Reactions of Cyclic 1,3-Dienes with Ethyne co-ordinated at a Dimetal Centre. Crystal Structure of $[Mo_2(CO)_2(\mu\text{-}\eta^2,\eta'^2\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ *

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The complex $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ reacts in refluxing octane with cyclo-octatetraene, cyclohexa-1,3-diene, cycloheptatriene, and cyclo-octa-1,3-diene to afford dimolybdenum compounds having the bridging bicyclic ligands $C_{10}H_{10}$, C_8H_{10}, C_9H_{10}, and $C_{10}H_{14}$ respectively, formed by formal Diels–Alder 1,4-addition of the diene to the $Mo_2(\mu\text{-}HC_2H)$ moiety. The molecular structure of the product from cyclo-octatetraene was established by an *X*-ray diffraction study. Crystals of $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ are monoclinic, *a* = 9.230(3), *b* = 16.561(4), *c* = 12.651(3) Å, β = 107.38(2)°, space group *Cc* (no. 9). The structure was solved by heavy-atom methods and has been refined to *R* 0.036 (*R'* 0.035) for 4 285 reflections. The bicyclo[4.2.2]deca-2,4,7,9-tetraene ligand bridges a Mo≡Mo triple bond [2.504(1) Å] with the double bonds at positions 7 and 9 each co-ordinated to a molybdenum atom. The two carbonyl ligands asymmetrically bridge the metal–metal bond [mean Mo–CO 1.99 and 2.33 Å]. The axis of the molecule through the metal–metal bond and the centroids of the $\eta\text{-}C_5H_5$ ligands is non-linear, with the two rings in a *cis* relationship. Hydrogen-1 and ^{13}C n.m.r. data for the complexes are reported and discussed. Variable-temperature ^{13}C n.m.r. studies on the product from cyclo-octa-1,3-diene revealed dynamic behaviour involving site exchange of the semi-bridging CO ligands ($\Delta G^‡$ *ca.* 47 kJ mol^{-1}).

THE dimolybdenum compound $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ reacts with cyclo-octatetraene (cot) and with cyclo-octa-1,5-diene (cod), in refluxing octane, to give the compounds $[Mo_2(CO)_2(C_8H_8)(\eta\text{-}C_5H_5)_2]$ [1] and $[Mo_2(CO)_3(C_8H_{10})(\eta\text{-}C_5H_5)_2]$ [2] respectively. Both species have molecular structures in which an alkyne group transversely bridges the metal–metal bond; hence in their formation a CH=CH group has been dehydrogenated. If a similar dehydrogenation took place in reactions between cot or cod and the dimolybdenum compound $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ [3-5] it might be anticipated that linkage of alkyne groups at the dimetal centre would occur. Investigation of these reactions revealed that addition of the C_8 fragments of cot or cod to the μ-bonded CH≡CH group did take place, but in an unexpected manner.[6]

RESULTS AND DISCUSSION

A brown crystalline compound $[Mo_2(CO)_2(C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (1) was obtained in *ca.* 25% yield after refluxing the complex $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with cot in octane for several hours. The composition of (1) was established by microanalysis and by mass spectrometry (Table 1). The i.r. spectrum in the carbonyl region showed a single band at 1 805 cm^{-1}, this frequency being indicative of bridging or semi-bridging CO ligands.[7] Examination of the ^1H and ^{13}C n.m.r. spectra (Table 2) of (1) was informative, but did not unambiguously define the structure of the compound. Thus both spectra indicated a single signal for the cyclopentadienyl ligands, although the resonance in the ^1H spectrum coincided with another signal integrating to two protons. Two multiplets (τ 3.58 and 3.93) in the ^1H spectrum, corresponding to two protons, are in a region characteristic of unco-ordinated olefinic hydrogen atoms. Apart from the C_5H_5 resonance in the ^{13}C spectrum, there is a signal for CO ligands at δ 253.5 p.p.m. in a region expected for bridging or semi-bridging carbonyl groups,[8-10] in agreement with the i.r. data. There are four other absorptions (relative intensity 2 : 2 : 4 : 2) assignable to ten carbon atoms of the $C_{10}H_{10}$ ligand. A partially ^1H-decoupled spectrum revealed each of these signals as doublets, thereby establishing that one hydrogen atom was attached to each of the carbon atoms, and no migrations of the hydrogen atoms had occurred.[1,2]

Since the spectroscopic data did not fully determine the molecular structure of (1), being especially inconclusive as to the nature of the $C_{10}H_{10}$ ligand, an *X*-ray diffraction study was carried out. The results are summarised in Tables 3 and 4, and the molecule is shown in Figure 1, together with the atomic numbering scheme.

