Dimolybdenum Complexes derived from Cyclo-octatetraene. Crystal and Molecular Structures of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (Two Isomers) and of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ *

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Reaction of the dimolybdenum compounds $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ or $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with cyclo-octatetraene in octane or heptane at reflux affords a complex mixture from which the species $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ were isolated and characterized. The maroon complex $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1) is stable in non-polar solvents but in polar solvents such as acetone, chloroform, or acetonitrile it transforms to an orange isomer (2). Carbon-13 n.m.r. spectroscopy revealed that (1) possessed mirror symmetry, in contrast to (2), and that in both isomers two carbons of the C_8H_8 ligands did not bear protons. The unprecedented rearrangement of cyclo-octatetraene at a Mo_2 centre and subsequent isomerisation were established by single-crystal *X*-ray diffraction studies on the two isomeric forms (1) and (2). In both structures the central spine of the molecule comprises a $(\eta\text{-}C_5H_5)Mo\text{–}Mo(CO)_2(\eta\text{-}C_5H_5)$ unit of approximate mirror symmetry, the mirror passing through the Mo–Mo bond and bisecting the angle (*ca.* 85°) between the carbonyl ligands (which are both attached to the same Mo atom). The cyclopentadienyl rings are in a *trans* relationship to the metal–metal bond, and the carbonyl ligands bend back towards the centre of the molecule, making the Mo–Mo–CO angle *ca.* 74°. The two isomers differ strikingly, however, in the mode of attachment of the C_8 ring. In both isomers there is η^2 attachment to the $Mo(CO)_2(\eta\text{-}C_5H_5)$ moiety, and η^6 attachment to the other Mo atom through six contiguous carbon atoms of the C_8 ring, the two common carbon atoms being in the form of a symmetrical transverse acetylenic bridge. In isomer (1) the two carbon atoms on either side of the transverse bridge form two π-ethylenic links to the metal atom, whereas in isomer (2) only one carbon atom forms a σ bond on one side of the bridge, and three carbon atoms form a π-allylic attachment on the other side. The remaining two methylenic carbon atoms bend away from the η^6 part of the C_8 ring, which is approximately planar, but in crystals of (1) there is a slight twist which destroys the mirror symmetry of the molecule as a whole. In (2) the entire attachment is asymmetric. Crystals of (1) are monoclinic maroon plates, $a = 8.629(2)$, $b = 39.580(10)$, $c = 15.759(7)$ Å, $\beta = 103.90(3)°$, and (remarkably) with space group $P2_1/c$, $Z = 12$. The three crystallographically distinct molecules are, however, stereochemically identical. The structure has been solved by heavy-atom methods from 4 013 independent intensities $[I \geqslant 2.5\sigma(I)]$ and refined to R 0.073. Crystals of (2) are monoclinic orange ' cubes,' $a = 8.081(4)$, $b = 11.808(9)$, $c = 17.409(15)$ Å, $\beta = 91.94(6)°$, space group $P2_1/n$. The structure has been solved by heavy-atom methods from 4 735 intensities (183 K) and refined to R 0.078. An *X*-ray crystallographic investigation of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3) was also undertaken since n.m.r. studies did not define the structure. The diffraction results revealed that (3) contained a dimeric form of cyclo-octatetraene, in which two ' tub ' form C_8 rings are joined by a single bond. Three carbon atoms of each ring, adjacent to the link bond, are η^3-bonded to an octahedral $Mo(CO)_2(\eta\text{-}C_5H_5)$ moiety, to give the whole molecule C_2 symmetry (crystallographically required). Remarkably, the molecules form a tetragonal unit cell of space group $I4_1cd$ (no. 110), the eight dimeric units occupying a cell of dimensions $a = 19.062(3)$, $c = 14.425(6)$ Å. The structure has been solved by heavy-atom methods from 1 479 independent intensities (298 K) and refined to R 0.040.

WE have recently described [1,2] the synthesis of pentalene complexes of ruthenium *via* dehydrogenative ring closure of cyclo-octatetraene. In an attempt to induce this transformation with another transition metal the reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with cyclo-octatetraene was investigated. No pentalene complexes were obtained, but a unique rearrangement of the tetraene was achieved, and is described herein. Aspects of the work have been reported in a preliminary communication.[3] In the following paper similar studies with other polyolefins are reported.[4]

RESULTS AND DISCUSSION

Heating the compound $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with cyclo-octatetraene in octane (21 h) or heptane (7 d) at reflux produces several complexes, most in very low yield and unidentified. Only two were formed in quantities sufficient for full characterisation. These are $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1) and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3), obtained in *ca.* 20 and 5% yields respectively. It is well known that on heating, $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ loses carbon monoxide to form very reactive $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, containing a metal–metal triple bond,[5,6] and it seemed probable that the tetracarbonyl complex was the active species in the reaction with cyclo-octatetraene. This was confirmed through its observation, by i.r. spectroscopy, during the course of the reaction, and also through treating pure $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with cyclo-octatetraene, when (1), (3), and the unidentified products were formed in yields comparable with those obtained previously.

The nature of complex (1) will be described initially, including its interesting isomerisation, and subsequently compound (3) will be discussed.

The Two Isomers of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$.—Only the maroon crystalline isomer (1) of $[Mo_2(CO)_2(\eta\text{-}$

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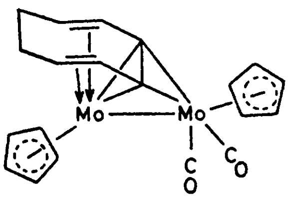
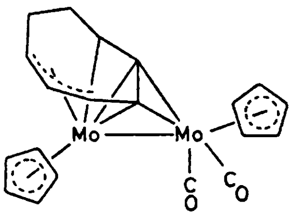
* 1,1-Dicarbonyl-μ-[1′—2′-η:5′—6′-η-cyclo-octa-1′,5′-dien-3′-yne-$C^{3',4'}$(Mo^1)$C^{3',4'}$(Mo^2)$C^{1'-2',5'-6'}$(Mo^2)]-1,2-bis(η-cyclopentadienyl)dimolybdenum(*Mo–Mo*) and 1,1-dicarbonyl-μ-[4′—6′-η-cyclo-oct-5′-en-2′-yne-1′,4′-diyl-$C^{2',3'}$(Mo^1)$C^{2',3'}$(Mo^2)$C^{4'-6'}$(Mo^2)]-1,2-bis(η-cyclopentadienyl)dimolybdenum(*Mo–Mo*); and μ-1—3-η:5—7-η′-(8,8′-bicyclo-octatrienyl)-bis[dicarbonyl(η-cyclopentadienyl)molybdenum].

$C_5H_5)_2(C_8H_8)]$ is produced in the reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with cyclo-octatetraene. It is stable in air and in non-polar solvents, but in polar solvents such as acetone, chloroform, acetonitrile *etc.* isomerisation to an orange species $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (2) occurs (see below).



(1)



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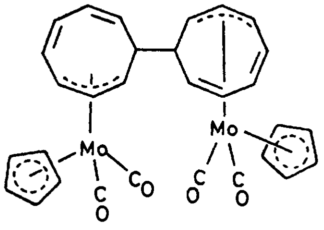

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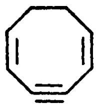
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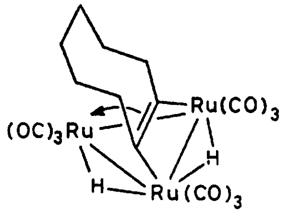

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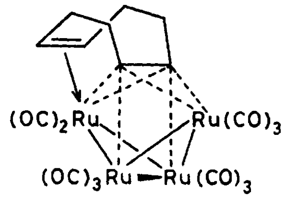

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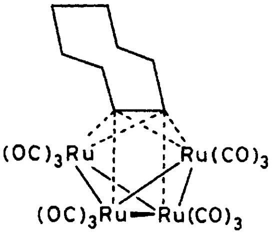

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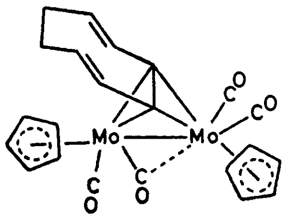

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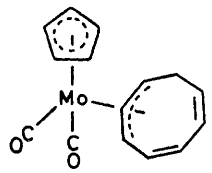

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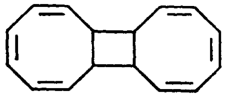

(10)

The two isomers of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ were characterized by elemental analyses and mass spectra, and from their i.r., ^1H and ^{13}C n.m.r. spectra. The mass spectra of (1) and (2) are identical, displaying a molecular ion with isotope pattern characteristic of two molybdenum atoms, and two ions at lower mass corresponding to the loss of two carbonyl groups. The ^{13}C n.m.r. spectra clearly reveal the existence of mirror symmetry for (1) and the lack of any symmetry in (2), in that the eight carbons of the C_8 ring appear as four sharp signals for (1) and eight signals for (2). Moreover, for (1) the lowest field ring-carbon signal (119.1 p.p.m.) has a lower intensity than the other three, while the same is true of the signals at 123.5 and 98.8 p.p.m. for (2). These indications that each isomer contains two carbons which do not bear a proton (hence having low-intensity n.m.r. signals due to the absence of the Nuclear Overhauser Effect) were confirmed when partially proton-decoupled ^{13}C n.m.r. spectra were recorded. With these measurements, the ^{13}C n.m.r. spectrum of (1) showed the signals at δ(p.p.m.) 119.1, 100.5, 65.8, and 35.2 as a singlet, doublet, doublet, and triplet, respectively. The corresponding spectrum of (2) had the ring carbon signals at δ 123.5, 107.9, 98.8, 91.8, 78.1, 59.8, 43.6, and 23.5 as a singlet, doublet, singlet, doublet, doublet, doublet, triplet, and triplet, respectively. The presence of four CH and two CH_2 groups in each of (1) and (2) was thereby also established. In accordance, the ^1H n.m.r. spectra have signals characteristic of four co-ordinated CH and two aliphatic methylene groups.

