New Chemistry of Binuclear Molybdenocene Compounds: Unexpected Synthesis of the Bis(fulvalene) Derivative $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$†

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The reaction of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_2]$ **1** with dihydrogen gives $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_4]$ whose crystal structure has been determined. Treatment of **1** with ethylene at 10 atm gives $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(C_2H_4)_2]$, whilst ethylene at 1 atm gives $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$ whose crystal structure has been determined. Treatment of **1** with but-2-yne gives a mixture of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(MeC{\equiv}CMe)_2]$ and $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(\mu\text{-}MeC{\equiv}CMe)]$; the latter is proposed to have a parallel-bridging alkyne group. Reaction of **1** with hex-3-yne gives $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(EtC{\equiv}CEt)_2]$.

The synthesis of dimeric molybdenocene complexes was first reported in 1977 when lithiation of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ followed by treatment with N_2O was shown to give a mixture of the yellow and thermally unstable isomers *cis*- and *trans*-$[\{Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)H\}_2]$.[1,2] Recrystallization from hot toluene resulted in their rearrangement to the dark green, fulvalene-bridged dimer $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_2]$ **1**. A more direct synthesis of **1** was reported by Smart and Curtis[3] who showed that the reaction between sodium cyclopentadienide and dimolybdenum tetraacetate gave **1** in good yields.

There have been several studies of the reactions of compound **1**, in particular with acids, strong bases, and with carbon monoxide.[4] In this paper we examine further the reactivity of the metallocene dimer $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_2]$ **1** in particular towards olefins and alkynes.

Results and Discussion

When compound **1** was stirred in toluene at 100 °C under 10 atm of H_2 large yellow crystals form in the reaction vessel. Elemental analysis was consistent with the stoichiometry $C_{20}H_{22}Mo_2$ corresponding to the formulation $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_4]$ **2**. The analytical and spectroscopic data for **2** and for all the other new compounds described below are given in Table 1. Compound **2** is insoluble in all common solvents at room temperature and only very slightly soluble in benzene at about 100 °C. The infrared spectrum of **2** shows two peaks at 1851 and 1817 cm^{-1} assignable to ν(Mo–H). The corresponding vibrations in $[Mo(\eta\text{-}C_5H_5)_2H_2]$ occur at 1847 cm^{-1}.[5] Since the reaction between **1** and CO gives the unsymmetrical complex $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_2(CO)]$ it must be possible for the hydrides of **1** to migrate between the two metal centres leaving one co-ordinatively unsaturated. By analogy, the formation of compound **2** is presumed to proceed by oxidative addition of H_2.

In view of the limited spectroscopic data available a single-crystal X-ray diffraction study of compound **2** was undertaken.

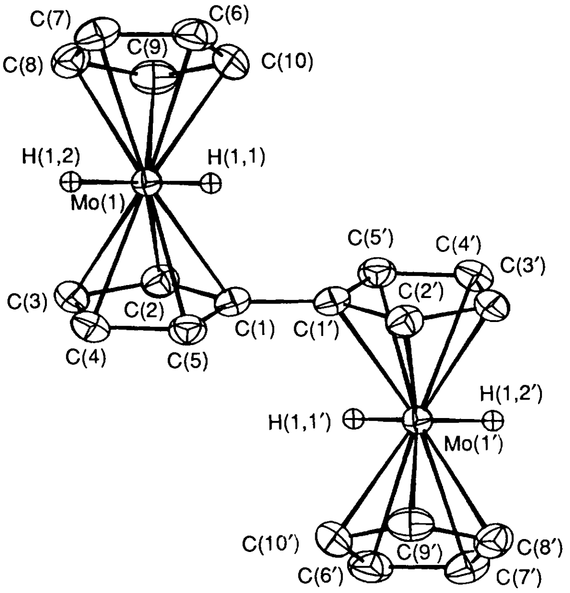

Fig. 1 Molecular structure of compound **2**. Primed atoms are generated from the asymmetric unit using inversion centres

