Cook, D. H., Fenton, D. E., Drew, M. G. B., Rodgers, A., McCann, M. & Nelson, S. M. (1979). *J. Chem. Soc. Dalton Trans.* pp. 414–419.

Drew, M. G. B. (1977). *Prog. Inorg. Chem.* 23, 67–213.

Drew, M. G. B., McFall, S. G., McIlroy, P. D. A. & Nelson, S. M. (1979). *J. Chem. Soc. Dalton Trans.* In the press.

Drew, M. G. B. & Nelson, S. M. (1979). Unpublished work.

Drew, M. G. B., Othman, A. H., McFall, S. G., McIlroy, P. D. A. & Nelson, S. M. (1977). *J. Chem. Soc. Dalton Trans.* pp. 438–446.

Drew, M. G. B., Rodgers, A., McCann, M. & Nelson, S. M. (1978). *Chem. Commun.* pp. 415–416.

Fenton, D. E., Cook, D. E., Nowell, I. W. & Walker, P. E. (1977). *Chem. Commun.* pp. 274–275.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Nelson, S. M., McFall, S. G., Drew, M. G. B., Othman, A. H. & Mason, N. B. (1977). *Chem. Commun.* pp. 167–168.

Shannon, R. D. (1976). *Acta Cryst.* A32, 751–767.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Wynne, K. J. (1973). *J. Chem. Educ.* 50, 328–330.

The Crystal and Molecular Structure of [Bromobis(tetrahydrofuran)magnesio]-bis(η-cyclopentadienyl)hydridomolybdenum

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Abstract

The crystal and molecular structure of the title compound has been determined by Patterson heavy-atom methods and refined to $R = 0.066$ {triclinic, $a = 11.708$ (5), $b = 11.596$ (5), $c = 7.750$ (3) Å, $\alpha = 86.33$ (2), $\beta = 82.92$ (2), $\gamma = 73.26$ (3)°, space group $P\bar{1}$, Mo $K\alpha$ radiation, 1334 reflections [$I > 3\sigma(I)$]}. The bis(η-cyclopentadienyl)molybdenum moiety has the eclipsed configuration and the Mo—Mg bond length is 2.732 Å. The presence of the hydrido ligand is inferred from the molecular geometry. The Mg atom has a distorted tetrahedral configuration.

Introduction

The crystals were prepared by the recrystallization from tetrahydrofuran of the reaction product of (η-C₅H₅)₂MoH₂ with the Grignard reagent isopropylmagnesium bromide. The preparation, reactions and structure of this compound have been the subject of a preliminary report (Davies, Green, Prout, Coda & Tazzoli, 1977). It was expected to have a structure analogous to that of the previously reported compound

bis-μ-[bis-(η-cyclopentadienyl)hydridomolybdenum]-bis{di-μ-bromo-[cyclohexylmagnesium][(diethyl ether)-magnesium]} (I) (Prout & Forder, 1975), but the structure analysis showed it to be a new type of compound (II). An irregular fragment, 0.3–0.4 mm thick, was chosen from the sample of air-unstable orange crystals, and was sealed under nitrogen in a glass capillary.

Experimental

Crystal data

(η-C₅H₅)₂Mo(H)Mg(C₄H₈O)₂Br, C₁₈H₂₇BrMg-MoO₂, [Mo{(C₅H₅)₂H[MgBr(C₄H₈O)₂]}], $M_r = 475.1$, triclinic, $a = 11.708$ (5), $b = 11.596$ (5), $c = 7.750$ (3) Å, $\alpha = 86.33$ (2), $\beta = 82.92$ (2), $\gamma = 73.26$ (3)°, $U = 1002.9$ Å³; $D_c = 1.57$ Mg m⁻³ for $Z = 2$; space group $P\bar{1}$ (C_i^1, No. 2) from intensity statistics and structure analysis, four-circle diffractometer data, Mo $K\alpha$ radiation (graphite monochromator), $\mu = 4.93$ mm⁻¹, 1334 independent reflections [$I > 3\sigma(I)$].

