The Sequential Linking of Alkynes at a Dimolybdenum Centre. Crystal Structures of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ and $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$

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Reaction of $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC{\equiv}CCO_2Me$ affords several products, one of which, of molecular formula $[Mo_2\{(HC_2H)(MeO_2CC_2CO_2Me)_3\}(\eta\text{-}C_5H_5)_2]$ (1), is here the subject of an *X*-ray diffraction study. Crystals of (1) are triclinic, space group $P\bar{1}$ (no. 2) with $Z = 2$ in a unit cell of dimensions $a = 11.519(7)$, $b = 18.602(9)$, $c = 8.709(3)$ Å, $\alpha = 86.65(4)$, $\beta = 100.99(4)$, $\gamma = 97.54(5)°$, and they encapsulate two molecules of solvent (CH_2Cl_2) per molecule of complex. The structure has been refined to R 0.054 for 3 450 reflections. The acetylenic moieties have joined to form a C_8 chain; within this chain the terminal atoms and the two central atoms are attached to one of the metal atoms, while the first three and the last three form π-allyl attachments to the other metal atom. The $(C_5H_5)Mo{=}Mo(C_5H_5)$ unit and the C_8 chain together form a framework of mirror symmetry, but the molecule as a whole does not possess C_s symmetry because of the methoxycarbonyl ligands which are bonded to C(11), C(12), C(13), C(14), C(17), and C(18). When a similar reaction is carried out with $[Mo_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$ as the starting material, one of the products is again a complex containing a C_8 chain with methoxycarbonyl ligands on all eight carbon atoms, $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (2). An *X*-ray diffraction study of (2) reveals a remarkable difference in the bonding mode. Crystals of (2) are monoclinic, space group $P2_1/c$ (no. 14) with $Z = 4$ in a unit cell of dimensions $a = 14.737(2)$, $b = 11.224(2)$, $c = 23.882(5)$ Å, $\beta = 115.92(1)°$, and the structure has been refined to R 0.088 for 4 897 reflections. The molecule (2) has idealised C_2 symmetry (not crystallographically required), and the C_8 chain forms a 'flyover' from one metal atom to the other. The two groups of four carbon atoms are each planar (and co-planar with the σ-bonded metal atom) and form a diene-type interaction with the other metal atom. A further marked difference from (1) is that the central bond of the C_8 chain, which in (1) is orthogonal to the Mo=Mo link, is in (2) parallel to that direction. The metal–metal distances, 2.618(1) Å in (1) and 2.635(1) Å in (2), are indicative of Mo–Mo double bonding.

In the foregoing paper [1] an account is given of the preparation of alkyne complexes of chromium and molybdenum by the reaction of dimetal species such as $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with alkynes. In particular, reaction of $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC{\equiv}CCO_2Me$ in refluxing octane affords an indigo-coloured mixture which, after chromatography, gives four products. One of these [1] is shown, in the structural study reported in this paper, to comprise a double-bonded $(\eta\text{-}C_5H_5)Mo{=}Mo(\eta\text{-}C_5H_5)$ species bridged by an eight-carbon chain formed by linkage of four alkyne groups, giving an overall molecular formula $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (1). In a similar synthetic investigation with $[Mo_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)]$ as the starting material, five products were obtained of which one (a dark red crystalline material) is here shown to be a species $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (2). The *X*-ray studies reveal a very interesting difference between the two structures investigated. Whereas in (1) the C_8 chain begins and ends with σ bonds to the same Mo atom, and the two central atoms of the chain are also η^2 bonded to this Mo atom, in (2) the chain begins and ends with σ bonds to different molybdenum atoms and the molecule has overall C_2 symmetry. In (1), atoms C(11)—C(13) and C(16)—C(18) of the C_8 chain form allylic moieties η^3 bonded to the same Mo atom, whereas in (2) atoms C(1)—C(4) form a diene-type interaction with Mo(1) while atoms C(5)—C(8) function similarly towards Mo(2). In both structures the terminal atoms, C(11), C(18) for (1) and C(1),C(8) for (2), are bonded to both metal atoms to form a slightly asymmetric bridge. The most characteristic difference is that in (1) the central bond of the C_8 chain [C(14)—C(15)] lies perpendicular to the Mo(1)–Mo(2) vector, while in (2) it lies parallel to this direction. A recent structure determination [2] of $[Mo_2\{\mu\text{-}(CMe)_8\}(\eta\text{-}C_5H_5)_2]$ shows it to be essentially of the same type as (1). A preliminary account of the structure of (1) has appeared earlier.[3] A structure closely similar to that found for (2) has also been reported,[4] for $[Cr_2\{\mu\text{-}(CH)_8\}(\eta\text{-}C_5H_5)_2]$.

RESULTS AND DISCUSSION

Crystal Structure of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (1).—The results of the *X*-ray diffraction study are given in Tables 1 and 2, and an illustration of the molecule, with the crystallographic numbering sequence, is shown in Figure 1. It is seen at once that the C_8 chain is symmetrically related to the two metal atoms, the central two carbon atoms C(14) and C(15) as well as the two terminal atoms C(11) and C(18) being directly bonded to Mo(2), while the two groups of three outer carbon atoms C(11)—C(13) and C(16)—C(18) are all within bonding distance of Mo(1). The two terminal atoms are therefore bound to both metal atoms but are closer to Mo(2) by about 0.15 Å. This is readily appreciated from the stereopair drawing (Figure 2). The binding of the C_8 chain to the Mo_2 fragment can be interpreted as beginning and ending with σ bonds to Mo(2); these are the shorter of the terminal C–Mo interactions. Atoms C(11)—C(13) and C(16)—C(18) are co-ordinated to Mo(1) *via* η^3-allylic interactions, whilst C(14) and C(15) form an η^2-olefinic linkage to Mo(2).