It is at once apparent that the cyclo-octatetraene ring has undergone 1,4-addition to the co-ordinated ethyne to form bicyclo[4.2.2]deca-2,4,7,9-tetraene, with the double bonds at positions 7 and 9 each co-ordinated to one molybdenum atom of the $Mo_2(CO)_2(\eta\text{-}C_5H_5)_2$ moiety. In the crystallographic numbering scheme, Mo(1) is bonded to C(11)–C(12), and Mo(2) to C(19)–C(20). The C_{10} ligand itself has *mm* symmetry, but because of the asymmetry of the carbonyl bonding, discussed below, the molecule as a whole has only two-fold symmetry. This two-fold symmetry is not, however, crystallographically required. The two-fold axis joins the mid-points of the Mo(1)–Mo(2) and C(15)–C(16) bonds. Within the C_{10} ring the atom sequences C(13)—(18), C(13),(12),(11),(18), and C(13),(20),(19),(18) are each co-planar, with a dihedral angle between the last two of 142°.

The distance apart of the two η^2-metal-bonded olefinic linkages is almost exactly equal to the length of the Mo≡Mo bond [2.504(1) Å], so that the angle subtended at each Mo atom by the other Mo atom and the midpoint of the bonded olefin is close to 90°. The carbonyl groups form asymmetric bridges across the two molyb-

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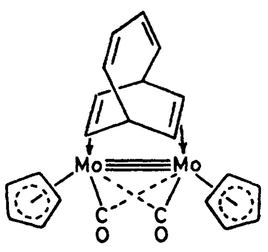
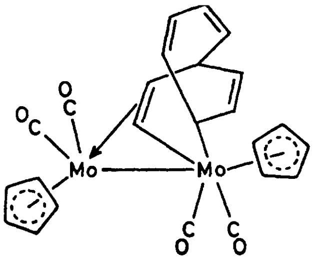
* μ-(7—8-η:9—10-η-Bicyclo[4.2.2]deca-2,4,7,9-tetraene)-bis-[carbonyl(η-cyclopentadienyl)molybdenum](3*Mo*–*Mo*).



(1)



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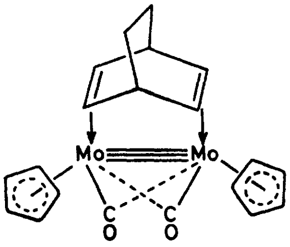

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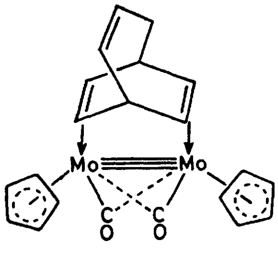

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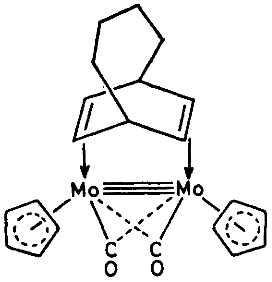

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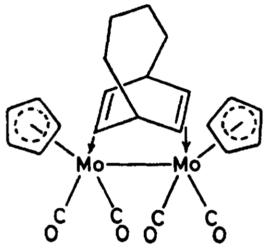


(6)

Table 1

Analytical [a] and physical data for the dimolybdenum complexes

Compound [b]	$\nu_{max.}$(CO) [c]	Analysis (%) C	Analysis (%) H	*M* [d]
(1) $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$	1 805s	51.9 (52.0)	3.8 (3.9)	508 (508)
(3) $[Mo_2(CO)_2(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$	1 819s	49.2 (49.6)	4.1 (4.1)	484 (484)
(4) $[Mo_2(CO)_2(\mu\text{-}C_9H_{10})(\eta\text{-}C_5H_5)_2]$	1 814s	48.1 (50.8)	3.8 (4.0)	496 (496)
(5) $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{14})(\eta\text{-}C_5H_5)_2]$	1 776s [e]	50.9 (51.6)	4.6 (4.7)	512 (512)
(6) $[Mo_2(CO)_4(\mu\text{-}C_{10}H_{14})(\eta\text{-}C_5H_5)_2]$	1 951m, 1 924s 1 880m, 1 853w	50.5 (50.7)	4.4 (4.2)	568 (568)

[a] Calculated values are given in parentheses. [b] All compounds are brown. [c] Measured in hexane. [d] Molecular weight measured from parent ion in mass spectrum. [e] Measured in dichloromethane.

