | 7(7) | 15(8) |
| O(2) | 212(15) | 235(14) | 209(12) | 109(24) | −184(21) | 32(21) |
| O(3) | 383(20) | 141(11) | 153(11) | 183(24) | −12(17) | −135(23) |
| C(4) | 201(21) | 257(21) | 172(17) | 129(36) | 57(30) | −30(31) |
| C(5) | 265(25) | 182(19) | 194(18) | 177(36) | −3(29) | −119(34) |
| C(6) | 294(28) | 202(22) | 253(22) | 98(41) | −61(35) | −238(40) |
| C(7) | 447(37) | 288(25) | 172(19) | 378(53) | −102(36) | −181(43) |
| C(8) | 269(25) | 168(17) | 189(17) | 167(35) | −13(28) | −109(34) |
| C(9) | 328(33) | 306(27) | 300(26) | 220(50) | −267(43) | 86(45) |
| C(10) | 433(42) | 495(40) | 330(31) | 536(70) | −280(57) | 33(56) |
| C(11) | 290(31) | 472(39) | 326(30) | 372(60) | 180(55) | 283(50) |
| C(12) | 187(27) | 494(42) | 430(37) | −124(53) | −440(63) | 153(49) |
| C(13) | 528(44) | 235(25) | 215(21) | 207(55) | 10(37) | −245(49) |
| C(14) | 672(52) | 227(4) | 200(21) | 350(60) | 107(36) | 74(52) |
| C(15) | 389(34) | 186(20) | 226(21) | 178(44) | 2(33) | −105(43) |
| C(16) | 370(34) | 199(20) | 216(20) | 157(44) | −61(33) | −115(41) |

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

TABLE 3

BOND LENGTHS (Å) FOR $[(CH_2)_5Mg]_2 \cdot 4THF$

| Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|
| Mg(1)—O(2) | 2.089(9) | C(4)—H(25) | 0.88(7) |
| Mg(1)—O(3) | 2.110(7) | C(4)—H(26) | 0.95(7) |
| Mg(1)—C(4) | 2.15(1) | C(5)—H(27) | 0.92(7) |
| Mg(1)—C(8)′ [a] | 2.13(1) | C(5)—H(28) | 1.06(8) |
| O(2)—C(9) | 1.40(2) | C(6)—H(29) | 1.03(7) |
| O(2)—C(12) | 1.38(2) | C(6)—H(30) | 1.18(7) |
| O(3)—C(13) | 1.41(2) | C(7)—H(31) | 1.08(7) |
| O(3)—C(16) | 1.43(1) | C(7)—H(32) | 1.01(8) |
| C(4)—C(5) | 1.50(2) | C(8)—H(33) | 0.95(8) |
| C(5)—C(6) | 1.49(2) | C(8)—H(34) | 1.13(7) |
| C(6)—C(7) | 1.44(2) | C(9)—H(17) | 1.02(7) |
| C(7)—C(8) | 1.53(2) | C(9)—H(35) | 1.07(8) |
| C(9)—C(10) | 1.40(2) | C(10)—H(18) | 0.97(8) |
| C(10)—C(11) | 1.45(2) | C(10)—H(36) | 1.05(7) |
| C(11)—C(12) | 1.36(2) | C(11)—H(19) | 1.07(8) |
| C(13)—C(14) | 1.44(2) | C(11)—H(37) | 1.12(7) |
| C(14)—C(15) | 1.43(2) | C(12)—H(20) | 0.97(8) |
| C(15)—C(16) | 1.46(2) | C(12)—H(38) | 0.98(8) |
| | | C(13)—H(21) | 1.10(7) |
| | | C(13)—H(39) | 1.13(8) |
| | | C(14)—H(22) | 0.93(8) |
| | | C(14)—H(40) | 0.98(8) |
| | | C(15)—H(23) | 1.15(7) |
| | | C(15)—H(41) | 0.98(8) |
| | | C(16)—H(24) | 1.03(8) |
| | | C(16)—H(42) | 1.04(7) |