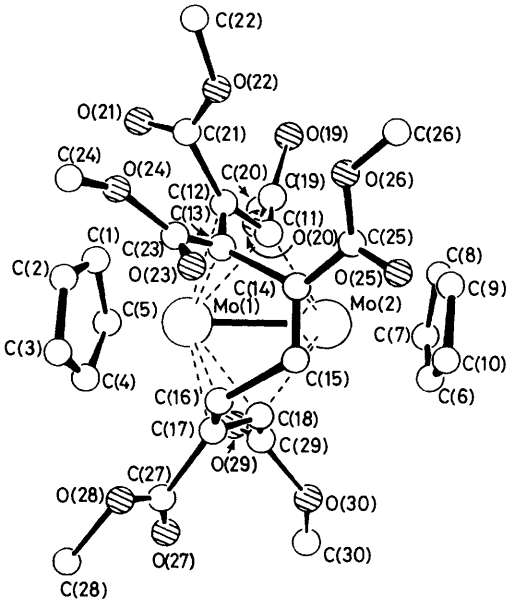

FIGURE 1 Molecular structure of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)\text{-}(HC_2H)(MeO_2CC_2CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (1), showing the crystallographic numbering

This description of the binding requires the $\mu\text{-}C_8H_2(CO_2Me)_6$ moiety to function as a neutral 10-electron donor ligand, thus requiring a formal metal–metal bond order of two by the Effective Atomic Number (EAN) rule; according to this formalism, Mo(1) has 19 valence electrons and Mo(2), 17.

variation and lie in the range appropriate for π-bound C–C bonds [min. 1.403(13), max. 1.442(12), mean 1.424(7) Å].

The cyclopentadienyl rings show no unusual features, being planar and having a mean C–C bond length 1.390(5) Å and mean Mo–C distance 2.352(8) Å. Likewise, the methoxycarbonyl groups show the expected geometry, being planar about the sp^2 carbon and having typical carbon–oxygen bond lengths [mean C=O 1.196(4), mean C–O(Me) 1.330(5), mean O–CH_3 1.442(5) Å]. The Mo–Mo distance [2.618(1) Å] reflects the formal double-bond character [5] and falls within the range of values observed for other Mo=Mo species: *e.g.* $[Mo_2(\mu\text{-}C_2Ph_2)(\mu\text{-}C_5Ph_4O)(\eta^4\text{-}C_4Ph_4)(CO)_3]$, Mo=Mo 2.772(4) Å; [6] $[Mo_2(\mu\text{-}SBu^t)_2(CO)_2(\eta\text{-}C_5H_5)_2]$, Mo=Mo 2.616(2) Å; [7] $[Mo_2(OPr^i)_8]$, Mo=Mo 2.523(1) Å; [8] $[Mo_2(\mu\text{-}CO)(\mu\text{-}OBu^t)_2(OBu^t)_4]$, Mo=Mo 2.498(1) Å; [9] $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}(MeC_2Me)_4\}]$, Mo=Mo 2.595(1) Å; [2] $[Mo_2H(\eta\text{-}C_5H_5)_2\{\mu\text{-}(MeC_2Me)_4\}]^+$, Mo=Mo 2.614(1) Å; [2] $[Mo_2(\eta\text{-}C_5H_5)\{\mu\text{-}(Bu^tC_2H)_4\}]$, Mo=Mo 2.635(1) Å.[10] These last three values reflect the extraordinary stability of this $Mo_2(\mu\text{-}C_8)(\eta\text{-}C_5H_5)_2$ unit, preserving its integrity and showing almost negligible changes in geometry despite the widely differing bulk, electronegativity, and charge of the substituents. The geometry of this core shows near-perfect (though non-crystallographic) mirror symmetry, the plane being defined by Mo(1), Mo(2) and the midpoint of C(14)–C(15). This symmetry is reflected in the five torsion angles within the C_8 chain, starting from C(11); 34, −115, 2, 118, −32°. The cyclopentadienyl groups are,

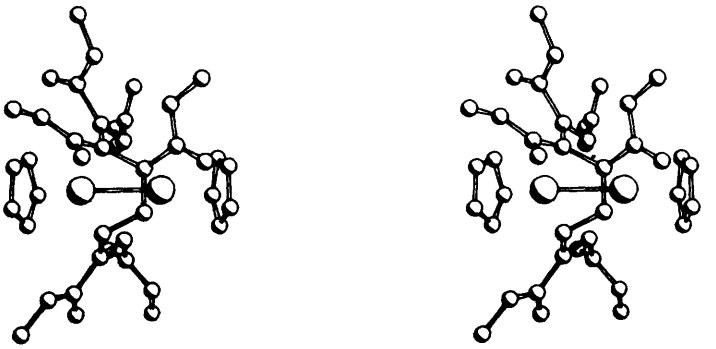

FIGURE 2 Stereoscopic view of the molecular structure of complex (1)

The η^3-allyl type attachments are significantly asymmetric, the terminal C–Mo(1) distances being shorter (mean 2.23_4 Å) than the other pairs of C–Mo(1) distances [formed by C(16), C(17), C(12), and C(13), mean 2.33_3 Å]. The η^2 interaction between C(14)–C(15) and Mo(2) has a mean C–Mo distance of 2.21_9 Å. The bond lengths within the C_8 chain are consistent with the formal description of its bonding given above. The two bonds linking allylic and olefinic fragments show the longest C–C distances within the chain [C(13)–C(14) 1.507(11), C(15)–C(16) 1.505(13) Å *]; these distances are appropriate for sp^2–sp^2 C–C single bonds as indicated by the six C–C(O_2Me) bonds [mean 1.500(6) Å]. The remaining five C–C distances within the chain show no significant however, tilted slightly differently with respect to the Mo(1)–Mo(2) axis, the angles between this axis and the ring normals being 22° for C(1)—C(5) and 11° for C(6)—C(10). The complex (1) crystallises from dichloromethane–hexane solution with two molecules of CH_2Cl_2 per molecule of complex incorporated within the crystal structure. These solvent molecules show a mean C–Cl

* Here and throughout this paper, numbers in parentheses are estimated standard deviations in the reported parameter values. For single values these estimates are derived from least-squares refinements; when the value is the mean of n measurements (where $n \geqslant 5$) the standard deviation s is estimated externally by the formula $s = \left[\sum_{i=1,n} (x_i - \bar{x})^2/n(n-1)\right]^{\frac{1}{2}}$.