These data suggested an unprecedented rearrangement of cyclo-octatetraene upon co-ordination, and a unique isomerisation of the new ligand. *X*-Ray diffraction studies were therefore undertaken on both (1) and (2).

The molecular structure of the maroon isomer (1) is shown in Figure 1, with the crystallographic numbering sequence. As there are three crystallographically distinct molecules in the asymmetric unit of the structure ($P2_1/c$ with $Z = 12$; see Experimental section) a system of atom numbering has been adopted whereby the Mo atoms are labelled 1 and 2 for the first molecule, 3 and 4 for the second, and 5 and 6 for the third. In Table 1, which lists the atomic positional parameters, the atom numbers for the cyclopentadienyl rings are prefixed by the number of the Mo atom to which they are attached, and for the C_8 ring the atom numbers are prefixed by the two numbers of the Mo atoms for that molecule. The three molecules are not significantly different from one another, so in Table 2 corresponding bond lengths and angles are listed in three columns for easy comparison using the simple atom numbering scheme of Figure 1.

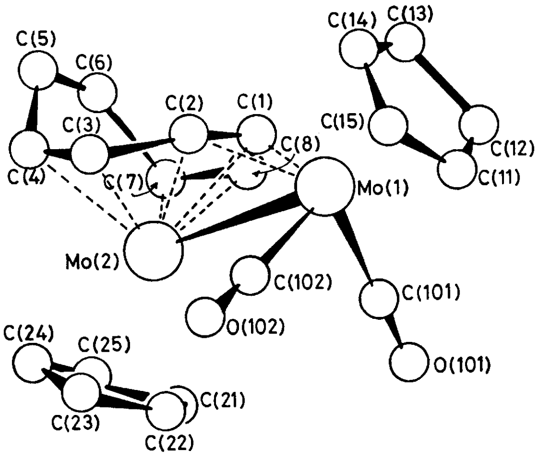


FIGURE 1 Molecular structure of the maroon isomer (1) of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ showing the crystallographic numbering. (The corresponding diagram in the preliminary publication, ref. 3, is incorrectly labelled)

The atom numbers in the C_8 ring for the three molecules listed in Table 1 increase in a clockwise direction when the molecule is viewed with the carbonyl groups pointing away from the observer. The two carbon atoms of the transverse bridge are labelled C(1) and C(2), and the two carbonyl ligands are labelled so that C(01)–O(01) is nearer to C(1), and C(02)–O(02) to C(2).

TABLE 1

Atomic positional parameters (fractional cell co-ordinates) for the maroon isomer of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1), with estimated standard deviations in parentheses

Atom	x	y	z
Molecule (i)			
Mo(1)	0.841 07(22)	0.273 44(5)	0.076 20(11)
Mo(2)	0.561 04(22)	0.228 34(5)	−0.012 99(11)
C(11)	1.099(3)	0.273(1)	0.165(2)
C(12)	1.074(4)	0.305(1)	0.122(2)
C(13)	0.998(4)	0.272(1)	0.220(2)
C(14)	0.953(4)	0.321(1)	0.150(2)
C(15)	0.907(3)	0.302(1)	0.210(2)
C(21)	0.458(3)	0.193(1)	−0.132(2)
C(22)	0.593(3)	0.208(1)	−0.144(2)
C(23)	0.346(4)	0.221(1)	−0.132(2)
C(24)	0.420(4)	0.251(1)	−0.147(2)
C(25)	0.572(3)	0.243(1)	−0.154(2)
C(101)	0.711(3)	0.302(1)	−0.018(2)
O(101)	0.640(3)	0.321(1)	−0.069(1)
C(102)	0.907(3)	0.249(1)	−0.018(2)
O(102)	0.963(2)	0.235(1)	−0.069(1)
C(121)	0.732(3)	0.229(1)	0.113(1)
C(122)	0.631(3)	0.257(1)	0.109(2)
C(123)	0.464(3)	0.262(1)	0.073(2)
C(124)	0.364(3)	0.231(1)	0.061(2)
C(125)	0.388(5)	0.205(1)	0.131(3)
C(126)	0.465(5)	0.175(1)	0.119(3)
C(127)	0.579(3)	0.179(1)	0.063(2)
C(128)	0.721(3)	0.196(1)	0.080(2)
Molecule (ii)			
Mo(3)	0.574 22(26)	0.093 00(5)	0.716 49(14)
Mo(4)	0.863 86(25)	0.076 02(5)	0.864 72(13)
C(31)	0.347(4)	0.095(1)	0.607(2)
C(32)	0.465(5)	0.106(1)	0.570(2)
C(33)	0.524(4)	0.136(1)	0.608(2)
C(34)	0.435(4)	0.143(1)	0.663(2)
C(35)	0.332(4)	0.119(1)	0.665(2)
C(41)	0.934(4)	0.022(1)	0.850(2)
C(42)	0.809(14)	0.021(1)	0.871(2)
C(43)	0.823(3)	0.033(1)	0.956(2)
C(44)	0.975(4)	0.041(1)	0.985(2)
C(45)	1.061(4)	0.037(1)	0.923(2)
C(301)	0.497(3)	0.063(1)	0.804(2)
O(301)	0.437(3)	0.050(1)	0.848(1)
C(302)	0.666(3)	0.050(1)	0.683(2)
O(302)	0.713(3)	0.027(1)	0.655(1)
C(341)	0.804(3)	0.115(1)	0.765(2)
C(342)	0.717(3)	0.120(1)	0.823(2)
C(343)	0.738(3)	0.116(1)	0.915(2)
C(344)	0.899(4)	0.116(1)	0.970(2)
C(345)	1.024(7)	0.139(1)	0.967(4)
C(346)	1.085(5)	0.140(1)	0.899(3)
C(347)	1.080(5)	0.106(1)	0.846(3)
C(348)	0.920(4)	0.102(1)	0.768(2)
Molecule (iii)			
Mo(5)	1.012 31(25)	0.119 30(5)	0.338 69(13)
Mo(6)	0.775 25(27)	0.060 74(5)	0.311 40(13)
C(51)	1.060(4)	0.175(1)	0.374(2)
C(52)	1.207(4)	0.160(1)	0.386(2)
C(53)	1.222(4)	0.149(1)	0.306(2)
C(54)	1.084(4)	0.159(1)	0.244(2)
C(55)	0.988(4)	0.174(4)	0.286(2)
C(61)	0.750(4)	0.042(1)	0.444(2)
C(62)	0.900(4)	0.034(1)	0.440(2)
C(63)	0.901(4)	0.012(1)	0.373(2)
C(64)	0.744(4)	0.005(1)	0.334(2)
C(65)	0.657(4)	0.018(1)	0.378(2)
C(501)	1.151(4)	0.079(8)	0.367(2)
O(501)	1.234(2)	0.056(1)	0.386(2)
C(502)	0.953(3)	0.113(1)	0.450(2)
O(502)	0.924(3)	0.112(1)	0.518(1)
C(561)	0.773(3)	0.114(1)	0.269(1)
C(562)	0.866(4)	0.096(1)	0.229(2)
C(563)	0.861(3)	0.062(1)	0.193(2)
C(564)	0.711(4)	0.046(1)	0.167(2)
C(565)	0.562(5)	0.068(1)	0.118(3)
C(566)	0.446(4)	0.074(1)	0.169(2)
C(567)	0.523(4)	0.081(1)	0.264(2)
C(568)	0.631(3)	0.106(1)	0.299(2)

It is at once clear that the C_8 ring is η^6-bonded to Mo(2) and η^2-bonded to Mo(1), the two common carbon atoms, C(1) and C(2), devoid of hydrogen atoms, forming a symmetrical transverse bridge. Only the methylenic carbon atoms C(5) and C(6) are non-bonded, and these bend away from the other six atoms in a direction *exo* to the metal atoms. The bond lengths and the near planarity (within 0.18 Å) of the η^6 system suggest extensive delocalisation, though the bonding is perhaps most easily described in terms of an acetylenic bridge [C(1) and C(2)] and two symmetrically arranged η^2-olefinic links [C(3), C(4) and C(7), C(8)]. The axis of the molecule, through the centroids of the cyclopentadienyl rings and the two molybdenum atoms, is non-linear, though the $Mo_2(CO)_2(\eta\text{-}C_5H_5)_2$ moiety retains mirror symmetry.

Close examination of the interbond angles, however, reveals that the molecule as a whole does not possess exact mirror symmetry in the crystal. The C(5)–C(6) bond, which joins the two methylene groups in the C_8 ring, is slightly twisted relative to the C(4) · · · C(7) vector so that the C–C–C angles at C(4) and C(7) are not equal. Inspection of Table 2 shows further that the angles at C(4) and C(7) in molecules (i) and (iii), seen in the molecular packing diagram (Figure 2), correspond closely to the angles at C(7) and C(4), respectively, in molecule (ii). On this basis, therefore, molecule (ii) is the enantiomorph of molecules (i) and (iii); but as the space group is centrosymmetric, equal numbers of each enantiomorph are present in the unit cell. The departure from mirror symmetry is in any case slight, and from the n.m.r. evidence the two forms are indistinguishable in solution.