The structure is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The molecule is centrosymmetric and the fulvalene unit is planar. The molecules lies in the sterically favoured *anti* conformation. This conformation is unusual for an early transition-metal dimer. In most of these complexes either metal–metal bonds or bridging ligands (or both), necessary to fulfil the effective atomic number rule, are present and serve to stabilize the *syn* conformation. The 32-electron complex $[Zr_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(SPh)_4]$ adopts the *trans* conformation for steric reasons.[6] It has been shown recently that the conformation of a fulvalene-bridged dimer can be decided simply by altering the electron count at the metal. Thus treatment of *anti*-$[Rh_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(CO)_4]$ with the carbonyl-abstracting reagent trimethylamine *N*-oxide gives the corresponding tricarbonyl $[Rh_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\mu\text{-}CO)(CO)_2]$, which contains both a metal–metal bond and a bridging ligand

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† *Supplementaty data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: 1 atm ≈ 101 325 Pa.

Fulvalene = 5-(cyclopenta-2,4-dien-1-ylidene)cyclopenta-1,3-diene.

Table 1 Analytical and spectroscopic data

		Analysis[a] (%)		
Compound	Colour, habit	C	H	Spectroscopic data[b]
2 $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_4]$	Yellow, blocks	52.60 (52.90)	4.85 (4.90)	IR: 1851 (sh), 1817 (sh)
3 $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(C_2H_4)_2]$	Deep red, microcrystals	56.50 (56.95)	5.20 (5.20)	^1H NMR (C_6D_6): 4.28 (AA'BB', 4 H, $C_5H_2\mathit{H}_2$), 4.21 (AA'BB', 4 H, $C_5\mathit{H}_2H_2$), 4.18 (s, 10 H, C_5H_5), 1.30 (AA'BB', 2 H, CH_2), 1.00 (AA'BB', 2 H, CH_2) ^{13}C NMR (C_6D_6): 96.2 (s), 81.3 (d, *J* 176), 79.8 (d, *J* 174), 77.9 (d, *J* 175), 13.9 (t, *J* 142)
4 $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$	Dark brown, blocks	52.35 (53.35)	4.05 (3.90)	IR: 1829 (w)
5 $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(MeC{\equiv}CMe)_2]$	Orange, plates	57.30 (60.20)	5.20 (5.40)	^1H NMR (C_6D_6): 4.27 (AA'BB', 4 H, $C_5H_2\mathit{H}_2$), 4.22 (s, 10 H, C_5H_5), 4.17 (AA'BB', 4 H, $C_5\mathit{H}_2H_2$), 2.33 (s, 6 H, CH_3) ^{13}C NMR (C_6D_6): 117 (s, C≡C), 100.5 (s, *ipso*-C), 84.5 (d, *J* 176, C_5H_5), 81.7 (d, *J* 176, $C_2\mathit{C}_2CH_4$), 79.8 (d, *J* 176, $\mathit{C}_2C_2CH_4$), 19.0 (q, *J* 126, CH_3)
6 $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(\mu\text{-}MeC{\equiv}CMe)]$	Black, powder	57.20 (57.15)	5.20 (4.80)	^1H NMR (C_6D_6): 4.96 (ABCD, 2 H, C_5H_4), 4.31 (s, 10 H, C_5H_5), 3.06 (ABCD, 2 H, C_5H_4), 3.02 (ABCD, 2 H, C_5H_4), 2.82 (ABCD, 2 H, C_5H_4), 1.62 (s, 6 H, CH_3) ^{13}C NMR (C_6D_6):[c] 94.8 (d, *J* 176, C_5H_4), 84.1 (d, *J* 176, C_5H_5), 74.4 (d, *J* 175, C_5H_4), 70.9 (d, *J* 175, C_5H_4), 59.9 (d, *J* 176, C_5H_4), 28.9 (q, *J* 126, CH_3)
7 $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(EtC{\equiv}CEt)_2]$	Red, needles	60.55 (62.55)	6.25 (6.35)	^1H NMR (C_6D_6): 4.28 (AA'BB', 4 H, $C_5H_2\mathit{H}_2$), 4.23 (s, 10 H, C_5H_5), 4.15 (AA'BB', 4 H, $C_5\mathit{H}_2H_2$), 2.60 (AA'BB'X_3, 8 H, *J* 7.3, CH_2), 1.26 (AA'BB'X_3, 12 H, *J* 7.3, CH_3) ^{13}C NMR (C_6D_6): 123 (s, C≡C), 99.7 (s, *ipso*-C), 89.0 (d, *J* 176, C_5H_5), 80.8 (d, *J* 176, C_4CH_4), 27.8 (q, *J* 126, CH_2), 15.6 (q, *J* 125, CH_3)