Table 2

Hydrogen-1 and ^{13}C n.m.r. data [a] for the dimolybdenum compounds

Compound	^1H (τ)	^{13}C (δ/p.p.m.) [b,c]
(1)	3.58 (m, 2 H), 3.93 (m, 2 H), 5.19 (m, 12 H), 6.30 [t, 4 H, *J*(HH) 2]	253.5 (CO), 144.9 (C^d), 125.9 (C^c), 91.4 (C_5H_5), 56.3 (C^a), 49.0 (C^b)
(3)	5.19 (s, 10 H), 5.51 (br, 2 H), 6.61 [t, 4 H, *J*(HH) 3], 8.04 (m, 4 H)	92.1 (C_5H_5), 59.1 (C^a), 51.1 (C^b), 31.2 (CH_2)
(4)	3.40 (m, 1 H), 4.05 (m, 1 H), 5.16 (s, 10 H), 5.57 (m, 2 H), 6.0 [dd, 2 H, *J*(HH) 10, 4], 6.58 [dd, 2 H, *J*(HH) 10, 4], 7.31 [quartet, 2 H, *J*(HH) 3]	251.4 (CO), 138.8 (CH), 130.2 (CH), 91.9 (C_5H_5), 62.4 (C^a), 54.4 (C^a), 50.7 (C^b), 50.2 (C^b)
(5)	5.19 (s, 10 H), 5.38 (br, 2 H), 6.49 [t, 4 H, *J*(HH) 2], 7.98 (m, 8 H)	91.5 (C_5H_5), 60.9 (C^a), 49.3 (C^b), 42.8 (CH_2), 25.9 (CH_2) [d] 254.7 (CO), 91.3 (C_5H_5), 63.1 (C^a), 58.4 (C^a), 48.6 (C^b), 42.2 (CH_2), 25.3 (CH_2)
(6)	5.04 (s, 10 H), 6.58 (m, 2 H), 7.35 (m, 2 H), 8.33 (m, 10 H)	[d] 240.1 (CO), 93.2 (C_5H_5), 63.0 (C^a), 40.6 (C^b), 32.0 (CH_2), 26.7 (CH_2)

[a] Measured in $CDCl_3$ at room temperature, unless otherwise stated. Coupling constants in Hz. [b] Chemical shifts relative to $SiMe_4$ (0.0 p.p.m.). [c] For all compounds C^a refers to the η^2-CH=CH group and C^b to the bridgehead carbon atoms. For (1), C^c is the CH group adjacent to C^b, and C^d the remaining CH group. [d] Measured at −60 °C.

denum atoms, giving rise to mean Mo–C distances of 1.99 and 2.33 Å. These two carbonyl ligands are ' semi-bridging ' in the sense that the carbon atom is within bonding range of both metal atoms but the oxygen atom is not. The shorter Mo–C bond is associated with a bond angle at the C–O link (1.15 Å) of *ca.* 162°, whereas the longer M–C link makes an angle of *ca.* 128° with the carbonyl group. In a symmetrical carbonyl bridge across a molybdenum–molybdenum triple bond these angles would be equal, and of magnitude *ca.* 137°. The carbonyl ligand bonding situation in (1) contrasts interestingly with that found [7] in $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ where the Mo–C–O linkage remains almost linear, where the two Mo–C distances are 2.13 and 2.56 Å (*i.e.* both appreciably longer than in the title compound), but where also the centroids of the cyclopentadienyl ligands are collinear with the two molybdenum atoms. Indeed, arguments have been advanced[7] that in $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ the CO ligands are functioning as four-electron donors, being terminally bound to one Mo atom but also donating electron density from the CO π bonds to the second Mo atom. Neither the electron count nor the geometry of complex (1) suggests that the carbonyl ligands are other than two-electron donors, even though the correlation of the M–C–O angle with the bridge asymmetry is not very close in comparison with the examples given in ref. 7.

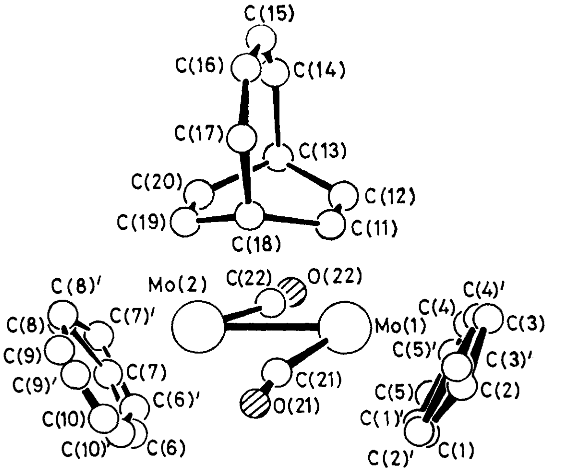


FIGURE 1 Molecular structure of $[Mo_2(CO)_2(\mu\text{-}\eta^2,\eta^{2\prime}\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (1)

Although each of the two bridging carbonyl ligands is coplanar with the Mo–Mo bond, the two planes so defined are not coplanar with each other; they bend slightly away from the C_{10} ring, so that the angle formed by the midpoint of the co-ordinated olefinic bond in the ring, the metal atom, and the corresponding carbonyl ligand is about 95°. The co-ordination around each molybdenum atom can be regarded as capped octahedral, with three sites for the cyclopentadienyl rings, one for the olefinic link, two for the bridging carbonyls, and a capping Mo≡Mo triple bond interaction, as required by the 18-electron rule.