[a] The prime notation refers to atoms related to those in Table 1 by a centre of symmetry at (1/2, 1/2, 1/2): $(x,y,z \rightarrow 1-x,\ 1-y,\ 1-z)$

TABLE 4

BOND ANGLES (°) FOR $[(CH_2)_5Mg]_2 \cdot 4THF$

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| O(2)—Mg(1)—O(3) | 90.8(3) | | |
| O(2)—Mg(1)—C(4) | 102.7(4) | C(7)—C(8)—H(33) | 100(4) |
| O(2)—Mg(1)—C(8)′ [a] | 106.8(4) | C(7)—C(8)—H(34) | 102(3) |
| Mg(1)—O(2)—C(9) | 128.5(7) | C(10)—C(11)—H(19) | 113(4) |
| Mg(1)—O(2)—C(12) | 125.2(7) | C(10)—C(11)—H(37) | 91(4) |
| O(3)—Mg(1)—C(4) | 103.9(4) | H(18)—C(10)—H(36) | 108(6) |
| O(3)—Mg(1)—C(8)′ | 99.9(4) | C(12)—C(11)—H(19) | 128(3) |
| Mg(1)—O(3)—C(13) | 125.0(6) | C(12)—C(11)—H(37) | 111(4) |
| Mg(1)—O(3)—C(16) | 125.8(6) | C(11)—C(12)—H(20) | 108(5) |
| C(4)—Mg(1)—C(8)′ | 141.5(3) | C(11)—C(12)—H(38) | 113(4) |
| Mg(1)—C(4)—C(5) | 124.5(7) | H(19)—C(11)—H(37) | 106(5) |
| Mg(1)—C(8)′—C(7)′ | 122.1(7) | H(20)—C(12)—H(38) | 101(6) |
| C(9)—O(2)—C(12) | 105(1) | C(14)—C(13)—H(21) | 115(3) |
| O(2)—C(9)—C(10) | 108(1) | C(14)—C(13)—H(39) | 115(4) |
| C(5)—C(6)—C(7) | 118(1) | C(14)—C(15)—H(23) | 114(3) |
| C(10)—C(11)—C(12) | 102(1) | C(14)—C(15)—H(41) | 106(4) |
| C(13)—C(14)—C(15) | 107(1) | H(22)—C(14)—H(40) | 110(6) |
| C(13)—O(3)—C(16) | 109(1) | C(16)—C(15)—H(23) | 116(4) |
| O(3)—C(13)—C(14) | 109(1) | C(16)—C(15)—H(41) | 108(4) |
| C(9)—C(10)—C(11) | 108(1) | C(15)—C(16)—H(24) | 115(4) |
| C(6)—C(7)—C(8) | 119(1) | C(15)—C(16)—H(42) | 114(4) |
| O(3)—C(16)—C(15) | 106(1) | H(23)—C(15)—H(41) | 102(5) |
| C(14)—C(15)—C(16) | 109(1) | H(24)—C(16)—H(42) | 101(6) |
| O(2)—C(12)—C(11) | 114(1) | C(13)—C(14)—H(22) | 108(4) |
| C(4)—C(5)—C(6) | 116(1) | C(13)—C(14)—H(40) | 112(4) |
| C(6)—C(7)—H(31) | 114(4) | H(21)—C(13)—H(39) | 94(5) |
| C(6)—C(7)—H(32) | 100(4) | C(15)—C(14)—H(22) | 105(4) |
| H(29)—C(6)—H(30) | 121(5) | C(15)—C(14)—H(40) | 114(4) |
| C(8)—C(7)—H(31) | 111(4) | C(9)—C(10)—H(18) | 109(4) |
| C(8)—C(7)—H(32) | 112(4) | C(9)—C(10)—H(36) | 111(4) |
| | | H(17)—C(9)—H(35) | 92(6) |
| | | C(11)—C(10)—H(18) | 103(4) |
| | | C(11)—C(10)—H(36) | 117(4) |
| | | C(4)—C(5)—H(27) | 108(4) |
| | | C(4)—C(5)—H(28) | 115(4) |
| | | H(25)—C(4)—H(26) | 101(6) |
| | | C(6)—C(5)—H(27) | 109(4) |
| | | C(6)—C(5)—H(28) | 107(4) |
| | | C(5)—C(6)—H(29) | 103(4) |
| | | C(5)—C(6)—H(30) | 117(3) |
| | | H(27)—C(5)—H(28) | 101(6) |
| | | C(7)—C(6)—H(29) | 113(4) |
| | | C(7)—C(6)—H(30) | 85(4) |
| | | O(3)—C(16)—H(24) | 113(4) |
| | | O(3)—C(16)—H(42) | 107(4) |
| | | C(5)—C(4)—H(25) | 108(5) |
| | | C(5)—C(4)—H(26) | 112(4) |
| | | H(31)—C(7)—H(32) | 97(6) |
| | | H(33)—C(8)—H(34) | 113(5) |
| | | Mg(1)—C(8)′—H(33)′ | 110(4) |
| | | Mg(1)—C(8)′—H(34)′ | 109(4) |
| | | C(10)—C(9)—H(17) | 126(4) |
| | | C(10)—C(9)—H(35) | 114(4) |
| | | Mg(1)—C(4)—H(25) | 108(5) |
| | | Mg(1)—C(4)—H(26) | 101(5) |
| | | O(2)—C(12)—H(20) | 112(4) |
| | | O(2)—C(12)—H(38) | 108(5) |
| | | O(3)—C(13)—H(21) | 113(4) |
| | | O(3)—C(13)—H(39) | 110(3) |
| | | O(2)—C(9)—H(17) | 103(4) |
| | | O(2)—C(9)—H(35) | 113(4) |