TABLE 1

Atomic positional parameters (fractional cell co-ordinates) for $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ (1) *

Atom	x	y	z
Mo(1)	0.198 2(1)	0.191 8(1)	−0.016 3(1)
Mo(2)	0.419 5(1)	0.182 6(1)	0.118 3(1)
C(1)	0.082 7(10)	0.178 8(6)	−0.266 1(12)
C(2)	0.033 4(10)	0.229 1(6)	−0.190 5(14)
C(3)	−0.010 4(10)	0.191 9(7)	−0.067 3(13)
C(4)	0.015 8(10)	0.120 0(7)	−0.065 9(13)
C(5)	0.073 0(10)	0.113 0(6)	−0.187 3(12)
C(6)	0.550 7(9)	0.111 0(6)	0.285 6(12)
C(7)	0.566 3(10)	0.103 2(6)	0.132 2(13)
C(8)	0.612 1(10)	0.169 9(7)	0.072 5(13)
C(9)	0.625 7(9)	0.219 3(6)	0.192 7(15)
C(10)	0.589 9(10)	0.183 2(6)	0.322 3(12)
C(11)	0.364 9(9)	0.217 2(5)	−0.112 9(10)
C(12)	0.315 0(8)	0.282 8(5)	−0.134 7(9)
C(13)	0.295 3(8)	0.310 0(4)	0.007 7(10)
C(14)	0.386 4(8)	0.295 5(5)	0.151 3(10)
C(15)	0.346 3(9)	0.249 2(5)	0.270 3(10)
C(16)	0.215 5(8)	0.221 6(5)	0.243 9(9)
C(17)	0.188 9(8)	0.143 9(5)	0.234 7(9)
C(18)	0.273 5(8)	0.112 3(5)	0.167 6(9)
C(19)	0.393 8(9)	0.183 2(5)	−0.250 0(9)
C(20)	0.366 2(11)	0.075 8(5)	−0.391 0(12)
C(21)	0.288 5(10)	0.322 0(5)	−0.294 3(11)
C(22)	0.354 1(12)	0.425 1(6)	−0.438 3(12)
C(23)	0.224 5(9)	0.370 9(5)	0.017 7(12)
C(24)	0.089 0(12)	0.446 4(6)	−0.117 3(15)
C(25)	0.491 2(9)	0.351 3(5)	0.192 5(11)
C(26)	0.614 0(11)	0.448 8(6)	0.098 6(14)
C(27)	0.081 4(9)	0.102 5(5)	0.284 6(10)
C(28)	−0.100 6(11)	0.107 9(7)	0.362 9(15)
C(29)	0.262 1(9)	0.031 7(5)	0.152 5(10)
C(30)	0.285 9(11)	−0.079 7(5)	0.288 2(13)
C(31)	0.653 6(13)	0.347 8(6)	−0.307 3(17)
C(32)	−0.004 1(19)	0.357 4(13)	0.345 2(20)
O(19)	0.452 4(8)	0.213 5(4)	−0.339 6(8)
O(20)	0.353 0(7)	0.113 1(3)	−0.256 7(7)
O(21)	0.222 6(8)	0.300 3(4)	−0.407 2(8)
O(22)	0.360 3(7)	0.383 7(3)	−0.291 7(7)
O(23)	0.227 9(7)	0.400 6(4)	0.137 8(8)
O(24)	0.157 9(7)	0.388 3(4)	−0.118 7(8)
O(25)	0.548 9(7)	0.360 3(4)	0.321 6(8)
O(26)	0.513 4(6)	0.392 6(8)	0.068 1(7)
O(27)	0.067 1(7)	0.037 7(4)	0.295 7(9)
O(28)	0.007 5(7)	0.145 1(4)	0.317 4(8)
O(29)	0.224 1(7)	−0.001 2(3)	0.035 1(7)
O(30)	0.306 2(6)	−0.001 7(3)	0.288 3(7)
Cl(1)	0.718 2(4)	0.436 1(2)	−0.274 5(5)
Cl(2)	0.750 1(4)	0.284 2(2)	−0.247 9(6)
Cl(3)	−0.086 8(4)	0.336 9(3)	0.167 6(6)
Cl(4)	−0.065 2(8)	0.397 0(5)	0.465 6(7)

* Estimated standard deviations are in parentheses in Tables 1—4.

distance of 1.69(2) Å and a mean Cl–C–Cl angle of 116(1)°. The packing of the molecules within the triclinic unit cell is shown in Figure 3.

Finally, it should be noted that the two carbon atoms of the C_8 chain with H substituents remain adjacent to one another in (1). These are presumably derived from the acetylenic bridge in the parent molecule $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ (3). There is therefore no structural evidence for cleavage of the C–C bond present in (3) and no requirement that mechanisms postulated to explain acetylene oligomerisation on (3) should involve such bond cleavage.

TABLE 2

Bond distances (Å) and angles (°) for (1)

(*i*) Distances

(*a*) Metal atoms and C_8 chain

Mo(1)–Mo(2)	2.618(1)		
Mo(1)–C(11)	2.225(10)	Mo(1)–C(18)	2.243(8)
Mo(1)–C(12)	2.339(9)	Mo(1)–C(17)	2.327(8)
Mo(1)–C(13)	2.335(8)	Mo(1)–C(16)	2.330(8)
Mo(2)–C(11)	2.082(8)	Mo(2)–C(18)	2.088(9)
Mo(2)–C(14)	2.227(9)	Mo(2)–C(15)	2.211(10)
C(11)–C(12)	1.403(13)	C(18)–C(17)	1.429(14)
C(12)–C(13)	1.434(13)	C(17)–C(16)	1.442(12)
C(13)–C(14)	1.507(11)	C(16)–C(15)	1.505(13)
C(14)–C(15)	1.414(12)		

(*b*) Carboxylate groups

C(11)–C(19)	1.494(14)	C(19)–O(19)	1.197(13)
C(12)–C(21)	1.528(12)	C(21)–O(21)	1.178(11)
C(13)–C(23)	1.496(14)	C(23)–O(23)	1.203(13)
C(14)–C(25)	1.488(12)	C(25)–O(25)	1.200(11)