The axis of the molecule, through the metal–metal bond and the centroids of the C_5H_5 ligands, is non-linear, with the two rings having a *cis* relationship. Both rings are inequivalently disordered relative to their staggered and nearly coplanar (*ca.* 6°) counterparts; the ring associated with Mo(1) in the ratio 0.70 : 0.30, and that associated with Mo(2) in the ratio 0.53 : 0.47. The more highly populated sites are associated (Table 3) with lower estimated standard deviations in the positional parameters. All C_5 rings were constrained to regular pentagonal geometry [C–C 1.42, C–H 0.95 Å] in the refinement of the structure.

The η^2,η'^2 $C_{10}H_{10}$ ligand in (1) may be regarded as being derived by a formal Diels–Alder addition of the co-ordinated ethyne ligand in $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with cot. This is significant, since HC≡CH itself is a poor dienophile in Diels–Alder reactions, typically requiring high pressure and temperature before reacting.[11,12] However, it is not envisaged that compound (1) forms by a $(4 + 2)\pi$ concerted process, but by a stepwise mechanism. A possible intermediate is (2), which by loss of CO could give (1). No free $C_{10}H_{10}$ was isolated from the reaction products, nor in attempts to cleave the ligand by passing CO through a refluxing octane solution of (1), which resulted only in the detection by i.r. of the complex $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.

TABLE 3

Atomic positional parameters (fractional cell co-ordinates) for the complex $[Mo_2(CO)_2(\mu\text{-}\eta^2,\eta'^2\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (1), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo(1)	0.000 00 *	0.111 29(2)	0.000 00 *
Mo(2)	0.194 53(4)	0.181 41(2)	−0.068 99(3)
C(1)	−0.209 9(8)	0.170 8(3)	0.032 4(7)
C(2)	−0.170 2(8)	0.109 1(3)	0.114 0(7)
C(3)	−0.191 6(8)	0.033 5(3)	0.058 6(7)
C(4)	−0.244 6(8)	0.048 4(3)	−0.057 1(7)
C(5)	−0.255 9(8)	0.133 3(3)	−0.073 3(7)
C(1)'	−0.237 3(20)	0.166 4(13)	−0.039 6(20)
C(2)'	−0.166 0(20)	0.176 1(13)	0.075 8(20)
C(3)'	−0.134 2(20)	0.098 1(13)	0.123 7(20)
C(4)'	−0.186 0(20)	0.040 2(13)	0.038 0(20)
C(5)'	−0.249 7(20)	0.082 4(13)	−0.063 0(20)
C(6)	0.166 8(12)	0.314 9(7)	−0.124 6(11)
C(7)	0.196 3(12)	0.271 5(7)	−0.212 7(11)
C(8)	0.348 3(12)	0.243 2(7)	−0.175 6(11)
C(9)	0.412 9(12)	0.269 1(7)	−0.064 4(11)
C(10)	0.300 7(12)	0.313 4(7)	−0.032 9(11)
C(6)'	0.142 6(14)	0.294 6(11)	−0.181 9(19)
C(7)'	0.236 2(14)	0.243 8(11)	−0.224 3(19)
C(8)'	0.379 8(14)	0.237 5(11)	−0.142 6(19)
C(9)'	0.374 9(14)	0.284 5(11)	−0.049 7(19)
C(10)'	0.228 4(14)	0.319 7(11)	−0.074 0(19)
C(11)	0.185 2(5)	0.022 2(2)	0.097 4(3)
C(12)	0.113 6(5)	−0.010 3(2)	−0.007 8(4)
C(13)	0.119 2(6)	−0.014 6(3)	−0.092 4(4)
C(14)	0.292 3(10)	−0.092 5(3)	−0.077 1(7)
C(15)	0.405 5(10)	−0.116 7(3)	0.010 6(8)
C(16)	0.479 8(8)	−0.082 1(4)	0.117 4(7)
C(17)	0.457 2(7)	−0.014 7(4)	0.166 6(6)
C(18)	0.345 1(5)	0.053 1(3)	0.123 3(4)
C(19)	0.373 3(5)	0.090 2(3)	0.021 3(4)
C(20)	0.302 4(6)	0.058 0(3)	−0.082 9(4)
C(21)	0.142 6(8)	0.186 8(3)	0.103 1(5)
O(21)	0.203 4(6)	0.226 7(3)	0.177 3(4)
C(22)	0.020 3(10)	0.124 9(5)	−0.175 1(5)
O(22)	−0.061 5(7)	0.103 8(3)	−0.258 1(3)

* Co-ordinates arbitrarily fixed at zero to define the origin.