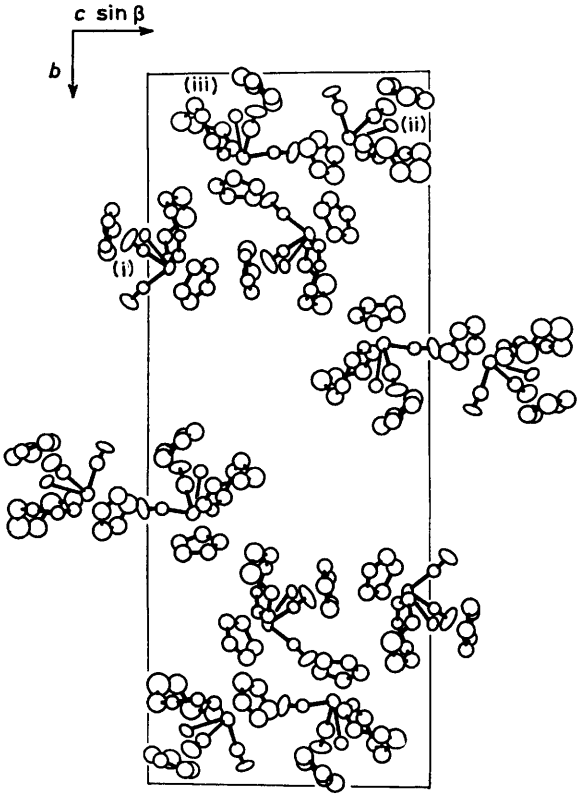


FIGURE 2 Contents of the monoclinic unit cell ($P2_1/c$) of (1), showing the three crystallographically independent molecules which comprise the asymmetric unit

The molecular structure of the orange isomer (2) is shown in Figure 3, with similar atom numbering to that used for (1). Atomic positional parameters for (2) are in Table 3; interatomic distances and angles are given in Table 4. Although there is still η^6 attachment of the C_8 ring to Mo(2), with atoms C(1) and C(2) forming a transverse bridge across the Mo(1)–Mo(2) bond and with η^2 attachment to both metal atoms, it is seen that atoms C(6) and C(7) are now the unattached ones (the methylene groups) and that only C(8) is bonded to Mo(2) on one side of the bridge, while C(3), C(4), and C(5) are bonded on the other side. The ring is therefore much less symmetrically attached than in isomer (1), and the bonding could here be described in terms of an acetylenic bridge with a σ bond on one side [Mo(2)–C(8)] and an η^3-allyl attachment on the other, Mo(2)–C(3—5). As with (1), the crystals of (2) contain equal numbers of enantiomorphous molecules because of the space group symmetry ($P2_1/n$). The packing of the molecules within the monoclinic unit cell is shown in Figure 4.

For both isomers the core of the molecule consists of a $Mo_2(CO)_2(\eta\text{-}C_5H_5)_2$ moiety in which the cyclopentadienyl rings lie *trans* to one another across the Mo–Mo bond, and the two carbonyl ligands are attached to the same metal atom, Mo(1). In both structures the carbonyl

TABLE 2

Bond lengths (Å) and angles (°) for the maroon complex $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1)

	Molecule (i)	Molecule (ii)	Molecule (iii)
(*a*) Distances			
Mo(1)–Mo(2)	3.061(3)	3.058(3)	3.053(3)
Mo(1)–C(1)	2.14(2)	2.12(2)	2.10(2)
Mo(1)–C(2)	2.11(3)	2.11(2)	2.10(3)
Mo(2)–C(1)	2.18(2)	2.16(2)	2.21(2)
Mo(2)–C(2)	2.18(2)	2.14(2)	2.18(3)
Mo(2)–C(3)	2.20(3)	2.17(3)	2.16(3)
Mo(2)–C(4)	2.28(3)	2.25(4)	2.29(3)
Mo(2)–C(7)	2.30(3)	2.28(4)	2.28(3)
Mo(2)–C(8)	2.18(2)	2.16(4)	2.17(3)
Mo(1)–C(101)	1.98(2)	2.05(3)	1.99(3)
Mo(1)–C(102)	1.96(3)	2.00(3)	1.95(3)
C(101)–O(101)	1.19(3)	1.09(4)	1.16(4)
C(102)–O(102)	1.18(3)	1.13(4)	1.17(4)
Mo(1)–C[mean, cp(1)] *	2.33(3)	2.33(3)	2.32(3)
Mo(2)–C[mean, cp(2)]	2.32(3)	2.31(3)	2.31(3)
C(1)–C(2)	1.39(3)	1.33(4)	1.35(4)
C(2)–C(3)	1.43(3)	1.43(4)	1.47(4)
C(3)–C(4)	1.49(4)	1.45(4)	1.40(4)
C(4)–C(5)	1.48(5)	1.42(7)	1.57(5)
C(5)–C(6)	1.41(6)	1.30(8)	1.44(6)
C(6)–C(7)	1.47(6)	1.59(6)	1.51(4)
C(7)–C(8)	1.39(4)	1.41(5)	1.38(4)
C(8)–C(1)	1.42(3)	1.44(4)	1.44(4)
C–C [mean, cp(1)]	1.39(4)	1.34(5)	1.37(5)
C–C [mean, cp(2)]	1.40(4)	1.38(6)	1.37(6)
C(4) · · · C(7)	2.77(4)	2.79(6)	2.85(5)
(*b*) Angles			
Mo(1)–C(1)–Mo(2)	90.5(8)	91.0(10)	90.0(8)
Mo(1)–C(2)–Mo(2)	91.1(10)	91.9(10)	91.0(11)
Mo(1)–Mo(2)–C(1)	44.2(6)	44.0(6)	43.5(6)
Mo(1)–Mo(2)–C(2)	43.5(7)	43.7(6)	43.4(7)
Mo(2)–Mo(1)–C(1)	45.2(5)	45.0(6)	46.5(6)
Mo(2)–Mo(1)–C(2)	45.5(6)	44.5(7)	45.6(9)
Mo(2)–Mo(1)–C(101)	75.0(7)	72.3(7)	76.6(9)
Mo(2)–Mo(1)–C(102)	73.1(7)	73.3(7)	73.3(7)
C(101)–Mo(1)–C(102)	85.4(10)	84.5(12)	87.9(12)
C(1)–Mo(1)–C(101)	117.3(9)	114.5(10)	120.2(11)
C(1)–Mo(1)–C(102)	92.3(10)	92.4(10)	90.9(10)
C(2)–Mo(1)–C(101)	89.4(10)	88.3(10)	92.3(12)
C(2)–Mo(1)–C(102)	117.3(10)	116.2(10)	116.5(11)
Mo(1)–C(101)–O(101)	173.0(20)	170.3(25)	178.2(26)
Mo(1)–C(102)–O(102)	172.7(19)	172.5(26)	172.5(22)
C(8)–C(1)–C(2)	137.1(20)	135.2(24)	133.4(24)
C(1)–C(2)–C(3)	133.4(22)	137.0(23)	134.8(28)
C(2)–C(3)–C(4)	116.0(22)	117.9(28)	117.5(28)
C(3)–C(4)–C(5)	119.9(25)	127.4(35)	119.9(29)
C(4)–C(5)–C(6)	117.7(38)	120.6(47)	114.6(32)
C(5)–C(6)–C(7)	113.9(35)	115.6(42)	112.7(30)
C(6)–C(7)–C(8)	128.1(26)	118.7(33)	129.3(30)
C(7)–C(8)–C(1)	121.2(24)	118.1(32)	124.8(27)
C–C–C [mean, cp(1)]	108.0(24)	108.0(32)	107.9(28)
C–C–C [mean, cp(2)]	108.0(22)	108.0(27)	107.7(33)

* cp = Cyclopentadienyl ring.

groups bend back towards the Mo–Mo bond at a Mo–Mo–C angle of *ca.* 74°, and the plane through the Mo–Mo bond bisecting the carbonyl directions is an approximate mirror plane for the $Mo_2(CO)_2(\eta\text{-}C_5H_5)_2$ moiety. It is interesting that the Mo–Mo bond in (1) appears to be significantly longer [mean 3.057(3) Å] than that in (2) [3.034(1) Å]. In both structures the bond angle between the two carbonyl ligands is less than 90°, presumably because of the effectively high co-ordination number of the molybdenum atom.

