# The Crystal Structures of the Cyclohexyl and Isopropyl Derivatives of Bis-μ-[bis-(η-cyclopentadienyl)hydridomolybdenum]-bis{di-μ-bromo-[alkylmagnesium][(diethyl ether)magnesium]}

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The structures of the cyclohexyl and isopropyl derivatives of the title complex are described. The cyclohexyl derivative is monoclinic, $a = 15\cdot671$, $b = 11\cdot996$, $c = 15\cdot085$ Å, $\beta = 109\cdot55°$, space group $C2/m$, four-circle diffractometer intensity measurements, Mo $K\alpha$ radiation, 1531 independent reflexions, final R 0·083. Problems of disorder/space group were encountered. The novel metal cluster system (I) with Mo–Mg bonds (2·85, 2·74 Å) was found.

(I)
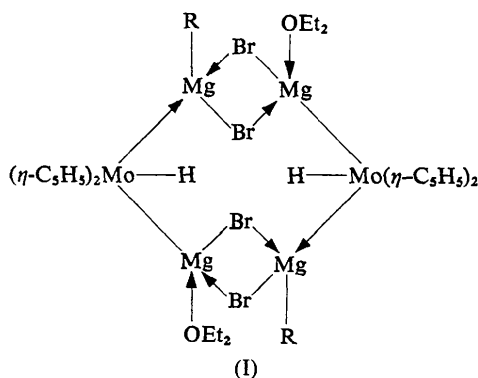
An incomplete determination of the structure of the isopropyl derivative (monoclinic, $a = 8\cdot566$, $b = 12\cdot955$, $c = 18\cdot617$ Å, $\beta = 93\cdot9°$, space group $P2_1/c$) revealed the same metal–bromine skeleton.

Introduction

During investigations of compounds containing Mo and W bound to light main-group elements Green and his coworkers (Benfield *et al.*, 1974) have obtained crystalline products from the reactions of $(\eta\text{-}C_5H_5)_2MH_2$ (M = Mo, W) with Grignard reagents, 'RMgBr', in ethers. X-ray diffraction studies of two products (M = Mo, R = isopropyl and cyclohexyl, diethyl ether solvent) were undertaken to characterize these unusual materials.

The isopropyl derivative was examined first, but crystal decomposition resulted in a data set of poor quality and, combined with apparent severe disorder in the crystal, permitted only a partial structure to be elucidated; the results of this investigation are described in the Appendix. The opportunities for disorder in the cyclohexyl derivative appeared to be more restricted and, although problems on that account were by no means absent, it was possible to put forward a more detailed description of this structure. A preliminary account of this work has been published (Green, Moser, Packer, Petit, Forder & Prout, 1974).

Experimental

Pale-yellow lath-like crystals from the reaction of $(\eta\text{-}C_5H_5)_2MoH_2$ and the Grignard reagent from cyclohexyl bromide in diethyl ether were supplied by Mr I. Packer and Dr M. L. H. Green. They were excessively sensitive to air and moisture and all manipulations were carried out in an atmosphere of dry nitrogen; crystals were mounted for X-ray examination in nitrogen-filled glass capillary tubes. It was not possible to measure their density.

After preliminary oscillation and Weissenberg photography, a crystal of approximate dimensions $0\cdot4 \times 0\cdot2 \times 0\cdot01$ mm was set up on a Hilger and Watts PDP8-controlled four-circle diffractometer: cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 20 reflexions (Dobler & Duerr, 1969). The intensities of at least two equivalents of each independent reflexion with $\sin\theta/\lambda < 0\cdot7$ were measured by an $\omega/2\theta$ scan and ordinate analysis (Watson, Shotton, Cox & Muirhead, 1970) with 50 steps of $0\cdot02°$. The 30 consecutive steps giving the highest total count were treated as peak and the remaining 20 as background. Mo $K\alpha$ radiation

from a graphite monochromator (Bragg angle 6·05°) was used. The intensities of three standard reflexions were monitored at regular intervals so that corrections for crystal decomposition could be made; these intensities decreased by some 15% over the period of the experiment.