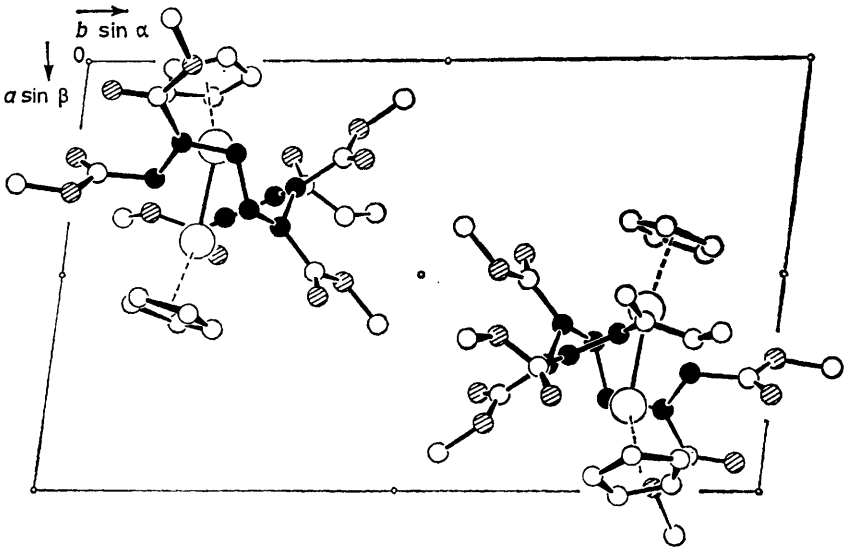

FIGURE 3 Contents of the triclinic cell (excluding solvent) for complex (1), seen in projection down *c* looking towards the origin

TABLE 2 (*continued*)

(*b*) Carboxylate groups (*continued*)

C(17)–C(27)	1.494(14)	C(27)–O(27)	1.196(12)
C(18)–C(29)	1.499(13)	C(29)–O(29)	1.202(11)
C(19)–O(20)	1.328(11)	O(20)–C(20)	1.436(13)
C(21)–O(22)	1.322(11)	O(22)–C(22)	1.447(12)
C(23)–O(24)	1.334(12)	O(24)–C(24)	1.423(16)
C(25)–O(26)	1.337(11)	O(26)–C(26)	1.450(13)
C(27)–O(28)	1.315(14)	O(28)–C(28)	1.455(14)
C(29)–O(30)	1.345(10)	O(30)–C(30)	1.441(11)

(*c*) Cyclopentadienyl ligands

Mo(1)–C(1)	2.332(10)	C(1)–C(2)	1.409(18)
Mo(1)–C(2)	2.348(11)	C(2)–C(3)	1.383(17)
Mo(1)–C(3)	2.359(11)	C(3)–C(4)	1.409(19)
Mo(1)–C(4)	2.316(11)	C(4)–C(5)	1.368(18)
Mo(1)–C(5)	2.307(10)	C(5)–C(1)	1.369(15)
Mo(2)–C(6)	2.375(10)	C(6)–C(7)	1.399(16)
Mo(2)–C(7)	2.369(12)	C(7)–C(8)	1.395(16)
Mo(2)–C(8)	2.371(12)	C(8)–C(9)	1.395(16)
Mo(2)–C(9)	2.359(10)	C(9)–C(10)	1.383(16)
Mo(2)–C(10)	2.382(10)	C(10)–C(6)	1.394(15)

(*d*) Solvent

C(31)–Cl(1)	1.727(12)	C(32)–Cl(3)	1.690(18)
C(31)–Cl(2)	1.720(15)	C(32)–Cl(4)	1.627(25)

(*ii*) Angles

(*a*) Metal atoms and C_8 chain

C(11)–Mo(1)–C(18)	94.5(3)	C(12)–Mo(1)–C(17)	137.8(3)
C(11)–Mo(2)–C(18)	103.8(3)	C(13)–Mo(1)–C(16)	73.1(3)
Mo(1)–Mo(2)–C(14,15) *	93.6(3)	Mo(1)–C(11)–Mo(2)	74.8(3)
		Mo(1)–C(18)–Mo(2)	74.3(3)
C(11)–C(12)–C(13)	113.3(7)	C(18)–C(17)–C(16)	112.6(8)
C(12)–C(13)–C(14)	115.3(8)	C(17)–C(16)–C(15)	114.5(8)
C(13)–C(14)–C(15)	117.0(8)	C(16)–C(15)–C(14)	116.7(7)

(*b*) Carboxylate groups

C(11)–C(12)–C(21)	122.9(8)	C(12)–C(13)–C(23)	125.2(8)
C(13)–C(12)–C(21)	123.8(8)	C(14)–C(13)–C(23)	115.7(8)
C(21)–C(21)–O(21)	127.3(9)	C(13)–C(23)–O(23)	122.8(9)
C(12)–C(21)–O(22)	108.7(7)	C(13)–C(23)–O(24)	113.3(9)
C(21)–O(22)–C(22)	116.1(7)	C(23)–O(24)–C(24)	116.1(9)
C(13)–C(14)–C(25)	117.8(7)	C(16)–C(17)–C(27)	122.7(9)
C(15)–C(14)–C(25)	119.7(7)	C(18)–C(17)–C(27)	124.6(8)
C(14)–C(25)–O(25)	125.2(9)	C(17)–C(27)–O(27)	122.6(10)
C(14)–C(25)–O(26)	112.0(7)	C(17)–C(27)–O(28)	112.6(8)
C(25)–O(26)–C(26)	115.4(7)	C(27)–O(28)–C(28)	115.2(8)
C(12)–C(11)–C(19)	119.5(7)	C(17)–C(18)–C(29)	120.2(8)
C(11)–C(19)–O(19)	125.0(9)	C(18)–C(29)–O(29)	126.4(8)
C(11)–C(19)–O(20)	112.1(8)	C(18)–C(29)–O(30)	111.6(7)
C(19)–O(20)–C(20)	117.2(8)	C(29)–O(30)–C(30)	114.8(7)

(*c*) Cyclopentadienyl ligands

C(1)–C(2)–C(3)	107.0(11)	C(6)–C(7)–C(8)	109.5(10)
C(2)–C(3)–C(4)	107.3(11)	C(7)–C(8)–C(9)	106.2(10)
C(3)–C(4)–C(5)	108.9(10)	C(8)–C(9)–C(10)	108.9(10)
C(4)–C(5)–C(1)	107.9(11)	C(9)–C(10)–C(6)	108.5(10)
C(5)–C(1)–C(2)	109.0(10)	C(10)–C(6)–C(7)	106.9(9)

(*d*) Solvent

Cl(1)–C(31)–Cl(2)	113.7(8)	Cl(3)–C(32)–Cl(4)	117.8(14)

* C(*x*,*y*) is the midpoint of the line joining C(*x*) to C(*y*).