TABLE 3

Atomic positional parameters (fractional cell co-ordinates) for the orange isomer of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (2)

Atom	*x*	*y*	*z*
Mo(1)	0.360 53(5)	0.084 52(4)	0.144 00(2)
Mo(2)	0.536 76(5)	0.089 39(4)	0.299 72(3)
C(1)	0.279 7(7)	0.071 2(4)	0.259 8(3)
C(2)	0.329 4(7)	0.181 7(5)	0.246 9(3)
C(3)	0.435 9(8)	0.264 3(5)	0.281 9(3)
H(3)	0.438(9)	0.325(6)	0.250(4)
C(4)	0.488 7(9)	0.254 3(6)	0.360 6(4)
H(4)	0.553(14)	0.300(10)	0.383(7)
C(5)	0.427 1(8)	0.164 4(6)	0.408 0(3)
H(5)	0.506(14)	0.169(9)	0.459(6)
C(6)	0.246 7(8)	0.134 3(6)	0.415 8(4)
H(61)	0.288(17)	0.185(12)	0.425(8)
H(62)	0.190(12)	0.199(8)	0.388(6)
C(7)	0.228 0(8)	0.008 8(6)	0.397 3(4)
H(71)	0.286(9)	−0.031(6)	0.436(4)
H(72)	0.120(9)	−0.008(7)	0.402(4)
C(8)	0.301 9(7)	−0.010 2(5)	0.319 3(3)
H(8)	0.304(11)	−0.085(7)	0.305(5)
C(11)	0.288 9(9)	0.076 7(7)	0.013 0(3)
H(11)	0.198(22)	0.059(14)	−0.007(10)
C(12)	0.178 9(8)	0.004 6(7)	0.051 4(4)
H(12)	0.172(10)	−0.079(6)	0.039(5)
C(13)	0.079 8(8)	0.072 2(7)	0.099 8(4)
H(13)	−0.009(9)	0.055(6)	0.141(4)
C(14)	0.133 0(9)	0.186 1(7)	0.091 6(4)
H(14)	0.106(8)	0.220(6)	0.099(4)
C(15)	0.261 3(9)	0.189 3(7)	0.038 7(4)
H(15)	0.306(9)	0.263(6)	0.038(4)
C(21)	0.768 4(7)	−0.006 6(5)	0.253 4(3)
H(21)	0.803(10)	−0.032(7)	0.214(5)
C(22)	0.699 9(8)	−0.073 8(5)	0.311 8(4)
H(22)	0.681(8)	−0.134(6)	0.301(4)
C(23)	0.713 0(9)	−0.011 6(7)	0.381 4(4)
H(23)	0.656(11)	−0.044(7)	0.425(5)
C(24)	0.789 6(9)	0.094 3(7)	0.366 0(4)
H(24)	0.806(7)	0.139(5)	0.411(4)
C(25)	0.822 4(7)	0.096 4(5)	0.286 2(4)
H(25)	0.871(7)	0.106(5)	0.282(3)
C(01)	0.462 6(7)	−0.067 7(5)	0.156 3(3)
O(01)	0.515 9(7)	−0.157 8(4)	0.157 4(3)
C(02)	0.584 5(7)	0.147 1(6)	0.129 2(3)
O(02)	0.711 1(6)	0.182 3(5)	0.111 3(3)

The structural identification of (1) shows unequivocally that cyclo-octatetraene has undergone a two-hydrogen shift upon reaction with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ to produce cyclo-octa-1,5-dien-3-yne (4) as a ligand. This hydrocarbon, which has only recently been isolated, is highly reactive when uncomplexed and decomposes above its melting point of −15 °C.[7] In chloroform at 27 °C it transforms to cyclo-octatetraene with a half-life of 2 h. Complex (1) therefore provides another of the increasing number of examples of the stabilisation of an unstable hydrocarbon through co-ordination with a transition metal. However, in (1) stabilisation of the ligand occurs at a dimetal centre, as found with pentalene.[1,2]

The probability that (1) is formed through the interaction of cyclo-octatetraene with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ contrasts with observations that the metal–metal triple bond is unreactive towards olefins.[8,9] However, it has recently been shown that $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ also reacts with 3,3-dimethylcyclopropene.[10] The intricacies of hydrogen removal from one double bond of cyclo-octatetraene, to give a μ-alkyne, and hydrogen addition to another are a matter for speculation. However, there is precedent for the transformation in reactions of cyclo-octa-1,5-diene with $[Ru_3(CO)_{12}]$, when the complexes $[Ru_3H_2(CO)_9(C_8H_{12})]$ (5), $[Ru_4(CO)_{11}(C_8H_{10})]$ (6), and $[Ru_4(CO)_{12}(C_8H_{12})]$ (7) are formed.[11] It is well known [12] that $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ does favour μ-alkyne co-ordination, and it seems clear that hydrogen transfer from olefin to metal will be involved. A subsequent intramolecular hydrogenation of the other double bond is plausible, leading to Scheme 1 as a proposal for the formation of (1).

TABLE 4

Bond lengths (Å) and angles (°) for the orange complex $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (2)

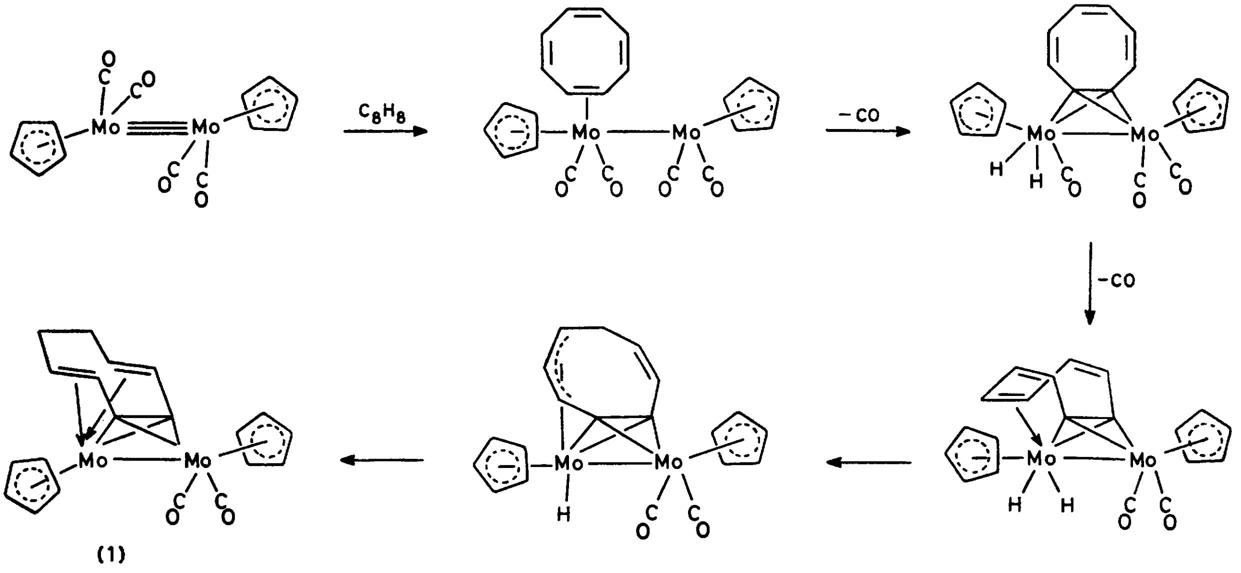
(*a*) Distances

Mo(1)–Mo(2)	3.033 9(6)	Mo(1)–C(11)	2.356(6)
Mo(1)–C(1)	2.164(5)	Mo(1)–C(12)	2.358(7)
Mo(1)–C(2)	2.171(6)	Mo(1)–C(13)	2.391(7)
Mo(2)–C(1)	2.193(5)	Mo(1)–C(14)	2.373(8)
Mo(2)–C(2)	2.193(6)	Mo(1)–C(15)	2.350(7)
Mo(2)–C(3)	2.267(6)	C(11)–C(12)	1.436(10)
Mo(2)–C(4)	2.287(7)	C(12)–C(13)	1.444(10)
Mo(2)–C(5)	2.312(6)	C(13)–C(14)	1.440(12)
Mo(2)–C(8)	2.293(6)	C(14)–C(15)	1.428(10)
C(1)–C(2)	1.405(8)	C(15)–C(11)	1.446(12)
C(2)–C(3)	1.437(8)	Mo(2)–C(21)	2.380(6)
C(3)–C(4)	1.433(9)	Mo(2)–C(22)	2.368(6)
C(4)–C(5)	1.461(10)	Mo(2)–C(23)	2.325(7)
C(5)–C(6)	1.525(10)	Mo(2)–C(24)	2.326(7)
C(6)–C(7)	1.543(10)	Mo(2)–C(25)	2.351(6)
C(7)–C(8)	1.534(9)	C(21)–C(22)	1.433(9)
C(8)–C(1)	1.434(8)	C(22)–C(23)	1.429(10)
Mo(1)–C(01)	2.012(6)	C(23)–C(24)	1.444(11)
Mo(1)–C(02)	2.000(6)	C(24)–C(25)	1.438(10)
C(01)–O(01)	1.163(8)	C(25)–C(21)	1.420(9)
C(02)–O(02)	1.168(8)	C(6)–H(62)	1.02(10)
C(3)–H(3)	1.01(7)	C(7)–H(71)	0.94(7)
C(4)–H(4)	0.84(11)	C(7)–H(72)	0.91(8)
C(5)–H(5)	1.08(11)	C(8)–H(8)	0.93(8)
C(6)–H(61)	0.71(14)	mean cp(1)–H	0.87(7)
C(5) · · · C(8)	2.777(9)	mean cp(2)–H	0.79(8)

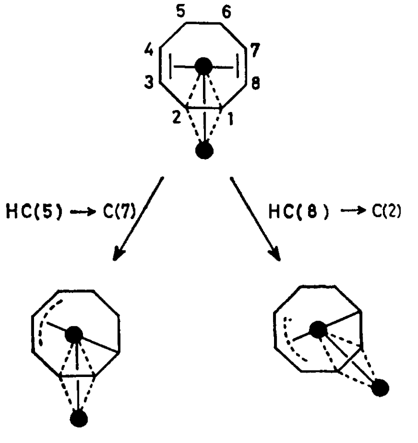
(*b*) Angles

Mo(2)–Mo(1)–C(01)	75.1(2)	C(8)–C(1)–C(2)	136.8(5)
Mo(1)–C(01)–O(01)	174.3(5)	C(1)–C(2)–C(3)	138.8(5)
Mo(2)–Mo(1)–C(02)	73.0(2)	C(2)–C(3)–C(4)	120.4(5)
Mo(2)–C(02)–O(02)	172.0(5)	C(3)–C(4)–C(5)	120.8(6)
C(01)–Mo(1)–C(02)	88.7(3)	C(4)–C(5)–C(6)	125.4(6)
Mo(1)–Mo(2)–C(1)	45.5(1)	C(5)–C(6)–C(7)	107.4(6)
Mo(1)–Mo(2)–C(2)	45.7(1)	C(6)–C(7)–C(8)	107.0(5)
Mo(1)–C(1)–Mo(2)	88.3(2)	C(7)–C(8)–C(1)	120.3(5)
Mo(1)–C(2)–Mo(2)	88.1(2)	C(25)–C(21)–C(22)	108.8(5)
C(15)–C(11)–C(12)	107.7(6)	C(21)–C(22)–C(23)	107.4(6)
C(11)–C(12)–C(13)	108.3(7)	C(22)–C(23)–C(24)	108.5(6)
C(12)–C(13)–C(14)	107.2(6)	C(23)–C(24)–C(25)	107.1(6)
C(13)–C(14)–C(15)	108.8(7)	C(24)–C(25)–C(21)	108.2(6)
C(14)–C(15)–C(11)	107.8(7)		