Reflexions with $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on simple counting statistics, or whose apparent centre was more than 0·14° from the predicted position were not included in subsequent calculations. Lorentz and polarization corrections were applied together with an empirical absorption correction (North, Phillips & Mathews, 1968) to yield a final set of 1531 independent structure amplitudes.

Crystal data

$\{(C_5H_5)_2Mo(H)[MgO(C_2H_5)_2]\}$ $[MgC_6H_{11}]Br_2\}_2$.-$(C_2H_5)_2O$, $C_{44}H_{74}Br_4Mg_4Mo_2O_3$, $M = 1259·8$. Monoclinic, $a = 15·671$ (8), $b = 11·996$ (5), $c = 15·085$ (8) Å; $\beta = 109·55$ (8)°, $U = 2672·3$ Å³. Systematic extinctions hkl: $h + k = 2n + 1$. Space group $C2$, Cm or $C2/m$; $C2/m$ (No. 12, C_{2h}^3) from structure analysis. $D_c = 1·57$ g cm⁻³ for $Z = 2$. Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å. $\mu = 37$ cm⁻¹.

Structure solution and refinement

Patterson and Fourier techniques revealed the Mo, Br and Mg atoms, together with the cyclopentadienyl rings; this partial structure refined well in space group $C2/m$ with the Mo and Mg atoms in the mirror plane and one Br atom and a cyclopentadienyl group in general positions. This centrosymmetric group of atoms, containing the bulk of the scattering matter, dictated the choice of the centrosymmetric space group for the structure as a whole. Two further atoms [C(1) and O(1)] were also located in the mirror plane at bonding distances from the Mg atoms, but no other atoms were well resolved. However, when displayed in appropriate sections of F_o syntheses (Fig. 1), the electron density in the region of Mg(1) could be interpreted in terms of a cyclohexyl group in the chair conformation with a crystallographic mirror plane.
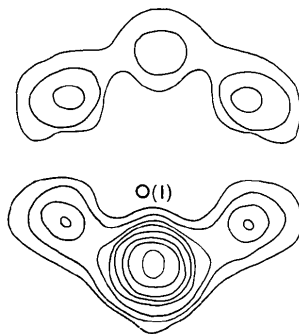

Fig. 1. F_{obs} map calculated in mean plane of refined cyclohexyl group. Phases calculated from model from which C(2), C(3) and C(4) had been deleted. Contours at 0·5 e Å⁻³.

The ligand attached to Mg(2) is more problematical: Fourier syntheses permitted the location with reasonable certainty of two further atoms, C(5) and C(7), bonded to O(1) and lying in the mirror plane, but the only other features were unresolved smudges of electron density trailing out from these atoms on either side of the mirror. From this and chemical evidence it is proposed that a diethyl ether ligand is present, disordered about the crystallographic mirror plane.

Fourier syntheses also showed the presence of further electron density in a compact region out of bonding contact with the structure described above, which has been interpreted as a disordered molecule of diethyl ether of crystallization. It is apparently planar, perpendicular to the mirror, with the oxygen atom located on the diad axis and the mirror plane approximately bisecting the two C–C bonds: it therefore overlaps its own mirror image. It is believed that the true space group is most probably $C2$, but with such a large proportion of the scattering model adequately represented by space group $C2/m$ it is impossible to distinguish this from the disordered model and if the non-centrosymmetric space group were used the refinement would be ill-conditioned.

Refinement was by full-matrix least-squares calculations with constraints (Waser, 1963; Rollett, 1969) applied to ill-resolved structural features. For the cyclohexyl group, unconstrained refinement led to unreasonable bond lengths and a noticeable tendency for the ring to be too flat at the C(1) end. Accordingly, the C–C bond lengths within the ring were constrained to their mean (recalculated between each cycle) with an estimated standard deviation of 0·01 Å; a similar procedure, with an e.s.d. of 1°, was adopted for the C–C–C and Mg–C–C angles (taken as one group). These means converged to 1·537 Å and 111·7° respectively, satisfactory values for a cyclohexyl group.

