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

ISAGO, T., OKAMOTO, K., OHMASA, M. & HIDAKA, J. (1980). *Chem. Lett.* pp. 319–322.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KOJIMA, M. & FUJITA, J. (1983). *Bull. Chem. Soc. Jpn*, **56**, 2958–2964.

MITSUI, Y., WATANABE, J., HARADA, Y., SAKAMAKI, T. & IITAKA, Y. (1976). *J Chem. Soc. Dalton Trans.* pp. 2095–2102.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

Acta Cryst. (1984). C**40**, 401–403

The Structure of Dicarbonyl(η^5-cyclopentadienyl) (η^3-2-methylallyl)molybdenum(II), $[Mo(C_4H_7)(C_5H_5)(CO)_2]$

BY NICHOLAS W. MURRALL AND ALAN J. WELCH

Dewar Crystallographic Laboratory, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland

(*Received* 27 *September* 1983; *accepted* 16 *November* 1983)

Abstract. $M_r = 272\cdot2$, monoclinic, $P2_1/n$, $a = 6\cdot1105$ (9), $b = 12\cdot7885$ (22), $c = 13\cdot7247$ (24) Å, $\beta = 98\cdot787$ (13)°, $U = 1059\cdot91$ Å^3, $D_x = 1\cdot705$ Mg m^{-3}, $Z = 4$, $F(000) = 544$ e, $\bar{\lambda}$(Mo $K\alpha$) = 0·71069 Å, $\mu = 1\cdot083$ mm^{-1}, $T = 188$ K. $R = 0\cdot025$ for 2867 unique reflections. The molecule crystallizes with the η^3-2-methylallyl ligand in the *endo* conformation, and the three Mo—C(allyl) distances are equal within experimental error, average 2·3163 (13) Å.

Introduction. There is currently considerable theoretical and experimental interest in the structural preferences of complexes containing the η^3-allyl or a substituted η^3-allyl ligand. Detailed NMR studies (Faller, Chen, Mattina & Jakubowski, 1973) had previously established that whilst both *exo* and *endo* (Schilling, Hoffmann & Faller, 1979) conformations of $[(\eta^5\text{-}C_5H_5)(2\text{-}R\text{-}\eta^3\text{-}C_3H_4)(CO)_2Mo]$ (R = H, Me) are present (and rapidly interconvert) in solution, the major isomer is *exo* for R = H and *endo* for R = Me. It is, furthermore, *exo*-$[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CO)_2Mo]$ (I) that crystallizes (Faller, Chodosh & Katahira, 1980). To establish if a similar correspondence exists between major solution isomer and that observed in the solid state when R = Me, we have determined the crystal structure of $[(\eta^5\text{-}C_5H_5)(2\text{-Me-}\eta^3\text{-}C_3H_4)(CO)_2Mo]$ (II).

Experimental. Yellow crystals, prepared according to the literature (Faller, Chen, Mattina & Jakubowski, 1973), 0·05 × 0·04 × 0·03 cm, from diethyl ether/*n*-heptane (1:1) by slow evaporation, mounted in Lindemann tube under N_2; preliminary unit cell and space group from oscillation and Weissenberg photography [λ(Cu $K\alpha$) = 1·54178 Å], $h0l$ $h+l = 2n+1$ and $0k0$ $k = 2n+1$ absent; CAD-4 diffractometer, 188 K (ULT-1 apparatus), 25 reflections (17° < θ < 18°) centred, graphite-monochromated Mo $K\alpha$ radiation; for data collection $\theta_{\max} = 30°$, ω–2θ scans in 96 steps, ω scan width 0·8° + 0·35° tan θ, rapid prescan after which reflections with $I \geq 0\cdot5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to a maximum measuring time of 90 s; two quadrants measured ($hk\pm l$ and $-h-k\pm l$) over 115 X-ray hours with no detectable decay or movement; data not corrected for absorption, observed structure factors determined and merged to give 3083 unique reflections, $R_{\rm merg} = 0\cdot0218$; for structure solution and refinement 2867 amplitudes for which $F \geq 2\sigma(F)$, Patterson synthesis (Mo), full-matrix least squares (on F) (Sheldrick, 1976), $w = [\sigma^2(F) + 0\cdot004524\,(F)^2]^{-1}$, anisotropic thermal parameters for all non-H atoms, $U_{\rm H}$* set at 0·04 Å^2, $R = 0\cdot0250$, $wR = 0\cdot0469$, data: variable ratio 17:1, $(\Delta/\sigma)_{\max}$ in final cycle <0·3, max. peak and min. trough in final ΔF synthesis 0·41 and $-1\cdot08$ e Å^{-3} respectively, neutral scattering factors for C, O, Mo (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965), computer programs *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1976), *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), and *ORTEP*II (Johnson, 1976).†

---

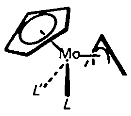
* The isotropic temperature factor is defined as $\exp[-8\pi^2U\times(\sin^2\theta)/\lambda^2]$.