A complex of formulation $[\{Fe(CO)_3\}_2(C_{10}H_{10})]$, obtained from heating bullvalene with $[Fe_2(CO)_9]$, has also been identified[13] as containing the bicyclo[4.2.2]-deca-2,4,7,9-tetraene ligand found in (1). Of more relevance to the present work, however, is the reaction of tricarbonyl(cyclo-octatetraene)iron with diphenylacetylene which has been shown to produce unco-ordinated 7,8-diphenylbicyclo[4.2.2]deca-2,4,7,9-tetraene.[14,15] Although this has been described[15] as an example of a thermally 'forbidden' $[2 + 6]\pi$ cyclo-addition made 'allowed' through metal participation, more recent work,[16] involving the formation of $[Fe(CO)_3\{\eta^4\text{-}C_6H_6(CF_3)_2\}]$ from $CF_3C{\equiv}CCF_3$ and buta-1,3-diene(tricarbonyl)iron, has suggested that such reactions of electrophilic alkynes with co-ordinated hydrocarbons proceed by a step-wise rather than a concerted mechanism.

Pauson and co-workers[17] have reported reactions related to that leading to the formation of (1). The bridged acetylenedicobalt complex [$Co_2(CO)_6(\mu\text{-}HC_2H)$] reacts with norbornene and with cyclobutene derivatives to afford in good yield non-cobalt-containing fused cyclopentenone compounds. Insertion of CO into the bicyclic ring systems is in accord with a step-wise process, as postulated for production of (1).

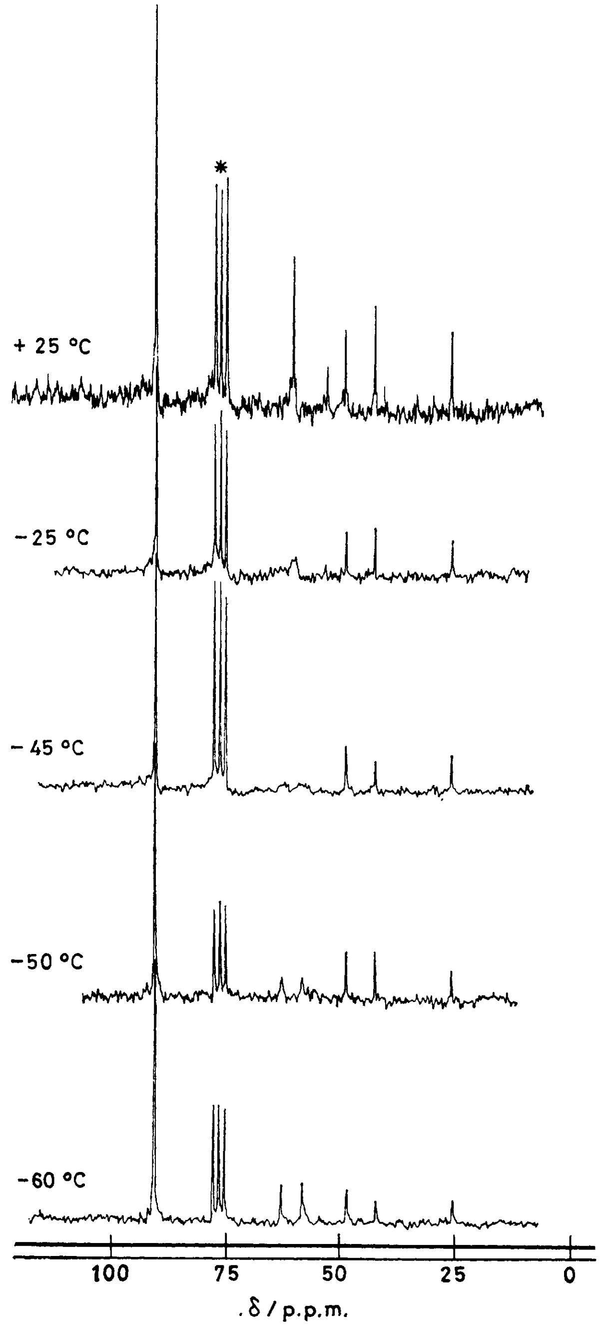
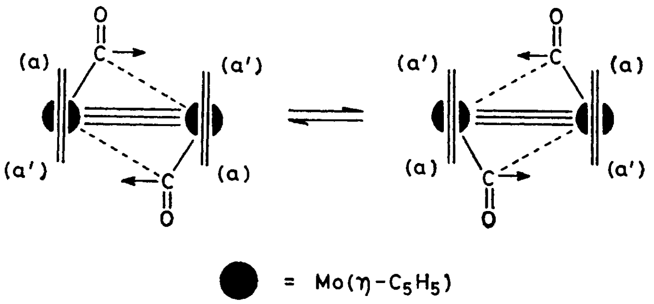


FIGURE 2 Variable-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of complex (5) from 25 to −60 °C measured in $CDCl_3$ solution. Solvent peaks are marked (*)