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[a] See footnote to Table 3.

TABLE 5

TORSION ANGLES (in degrees)

| | | | |
|---|---|---|---|
| *In the twelve membered ring* [a] | | | |
| C(8)'—Mg(1)—C(4)—C(5) | 2.1 | | |
| Mg(1)—C(4)—C(5)—C(6) | −51.4 | −51 [b] | |
| C(4)—C(5)—C(6)—C(7) | −72.9 | −69 | |
| C(5)—C(6)—C(7)—C(8) | −171.4 | −173 | |
| C(6)—C(7)—C(8)—Mg(1)' | −41.3 | −54 | |
| C(7)—C(8)—Mg(1)'—C(4)' | −51.1 | −51 | |
| *In bonds around Mg involving the THF molecules* | | | |
| C(4)—Mg(1)—O(2)—C(9) | −22.8 | | |
| C(16)—O(3)—Mg(1)—C(8)' | −4.8 | | |
| O(2)—Mg(1)—C(4)—C(5) | 141.5 | | |
| O(3)—Mg(1)—C(4)—C(5) | −124.5 | | |
| O(2)—Mg(1)—C(8)'—C(7)' | −92.7 | | |
| O(3)—Mg(1)—C(8)'—C(7)' | 178.8 | | |
| *In bonds in the THF ring* | | | |
| O(2)—C(9)—C(10)—C(11) | −13.6 | O(3)—C(13)—C(14)—C(15) | −7.8 |
| C(9)—C(10)—C(11)—C(12) | 17.2 | C(13)—C(14)—C(15)—C(16) | 6.4 |
| C(10)—C(11)—C(12)—O(2) | −15.3 | C(14)—C(15)—C(16)—O(3) | −2.7 |
| C(11)—C(12)—O(2)—C(9) | 7.6 | C(15)—C(16)—O(3)—C(13) | −2.2 |
| C(12)—O(2)—C(9)—C(10) | 4.2 | C(16)—O(3)—C(13)—C(14) | 6.2 |

[a] The signs of the torsion angles are defined positive for a clockwise rotation along the axis atom(2)—atom(3). [b] Comparison with corresponding angles in ref. 14.