† Lists of structure factors, H-atom coordinates, Tables 3 and 4, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39027 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

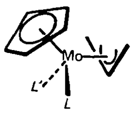
0108-2701/84/030401-03\$01.50

Discussion. The derived fractional coordinates are given in Table 1. Table 2 lists important molecular dimensions. Coordinates and bond lengths and angles involving H atoms have been deposited as Table 3 and full details of molecular planes are deposited as Table 4.* Fig. 1 is a perspective view of a single molecule.

In $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-allyl})LL'\text{Mo}]$ complexes there are two limiting molecular conformations, *exo* (*A*) and *endo* (*B*) (Schilling, Hoffmann & Faller, 1979). For (I) and for a number of its substituted-allyl analogues both conformers have been shown to co-exist in solution at ambient temperatures, and barriers to interconversion have been estimated at *ca* 63 kJ mol^{-1} for (I) and (II) (Faller, Chen, Mattina & Jakubowski, 1973). For (I) the *exo* conformer predominates in solution, and is, moreover, the conformation characterized in the solid state. It is of interest that this conformational preference is not supported by the result of molecular-orbital calculations.



(*A*)



(*B*)

In contrast, the major solution isomer of (II) has an *endo* conformation, and the present study clearly demonstrates that this, too, is retained upon crystallization. Clearly, an important influence upon the preferred stereochemistry of (II) is the steric requirement of the 2-methyl substituent, and we have calculated that in the alternative *exo* conformation a repulsive $H(Me)\cdots H(\eta^5\text{-}C_5H_5)$ contact would result, whereas there is no intramolecular congestion in the observed, *endo* conformation.

Unusually the Mo—C(allyl) distances in (II) are equal; this contrasts with the great majority of seven-coordinate molybdenum(II) allyls that have been structurally studied (Faller, Chodosh & Katahira, 1980; Allen, Baker, Barnes, Bottrill, Green, Orpen & Welch, 1983; Graham, Akrigg & Sheldrick, 1976, and references therein) in which the Mo—C(central) bond is found to be significantly the shortest.

Table 4 (deposited) presents the results of least-squares-planes' calculations. With respect to the (precise) plane through the allyl atoms C(1), C(2) and C(3), the methyl carbon C(4) and the 1,3-*syn* H atoms [H(12) and H(32)] are all displaced *towards* the metal whereas H(11) and H(31) bend away. This kind of distortion has previously been observed in other

Table 1. *Fractional atomic coordinates with standard deviations*

$$U_{eq}=\tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Mo	0·46349 (2)	0·19301 (1)	0·12509 (1)	0·0201
C(1)	0·2065 (4)	0·29750 (17)	0·18619 (19)	0·0390
C(2)	0·3405 (4)	0·36310 (14)	0·13794 (14)	0·0321
C(3)	0·5683 (4)	0·36159 (16)	0·17359 (17)	0·0357
C(4)	0·2461 (5)	0·42399 (19)	0·04816 (18)	0·0440
C(5)	0·7513 (4)	0·07415 (24)	0·16929 (24)	0·0585
C(6)	0·7330 (5)	0·12972 (20)	0·25498 (24)	0·0571
C(7)	0·5294 (6)	0·11132 (22)	0·28080 (17)	0·0567
C(8)	0·4165 (4)	0·04157 (21)	0·21231 (25)	0·0552
C(9)	0·5559 (6)	0·01847 (18)	0·14263 (19)	0·0528
C(10)	0·2145 (3)	0·16906 (18)	0·01913 (16)	0·0335
C(11)	0·5812 (3)	0·24101 (15)	0·00806 (14)	0·0324
O(1)	0·0755 (3)	0·15168 (19)	−0·04488 (17)	0·0588
O(2)	0·6451 (3)	0·27005 (18)	−0·06222 (14)	0·0552

Table 2. *Interatomic distances* (Å) *and angles* (°) *and deviations of atoms from planes* (Å)