Cyclohexa-1,3-diene, cycloheptatriene, and cyclo-octa-1,3-diene also reacted with [$Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2$] in refluxing octane to give the compounds (3)—(5), respectively, but interestingly no analogous product was obtained from *cyclo*-C_5H_6 which also contains a 1,3-diene system. In their i.r. spectra, compounds (3)—(5) all show (Table 1) a single CO stretching band of relatively low frequency, as seen in the spectrum of (1). Evidently the complexes are of similar structure. Comparison of the ^1H n.m.r. spectra (Table 2) shows that in each compound there are two protons which resonate in the very narrow range τ 5.2—5.6 and these we assign to the bridgehead CH groups. Similarly, the bands in the range τ 6.3—6.6 are assigned to the co-ordinated olefinic protons. These trends are reflected in the ^{13}C n.m.r. spectra. Signals assigned to the bridgehead carbon atoms lie in the range δ 49—51 p.p.m., while the co-ordinated carbon atom resonances are in the range 54—63 p.p.m.



SCHEME Site exchange of co-ordinated carbon atoms in the bridge system of the dimolybdenum complexes. Only metal-bonded carbon atoms are shown for clarity

Examination of the ^{13}C n.m.r. spectrum of (5) over the range 25 to −60 °C revealed that the compound undergoes dynamic behaviour in solution (Figure 2). The resonance at δ 60.9 p.p.m. assigned to the four metal-bonded olefinic carbon atoms collapses on cooling and reappears as two signals, showing that in the static molecule these carbon atoms exist in two pairs of environments. All other absorptions remain unchanged over the temperature range studied.

Inspection of the molecular structure of (1) (Figure 1) shows that there are indeed two chemical environments for the co-ordinated carbon atoms, as a result of the two-fold molecular symmetry. It is suggested, therefore, that the averaging process for (5) is a carbonyl exchange between the two metal atoms as shown in the Scheme, thus accounting for the interchange of the two environments (a) and (a'). The free energy of activation for the averaging process was estimated, from the coalescence temperature and frequency difference between the two coalescing signals,[18] as 47.2 kJ mol^{-1}. This value compares well with the free energy of activation for bridge–terminal carbonyl exchange in [$Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2$] of 43.5 kJ mol^{-1}.[19]

A second product was isolated from the reaction of cyclo-octa-1,3-diene with [$Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2$]

in low yield, and was tentatively identified as compound (6) on the basis of analytical data, the mass spectrum, and the ^1H n.m.r. spectrum. There are four signals in the ^{13}C n.m.r. spectrum (Table 2) assigned to the $C_{10}H_{14}$ ligand, but the spectrum was weak, preventing firm conclusions from being drawn. Hence the structural assignment for (6) must remain tentative.

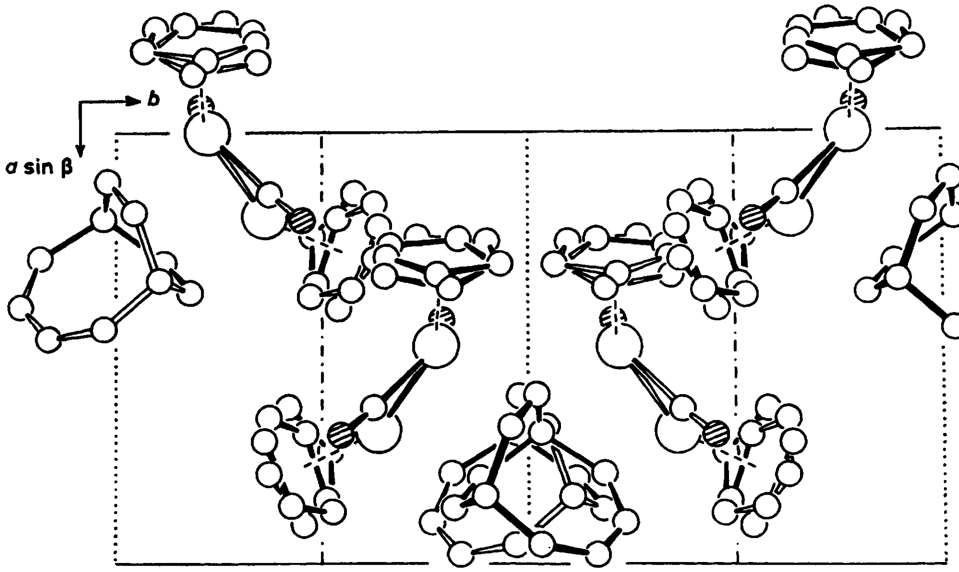


FIGURE 3 Packing of molecules of complex (1) in the monoclinic unit cell (*Cc*) viewed down *c* looking towards the origin