The coordinated ether molecule was even less susceptible to refinement. Bonds O(1)–C(5) and O(1)–C(7) were constrained to 1·45 Å (e.s.d. 0·01 Å), but C(6) and C(8) had to be introduced with zero occupancies and constrained to lie exactly in idealized mean positions in the mirror plane. The ether of crystallization [O(2) and C(9)] was refined without constraint, but with the assumption that carbon atoms adjacent to the oxygen in one molecule fall in the position occupied by the terminal carbon atoms of the molecule related by the mirror plane.

The metal, bromine and cyclopentadienyl carbon atoms were assigned anisotropic temperature factors, whilst all others were refined isotropically, except C(6) and C(8) where the temperature factor has no relevance. Each reflexion was assigned a weight according to the expression $w^{-1} = 1 + (((|F_o| - 19)/22)^2$, chosen to minimize the variation of $w(|F_o| - |F_c|)^2$ with F_o. The final R was 0·083. Complex neutral-atom scattering factors were taken from International Tables for X-ray Crystallography (1962) and all calculations were performed with the Oxford package of crystallographic pro-

grams (Carruthers & Rollett, 1973) on the Oxford University ICL 1906 A computer.

Results

The final atomic parameters are given in Tables 1 and 2. Bond distances and interbond angles, with estimated standard deviations calculated from the full variance-covariance matrix are given in Table 3 and a projection of the molecule is shown in Fig. 2.*

Table 1. *Cyclohexyl derivative: fractional atomic coordinates* (× 10^4) *and isotropic temperature factors*

	x/a	y/b	z/c	U_{iso}
Mo	1526 (1)	0	7244 (1)	
Br	−1237 (1)	1565 (1)	5627 (1)	
Mg(1)	−384 (5)	0	6865 (5)	
Mg(2)	1849 (4)	0	5570 (4)	
C(1)	−869 (13)	0	8087 (13)	0·09 (1)
C(2)	−1365 (15)	1065 (9)	8182 (17)	0·27 (2)
C(3)	−1584 (18)	1056 (9)	9108 (17)	0·28 (2)
C(4)	−2120 (21)	0	9169 (23)	0·19 (2)
O(1)	3200 (12)	0	5658 (12)	0·11 (1)
C(5)	3969 (22)	0	6527 (20)	0·19 (2)
C(6)	4867 (16)	0	6333 (56)	
C(7)	3492 (31)	0	4837 (23)	0·20 (2)
C(8)	2682 (54)	0	3923 (17)	
O(2)	5000	1351 (63)	0	0·23 (3)
C(9)	4423 (22)	765 (29)	383 (22)	0·21 (1)
C(11)	996 (13)	1644 (12)	7663 (11)	
C(12)	1203 (11)	1869 (12)	6823 (11)	
C(13)	2191 (10)	1690 (13)	7023 (10)	
C(14)	2568 (14)	1342 (16)	7969 (13)	
C(15)	1771 (13)	1335 (15)	8365 (12)	

Discussion

The molecule represents a novel type of metal cluster compound, the first shown to contain Mo–Mg bonds (Fig. 2). Since the isopropyl derivative (see Appendix and Fig. 3) contains the same metal–bromine skeleton, it seems likely that these products are typical of those obtained from the reactions under investigation.