Mo—C(1)	2·3146 (25)	C(1)—C(2)	1·407 (3)
Mo—C(2)	2·3169 (20)	C(2)—C(3)	1·403 (3)
Mo—C(3)	2·3175 (22)	C(2)—C(4)	1·497 (3)
Mo—C(5)	2·333 (3)	C(5)—C(6)	1·393 (4)
Mo—C(6)	2·377 (3)	C(5)—C(9)	1·390 (4)
Mo—C(7)	2·358 (3)	C(6)—C(7)	1·365 (4)
Mo—C(8)	2·318 (3)	C(7)—C(8)	1·399 (4)
Mo—C(9)	2·306 (3)	C(8)—C(9)	1·406 (4)
Mo—C(10)	1·9615 (22)	C(10)—O(1)	1·147 (3)
Mo—C(11)	1·9563 (19)	C(11)—O(2)	1·156 (3)
C(1)—Mo—C(2)	35·36 (8)	C(7)—Mo—C(8)	34·81 (10)
C(1)—Mo—C(3)	62·09 (8)	C(7)—Mo—C(9)	58·08 (10)
C(1)—Mo—C(5)	143·90 (10)	C(7)—Mo—C(10)	127·50 (10)
C(1)—Mo—C(6)	110·83 (10)	C(7)—Mo—C(11)	148·21 (9)
C(1)—Mo—C(7)	87·64 (10)	C(8)—Mo—C(9)	35·40 (10)
C(1)—Mo—C(8)	98·68 (10)	C(8)—Mo—C(10)	96·27 (10)
C(1)—Mo—C(9)	133·62 (10)	C(8)—Mo—C(11)	140·93 (9)
C(1)—Mo—C(10)	82·32 (9)	C(9)—Mo—C(10)	94·37 (10)
C(1)—Mo—C(11)	118·11 (8)	C(9)—Mo—C(11)	105·93 (9)
C(2)—Mo—C(3)	35·25 (7)	C(10)—Mo—C(11)	77·36 (8)
C(2)—Mo—C(5)	146·32 (9)	Mo—C(1)—C(2)	72·41 (13)
C(2)—Mo—C(6)	117·28 (9)	Mo—C(2)—C(1)	72·23 (13)
C(2)—Mo—C(7)	111·07 (9)	Mo—C(2)—C(3)	72·40 (12)
C(2)—Mo—C(8)	132·69 (9)	Mo—C(2)—C(4)	120·96 (15)
C(2)—Mo—C(9)	167·94 (9)	C(1)—C(2)—C(3)	116·45 (19)
C(2)—Mo—C(10)	88·81 (8)	C(1)—C(2)—C(4)	121·27 (20)
C(2)—Mo—C(11)	86·11 (7)	C(3)—C(2)—C(4)	122·08 (19)
C(3)—Mo—C(5)	111·54 (9)	Mo—C(3)—C(2)	72·35 (12)
C(3)—Mo—C(6)	88·40 (9)	Mo—C(5)—C(6)	74·50 (18)
C(3)—Mo—C(7)	98·65 (9)	Mo—C(5)—C(9)	71·50 (17)
C(3)—Mo—C(8)	132·81 (9)	C(6)—C(5)—C(9)	107·9 (3)
C(3)—Mo—C(9)	144·88 (9)	Mo—C(6)—C(5)	71·11 (18)
C(3)—Mo—C(10)	120·48 (8)	Mo—C(6)—C(7)	72·49 (18)
C(3)—Mo—C(11)	79·85 (8)	C(5)—C(6)—C(7)	109·0 (3)
C(5)—Mo—C(6)	34·40 (11)	Mo—C(7)—C(6)	74·01 (18)
C(5)—Mo—C(7)	57·18 (10)	Mo—C(7)—C(8)	71·03 (17)
C(5)—Mo—C(8)	57·94 (11)	C(6)—C(7)—C(8)	108·1 (3)
C(5)—Mo—C(9)	34·86 (10)	Mo—C(8)—C(7)	74·16 (17)
C(5)—Mo—C(10)	124·01 (10)	Mo—C(8)—C(9)	71·85 (17)
C(5)—Mo—C(11)	93·49 (9)	C(7)—C(8)—C(9)	107·7 (3)
C(6)—Mo—C(7)	33·50 (10)	Mo—C(9)—C(5)	73·64 (17)
C(6)—Mo—C(8)	56·92 (10)	Mo—C(9)—C(8)	72·75 (17)
C(6)—Mo—C(9)	57·41 (10)	C(5)—C(9)—C(8)	107·4 (3)
C(6)—Mo—C(10)	150·82 (10)	Mo—C(10)—O(1)	176·61 (21)
C(6)—Mo—C(11)	115·04 (9)	Mo—C(11)—O(2)	178·18 (18)

Plane 1: C(1)—C(3) Mo −1·893 (1), C(4) −0·111 (3), H(11) 0·45 (3), H(12) −0·10 (3), H(31) 0·47 (3), H(32) −0·18 (3)

Plane 2: C(5)—C(9) Mo −2·016 (1), C(5) −0·005 (3), C(6) 0·007 (3), C(7) −0·005 (3), C(8) 0·002 (3), C(9) 0·002 (3)

Dihedral angle: plane 1, plane 2 73·5°

---

* See deposition footnote.