The unit-cell dimensions were determined on a Philips PW 1100 four-circle automatic diffractometer using the manufacturer's routine *LAT*: this performs an accurate scan of the rows $h00$, $0k0$, $00l$, $hh0$, $h0h$, $0kk$, $0\bar{k}k$, hhh, $\bar{h}hh$, $h\bar{h}h$ and $hh\bar{h}$ in the range $\theta = 2$–$20°$, and afterwards minimizes the differences between

observed and calculated spacings by least squares. The intensity data were measured in the $\omega/2\theta$ scan mode with $\Delta\omega$ $1\cdot5°$ and scanning speed $0\cdot1°$ s^{-1}. A maximum of four scans were used and reflections were skipped after the first scan when $I_{top} - I_{bck} < 2\sqrt{I_{top}}$ where I_{top} is the intensity at the top of the reflection, I_{bck} is the mean intensity of the two background counts from preliminary counting 5 s each side of the reflection. Of the 1872 reflections measured, 1506 had $I > \sigma(I)$ and 1334 $I > 3\sigma(I)$. The fall off of I with θ was rapid and reflections with $\theta > 20°$ were not observed. The reference reflections 202, 0$\bar{1}$1 and 1$\bar{1}$1 were measured frequently during the two days of data collection. During this time their intensities fell by about 30% due to decomposition of the crystal. To counter this decline a continuous scaling correction was applied. The intensities were corrected for Lorentz and polarization effects but not absorption.

Structure determination and refinement

The structure was determined by heavy-atom Patterson methods and refined by full-matrix least squares. The 1334 reflections with $I > 3\sigma(I)$ were used and were given unit weights. At no stage could H atoms be located in the difference syntheses but those associated with the η-C₅H₅ groups were placed geometrically. The addition of those H atoms improved the final R by $0\cdot008$. The C₄H₈O H atoms when placed geometrically lead to an increase in R. The final R was $0\cdot066$. There was no evidence in the difference syntheses for the H attached to Mo.

All calculations were carried out on the Honeywell 6030 computer at the Centro di Calcolo dell'Università di Pavia with programs developed locally. The atomic scattering factors were taken from Hanson, Herman Lea & Skillman (1964) and anomalous-dispersion corrections from Cromer & Liberman (1970). The final atomic parameters are given in Table 1.*

Results and discussion

The crystal structure is shown in Fig. 1 and the molecule projected on to the plane perpendicular to that of the normals to the η-C₅H₅ rings in Fig. 2. The inter-atomic distances and interbond angles with standard deviations calculated from the full variance–covariance matrix are given in Table 2.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34279 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates with estimated standard deviations in parentheses*

The hydrogen coordinates are given after geometrical consideration.

|	x	y	z
Mo	0·3455 (2)	0·3359 (2)	0·3778 (2)
Br	0·1215 (3)	0·1050 (3)	0·6859 (3)
Mg	0·2102 (5)	0·1780 (5)	0·4033 (6)
O(1)	0·0638 (9)	0·2334 (9)	0·2680 (14)
O(2)	0·2799 (10)	0·0156 (9)	0·2794 (15)
C(1)	0·4920 (18)	0·1975 (21)	0·2104 (22)
C(2)	0·3806 (18)	0·2401 (19)	0·1157 (22)
C(3)	0·3644 (19)	0·3666 (22)	0·0889 (22)
C(4)	0·4591 (23)	0·4036 (24)	0·1547 (25)
C(5)	0·5355 (19)	0·3013 (27)	0·2352 (29)
C(6)	0·2564 (16)	0·3675 (15)	0·6618 (20)
C(7)	0·1625 (15)	0·4048 (15)	0·5464 (24)
C(8)	0·1869 (19)	0·5010 (18)	0·4445 (22)
C(9)	0·3034 (19)	0·5221 (17)	0·4801 (26)
C(10)	0·3404 (16)	0·4392 (16)	0·6259 (21)
C(11)	0·0619 (20)	0·3174 (20)	0·1151 (26)
C(12)	−0·0666 (21)	0·3389 (22)	0·0687 (31)
C(13)	−0·1106 (20)	0·2367 (29)	0·1513 (36)
C(14)	−0·0499 (15)	0·2049 (19)	0·3123 (26)
C(15)	0·3848 (22)	−0·0712 (18)	0·3413 (39)
C(16)	0·3689 (24)	−0·1866 (19)	0·3118 (38)
C(17)	0·2723 (21)	−0·1735 (17)	0·2041 (33)
C(18)	0·2194 (23)	−0·0436 (18)	0·1793 (34)
H(1)	0·5284	0·1158	0·2481
H(2)	0·3318	0·1930	0·0815
H(3)	0·2991	0·4204	0·0347
H(4)	0·4690	0·4831	0·1447
H(5)	0·6030	0·3002	0·2954
H(6)	0·2623	0·3041	0·7501
H(7)	0·0974	0·3705	0·5409
H(8)	0·1357	0·5479	0·3622
H(9)	0·3431	0·5769	0·4196
H(10)	0·4087	0·4337	0·6877
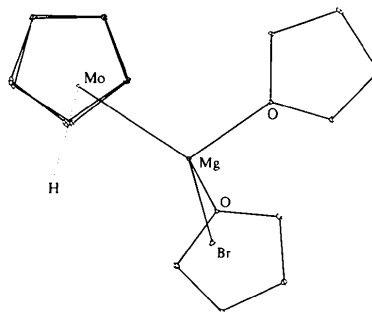
Fig. 1. Molecule projected down Z_R on to the plane $X_R Y_R$ (see text for reference system).
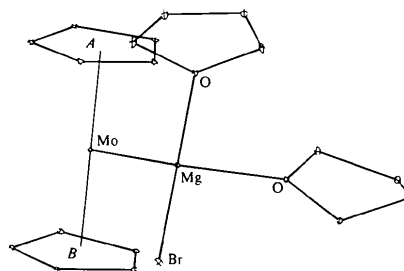