Crystal Structure of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (2).—The molecular configuration of (2), with the crystallographic numbering sequence, is given in Figure 4, and a stereopair drawing in Figure 5. The atom coordinates are in Table 3; bond lengths and angles in Table 4. The structure is notably different from that of (1). Again we have a C_8 chain, here with every carbon atom carrying a CO_2Me group, but now the chain begins with a σ attachment to Mo(2) while the first four carbon atoms of the chain form a diene-type interaction with Mo(1), and this pattern is repeated in converse manner for the other half of the chain. The C_8 chain thus forms a 'fly-over' between Mo(2) and Mo(1); indeed, the entire molecule possesses (non-crystallographic) C_2 symmetry about an axis passing through the midpoints of Mo(1)–Mo(2) and C(4)–C(5). In contradistinction to

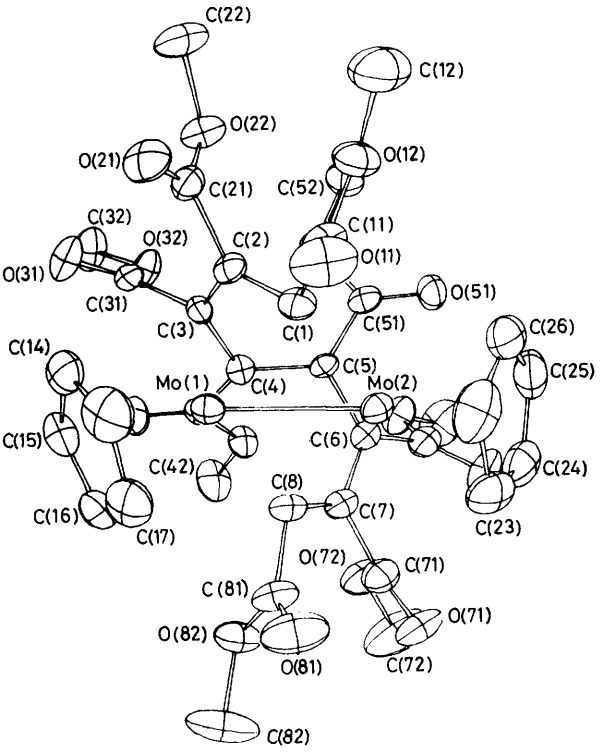

FIGURE 4 Molecular structure of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (2), showing the crystallographic numbering

(1), the central bond C(4)–C(5) of the C_8 chain in (2) lies almost parallel to the metal–metal bond. The terminal atoms of the chain, C(1) and C(8), are bonded to both molybdenum atoms, and the difference between the lengths of the two bridge bonds is only *ca.* 0.03 Å (Table 4). The diene fragments of the chain C(1)—C(4) and C(5)—C(8) are each planar, with C–C bonds essentially equivalent at 1.42 Å and with a mean Mo–C distance 2.26 Å. Each diene fragment is also essentially coplanar with the molybdenum atom to which it is not π-bonded. The central link of the chain, C(4)–C(5), is notably longer than the other bonds, at 1.47 Å; it links the two planar sections at a dihedral angle of 105°.

These structural characteristics are therefore consistent with the μ-C_8 fly-over chain acting as a neutral 10-electron donor ligand and hence, as for (1), the Mo–Mo bond order in (2) is given to be two by the EAN rule. The differing modes of the C_8 chain in (1) and (2) might be summarised as $\eta^1,\eta^3,\eta^2,\eta^3,\eta^1$ and $\eta^1,\eta^4,\eta^4,\eta^1$ respectively. As in complex (1), the Mo–Mo distance [2.635(1) Å] is consistent with this formalism, and the mean C–C distance within the π-bound dienoid fragments of the

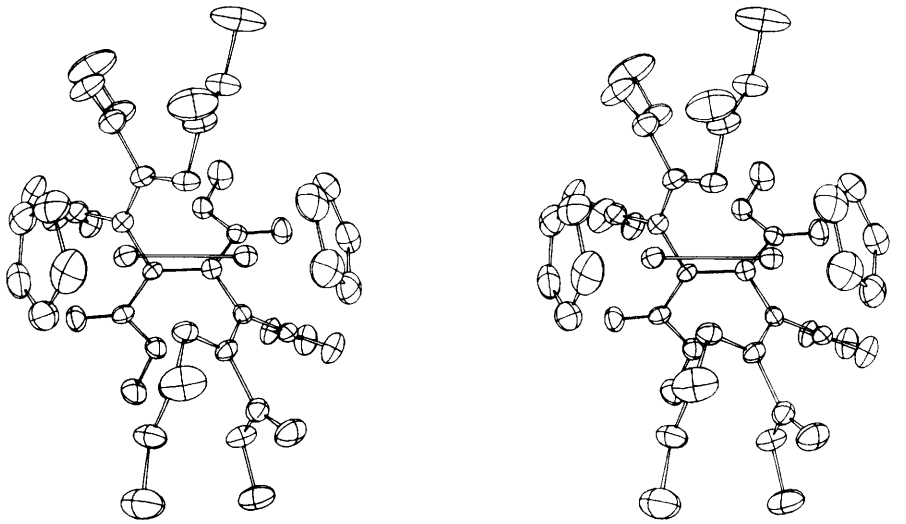

FIGURE 5 Stereoscopic view of the molecular structure of complex (2)

chain is typical [C–C 1.424(5) Å]. Likewise, the methoxycarbonyl groups are planar and show similar geometric parameters to those in (1): mean C–C(chain) 1.499(5), mean C=O 1.197(3), mean C–O(Me) 1.337(3), mean O–CH_3 1.448(4) Å.

Complex (2) is structurally related to $[Cr_2\{\mu\text{-}(CH)_8\}(\eta\text{-}C_5H_5)_2]$ which also has an eight-carbon fly-over leading to a formal metal–metal bond order of two. In the case of the chromium compound it was noted that there was no build up of electron density, as revealed by X–X′ Fourier maps, between the metals either along or near the M–M axis. This observation leads to the conclusion that electron pairing in the M–M double bond of the diamagnetic molecule $[Cr_2\{\mu\text{-}(CH)_8\}(\eta\text{-}C_5H_5)_2]$ does not lead to localised charge-density peaks, as has been frequently noted in the case of, for example, bonds between first-row elements. However, in this regard, it should be noted that the Mo=Mo double bond [2.635(1) Å] in (2) is actually *shorter* than the Cr=Cr double bond [2.656(1) Å] in $[Cr_2\{\mu\text{-}(CH)_8\}(\eta\text{-}C_5H_5)_2]$. This might be taken to imply a stronger, more localised M–M interaction in (2) than in the formally analogous chromium complex.