As judged by the length of their bonds to carbon, the covalent radius of Mg is some 0·15 Å greater than

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30751 (16pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

that of Al, and, since Mo–Al single bonds have been observed in the range 2·65–2·66 Å (Forder & Prout, 1974a), the expected Mo–Mg single-bond distance can be estimated at about 2·8 Å. Again, in the only other transition metal–magnesium compound whose detailed structure is known, (η-C_5H_5) (diphos)FeMgBr . 3-THF (Felkin *et al.*, 1974), the Fe–Mg bond length is 2·59 Å. Now the covalent radius of Mo is about 0·2 Å greater than that of Fe (by considering, for example, the contacts to η-cyclopentadienyl ligands), so that the same estimate of 2·8 Å for Mo–Mg is obtained. There is little reason to doubt therefore that Mo–Mg distances in the observed range of 2·74–2·85 Å represent single, covalent bonds.

The observed approximately tetrahedral coordination of Mg is not uncommon either in Grignard derivatives (see, for example, Stucky & Rundle, 1964; Guggenberger & Rundle, 1968) or in other essentially covalent compounds of the element. The double bromine bridge has been observed in (Et_3N) (Et)MgBr₂Mg(Et) (NEt₃) (Toney & Stucky, 1967) where the Mg–Br bond length of 2·57 Å agrees reasonably well with that found in the present work. The Mg–C and Mg–O distances are in good agreement with the literature values.
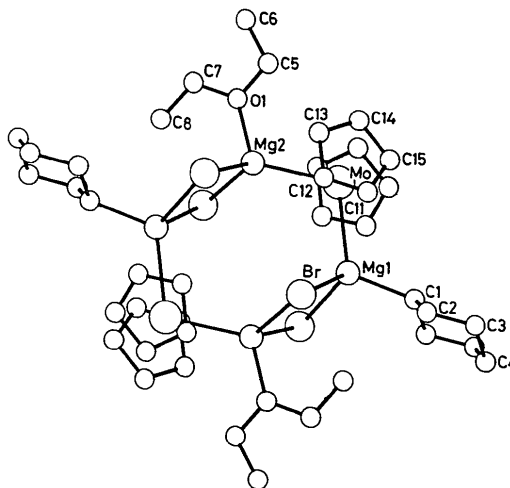

Fig. 2. Projection of cyclohexyl derivative at angle of 15° from **b**.

Table 2. *Cyclohexyl derivative: anisotropic temperature factor components* (× 10^3)

$$T = \exp\left[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23} + \ldots)\right]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	84 (1)	74 (1)	65 (1)	0	22 (1)	0
Br	94 (1)	68 (1)	85 (1)	−5 (1)	29 (1)	8 (1)
Mg(1)	85 (4)	79 (4)	76 (4)	0	33 (3)	0
Mg(2)	74 (4)	71 (4)	79 (4)	0	30 (3)	0
C(11)	130 (13)	73 (9)	95 (10)	−17 (8)	50 (10)	−8 (9)
C(12)	105 (10)	69 (8)	96 (10)	−12 (7)	32 (8)	−4 (8)
C(13)	87 (9)	99 (11)	89 (9)	−8 (8)	31 (8)	−9 (8)
C(14)	130 (15)	101 (12)	108 (12)	−27 (10)	17 (11)	−18 (11)
C(15)	122 (13)	94 (11)	94 (10)	−27 (9)	33 (10)	−9 (10)

Mg(1) and Mg(2) are not only crystallographically but also chemically distinct. Each Mg is bonded to two Br and one Mo, but, whereas at Mg(1) the fourth ligand is the one-electron donor cyclohexyl carbon atom, at Mg(2) it is the two-electron donor ether oxygen atom. In consequence, a simple valence-bond formulation of the structure requires an asymmetrical distribution of normal and dative covalent bonds (I), the latter including one of the Mo–Mg bonds. Such a formulation would, of course, be at variance with the 18-electron rule, which provides a very useful rationalization of much organomolybdenum chemistry, were it not for evidence that there is a further hydrogen atom associated with each Mo. This evidence is both spectroscopic and structural.