Fig. 2. Molecule projected down Y_R on to the plane $X_R Z_R$ (see text).

Table 2. *Interatomic distances* (Å) *and interbond angles* (°)

Mo—Mg	2·732 (5)	Mo—C(6)	2·32 (2)	C(6)—C(7)	1·46 (3)	O(2)—C(15)	1·46 (2)
Mg—Br	2·514 (5)	Mo—C(7)	2·32 (2)	C(7)—C(8)	1·40 (3)	C(15)—C(16)	1·44 (3)
Mg—O(1)	2·04 (1)	Mo—C(8)	2·29 (2)	C(8)—C(9)	1·52 (3)	C(16)—C(17)	1·46 (3)
Mg—O(2)	2·07 (1)	Mo—C(9)	2·25 (2)	C(9)—C(10)	1·46 (3)	C(17)—C(18)	1·47 (3)
		Mo—C(10)	2·32 (2)	C(10)—C(6)	1·45 (3)	C(18)—O(2)	1·44 (2)
Mo—C(1)	2·31 (2)	C(1)—C(2)	1·52 (3)	O(1)—C(11)	1·48 (2)		
Mo—C(2)	2·31 (2)	C(2)—C(3)	1·43 (3)	C(11)—C(12)	1·54 (3)		
Mo—C(3)	2·24 (2)	C(3)—C(4)	1·46 (3)	C(12)—C(13)	1·50 (3)		
Mo—C(4)	2·29 (2)	C(4)—C(1)	1·42 (3)	C(13)—C(14)	1·49 (3)		
Mo—C(5)	2·30 (2)	C(5)—C(1)	1·47 (3)	C(14)—O(1)	1·46 (2)		

Mo—Mg—Br	124·2 (2)	C(6)—C(7)—C(8)	105·6 (1·6)	O(2)—C(15)—C(16)	104·3 (1·8)
Mo—Mg—O(1)	113·6 (4)	C(7)—C(8)—C(9)	111·8 (1·6)	C(15)—C(16)—C(17)	110·9 (1·8)
Mo—Mg—O(2)	118·4 (4)	C(8)—C(9)—C(10)	103·7 (1·6)	C(16)—C(17)—C(18)	105·8 (1·2)
Br—Mg—O(1)	101·4 (4)	C(9)—C(10)—C(6)	108·1 (1·5)	C(17)—C(18)—O(2)	107·2 (1·5)
Br—Mg—O(2)	99·5 (4)	C(10)—C(6)—C(7)	110·4 (1·5)	C(18)—O(2)—C(15)	110·1 (1·3)
O(1)—Mg—O(2)	94·5 (5)	O(1)—C(11)—C(12)	101·5 (1·6)		
C(1)—C(2)—C(3)	103·9 (1·8)	C(11)—C(12)—C(13)	106·9 (1·7)	Shortest intermolecular distance, not
C(2)—C(3)—C(4)	111·5 (2·0)	C(12)—C(13)—C(14)	104·3 (1·8)	involving H atoms
C(3)—C(4)—C(5)	108·4 (2·0)	C(13)—C(14)—O(1)	104·1 (1·6)	
C(4)—C(5)—C(1)	107·3 (2·0)	C(14)—O(1)—C(11)	112·7 (1·3)	C(4)···C(4) (1 − x, 1 − y, −z) 3·41 (3)
C(5)—C(1)—C(2)	108·8 (1·9)			