The cyclopentadienyl rings are in a *cis* configuration and are much more sharply inclined to the metal–metal axis than in (1), the dihedral angle between them being 64°. The CO_2Me groups are of course individually planar and conform in their orientations to the molecular C_2 symmetry. All this is readily seen from the stereo-pair drawing (Figure 5), while the packing of the molecules within the unit cell is shown in Figure 6.

TABLE 3

Atomic positional parameters (fractional cell co-ordinates) for $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (2)

	x	*y*	*z*
Mo(1)	0.196 2(1)	0.250 1(1)	0.544 7(1)
Mo(2)	0.247 7(1)	0.116 9(1)	0.472 4(1)
C(1)	0.333 5(5)	0.145 8(6)	0.570 2(3)
C(2)	0.368 7(5)	0.255 3(7)	0.601 8(3)
C(3)	0.330 6(5)	0.367 8(6)	0.572 8(3)
C(4)	0.277 6(5)	0.377 9(6)	0.507 0(3)
C(5)	0.310 7(5)	0.303 6(6)	0.468 9(3)
C(6)	0.236 1(5)	0.267 8(6)	0.408 2(3)
C(7)	0.135 3(5)	0.242 2(6)	0.398 2(3)
C(8)	0.108 7(5)	0.217 8(6)	0.446 8(3)
C(13)	0.146 4(7)	0.184 7(9)	0.619 2(4)
C(14)	0.186 9(7)	0.298 6(8)	0.637 7(4)
C(15)	0.123 0(6)	0.379 8(8)	0.591 8(4)
C(16)	0.045 9(6)	0.315 2(9)	0.545 6(4)
C(17)	0.061 3(7)	0.194 4(9)	0.563 1(4)
C(23)	0.173 0(7)	−0.059 1(7)	0.423 7(4)
C(24)	0.224 9(7)	−0.015 2(7)	0.391 5(4)
C(25)	0.327 7(7)	−0.015 4(7)	0.430 8(4)
C(26)	0.340 9(7)	−0.060 7(7)	0.488 4(4)
C(27)	0.244 9(8)	−0.087 0(6)	0.485 7(4)
C(11)	0.379 2(6)	0.039 9(7)	0.612 8(3)
O(11)	0.335 4(4)	−0.036 8(5)	0.626 0(3)
O(12)	0.479 8(4)	0.041 7(4)	0.632 2(2)
C(12)	0.537 9(7)	−0.044 5(8)	0.679 8(4)
C(21)	0.439 9(5)	0.252 7(7)	0.670 2(3)
O(21)	0.426 9(4)	0.205 8(5)	0.710 6(2)
O(22)	0.525 1(4)	0.307 2(5)	0.677 5(2)
C(22)	0.610 4(7)	0.294 3(9)	0.738 4(4)
C(31)	0.358 3(5)	0.476 1(6)	0.614 7(3)
O(31)	0.350 6(4)	0.486 5(5)	0.662 6(2)
O(32)	0.398 1(4)	0.557 4(4)	0.592 0(2)
C(32)	0.417 6(8)	0.674 2(7)	0.622 4(4)
C(41)	0.219 4(5)	0.489 2(6)	0.482 2(3)
O(41)	0.190 8(4)	0.556 9(4)	0.510 4(2)
O(42)	0.200 0(4)	0.506 6(4)	0.422 5(2)
C(42)	0.137 6(8)	0.606 8(8)	0.390 4(4)
C(51)	0.416 8(5)	0.297 0(6)	0.478 9(3)
O(51)	0.448 8(4)	0.236 4(5)	0.450 2(2)
O(52)	0.475 9(4)	0.365 5(4)	0.527 5(2)
C(52)	0.582 7(6)	0.360 4(8)	0.546 8(4)
C(61)	0.257 2(6)	0.269 7(6)	0.352 2(3)
O(61)	0.235 6(5)	0.195 1(5)	0.313 1(2)
O(62)	0.298 5(4)	0.373 7(5)	0.349 3(2)
C(62)	0.314 4(9)	0.393 4(10)	0.294 6(4)
C(71)	0.058 9(6)	0.224 3(7)	0.331 5(3)
O(71)	0.008 3(4)	0.138 2(5)	0.310 0(2)
O(72)	0.052 5(4)	0.324 5(5)	0.300 2(2)
C(72)	−0.012 3(11)	0.321 7(11)	0.233 8(4)
C(81)	0.001 8(6)	0.179 9(7)	0.424 8(3)
O(81)	−0.028 4(5)	0.084 5(5)	0.431 9(3)
O(82)	−0.060 5(4)	0.269 8(5)	0.395 8(2)
C(82)	−0.167 0(6)	0.245 0(12)	0.370 0(6)

TABLE 4

Bond distances (Å) and angles (°) for (2)

(*i*) Distances

(*a*) Metal atoms and C_8 chain

Mo(1)–Mo(2)	2.635(1)		
Mo(1)–C(1)	2.182(7)	Mo(2)–C(8)	2.181(7)
Mo(1)–C(2)	2.302(6)	Mo(2)–C(7)	2.301(6)
Mo(1)–C(3)	2.227(7)	Mo(2)–C(6)	2.241(7)
Mo(1)–C(4)	2.291(8)	Mo(2)–C(5)	2.309(7)
Mo(1)–C(8)	2.152(7)	Mo(2)–C(1)	2.140(7)
C(1)–C(2)	1.418(10)	C(8)–C(7)	1.404(12)
C(2)–C(3)	1.431(10)	C(7)–C(6)	1.428(11)
C(3)–C(4)	1.420(9)	C(6)–C(5)	1.441(8)
C(4)–C(5)	1.467(11)		