The infrared spectrum of the product from $(C_5H_5)_2MoH_2$ and cyclohexyl Grignard shows bands at 1740, 1720 cm^{-1} assignable to $v(Mo–H)$. When the preparation is carried out with $(C_5H_5)_2MoD_2$, these bands are absent, but a new band at 1260 cm^{-1} appears assigned to $v(Mo–D)$; $v(Mo–H)/v(Mo–D) = 1.39$ (Green et al., 1974). Structurally, the Mg–Mo–Mg angle of 109° is substantially larger than the acute angles usually found in d^2 $(\eta$-$C_5H_5)_2MoX_2$ complexes (Prout, Cameron, Forder, Critchley, Denton & Rees,

1974). This is not an obvious steric requirement of the metal–bromine skeleton and probably results from the hydrogen atom lying in the Mg–Mo–Mg plane, inside the angle. In fact, the situation is very similar to that in $[(\eta$-$C_5H_5)_2Mo(H)Li]_4$ (Forder & Prout, 1974b) where the Li–Mo–Li angle is 99°. This similarity extends to the geometry of the $(C_5H_5)_2Mo$ groups: in the present work the Mo was found to lie 1.95 Å from the mean planes of the cyclopentadienyl rings and the angle between ring normals was 146°, the corresponding values in the Li compound being 1.90–1.93 Å and 148–149°. These values are significantly different from those found in more typical $(\eta$-$C_5H_5)_2MoX_2$ complexes.

The significant differences in the lengths of the Mg–Mo and Mg–Br bonds at Mg(1) and Mg(2) may reflect this electronic asymmetry. However, a molecule of the form (I) has symmetry C_i whereas the molecule found was unavoidably constrained to have the higher C_{2h} symmetry by the choice of the space group $C2/m$. Neither of the alternative space groups $C2$ and Cm could have led to a molecule of symmetry C_i.

Table 3. *Cyclohexyl derivative*: bond distances (Å) and interbond angles (°)

Symmetry-operator superscripts: i $x, -y, z$; ii $1-x, y, -z$; iii $-x, y, 1-z$; iv $-x, -y, 1-z$.

Mo——Mg(1)	2.853 (7)	Mo——Mg(2)	2.737 (6)
Mg(1)–Br	2.670 (5)	Mg(2)–Br^{iii}	2.559 (4)
Mo——C(11)	2.31 (1)	C(11)–C(12)	1.43 (2)
Mo——C(12)	2.34 (2)	C(12)–C(13)	1.49 (2)
Mo——C(13)	2.35 (2)	C(13)–C(14)	1.41 (2)
Mo——C(14)	2.29 (2)	C(14)–C(15)	1.55 (3)
Mo——C(15)	2.27 (2)	C(15)–C(11)	1.37 (2)
Mg(1)-C(1)	2.22 (2)	Mg(2)–O(1)	2.08 (2)
C(1)——C(2)	1.53*	O(1)——C(5)	1.45*
C(2)——C(3)	1.55*	O(1)——C(7)	1.46*
C(3)——C(4)	1.54*	C(5)——C(6)	1.53*
O(2)——C(9)	1.41 (5)	C(7)——C(8)	1.53*
C(9)——C(9)^i	1.84 (7)	Mg(1)···Mg(2)	3.623 (9)
Mg(1)-Mo——Mg(2)	108.7 (4)	Mg(1)-Br——Mg(2^{iii})	87.7 (2)
Mo——Mg(1)-Br	112.7 (3)	Mo——Mg(2)-Br^{iii}	120.6 (3)
Mo——Mg(1)-C(1)	117.5 (14)	Mo——Mg(2)-O(1)	116.1 (14)
Br——Mg(1)-Br^i	89.4 (2)	Br^{iii}——Mg(2)-Br^{iv}	94.4 (6)
Br——Mg(1)-C(1)	110.5 (15)	Br^{iii}——Mg(2)-O(1)	100.3 (17)
Mg(1)-C(1)——C(2)	114*	Mg(2)-O(1)——C(5)	125 (2)
C(2)——C(1)——C(2^i)	114*	Mg(2)-O(1)——C(7)	123 (2)
C(1)——C(2)——C(3)	111*	C(5)——O(1)——C(7)	111 (3)
C(2)——C(3)——C(4)	110*	O(1)——C(5)——C(6)	111*
C(3)——C(4)——C(3^i)	111*	O(1)——C(7)——C(8)	111*
C(9)——O(2)——C(9^{ii})	120 (10)	O(2)——C(9)——C(9)^i	120 (7)

* Constrained: see text.