The reversible transfer of hydrogen from C_8 ring to metal brings us to the isomerisation of (1) into (2) in polar solvents. The *X*-ray diffraction studies of (1) and (2), discussed above, characterise the isomerisation as a hydrogen shift, and the intermediacy of metal hydrides in such rearrangements of metal–hydrocarbon complexes is well established. The shift may occur from C(5) to C(7) or from C(8) to C(2), in either case being a 1,3-shift (Scheme 2). The shift from C(8) to C(2) involves a twist of the C_8 ligand relative to the metal–metal axis, and substantial interference with the μ-alkyne Mo_2 link. On the other hand, that from C(5) to C(7) represents a relatively minor change in ring conformation, and is perhaps favoured by relief of ring strain. For these reasons we favour the latter route to isomerisation. No isomerisation of (1) occurs when it is subjected to u.v. irradiation, but when heated to its melting point in air (2) is formed amid much decomposition.



SCHEME 1



SCHEME 2

Although the maroon isomer (1) is stable in alkane solvents and in benzene or carbon tetrachloride, in nitromethane and acetonitrile the conversion to orange isomer (2) is so rapid as to be complete before an n.m.r. spectrum can be recorded. In chloroform, dichloromethane, and acetone the isomerisation proceeds at rates which allow its monitoring conveniently by n.m.r. spectroscopy. Such monitoring revealed concentration-independent half-lives for the isomerisation of (1) of 31 min in $CDCl_3$, 6 min in CD_2Cl_2, and ranging from 13 min to 22 h in $[^2H_6]$acetone. The half-life in acetone is longest when the solvent has been rigorously dried. The rate of isomerisation, therefore, appears to be largely dependent on the degree of water impurity in the solvent employed. This suggested proton involvement in the process, and addition of a trace of CF_3CO_2H to a solution of (1) in C_6D_6, in which solvent it is otherwise stable, does induce an immediate isomerisation to (2). The effect is a catalytic one. Addition of an excess of CF_3CO_2D to (1) in C_6D_6 afforded (2) containing no deuterium, as shown by ^1H n.m.r. spectroscopy. Neither was deuterium incorporated when the isomerisation was

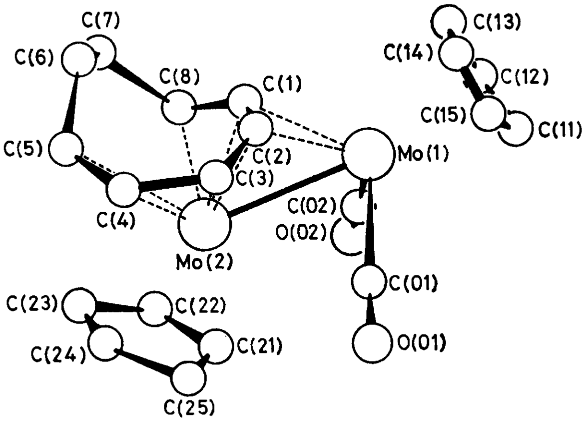


FIGURE 3 Molecular structure of the orange isomer (2) of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$; the numbering follows the same sequence as for (1) (Figure 1)

allowed to proceed in [$^2H_6$]acetone to which D_2O had been added. It has recently been shown [13] that protonation of the μ-alkyne dimolybdenum complex [$Mo_2(CO)_4(\mu\text{-}C_2H_2)(\eta\text{-}C_5H_5)_2$], which is closely related to (1), generates a μ-vinyl cation [$Mo_2(CO)_4(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2$]$^+$. In this light we propose that the proton-catalysed isomerisation of (1) proceeds *via* initial formation of such a μ-vinyl cation, which then undergoes rearrangement through a metal–hydride intermediate before release of H^+ to give (2). For catalysis by D^+ this proposal is presented in Scheme 3. The (1) ⟶ (2) isomerisation is apparently irreversible; neither the action of heat, of CO, or of dissolution in non-polar solvents has any effect on (2).

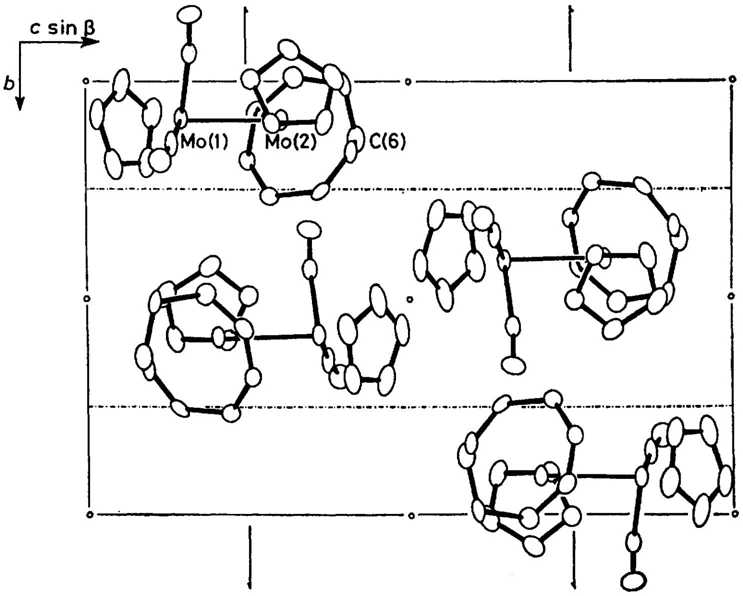
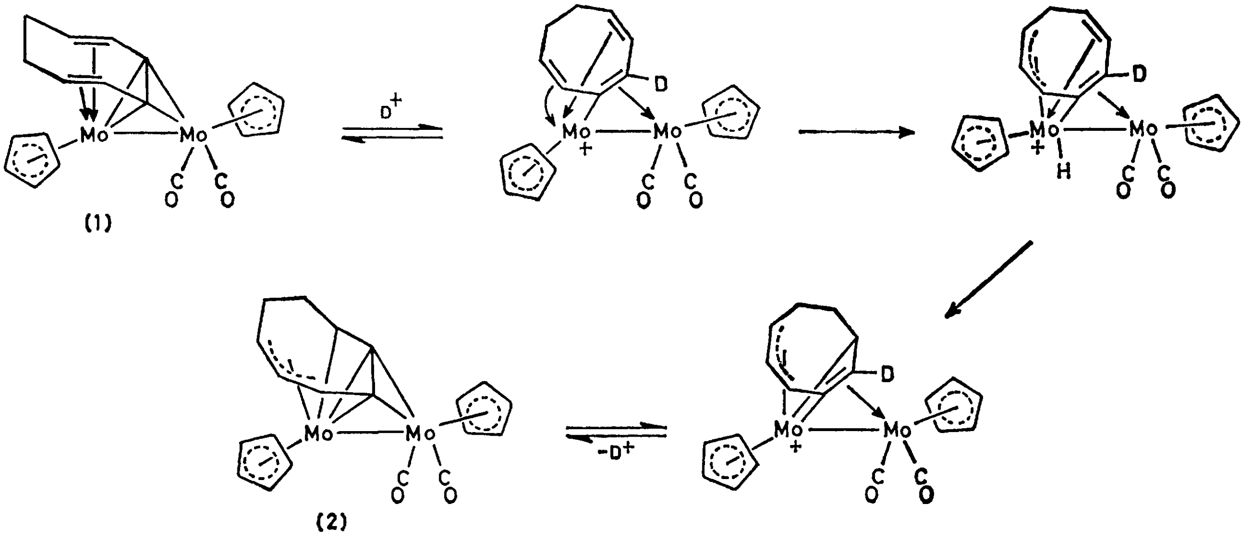


FIGURE 4 Contents of the monoclinic cell ($P2_1/n$) of (2)

It is worth noting that the structural study on complex (2) allows assignment of the unusually high field (τ 10.97) aliphatic proton resonance of the complex. This is attributed to a proton on C(6) which will be held in a shielding region above the delocalised η^6-ring system bonded to Mo(2). Similar shifts have been observed for aliphatic protons held above the postulated homotropylium (C_7, 6π) system in [$Mo(CO)_3(\eta^7\text{-}C_8H_9)$]$^+$ (τ 10.14),[14] and in $C_8H_9^+$ (τ 10.67).[15] However, any implication that in (2) orbital overlap between C(5) and C(8) allows a ring current in a homoaromatic C(1)—C(5),C(8) electronic system must be viewed against a C(5) ··· C(8) distance of 2.78 Å. That the high-field resonance is indeed due to the position of the aliphatic proton is shown by the ^{13}C n.m.r. spectrum of (2), in which neither of the two CH_2 carbons appears at an unusual shift.