(*b*) Carboxylate groups

C(1)–C(11)	1.516(10)	C(11)–O(11)	1.198(11)
C(2)–C(21)	1.507(8)	C(21)–O(21)	1.186(10)
C(3)–C(31)	1.514(10)	C(31)–O(31)	1.202(11)
C(4)–C(41)	1.485(9)	C(41)–O(41)	1.206(10)
C(5)–C(51)	1.477(11)	C(51)–O(51)	1.200(10)
C(6)–C(61)	1.498(12)	C(61)–O(61)	1.190(9)
C(7)–C(71)	1.509(9)	C(71)–O(71)	1.191(10)
C(8)–C(81)	1.489(11)	C(81)–O(81)	1.199(11)
C(11)–O(12)	1.346(10)	O(12)–C(12)	1.453(10)
C(21)–O(22)	1.339(10)	O(22)–C(22)	1.455(8)
C(31)–O(32)	1.322(10)	O(32)–C(32)	1.465(9)
C(41)–O(42)	1.339(9)	O(42)–C(42)	1.443(10)
C(51)–O(52)	1.346(7)	O(52)–C(52)	1.435(9)
C(61)–O(62)	1.333(10)	O(62)–C(62)	1.441(14)
C(71)–O(72)	1.331(10)	O(72)–C(72)	1.451(10)
C(81)–O(82)	1.337(9)	O(82)–C(82)	1.440(10)

(*c*) Cyclopentadienyl ligands

Mo(1)–C(13)	2.320(12)	C(13)–C(14)	1.397(13)
Mo(1)–C(14)	2.347(10)	C(14)–C(15)	1.419(11)
Mo(1)–C(15)	2.368(10)	C(15)–C(16)	1.392(11)
Mo(1)–C(16)	2.340(10)	C(16)–C(17)	1.407(14)
Mo(1)–C(17)	2.301(12)	C(17)–C(13)	1.384(11)
Mo(2)–C(23)	2.313(7)	C(23)–C(24)	1.391(16)
Mo(2)–C(24)	2.341(9)	C(24)–C(25)	1.390(12)
Mo(2)–C(25)	2.368(11)	C(25)–C(26)	1.397(15)
Mo(2)–C(26)	2.355(9)	C(26)–C(27)	1.419(17)
Mo(2)–C(27)	2.313(7)	C(27)–C(23)	1.430(11)

(*ii*) Angles

(*a*) Metal atoms and C_8 chain

C(1)–Mo(1)–C(8)	104.8(3)	Mo(1)–C(1)–Mo(2)	75.1(2)
C(1)–Mo(2)–C(8)	105.2(3)	Mo(1)–C(8)–Mo(2)	74.9(2)
C(1)–C(2)–C(3)	122.2(5)	C(8)–C(7)–C(6)	123.2(5)
C(2)–C(3)–C(4)	121.0(6)	C(7)–C(6)–C(5)	120.3(7)
C(3)–C(4)–C(5)	118.1(6)	C(6)–C(5)–C(4)	118.0(6)

(*b*) Carboxylate groups

C(1)–C(2)–C(21)	118.6(6)	C(8)–C(7)–C(71)	119.8(7)
C(3)–C(2)–C(21)	118.8(6)	C(6)–C(7)–C(71)	116.4(7)
C(2)–C(21)–O(21)	127.4(7)	C(7)–C(71)–O(71)	127.0(7)
C(2)–C(21)–O(22)	107.5(6)	C(7)–C(71)–O(72)	108.5(6)
C(21)–O(22)–C(22)	115.8(7)	C(71)–O(72)–C(72)	116.6(7)
C(2)–C(3)–C(31)	116.9(5)	C(7)–C(6)–C(61)	117.4(5)
C(4)–C(3)–C(31)	121.8(6)	C(5)–C(6)–C(61)	121.9(7)
C(3)–C(31)–O(31)	126.6(7)	C(6)–C(61)–O(61)	127.1(8)
C(3)–C(31)–O(32)	108.7(7)	C(6)–C(61)–O(62)	109.7(6)
C(31)–O(32)–C(32)	116.1(7)	C(61)–O(62)–C(62)	116.2(7)
C(3)–C(4)–C(41)	116.8(6)	C(6)–C(5)–C(51)	115.9(7)
C(5)–C(4)–C(41)	121.4(6)	C(4)–C(5)–C(51)	122.9(5)
C(4)–C(41)–O(41)	126.1(7)	C(5)–C(51)–O(51)	126.1(6)
C(4)–C(41)–O(42)	111.4(7)	C(5)–C(51)–O(52)	110.6(7)
C(41)–O(42)–C(42)	118.0(7)	C(51)–O(52)–C(52)	117.3(7)
C(2)–C(1)–C(11)	111.8(5)	C(7)–C(8)–C(81)	113.5(6)
C(1)–C(11)–O(11)	127.3(7)	C(8)–C(81)–O(81)	127.3(7)
C(1)–C(11)–O(12)	108.6(7)	C(8)–C(81)–O(82)	110.3(7)
C(11)–O(12)–C(12)	116.3(7)	C(81)–O(82)–C(82)	116.6(8)

TABLE 4 (*continued*)

(*c*) Cyclopentadienyl ligands

C(13)–C(14)–C(15)	107.2(8)	C(23)–C(24)–C(25)	109.0(8)
C(14)–C(15)–C(16)	108.3(8)	C(24)–C(25)–C(26)	107.9(10)
C(15)–C(16)–C(17)	107.3(7)	C(25)–C(26)–C(27)	108.9(8)
C(16)–C(17)–C(13)	108.9(8)	C(26)–C(27)–C(23)	105.9(10)
C(17)–C(13)–C(14)	108.3(8)	C(27)–C(23)–C(24)	108.2(9)