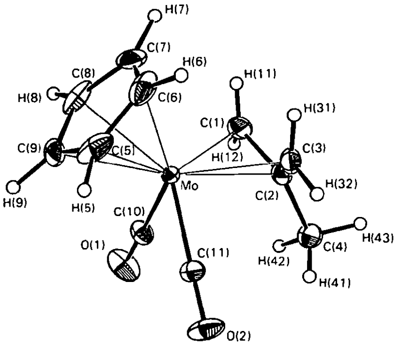


Fig. 1. Perspective view of $[(\eta^5\text{-}C_5H_5)(2\text{-Me-}\eta^3\text{-}C_3H_4)(CO)_2Mo]$ (II), with thermal ellipsoids drawn at the 30% probability level, except for H atoms which have an artificial radius of 0·1 Å for clarity.

accurately determined structures of 2-methylallyl complexes where sterically permitted (see, for example, Bandoli & Clemente, 1981), and its origin may be traced to rehybridization of the allyl π molecular orbitals upon complex formation (Elian, Chen, Mingos & Hoffmann, 1976).

The cyclopentadienyl ligand shows some degree of rotational disorder as evidenced by the fact that the three highest residues in the final ΔF synthesis occur between atoms C(8) and C(9), C(9) and C(5), and C(5) and C(6). However, refinement of a model involving two independent C_5 rings would not converge satisfactorily, carbon atoms tending to merge with concomitant reappearance of the residues.* The present model was therefore adopted as more suitable.

The general orientation of the $\eta^5\text{-}C_5H_5$ ligand does not conform to the effective C_s symmetry of the rest of the complex. Furthermore, the ligand is not bound symmetrically to the metal atom, and is not planar. Atoms C(6) and C(7) are significantly further from Mo than C(5), C(8) and C(9), and the short C(6)—C(7) bond implies some π localization. Thus this ligand is 'slipped' (by *ca* 0·08 Å) towards a cyclic η^3-allyl function (Green, Nyathi, Scott, Stone, Welch & Woodward, 1978, and references therein). The nonplanarity of the C_5 ring, however, does not readily correlate with this slippage, being of envelope conformation folded away from Mo about the C(5)···C(7) vector.

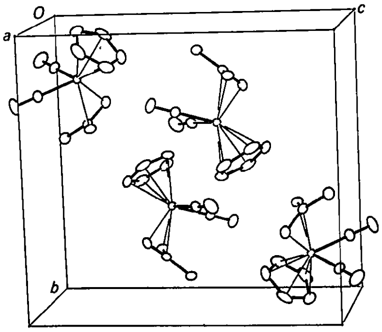


Fig. 2. Crystal-packing diagram for (II), with H atoms omitted for clarity.

Molecular parameters within the $Mo(CO)_2$ fragment are quite normal for a complex of this class. Fig. 2 is a perspective view of the contents of one unit cell. There are no significant intermolecular interactions.

We thank the Department of Chemistry, University of Edinburgh, for support (NWM).

References

Allen, S. R., Baker, P. K., Barnes, S. G., Bottrill, M., Green, M., Orpen, A. G. & Welch, A. J. (1983). *J. Chem. Soc. Dalton Trans.* pp. 927–939.

Bandoli, G. & Clemente, D. A. (1981). *Acta Cryst.* B**37**, 490–491.

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

Elian, M., Chen, M. M. L., Mingos, D. M. P. & Hoffmann, R. (1976). *Inorg. Chem.* **15**, 1148–1155.

Faller, J. W., Chen, C.-C., Mattina, M. J. & Jakubowski, A. (1973). *J. Organomet. Chem.* **52**, 361–387.

Faller, J. W., Chodosh, D. F. & Katahira, D. (1980). *J. Organomet. Chem.* **187**, 227–231.

Graham, A. J., Akrigg, D. & Sheldrick, B. (1976). *Cryst. Struct. Commun.* **5**, 891–898.

Green, M., Nyathi, J. Z., Scott, C., Stone, F. G. A., Welch, A. J. & Woodward, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1067–1080.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Roberts, P. & Sheldrick, G. M. (1976). *XANADU*. Univ. of Cambridge, England.

Schilling, B. E. R., Hoffmann, R. & Faller, J. W. (1979). *J. Am. Chem. Soc.* **101**, 592–598.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ of Cambridge, England.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY*76 system. Tech. Rep. TR446. Computer Science Centre, Univ. Maryland, College Park, Maryland, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

---

* In all refinements the C_5 rings were *not* idealized to regular pentagons as there is clear asymmetry in C—C distances, reflecting asymmetric Mo—($\eta^5\text{-}C_5H_5$) bonding, that we did not wish to override.