We have drawn attention above to the existence of a



SCHEME 3

μ-alkyne link in (1). In this connection it is interesting to record that treatment of (1) with CO (150 atm, 100 °C) * released the two double bonds [C(3)–(4) and C(7)–(8)] from co-ordination to give a low yield of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}C_8H_8)]$ (8), in which cyclo-octa-1,5-dien-3-yne acts as a simple μ-alkyne ligand. This air-stable compound displays an i.r. spectrum in the carbonyl region typical of a $[Mo_2(CO)_4(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2]$ complex.[12] Comparison of the ^1H n.m.r. spectra of (1) and (8) shows a shift to low field of the two multiplets due to olefinic protons, to a position characteristic of unco-ordinated olefinic protons. A similar effect is observed in the ^{13}C n.m.r. spectrum.

TABLE 5

Atomic positional co-ordinates (fractional cell co-ordinates) for $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3)

Atom	*x*	*y*	*z*
C(1)	0.035 7(4)	0.097 1(3)	−0.134 4(5)
C(2)	0.014 4(4)	0.167 7(3)	−0.145 4(5)
C(3)	−0.042 0(4)	0.197 6(4)	−0.097 4(6)
C(4)	−0.113 5(4)	0.170 6(5)	−0.080 6(8)
C(5)	−0.151 5(5)	0.123 3(4)	−0.131 1(8)
C(6)	−0.127 0(5)	0.081 4(4)	−0.207 7(7)
C(7)	−0.068 8(4)	0.045 0(4)	−0.210 6(6)
C(8)	−0.019 0(3)	0.036 9(3)	−0.129 7(5)
C(9)	0.080 7(6)	0.073 4(4)	0.032 5(5)
C(10)	−0.025 5(5)	0.149 1(5)	0.080 7(6)
C(11)	0.124 8(5)	0.218 5(5)	0.111 7(7)
C(12)	0.078 6(4)	0.272 7(4)	0.079 4(7)
C(13)	0.094 6(4)	0.286 5(4)	−0.011 3(8)
C(14)	0.150 7(5)	0.242 0(5)	−0.040 3(8)
C(15)	0.168 4(5)	0.199 9(5)	0.036 5(8)
H(1)	0.090 9	0.084 9	−0.129 1
H(2)	0.043 2	0.200 2	−0.193 4
H(3)	−0.031 5	0.248 6	−0.067 9
H(4)	−0.139 5	0.191 2	−0.019 9
H(5)	−0.205 7	0.116 6	−0.111 5
H(6)	−0.159 8	0.079 9	−0.268 7
H(7)	−0.055 5	0.019 2	−0.274 9
H(8)	−0.049 7(42)	0.037 5(43)	−0.074 0(57)
H(11)	0.125 9	0.196 1	0.180 5
H(12)	0.038 2	0.298 3	0.119 7
H(13)	0.068 8	0.325 1	−0.054 2
H(14)	0.174 9	0.240 9	−0.108 0
H(15)	0.208 6	0.160 0	0.037 7
O(9)	0.100 9(5)	0.018 4(3)	0.058 8(5)
O(10)	−0.069 9(5)	0.141 1(5)	0.133 0(6)
Mo	0.052 91(3)	0.168 95(2)	0.000 0 *

* The *z* co-ordinate of Mo was fixed arbitrarily at zero.

TABLE 6

Bond distances (Å) and angles (°) for the complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3) *

(*a*) Distances

Mo–C(1)	2.396(6)	C(4)–C(5)	1.366(12)
Mo–C(2)	2.222(7)	C(5)–C(6)	1.441(14)
Mo–C(3)	2.355(8)	C(6)–C(7)	1.309(12)
		C(7)–C(8)	1.513(10)
C(1)–C(2)	1.414(9)	C(8)–C(1)	1.552(8)
C(2)–C(3)	1.400(11)	C(8)–C(8)′	1.581(13)
C(3)–C(4)	1.476(12)	C(8)–H(8)	0.99(8)
Mo–C(9)	1.954(8)	C(9)–O(9)	1.171(10)
Mo–C(10)	1.933(8)	C(10)–O(10)	1.143(11)
Mo–C(11)	2.316(8)	C(11)–C(12)	1.436(12)
Mo–C(12)	2.338(7)	C(12)–C(13)	1.369(14)
Mo–C(13)	2.384(7)	C(13)–C(14)	1.427(12)
Mo–C(14)	2.398(8)	C(14)–C(15)	1.410(14)
Mo–C(15)	2.338(6)	C(15)–C(11)	1.411(13)

(*b*) Angles

C(8)–C(1)–C(2)	121.0(6)	Mo–C(9)–O(9)	174.8(7)
C(1)–C(2)–C(3)	123.6(7)	Mo–C(10)–O(10)	174.8(8)
C(2)–C(3)–C(4)	130.4(7)	C(9)–Mo–C(10)	83.3(4)
C(3)–C(4)–C(5)	129.1(9)		
C(4)–C(5)–C(6)	127.1(9)		
C(5)–C(6)–C(7)	126.3(8)	C(15)–C(11)–C(12)	107.0(8)
C(6)–C(7)–C(8)	124.2(8)	C(11)–C(12)–C(13)	108.2(7)
C(7)–C(8)–C(1)	108.2(5)	C(12)–C(13)–C(14)	109.4(8)
C(7)–C(8)–C(8)′	112.3(5)	C(13)–C(14)–C(15)	106.7(9)
C(1)–C(8)–C(8)′	110.5(5)	C(14)–C(15)–C(11)	108.7(8)
H(8)–C(8)–C(1)	115(5)		
H(8)–C(8)–C(7)	105(5)		
H(8)–C(8)–C(8)′	106(5)		

* C(8)′ is the C_2 counterpart of C(8).

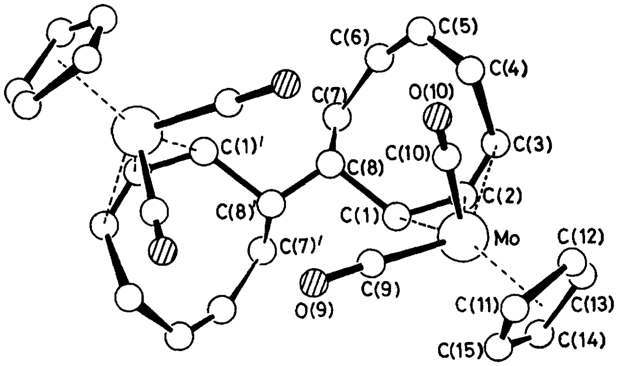


FIGURE 5 Molecular structure of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3), showing the crystallographic numbering of the asymmetric unit

The Complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3).—This yellow, crystalline, and air-stable complex was assigned the formula indicated on the basis of the mass spectrum and elemental analyses. The mass spectrum displays a molecular ion and ions due to the loss of four carbonyl groups, but also an ion corresponding to $[Mo(CO)_2(\eta\text{-}C_5H_5)(C_8H_8)]^+$. Neither the i.r. nor ^1H n.m.r. spectrum provided definitive structural information, and an *X*-ray diffraction study was therefore undertaken, the results of which (Tables 5 and 6) show several unexpected features, not least that the crystals are tetragonal with a very beautiful internal arrangement of the molecules, and that the molecules contain a dimeric form of cyclo-octatetraene. The molecular structure, with the crystallographic numbering sequence, is shown in Figure 5; the two-fold symmetry of the molecule is clearly apparent. A stereoscopic view is given in Figure 6, orthogonal to the viewpoint of Figure 5 so that the two-fold axis is now in the plane of the diagram, and bisects the molecule vertically. The 'tub' configuration of the C_8 rings, and their linkage *via* a single bond astride the C_2 axis, can be clearly seen. The two $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragments are not connected to each other, but each Mo atom is η^3-bonded to the novel $C_{16}H_{16}$ ligand [Mo–C(1) 2.396(6), Mo–C(2) 2.222(7), Mo–C(3) 2.355(8) Å]. The $C_{16}H_{16}$ ligand comprises two mono-

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* Throughout this paper: 1 atm = 101 325 N m^{-2}.

cyclic C_8H_8 units connected together through a single C–C bond [C(8)–C(8)′ 1.58(1) Å]; the crystallographic C_2 axis passes through the midpoint of this bond. The remaining four carbon atoms C(4)—(7) of each C_8 ring form a non-conjugated diene system, as the bond lengths in Table 6 show, while those of the η^3-allyl group C(1)—(3) show the expected intermediate bond length (mean 1.407 Å). The stereopair drawing (Figure 6) and the torsion angles within the dimeric ligand (Table 7) both show that the atom sequence C(2), C(1), C(8), C(8)′, C(1)′, C(2)′ is substantially coplanar. Indeed, these atoms are related to one another by the crystallographic C_2 axis and all have similar *z* co-ordinates. Other coplanar sequences, arising from the diene system, are C(3)—C(6) and C(5)—C(8). It is also evident from Table 6 that the atom C(8) retains sp^3 character. If the co-ordination around the molybdenum atom is considered to be octahedral, it is necessary to postulate that the η^3-attachment of the C_8 ring occupies only one co-ordination site; in which case, although the bond lengths in the $Mo(CO)_2(\eta\text{-}C_5H_5)$ moiety are all normal, it is hardly surprising that the bond angle between the two carbonyl ligands is less than 90° (83.3°).