[a] Calculated values in parentheses. [b] NMR data given as: chemical shift (δ), multiplicity, relative intensity, *J* in Hz, assignment, ^1H at 300 MHz, ^{13}C at 62.9 MHz, ^{31}P at 101 MHz, unless otherwise stated. The labelling of atoms is as given in Scheme 1. [c] *ipso* and C≡C not observed.

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Mo(1)–C(1)	2.286(1)	Mo(1)–Cp*	1.948
Mo(1)–C(2)	2.243(2)	C(1)–C(1')	1.465(3)
Mo(1)–C(3)	2.279(2)	C(1)–C(2)	1.441(2)
Mo(1)–C(4)	2.327(2)	C(1)–C(5)	1.432(2)
Mo(1)–C(5)	2.326(2)	C(2)–C(3)	1.436(2)
Mo(1)–C(6)	2.328(2)	C(3)–C(4)	1.421(3)
Mo(1)–C(7)	2.326(2)	C(4)–C(5)	1.413(2)
Mo(1)–C(8)	2.278(2)	C(6)–C(7)	1.403(3)
Mo(1)–C(9)	2.247(2)	C(6)–C(10)	1.414(3)
Mo(1)–C(10)	2.277(2)	C(7)–C(8)	1.419(3)
Mo(1)–H(1,1)	1.59(3)	C(8)–C(9)	1.427(3)
Mo(1)–H(1,2)	1.58(3)	C(9)–C(10)	1.425(3)
Mo(1)–Fu*	1.944		
H(1,1)–Mo(1)–H(1,2)	79.5(1.7)	C(1)–C(2)–C(3)	108.2(1)
H(1,1)–Mo(1)–Fu	102.2	C(2)–C(3)–C(4)	107.7(1)
H(1,1)–Mo(1)–Cp	101.2	C(3)–C(4)–C(5)	108.4(2)
H(1,2)–Mo(1)–Fu	102.2	C(1)–C(5)–C(4)	109.1(2)
H(1,2)–Mo(1)–Cp	100.6	C(7)–C(6)–C(10)	109.1(2)
Fu–Mo(1)–Cp	149.9	C(6)–C(7)–C(8)	108.3(2)
Mo(1)–C(1)–C(1')	125.4(1)	C(7)–C(8)–C(9)	107.2(2)
C(1')–C(1)–C(2)	126.8(2)	C(8)–C(9)–C(10)	108.3(2)
C(1')–C(1)–C(5)	126.5(2)	C(6)–C(10)–C(9)	107.1(2)
C(2)–C(1)–C(5)	106.6(1)		

* Fu and Cp denote the centroids of the rings C(1)–C(5) and C(6)–C(10) respectively.

and adopts a *syn* conformation.[7] Drage and Vollhardt[8] have made similar observations in studies of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(CO)_6]$ which contains a metal bond and is *syn*. The distribution of the bond lengths in the fulvalene ligand is unexceptional. The Cp(centroid)–Mo–Fu(centroid) angle is 149.9°.

The Mo–H distances 1.59(3) and 1.58(3) Å and H–Mo–H bond angle 79.5(1.7)° as well as the Cp–Fu bending angle 144.6° and Mo–Cp distance along the vector normal to the ring plane 1.95 Å are comparable with the corresponding values of 1.685(3) Å, 75.5(3)°, 145.8° and 1.94 Å obtained from the neutron-diffraction investigation of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$.[9] The Cp and Fu rings are oriented in an eclipsed configuration.