EXPERIMENTAL

All reactions were carried out under an atmosphere of oxygen-free nitrogen. Solvents were dried and distilled prior to use. Alumina (Brockman activity II) was used for chromatography of mixtures. Infrared spectra were measured on a Perkin-Elmer 257 Grating Infrared Spectrometer. Mass spectra were recorded on an AEI MS902 spectrometer operating at 70 eV,* and n.m.r. spectra were obtained with JEOL PS-100 and PFT-100 instruments. The complex $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ was prepared as described previously.[3]

Reactions of $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ *with Cyclo*-1,3-*dienes*.—(*a*) An octane (80 cm^3) solution of $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ (0.5 g, 1.09 mmol) and cot (2 g, 19.2 mmol) was refluxed for 19 h, affording a brown solution. Solvent was removed *in vacuo* and the residue, in dichloromethane–hexane (1 : 9), chromatographed to give some unreacted dimolybdenum compound. Further elution with CH_2Cl_2–hexane (1 : 1) gave after evaporation of solvent an oily brown solid. Re-chromatography, and elution with CH_2Cl_2–hexane (1 : 4), gave a yellow and a brown fraction. The former was not identified, while the latter afforded brown *crystals* of $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (1) (128 mg, 23%).

The complexes $[Mo_2(CO)_2(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (3) (35%) and $[Mo_2(CO)_2(\mu\text{-}C_9H_{10})](\eta\text{-}C_5H_5)_2$ (4) (3%) were obtained in a similar manner.

(*b*) Cyclo-octa-1,3-diene (1.5 g, 13.9 mmol) and $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ (1.5 g, 3.26 mmol) in octane (80 cm^3) were refluxed for 19 h. Chromatography, eluting with dichloromethane–hexane (1 : 3), gave trace amounts of unreacted dimolybdenum compound. Elution with CH_2Cl_2–hexane (2 : 3) gave a brown band containing two products not separable by further chromatography. Separation was achieved by fractional crystallisation, providing *crystals* of $[Mo_2(CO)_4(\mu\text{-}C_{10}H_{14})(\eta\text{-}C_5H_5)_2]$ (6) (36 mg, 3%) from hexane, and *crystals* of $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{14})(\eta\text{-}C_5H_5)_2]$ (5) (21 mg, 2%) from CH_2Cl_2–hexane.

Crystal Structure Determination of $[Mo_2(CO)_2(\mu\text{-}\eta^2,\eta'^2\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (1).—Crystals of (1) grow as opaque, grey-black rhombs from dichloromethane-hexane at −30 °C. Diffracted intensities were recorded at room temperature on a Syntex $P2_1$ four-circle diffractometer to $2\theta = 70°$. Of the 4 289 intensities so obtained, only 4 were deleted for reasons of coincidence-correction or tape-write errors; otherwise all the data were used in the solution and refinement of the structure. During the 95 h of crystal exposure to *X*-rays a mean intensity decay of *ca*. 2% was observed. The data were corrected for Lorentz, polarisation, and crystal decay effects, but not for the effects of *X*-ray absorption $[\mu(Mo\text{-}K_\alpha) = 12.3\ cm^{-1}]$.

Crystal data. $C_{22}H_{20}Mo_2O_2$, $M = 508.2$, Monoclinic, $a = 9.230(3)$, $b = 16.561(4)$, $c = 12.651(3)$ Å, $\beta = 107.38(2)°$, $U = 1\,845.4(9)$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.83$ g cm^{-3}, $F(000) = 1\,008$, space group *Cc* (no. 9), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(Mo\text{-}K_\alpha) = 12.3\ cm^{-1}$.

Structure solution and refinement. With $Z = 4$ in a monoclinic *C* cell with translational symmetry *c*, and with a molecule of possible two-fold symmetry, ambiguity arises as to whether the space group is *Cc* or *C*2/*c*. A solution was sought initially in *Cc*, by heavy-atom methods, from which successive electron-density difference syntheses revealed an atomic array of 2-fold symmetry but for which the two-fold axis was not parallel to *b*. Refinement was therefore effected in space group *Cc* with the origin fixed by one Mo atom ($x = z = 0$). The cyclopentadienyl rings were constrained to regular pentagonal symmetry [C–C 1.42, C–H 0.95 Å], but were found to be inequivalently disordered. The atomic positional parameters for the atoms of lower