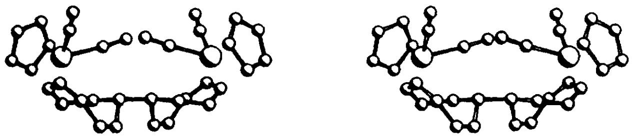

FIGURE 6 Stereoscopic view of (3) normal to the C_2 axis which lies vertically in the plane of the diagram

The formation of (3) from $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ is probably achieved through dimerisation of a radical $[Mo(CO)_2(\eta\text{-}C_5H_5)(\eta^3\text{-}C_8H_8)]$ (9), derived from the interaction of $[Mo(CO)_2(\eta\text{-}C_5H_5)]$ with cyclo-octatetraene. It has been proposed that cleavage of the Mo–Mo bond of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ does occur, followed by CO loss, to give the $[Mo(CO)_2(\eta\text{-}C_5H_5)]$ radical which then dimerises to afford triply-bonded $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[6] For (3) to be formed from $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, thermal scission of the triple bond must occur to give this same radical.

Although the hydrocarbon within (3) would not exist as a stable species when unco-ordinated, being then a diradical, it was possible that C–C bond formation might occur to form the known dimer of cyclo-octatetraene (10). However, treatment of (3) with Me_3NO, which has been shown to cleave $C_{16}H_{16}$ hydrocarbons from

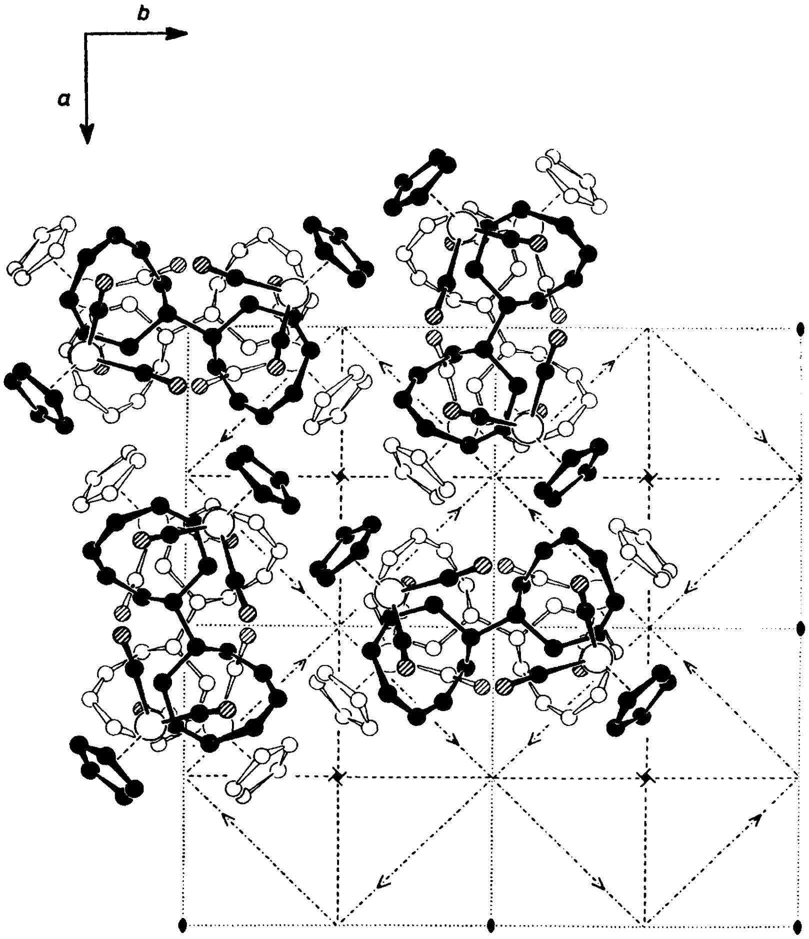

FIGURE 7 Contents of the tetragonal unit cell (space group $I4_1cd$) of (3) viewed in projection down *c* looking towards the origin. The open-bonded molecule whose $C_{16}H_{16}$ ligand lies astride the origin is the one for which atom co-ordinates are listed in Table 5

carbonyl-iron, -ruthenium, and -molybdenum groups,[16,17] did not lead to the isolation of any $C_{16}H_{16}$ hydrocarbon.

TABLE 7

Torsion angles (°) within the $C_{16}H_{16}$ ligand of complex (3) *

I	J	K	L	*W*
C(8)	C(1)	C(2)	C(3)	43.2
C(1)	C(2)	C(3)	C(4)	−45.8
C(2)	C(3)	C(4)	C(5)	−25.2
C(3)	C(4)	C(5)	C(6)	8.4
C(4)	C(5)	C(6)	C(7)	46.9
C(5)	C(6)	C(7)	C(8)	4.5
C(6)	C(7)	C(8)	C(1)	−90.2
C(7)	C(8)	C(1)	C(2)	49.8
C(6)	C(7)	C(8)	C(8)′	147.6
C(2)	C(1)	C(8)	C(8)′	173.1
C(1)	C(8)	C(8)′	C(1)′	−174.7
C(1)	C(8)	C(8)′	C(7)′	−53.8

* The torsion angle *W*(IJKL) is defined as the angle between the vector JI and the vector KL when viewed down JK. The sign of *W* is positive if JI is to be rotated clockwise into KL and negative if anticlockwise.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 257 spectrometer, and calibrated *via* the 1 601 cm^{-1} absorption of polystyrene. Proton and ^{13}C n.m.r. spectra were obtained with Varian Associates HA100, JEOL PS-100 and PFT-100 instruments, and mass spectra with an AEI MS902 spectrometer. Reactions were performed under a nitrogen atmosphere, employing solvents dried by distillation from calcium hydride (alkanes and dichloromethane) or Na–K alloy (toluene and benzene). Separation of products was achieved by chromatography on alumina columns.

Preparation of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$.—The literature method,[5] namely heating $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene at reflux for *ca.* 16 h while simultaneously purging with nitrogen, was employed. Another method is to heat solid $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ to fusion (215—217 °C) under vacuum for 5 min. This provides black, solid $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ which is pure by i.r. spectroscopy. The much shortened reaction time makes this a useful alternative route.

Reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ *with Cyclo-octatetraene.*—A mixture of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2.0 g, 4.1 mmol) and cyclo-octatetraene (2.0 g, 19.2 mmol) was heated in octane (200 cm^3) at reflux for 21 h. The resulting brown solution was concentrated and chromatographed. Elution with hexane afforded several unidentified yellow compounds in very low yield, and a maroon band which provided 280 mg (14%) of maroon *crystals* of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1) after crystallisation from hexane, m.p. 151—153 °C (decomp.); ν(CO) (hexane) 1 930s and 1 868s cm^{-1}; ^{1}H n.m.r. (C_6D_6), τ 4.35 (d, 2 H, *J* 6 Hz), 4.84 (s, 5 H), 5.30 (s, 5 H), 6.70 (m, 2 H), 8.16 (m, 2 H), 8.76 (m, 2 H); ^{13}C n.m.r. (C_6D_6), δ(p.p.m.) 237.7 (CO), 119.1 (C), 100.5 (CH), 92.3 (C_5H_5), 89.1 (C_5H_5), 65.8 (CH), 35.2 (CH_2) (Found: C, 49.3; H, 3.8; *M* 482. $C_{20}H_{18}Mo_2O_2$ requires C, 49.8; H, 3.7%; *M* 482). This was followed on the column by a red-grey band which appeared to contain several compounds, but which could not be separated or identified. Elution with dichloromethane removed material which was then rechromatographed using dichloromethane–hexane (1 : 4). This afforded four yellow bands, of which only the fourth gave any quantity of product, 236 mg (5%) of yellow *crystals* of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3) from dichloromethane–hexane, m.p. 173 °C (decomp.); ν(CO)-(CD_2Cl_2) 1 955s, 1 939s, and 1 872s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), τ 3.86 (m, 6 H), 4.50 (m, 2 H), 4.84 (s, 10 H), 5.84 (m, 4 H), 6.49 (m, 2 H), 7.17 (m, 2 H) (Found: C, 55.3; H, 3.7; *M* 642. $C_{30}H_{26}Mo_2O_4$ requires C, 56.0; H, 4.0%; *M* 642).

The same quantities of reagents heated in heptane at reflux for 7 d gave a 25% yield of (1) and a 2% yield of (3).

Treatment of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, derived by heating 1.5 g of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene (100 cm^3) at reflux, with cyclo-octatetraene (2 g) provided (1) and (3) in 15 and 2% yields, respectively.

Isomerisation of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1)→(2).—The isomerisation in chloroform is typical. A maroon solution of isomer (1) in this solvent gradually became orange. Removal of solvent and crystallisation of the residue then afforded, quantitatively, orange *crystals* of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (2), m.p. 133—134 °C; ν(CO) (hexane) 1 928s and 1 864s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), τ 3.48 (d of t, 1 H, *J* 1 and 5), 4.60 (s, 5 H), 4.70 (m, br, 1 H), 5.18 (s, 5 H), 5.74 (d of d, 1 H, *J* 5 and 8), 7.43 (m, 1 H), 7.55 (m, 1 H), 7.77 (t of d of d, 1 H, *J* 3, 5, and 13 Hz), 8.50 (m, 1 H), 10.97 (m, 1 H); ^{13}C n.m.r. (C_6D_6), δ(p.p.m.) 235.0 (CO), 123.5 (C), 107.9 (CH), 98.8 (C), 92.4 (C_5H_5), 91.8 (CH), 88.8 (C_5H_5), 78.1 (CH), 59.8 (CH), 43.6 (CH_2), 23.5 (CH_2) (Found: C, 50.0; H, 3.9; *M* 482. $C_{20}H_{18}Mo_2O_2$ requires C, 49.8; H, 3.7%; *M* 482).