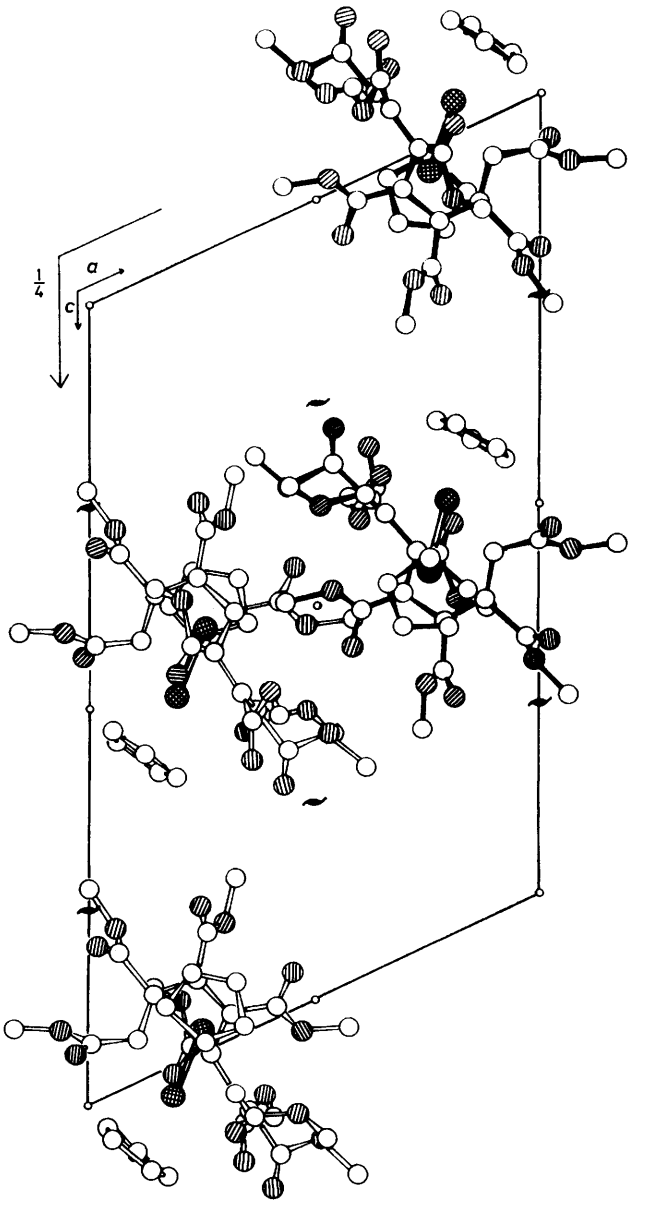

FIGURE 6 Contents of the monoclinic cell for complex (2), seen in projection down *b* looking towards the origin

EXPERIMENTAL

Structure Determination of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ (1).—Complex (1) crystallises as black prisms, elongated along *c*, from dichloromethane–hexane solution; the one chosen for collection of intensity data was of dimensions 0.09 × 0.20 × 0.25 mm. Scan rates were varied between 0.05 and 0.5° s^{-1} according to the magnitude of a preliminary 2-s count in the

range 150 to 1 500 counts. Intensities were collected on a Syntex $P2_1$ four-circle diffractometer to $2\theta = 50°$. Those for three check reflections showed an overall decrease of 27% during the 158 h of crystal exposure to *X*-rays; a correction was made to all measured intensities assuming exponential crystal decay. Correction was also made for Lorentz and polarisation, but not for *X*-ray absorption, effects [μ(Mo-K_α) = 9.4 cm^{-1}]. Refinement was carried out with 3 450 independent intensities for which $I \geqslant 3.0\sigma(I)$.

Crystal Data for (1).—$C_{30}H_{30}Mo_2O_{12}\cdot 2CH_2Cl_2$, M = 944.2, Triclinic, a = 11.519(7), b = 18.602(9), c = 8.709(3) Å, α = 86.65(4), β = 100.99(4), γ = 97.54(5)°, U = 1 815(2) Å^3, D_m = 1.72, Z = 2, D_c = 1.73 g cm^{-3}, $F(000)$ = 948, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 9.4 cm^{-1}.

Structure Solution and Refinement for (1).—The structure was solved by heavy-atom methods except for the hydrogen atom locations. These were calculated using a 'riding' model (C–H 0.95 Å). The structure was refined by blocked full-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms and with a fixed $U_{iso.}$ = 0.05 Å^2 for all hydrogen atoms. Difference syntheses showed clearly the positions of two molecules of CH_2Cl_2 and these were incorporated into the refinement model. Weights were applied according to the scheme $w = 2.170-[\sigma^2(F_o) + 0.004(F_o)^2]^{-1}$ and this gave a satisfactory analysis of variance, $\Sigma w\Delta^2$ *versus* $|F|$, sinθ, and indices. Refinement converged at R 0.054 (R' 0.052), and a final electron-density difference synthesis showed no peaks >1.0 or < -0.6 e Å^{-3}. Atomic scattering factors for hydrogen were taken from ref. 11 and complex neutral-atom scattering factors were used for all other atoms.[12, 13]

Computations were carried out on the South-Western Universities' Network with the SHELX system of programs.[14] Observed and calculated structure factors, all hydrogen atom co-ordinates, and all thermal parameters are listed in Supplementary Publication No. SUP 23187 (51 pp.).*

Structure Determination of $[Mo_2\{\mu\text{-}(MeO_2CC_2CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (2).—Complex (2) is obtained as red-black prisms from dichloromethane–hexane. Intensities were collected from a crystal of dimensions 0.09 × 0.13 × 0.25 mm to $2\theta = 55°$ on a Syntex $P3m$ four-circle diffractometer. Of the 9 371 intensities measured, 4 897 had $I \geqslant 1.5\sigma(I)$ and only these were used in the solution and refinement of the structure. Corrections were made for Lorentz, polarisation, crystal decay, and *X*-ray absorption effects.

Crystal Data for (2).—$C_{34}H_{34}Mo_2O_{16}$, M = 890.0, Monoclinic, a = 14.737(2), b = 11.224(2), c = 23.882(5) Å, β = 115.92(1)°, U = 3 553(1) Å^3, D_m = 1.66, Z = 4, D_c = 1.66 g cm^{-3}, $F(000)$ = 1 800, space group $P2_1/c$ (no. 14), μ(Mo-K_α) = 7.3 cm^{-1}.

Structure Solution and Refinement for (2).—This was as for (1) except that hydrogen atoms were incorporated at calculated positions even though some were detected on electron-density maps; a common isotropic thermal parameter was refined for all cyclopentadienyl H atoms and for all methyl H atoms, keeping the methyl ligands as rigid tetrahedral groups (C–H 0.96 Å, H–C–H 109.5°). A satisfactory analysis of variance was obtained with $w = [\sigma^2(F_o)]^{-1}$. Refinement converged at R 0.088 (R' 0.053), and a final electron-density difference map showed one peak of 1.3 e within 0.2 Å of a molybdenum atom; all other residual features were smaller and none was in a position of chemical significance. Computational details of refinement, scattering factors, and programs were as for (1).

[1/893 *Received*, 2nd *June*, 1981]

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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