Table 4. *Isopropyl derivative*: bond distances (Å) and interbond angles (°)

Mo——Mg(1)	2.76 (3)	Mo——Mg(2)	2.81 (3)
Mg(1)–Br(1)	2.58 (3)	Mg(2)–Br(1)	2.61 (3)
Mg(1)–Br(2)	2.51 (3)	Mg(2)–Br(2)	2.59 (3)
Mg(1)-Mo——Mg(2)	104 (2)	Mg(1)-Br(1)——Mg(2)	86 (1)
Mo——Mg(1)-Br(1)	118 (2)	Mg(1)-Br(2)——Mg(2)	88 (1)
Mo——Mg(1)-Br(2)	120 (2)	Mo——Mg(2)-Br(1)	118 (2)
Br(1)——Mg(1)-Br(2)	94 (3)	Mo——Mg(2)-Br(2)	113 (2)
		Br(1)——Mg(2)-Br(2)	91 (3)

APPENDIX

Yellow crystals from the reaction of $(\eta\text{-}C_5H_5)_2MoH_2$ and the Grignard reagent from isopropyl bromide in diethyl ether were supplied by Dr D. M. Roe and Dr M. L. H. Green. Experimental work proceeded in the same manner as for the cyclohexyl derivative and the following crystal data were obtained.

Monoclinic, $a = 8.566$ (8), $b = 12.955$ (12), $c = 18.617$ (15) Å, $\beta = 93.9$ (1)°, $U = 2064.5$ Å^3. Systematic extinctions $h0l$: $l = 2n + 1$; $0k0$: $k = 2n + 1$. Space group $P2_1/c$. $Z = 2$ ([$MoMg_2Br_2$]$_2$ units). Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å.

Considerable crystal decomposition resulted in high background scatter, and only 723 independent observed reflexions were measured. Patterson and Fourier methods located Mo, Mg and Br atoms in a skeleton closely similar to that of the cyclohexyl compound, except that, although lying about a centre, it lacks mirror symmetry; there are thus two refinable Br atoms. Cyclopentadienyl groups were placed with difficulty and an atom apparently bound to each Mg was found, but the remainder of these ligands could not confidently be placed. Least-squares refinement of this partial structure (Fig. 3), with anisotropic Mo and Br atoms and bond lengths and angles within the cyclopentadienyl groups constrained to 1.41 Å and 108° respectively, converged to $R = 0.14$. Principal bond lengths and angles are given in Table 4.

Fig. 3. Projection of isopropyl derivative at angle of 15° from normal to Mg(1)–Mo–Mg(2) plane.

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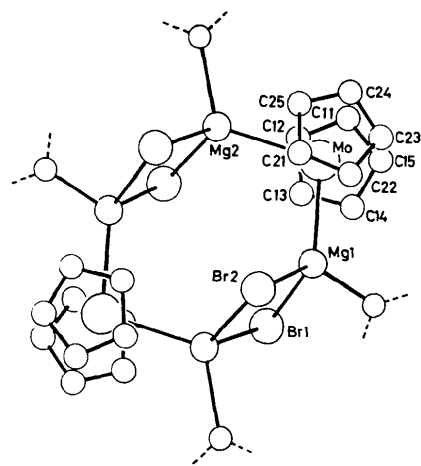Forder, R. A. & Prout, K. (1974a). *Acta Cryst.* B30, 2312–2317.

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