Fourier showed no peaks above 0.25 $e\text{Å}^{-3}$, thus showing that no more atoms are present in the structure.

## Discussion

In the crystalline state, "magnesiacyclohexane" occurs exclusively as the dimer which has the twelve-membered ring structure 1,7-dimagnesiacyclododecane (IV). The dimer lies on a crystallographic inversion centre. Magnesium achieves tetracoordination by attachment of two molecules tetrahydrofuran. The tetrahydrofuran rings are puckered. The stereochemistry of IV is shown in the stereoscopic drawing (Fig. 2). Bond lengths, bond angles and torsion angles are given in Tables 3, 4 and 5, respectively.

It is of interest to compare IV with its twelve-membered carbon analog cyclododecane [20] on the one hand and with its ten-membered lower homolog, 1,6-dimagnesiacyclodecane (V) [14] on the other.

With one exception, all bonds in IV are approximately staggered, one pair having the *trans*, the others the *gauche* conformation; one pair of carbon magnesium bonds, C(4)—Mg(1), is eclipsed. As in cyclododecane, we recognize in the four carbon unit C(5), C(6), C(7), C(8) the beginning of the zig zag folding which is typical for normal alkanes and large-membered cycloalkanes [21,22]. However, in cyclododecane these *trans* butane units are connected on both sides via two atoms [21] in such a way that — including the common end points — two further *trans* butane units are formed, whereas in IV these two atoms

TABLE 5

TORSION ANGLES (in degrees)

| | | | | |
|---|---|---|---|---|
| *In the twelve membered ring* [a] | | | | |
| C(8)'—Mg(1)—C(4)—C(5) | 2.1 | | | |
| Mg(1)—C(4)—C(5)—C(6) | −51.4 | −51 [b] | | |
| C(4)—C(5)—C(6)—C(7) | −72.9 | −69 | | |
| C(5)—C(6)—C(7)—C(8) | −171.4 | −173 | | |
| C(6)—C(7)—C(8)—Mg(1)' | −41.3 | −54 | | |
| C(7)—C(8)—Mg(1)'—C(4)' | −51.1 | −51 | | |
| *In bonds around Mg involving the THF molecules* | | | | |
| C(4)—Mg(1)—O(2)—C(9) | −22.8 | | | |
| C(16)—O(3)—Mg(1)—C(8)' | −4.8 | | | |
| O(2)—Mg(1)—C(4)—C(5) | 141.5 | | | |
| O(3)—Mg(1)—C(4)—C(5) | −124.5 | | | |
| O(2)—Mg(1)—C(8)'—C(7)' | −92.7 | | | |
| O(3)—Mg(1)—C(8)'—C(7)' | 178.8 | | | |
| *In bonds in the THF ring* | | | | |
| O(2)—C(9)—C(10)—C(11) | −13.6 | | O(3)—C(13)—C(14)—C(15) | −7.8 |
| C(9)—C(10)—C(11)—C(12) | 17.2 | | C(13)—C(14)—C(15)—C(16) | 6.4 |
| C(10)—C(11)—C(12)—O(2) | −15.3 | | C(14)—C(15)—C(16)—O(3) | −2.7 |
| C(11)—C(12)—O(2)—C(9) | 7.6 | | C(15)—C(16)—O(3)—C(13) | −2.2 |
| C(12)—O(2)—C(9)—C(10) | 4.2 | | C(16)—O(3)—C(13)—C(14) | 6.2 |

[a] The signs of the torsion angles are defined positive for a clockwise rotation along the axis atom(2)—atom(3). [b] Comparison with corresponding angles in ref. 14.