Reaction of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1) *with* CO.—A hexane (100 cm^3) solution of (1) (150 mg, 0.31 mmol) was heated (17 h, 100 °C) in an autoclave charged to 150 atm with carbon monoxide. Chromatography of the reaction mixture, eluting with dichloromethane–hexane (1 : 6), gave an orange band which provided the orange isomer (2), followed by a maroon band which afforded 23 mg (5%) of black *crystals* of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (8); ν(CO) (hexane) 1 985m, 1 926s, and 1 845m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), τ 3.45 (d, 2 H, *J* 10 Hz), 4.20 (m, 2 H), 4.77 (s, 10 H), 7.83 (m, 4 H); ^{13}C n.m.r. ($CDCl_3$), δ(p.p.m.) 230.2 (CO), 133.5 (CH), 130.8 (CH), 92.8 (C), 92.5 (C_5H_5), 29.6 (CH_2) (Found: C, 48.7; H, 3.3%; *M* 538. $C_{22}H_{18}Mo_2O_4$ requires C, 49.1; H, 3.3%; *M* 538).

Structural Studies by Single-crystal X-*Ray Diffraction.*—(*a*) *Maroon isomer* $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (1). Crystals of (1) grow as maroon plates with well developed (010) faces. The crystal used for intensity measurements was measured carefully (0.450 × 0.025 × 0.400 mm) so that a numerical correction for the effects of *X*-ray absorption could be applied[18] [$A^*_{\text{max.}}$ 1.28 ($74\bar{5}$); $A^*_{\text{min.}}$ 1.03 (013)]. A total of 6 032 reflections was measured; of these, 4 013 satisfied the criterion $I \geqslant 2.5\,\sigma(I)$, and only these were used in the solution and refinement of the structure. The scan rate was 0.001 17*c*° s^{-1} (where *c* is a preliminary 2-s peak count) for $200 \leqslant c \leqslant 1\,000$, 0.07° s^{-1} for $c < 200$, and 1.0° s^{-1} for $c > 1\,000$. Three standard reflections were remeasured after every 40 reflections and showed no significant decay.

Crystal data for (1). $C_{20}H_{18}Mo_2O_2$, $M = 482.2$, Monoclinic, $a = 8.629(2)$, $b = 39.580(10)$, $c = 15.759(7)$ Å, $\beta = 103.90(3)°$, $U = 5\,224(3)$ Å^3 at 293 K, $D_m = 1.83$ g cm^{-3}, $Z = 12$, $D_c = 1.84$ g cm^{-3}, $F(000) = 2\,856$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 14.2 cm^{-1}.

Structure solution and refinement for (1). The crystal structure of (1) is remarkable in that the monoclinic cell ($P2_1/c$) contains twelve molecules of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$, so that the asymmetric unit of the crystal structure comprises three distinct molecules. (The crystallographic numbering is described in the main text.) Checks for the absence of any higher symmetry, especially trigonal or hexagonal, were done using a real-space vector search program.[19] The six Mo atoms of the asymmetric unit were located (with difficulty!) from a Patterson synthesis. Subsequent electron-density difference syntheses revealed the locations of all other atoms except hydrogen. These were incorporated into the refinement at calculated positions (C–H 0.95 Å), but their positional and thermal parameters were kept invariant ($U_H = 0.083$ Å^2). The blocked-matrix least-squares refinement, which ascribed anisotropic thermal parameters only to molybdenum and oxygen atoms, and isotropic thermal parameters to all other atoms, converged at R 0.073 (R' 0.109). Weights were applied according to the scheme $w = (11.62—0.145|F_o| + 0.001|F_o|^2 - 0.000\,001|F_o|^3)^{-1}$, and this gave a satisfactory weight analysis. A final electron-density difference synthesis showed no peaks >0.8 or < -1.1 e Å^{-3}. Atomic scattering factors were the analytic types of ref. 20 for all atoms except hydrogen, and for the Mo atoms corrections were applied for the effects of anomalous dispersion ($\Delta f' = -1.7$, $\Delta f'' = 0.85$).[21] Atomic scattering factors for hydrogen were from ref. 22. All computations were carried out on the CDC 7600 at the University of London Computer Centre with the '*X*-Ray 72' system of programs.[18] Final positional parameters for (1) are in Table 1, bond lengths and angles in Table 2.

(*b*) *Orange isomer* $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (2). Crystals of (2) grow as large orange-red 'cubes' with faces defined by {100}. Intensities were measured from a small block of material cut from a larger crystal (dimensions 0.30 × 0.30 × 0.30 mm) and mounted on a glass fibre with low-temperature epoxy resin. The crystals assume a much brighter orange colour when cooled. The measurements were carried out at −90 °C, as described earlier.[23] The scan rate was $0.0003c°$ s^{-1} for $150 \leqslant c \leqslant 1\,000$, 0.03° s^{-1} for $c < 150$, and 1.0° s^{-1} for $c > 1\,000$. There was no significant crystal decay during the 87 h of exposure to *X*-rays, and no correction for *X*-ray absorption was made. Of the reflections measured to $2\theta = 65°$, 4 735 were deemed 'observed' and were used in the solution and refinement of the structure.

Crystal data for (2). $C_{20}H_{18}Mo_2O_2$, $M = 482.2$, Monoclinic, $a = 8.081(4)$, $b = 11.808(9)$, $c = 17.409(15)$ Å, $\beta = 91.94(6)°$, $U = 1\,660(2)$ Å^3 at 183 K, $D_m = 1.85$ g cm^{-3}, $Z = 4$, $D_c = 1.87$ g cm^{-3}, $F(000) = 952$, space group $P2_1/n$ (non-standard setting of $P2_1/c_1$, no. 14), *X*-radiation as for (1), $\mu(\text{Mo-}K_\alpha) = 14.9$ cm^{-1}. The unit cell parameters were also measured at 298 K; these were used in the computation of bond lengths and angles: $a = 8.150(3)$, $b = 11.978(9)$, $c = 17.529(10)$ Å, $\beta = 92.28(4)°$, $U = 1\,710(2)$ Å^3.

Structure solution and refinement for (2). The structure was solved by heavy-atom methods, leading to the location of all atoms, including hydrogen. Blocked-matrix least-squares refinement allowed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all other atoms. Weights were applied according to the scheme $w = (3.163 - 0.132|F_o| + 0.003\,1\,|F_o|^2 - 0.000\,01|F_o|^3)^{-1}$, and in the final stages of refinement the H atom thermal parameters were held invariant. Convergence was obtained at R 0.078 (R' 0.080). A final electron-density difference synthesis showed no peaks >0.5 or < -0.5 e Å^{-3}. Scattering factor sources and corrections were as for (1). Final positional parameters for (2) are in Table 3, bond lengths and angles in Table 4.

(*c*) $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3,\eta'^3\text{-}C_{16}H_{16})]$ (3). Crystals of (3) grow from dichloromethane–hexane solution as air-stable yellow needles elongated along [001]. Systematic absences ($hkl: h + k + l = 2n + 1$; $0kl: l(k) = 2n + 1$; $hhl: 2h + l \neq 4n$) indicated space group $I4_1cd$ (no. 110), which is most unusual for an organometallic complex. Diffracted intensities were collected to $2\theta = 55°$ for $h \geqslant 0$, $k \geqslant 0, l \geqslant 0$, and $k \geqslant h$. As before, scan rates were proportionated between a lower limit of 0.048 8° s^{-1} for reflections with pre-scan counts of <150, to 0.488° s^{-1} for those with counts $> 1\,500$. The three standard reflections which were remeasured every 40 reflections showed no significant decay during the 45 h of crystal exposure to *X*-rays. Of 1 719 independent measured intensities 1 479 had $I > 1.0\sigma(I)$, and only these were used in the solution and refinement of the structure.

Crystal data for (3). $C_{30}H_{26}Mo_2O_4$, $M = 642.3$, Tetragonal, $a = 19.062(3)$, $c = 14.425(6)$ Å at 298 K, $U = 5\,242(4)$ Å^3, $D_m = 1.55$ g cm^{-3}, $Z = 8$, $D_c = 1.63$ g cm^{-3}, $F(000) = 2\,576$, space group $I4_1cd$ (no. 110), *X*-radiation as for (1), $\mu(\text{Mo-}K_\alpha) = 8.8$ cm^{-1}.

Structure solution and refinement for (3). With space group symmetry $I4_1cd$ and $Z = 8$ it is clear[24] that the molecules must possess two-fold symmetry and hence that the crystallographic asymmetric unit is one-half of a molecule, $Mo(CO)_2(\eta\text{-}C_5H_5)(C_8H_8)$. The molybdenum atom was located from a Patterson synthesis and was given a z coordinate of zero to define the origin of the unit cell. Subsequent electron-density difference syntheses revealed the locations of all non-hydrogen atoms, and these were refined with anisotropic thermal parameters. Of the hydrogen atoms, only H(8) adjoining the 'bridge' was located directly. Positional parameters for H(8) were refined, and all other H atoms were included at calculated positions (C–H = 0.95 Å) so as to 'ride' on the adjoining carbon atom; all were given isotropic thermal motion ($U_{iso.} = 0.05$ Å^2). Weights were applied according to the scheme $w = 0.746[\sigma^2(F_o) + 0.0007(F_o)^2]^{-1}$. Refinement by blocked-matrix least squares converged at R 0.040 (R' 0.039). A final electron-density difference synthesis showed no peaks > 1.0 or < -0.3 e Å^{-3}. Final positional parameters for (3) are in Table 5, bond lengths and angles in Table 6, and selected torsion angles in Table 7. Lists of observed and calculated structure factors and all thermal parameters for the three compounds (1), (2), and (3) are in Supplementary Publication No. SUP 23140 (52 pp.).*

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