Attempts to protonate compound **2** using $HBF_4{\cdot}Et_2O$ yielded a red acetone-soluble oil from which no solid material could be isolated. The ^1H NMR spectra of the oil were consistent with the presence of small amounts of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_3]BF_4$ as the only hydride-containing species.

When compound **1** was stirred in toluene at 100 °C under 10 atm of C_2H_4, the solution changed from deep green to red and on cooling gave red crystals of compound **3**. Elemental analysis of **3** was consistent with the stoichiometry $C_{24}H_{26}Mo_2$. The electron-impact mass spectrum shows a parent ion at *m/z* 504, also consistent with this stoichiometry. Compound **3** is insoluble in light petroleum and only slightly soluble in benzene. Solutions of **3** in dichloromethane at room temperature decompose over several hours. In the 300 MHz ^1H NMR spectrum of **3** the peaks assignable to the olefinic protons appear as an AA'BB' system with multiplets centred around δ 1.0 and 1.3. The distinct proton environments imply that ethylene rotation is slow on the NMR time-scale. The ^{13}C NMR spectrum of **3** recorded in dichloromethane shows only a single peak which may be assigned to two symmetrically co-ordinated ethylene ligands, one peak assignable to the cyclopentadienyl ligands, and the three peaks expected for a symmetrical fulvalene ligand. The chemical shifts of the latter are similar to those reported by Davison and Wreford[10] for the 'titanocene'

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

Mo(1)–Mo(2)	3.1428(4)	Mo(2)–C(6)	2.296(3)	C(1)–C(2)	1.422(5)	C(11)–C(12)	1.433(5)
Mo(1)–C(1)	2.292(3)	Mo(2)–C(7)	2.261(3)	C(1)–C(5)	1.439(5)	C(11)–C(15)	1.428(5)
Mo(1)–C(2)	2.256(3)	Mo(2)–C(8)	2.247(3)	C(1)–C(6)	1.449(4)	C(11)–C(16)	1.446(5)
Mo(1)–C(3)	2.249(3)	Mo(2)–C(9)	2.279(3)	C(2)–C(3)	1.424(5)	C(12)–C(13)	1.429(5)
Mo(1)–C(4)	2.282(4)	Mo(2)–C(10)	2.297(3)	C(3)–C(4)	1.427(6)	C(13)–C(14)	1.433(6)
Mo(1)–C(5)	2.303(3)	Mo(2)–C(16)	2.294(3)	C(4)–C(5)	1.408(5)	C(14)–C(15)	1.425(5)
Mo(1)–C(11)	2.299(3)	Mo(2)–C(17)	2.306(3)	C(6)–C(7)	1.429(5)	C(16)–C(17)	1.423(5)
Mo(1)–C(12)	2.300(3)	Mo(2)–C(18)	2.286(3)	C(6)–C(10)	1.425(5)	C(16)–C(20)	1.423(5)
Mo(1)–C(13)	2.281(4)	Mo(2)–C(19)	2.242(4)	C(7)–C(8)	1.419(5)	C(17)–C(18)	1.409(5)
Mo(1)–C(14)	2.242(4)	Mo(2)–C(20)	2.257(4)	C(8)–C(9)	1.438(6)	C(18)–C(19)	1.434(6)
Mo(1)–C(15)	2.253(4)	Mo(2)–H(2,1)	1.74(8)	C(9)–C(10)	1.430(5)	C(19)–C(20)	1.437(5)
Mo(1)–H(1,1)	1.67(4)	Mo(2)–Fu(2)*	1.925				
Mo(1)–Fu(1)*	1.927	Mo(2)–Fu(4)*	1.927				
Mo(1)–Fu(3)*	1.923						