Fourier showed no peaks above 0.25 e$Å^{-3}$, thus showing that no more atoms are present in the structure.

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With one exception, all bonds in IV are approximately staggered, one pair having the *trans*, the others the *gauche* conformation; one pair of carbon magnesium bonds, C(4)—Mg(1), is eclipsed. As in cyclododecane, we recognize in the four carbon unit C(5), C(6), C(7), C(8) the beginning of the zig zag folding which is typical for normal alkanes and large-membered cycloalkanes [21,22]. However, in cyclododecane these *trans* butane units are connected on both sides via two atoms [21] in such a way that — including the common end points — two further *trans* butane units are formed, whereas in IV these two atoms is not a very likely structure for the following reasons: As alkyl bridges appear to be generally weaker than halogen bridges, dialkylmagnesium compounds do not possess the pronounced tendency towards association as Grignard reagents do; only in the unsolvated state [4,6] or in very weakly basic ethers [23,24] does alkyl bridging play an important role. Therefore, it would be difficult to device a reasonable explanation for the strong tendency of I to dimerize [2] on the basis of structure III. The same holds for magnesiacyclopentane (VI) which is completely dimerized in THF [3,25]; its dimer does indeed have the ten-membered ring structure V in the crystalline state [14].

The first of the two initially raised questions being solved, namely that concerning the structure of the dimer II, one may try to use the information now available to answer the second question: why do magnesiacyclopentane VI and magnesiacyclohexane I have a much stronger tendency towards dimerization than acyclic dialkylmagnesium compounds, while further polymerization does not occur? The absence of higher polymers in solutions of I and VI in THF is indicated by the association measurements (equilibrium between I and IV [2], and exclusively dimeric V [3]) and by the very fact that the compounds are soluble; higher polymers are not expected to dissolve in ether or THF.

Searching for possible causes for this apparently contradictory behaviour, a remarkable aspect of the molecular structure of IV comes to mind, namely the rather large valence angle C—Mg—C of 141.5°. Unfortunately, molecular structures have been determined of only two other Lewis complexes of dialkylmagnesium compounds, namely V [14] and $(CH_3)_3Mg \cdot 2$ quinuclidine [13] with C—Mg—C angles of 128° and 129°, respectively, so that generalizations must be made with some caution. Nevertheless, from the known examples one may derive the conclusion that magnesium prefers to have a rather large bond angle towards carbon atoms. Obviously, this preference will be in conflict with the geometric constraints of a six-membered ring, so that monomeric I will have considerable Baeyer strain. This strain is relieved on dimerization to IV; not only can the large angle easily be accommodated in the larger ring, but it will also tend to reduce unfavourable intraannular interactions (cf. also the eclipsing of the C(4)—Mg(1) bond). As the strain in five-membered VI would be even higher than in I, the complete absence of the former in solution can be considered as additional support for our hypothesis.

Relief of Baeyer strain must be responsible to a large extent, if not completely, for the exothermicity ($\Delta H = -11.5$ kcal mol$^{-1}$) of the dimerization of I to IV. Once the bond angle strain of the monomer has been alleviated in the dimer IV, it is not to be expected that formation of trimeric or higher polymeric species from the dimer will be accompanied by any appreciable enthalpy gain. It is possible, however, that the strongly negative entropy of dimerization will be of the same order of magnitude in the following association steps; although its origin is not known with certainty, it is probably connected with the loss of degrees of freedom in the higher associates. If this assumption is correct, $T \Delta S$ of ca. 7—8 kcal mol$^{-1}$ would overrule $\Delta H \approx 0$ kcal mol$^{-1}$ and make $\Delta G$ for the formation of higher polymers rather unfavourable. We thus have a system, which has the kinetic potential for rapid polymerization (due to the well known ligand shift in organomagnesium compounds [26]) but entropy forbids the formation of any polymer higher than the dimer.

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