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

population density are listed in Table 3 with primes. These atoms define five-membered rings which are staggered relative to the set with higher population density but are not quite coplanar (*ca.* 6° difference). The C_5 rings make angles of approximately 150° with the Mo–Mo axis. Hydrogen atoms were introduced at calculated positions to ride on the carbon atoms to which they are attached; they were given fixed isotropic thermal parameters $U_{iso.} = 0.03$ Å^2. All other atoms were allowed anisotropic thermal motion in a full-matrix least-squares refinement. Weights were applied according to the scheme $w = 0.272[\sigma^2(F_o) + 0.000\,5|F_o|^2]^{-1}$, and the refinement converged at R 0.036 (R' 0.035). A final difference synthesis showed no electron density >1.25 or < -0.60 e Å^{-3}. Scattering factors were from ref. 20 for all non-hydrogen atoms and from ref. 21 for hydrogen. All computational work was carried out on the South Western Universities' Computer Network with the SHELX system of programs.[22] Atomic positional parameters are in Table 3, relevant interatomic distances and interbond angles in Table 4, and the packing of the molecules in the unit cell is shown in Figure 3. Observed and calculated structure factors, hydrogen atom co-ordinates, and all thermal parameters are in Supplementary Publication SUP 23142 (26 pp).*

TABLE 4

Bond distances (Å) and angles (°) for the complex $[Mo_2(CO)_2(C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (1)

(*a*) Distances [a]			
(i) Molybdenum co-ordination			
Mo(1)–Mo(2)	2.504(1)		
Mo(1)–C(11)	2.315(4)	Mo(2)–C(19)	2.277(4)
Mo(1)–C(12)	2.286(4)	Mo(2)–C(20)	2.303(4)
Mo(1)–C(21)	1.994(6)	Mo(1)–C(22)	2.290(7)
Mo(2)–C(22)	1.994(8)	Mo(2)–C(21)	2.367(7)
Mo(1)–C(1)	2.286(17)	Mo(1)–C(1)′	2.317(5)
Mo(1)–C(2)	2.302(23)	Mo(1)–C(2)′	2.429(6)
Mo(1)–C(3)	2.278(21)	Mo(1)–C(3)′	2.474(6)
Mo(1)–C(4)	2.248(19)	Mo(1)–C(4)′	2.394(7)
Mo(1)–C(5)	2.253(19)	Mo(1)–C(5)′	2.294(7)
Mo(2)–C(6)	2.311(11)	Mo(2)–C(6)′	2.318(11)
Mo(2)–C(7)	2.356(12)	Mo(2)–C(7)′	2.350(17)
Mo(2)–C(8)	2.454(12)	Mo(2)–C(8)′	2.367(15)
Mo(2)–C(9)	2.471(13)	Mo(2)–C(9)′	2.346(17)
Mo(2)–C(10)	2.384(13)	Mo(2)–C(10)′	2.315(17)
(ii) Carbonyl			
C(21)–O(21)	1.148(6)	C(22)–O(22)	1.149(8)
(iii) $C_{10}H_{10}$			
C(11)–C(12)	1.405(6)	C(13)–C(14)	1.529(7)
C(12)–C(13)	1.510(6)	C(14)–C(15)	1.339(12)
C(13)–C(20)	1.517(7)	C(15)–C(16)	1.439(12)
C(20)–C(19)	1.390(8)	C(16)–C(17)	1.325(11)
C(19)–C(18)	1.519(6)	C(17)–C(18)	1.514(6)
C(18)–C(11)	1.503(6)		
(*b*) Angles [b]			
C(18)–C(11)–C(12)	119.3(4)	C(15)–C(16)–C(17)	132.8(5)
C(11)–C(12)–C(13)	119.5(4)	C(16)–C(17)–C(18)	129.8(6)
C(12)–C(13)–C(14)	110.1(4)	C(17)–C(18)–C(19)	109.6(4)
C(14)–C(13)–C(20)	110.0(5)	C(19)–C(18)–C(11)	111.0(3)
C(20)–C(13)–C(12)	110.8(3)	C(11)–C(18)–C(17)	110.3(4)
C(13)–C(14)–C(15)	128.9(6)	C(18)–C(19)–C(20)	119.9(4)
C(14)–C(15)–C(16)	133.9(5)	C(19)–C(20)–C(13)	119.1(3)
Mo(1)–C(21)–O(21)	164.2(7)	C(21)–Mo(1)–Mo(2)	62.2(3)
Mo(2)–C(21)–O(21)	126.2(6)	Mo(2)–Mo(1)–C(22)	48.8(3)
Mo(1)–C(22)–O(22)	129.3(8)	C(22)–Mo(2)–Mo(1)	60.1(3)
Mo(2)–C(22)–O(22)	159.3(8)	Mo(1)–Mo(2)–C(21)	48.3(3)
Mo(2)–Mo(1)–C(11,12) [c]	89.9(3)		
C(11,12)–Mo(1)–C(21)	95.1(6)		
Mo(1)–Mo(2)–C(19,20) [c]	89.7(3)		
C(19,20)–Mo(2)–C(22)	94.5(5)		

[a] For cyclopentadienyl rings C–C distances were fixed at 1.420 Å. [b] For cyclopentadienyl rings internal angles were fixed at 108.0°. [c] C(11,12) and C(19,20) are the midpoints of of the C(11)–C(12) and C(19)–C(20) bonds respectively.

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