The compound proved to be a novel adduct of $(\eta\text{-}C_5H_5)_2MoH_2$ and the magnesium Grignard with the elimination of the alkane. The $(\eta\text{-}C_5H_5)_2Mo$ moiety retains the eclipsed conformation of the hydride. The perpendicular distances from the Mo atom to the η-C_5H_5 rings, 1·923 Å [ring C(1)—C(5)] and 1·935 Å [ring C(6)—C(10)], are shorter than those found in non-hydrido complexes (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The angle between these perpendiculars is, at 145°, more than 10° larger than in the non-hydrido systems. However, these dimensions are very similar to those found in $(\eta\text{-}C_5H_5)_2MoH_2$ (Gerloch & Mason, 1965). The bond lengths and angles within the η-C_5H_5 rings have reasonable values.

In Fig. 2 the molecule is seen projected down Y_R on to the plane $X_R Z_R$.* This latter view corresponds very closely to the projection on to the MX_2 plane used in many descriptions of bent metal bis(η-cyclopentadienyl) compounds. The H atom position marked by a broken line in Fig. 1 is hypothetical; there is no direct evidence for its presence from the electron density distribution. However, its presence may be inferred on chemical grounds. A hydrido H is required to bring the Mo to the 18e configuration. With the hydrido H present the reaction has a reasonable stoichiometry

$$(\eta\text{-}C_5H_5)_2MoH_2 + C_3H_7Mg(C_4H_8O)_2Br \rightarrow$$

$$(\eta\text{-}C_5H_5)_2Mo(H)Mg(C_4H_8O)_2Br + C_3H_8.$$
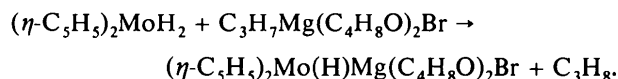
* X_R, Y_R and Z_R have the following definition. The origin is taken as the Mo atom and A and B are the points where the normals at Mo to the η-C_5H_5 rings, C(1)—C(5) and C(6)—C(10), pass through the best planes of those rings; then X_R is the normal to the plane containing A, B, and Mo; Y_R is the bisectrix of the angle A—Mo—B so that the positive direction forms an angle <90° with the bond Mo—Mg; and Z_R is perpendicular to the plane containing X_R and Y_R.

The skew position of the Mo—Mg bond is readily explained if there is a Mo—H bond in the neighbouring quadrant. In the absence of a Mo—H bond Mo—Mg would be expected to lie along Y_R. It is unfortunate that there are no reported structures of $(\eta\text{-}C_5H_5)_2MX$ monomers. The projection down X_R emphasizes that the $(\eta\text{-}C_5H_5)_2Mo$ group is symmetric about Y_R rather than about Mo—Mg. The Mo—Mg bond length is 2·732 Å. Prout & Forder (1975) have previously reported Mo—Mg bonds in (I). The Mo—Mg bonds in (I) are not electronically equivalent. In the longer bond, 2·853 (7) Å, Mo acts as a 2e ligand to Mg and in the shorter bond, 2·737 (6) Å, each metal acts as a 1e ligand. In the new compound the Mg acts as a 1e ligand and the bond length agrees remarkably well with the similar bond in (I).

The coordination of Mg is distorted tetrahedral. The distortions appear to be steric in origin and are consistent with the relative sizes of the four-ligand group (Table 2). The Mg—Br and Mg—O bond lengths are unexceptional. The tetrahydrofuran ligands are envelope shaped. In the ligand containing O(1) the departures from planarity are greater than in that containing O(2) (see Table 3) although the latter is less well resolved. In the former C(14), O(1), C(11) and C(12) are nearly coplanar, with C(13) 0·48 Å out of the plane, and in the latter C(16)—C(17)—C(18)—O(2) is the most nearly planar group with C(15) only 0·19 Å from the plane. These deviations from planarity contrast with the more usual tetrahydrofuran ligand in which the C atoms are coplanar and the O is bent out of the plane [e.g. bis(cyclooctatetraene)(tetrahydrofuran)zirconium (Brauer & Krüger, 1972), or dichloro(η-cyclooctatetraene)(tetrahydrofuran)zirconium (Brauer & Krüger, 1975)]. The Mg—O(1) bond makes an angle of 3·3° with the plane C(11), O(1), C(14) to give O(1) an essentially planar environment whereas

Table 3. *Torsion angles* (°), *with standard deviations in parentheses, in the tetrahydrofuran molecules*

A positive rotation is anticlockwise when viewed from atom 3 to atom 2.

1　　　2　　　3　　　4	
O(1)–C(11)–C(12)–C(13)	160·3 (2·2)
C(11)–C(12)–C(13)–C(14)	−148·1 (2·3)
C(12)–C(13)–C(14)–O(1)	149·3 (1·1)
C(13)–C(14)–O(1)–C(11)	−150·7 (1·8)
C(14)–O(1)–C(11)–O(12)	−179·8 (1·8)
O(2)–C(15)–C(16)–C(17)	−168·7 (2·1)
C(15)–C(16)–C(17)–C(18)	174·9 (2·3)
C(16)–C(17)–C(18)–O(2)	176·6 (2·4)
C(17)–C(18)–O(2)–C(15)	−169·3 (4·0)
C(18)–O(2)–C(15)–C(16)	166·6 (2·5)

the Mo–O(2) bond makes a much larger angle, 16·90°, with the C(15), O(2), C(1) plane. The thermal motion in the tetrahydrofuran ligands is high and they are less than well defined. However, attempts to force the ligands to be planar or to have the more usual distortion by the use of constrained refinement pro-

duced models that were, according to statistical tests, worse than the unconstrained model.

References

BRAUER, D. J. & KRÜGER, C. (1972). *J. Organomet. Chem.* **42**(1), 129–137.

BRAUER, D. J. & KRÜGER, C. (1975). *Inorg. Chem.* **14**(12), 3053–3056.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

DAVIES, S. G., GREEN, M. L. H., PROUT, C. K., CODA, A. & TAZZOLI, V. (1977). *J. Chem. Soc. Chem. Commun.* pp. 135–136.

GERLOCH, M. & MASON, R. (1965). *J. Chem. Soc.* pp. 296–304.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

PROUT, C. K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.

PROUT, C. K. & FORDER, R. A. (1975). *Acta Cryst.* **B31**, 852–856.

The Crystal Structure of Tetrakis[1-methylimidazoline-2(3H)-thione]cobalt(II) Diperchlorate

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Abstract

[Co(C₄H₆N₂S)₄](ClO₄)₂, C₁₆H₂₄CoN₈S₄²⁺.2ClO₄⁻, is tetragonal, $a = b = 12·359$ (4), $c = 19·932$ (4) Å, $Z = 4$, space group $I4_1/a$. $R = 0·0563$ for 1359 counter reflections. The ligand is monodentate and S-bonded to the metal [Co–S = 2·302 (1) Å]; the resultant CoS₄ tetrahedron is distorted by compression along the $\bar{4}$ axis. The discrete cations are grouped in pairs around symmetry centres. Distorted perchlorate anions with Cl–O = 1·306 (8), 1·375 (11) Å are H-bonded to the ligand by N–H···O contacts of 2·872 Å.

Introduction

The preparation and characterization of complexes of 1-methylimidazoline-2(3H)-thione with Co^II and Zn^II

halides and perchlorates have been described (Raper & Brooks, 1977). In these complexes the potentially ambidentate ligand was shown to be monodentate with metal–S rather than metal–N contacts. This X-ray study has been undertaken in order to verify the conclusions drawn from infrared and visible spectra and to provide detailed information on the coordination geometry.

Experimental

Crystal data

Deep-green, well formed crystals of the complex were obtained from anhydrous ethanol containing 5% (v/v) triethyl orthoformate. Cell constants were obtained from Weissenberg and precession photographs;