Mo(2)–Mo(1)–H(1,1)	81.7(14)	C(2)–C(3)–C(4)	108.7(3)	C(15)–C(11)–C(16)	124.0(3)
H(1,1)–Mo(1)–Fu(1)	100.3	C(3)–C(4)–C(5)	107.6(3)	C(11)–C(12)–C(13)	109.0(3)
H(1,1)–Mo(1)–Fu(3)	102.1	C(1)–C(5)–C(4)	108.5(3)	C(12)–C(13)–C(14)	106.8(3)
Fu(1)–Mo(1)–Fu(3)	150.9	C(1)–C(6)–C(7)	123.3(3)	C(13)–C(14)–C(15)	108.8(3)
Mo(1)–Mo(2)–H(2,1)	70.9(28)	C(1)–C(6)–C(10)	127.2(3)	C(11)–C(15)–C(14)	108.1(3)
H(2,1)–Mo(2)–Fu(2)	105.9	C(7)–C(6)–C(10)	108.0(3)	C(11)–C(16)–C(17)	127.4(3)
H(2,1)–Mo(2)–Fu(4)	99.6	C(6)–C(7)–C(8)	107.9(3)	C(11)–C(16)–C(20)	123.7(3)
Fu(2)–Mo(2)–Fu(4)	151.7	C(7)–C(8)–C(9)	108.6(3)	C(17)–C(16)–C(20)	107.6(3)
C(2)–C(1)–C(5)	107.5(3)	C(8)–C(9)–C(10)	107.0(3)	C(16)–C(17)–C(18)	109.7(3)
C(2)–C(1)–C(6)	124.1(3)	C(6)–C(10)–C(9)	108.5(3)	C(17)–C(18)–C(19)	106.8(3)
C(5)–C(1)–C(6)	126.5(3)	C(12)–C(11)–C(15)	107.3(3)	C(18)–C(19)–C(20)	108.5(3)
C(1)–C(2)–C(3)	107.7(3)	C(12)–C(11)–C(16)	126.7(3)	C(16)–C(20)–C(19)	107.3(3)

* Fu(1), Fu(2), Fu(3) and Fu(4) denote the centroids of the rings C(1)–C(5), C(6)–C(10), C(11)–C(15) and C(16)–C(20) respectively.

$[Ti_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(\mu\text{-}H)_2]$. The data suggest that compound **3** has the structure, $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(C_2H_4)_2]$, in which two metallocene units are linked *via* the fulvalene unit in an *anti* arrangement analogous to that observed in **2**. Each half of the molecule may be regarded as consisting of a '$[Mo(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)]$' unit.[11]

The mononuclear complex $[Mo(\eta\text{-}C_5H_5)_2H_2]$ has been shown to hydrogenate olefins.[12] It was proposed that the initial co-ordination of ethylene was accompanied by ring slippage to give $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(\eta\text{-}C_2H_4)H_2]$ and subsequent insertion of the olefin into the Mo–H bond to give the ethyl hydride complex $[Mo(\eta\text{-}C_5H_5)_2H(Et)]$ which could then reductively eliminate ethane. Ethane elimination would generate co-ordinatively unsaturated $[Mo(\eta\text{-}C_5H_5)_2]$ which could add a further olefin molecule to give the observed product, $[Mo(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)]$. Gas chromatographic analysis of the headspace gas of the reaction vessel after the synthesis of compound **3** revealed the presence of ethane, consistent with a similar hydrogenation-based mechanism.

Compound **3** is thermally stable and can be recrystallized from refluxing toluene even in the absence of ethylene. It is also inert to substitution: the complex was recovered intact after 12 h in toluene at 100 °C both under 1 atm of CO or in the presence of an excess of PMe_3. Attempts to protonate **3** using HCl and HBF_4 gave only red oils from which no pure compounds or useful NMR data could be extracted.

When compound **1** in toluene was stirred under only 1 atm of ethylene, a mixture of dark red and red-brown crystals was obtained. Extraction with hot toluene and cooling the extract at −20 °C gave analytically pure **3**. Elemental analysis of the residual dark red-purple crystals **4** was consistent with the formulation $C_{20}H_{20}Mo_2$. The crystals of **4** were found to be insoluble in all common solvents. In view of our inability to obtain NMR spectra of the complex a single-crystal X-ray diffraction study was carried out. Its structure, $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$, is interesting and quite unexpected and is given in Fig. 2. Selected bond lengths and angles are given in Table 3. The two cyclopentadienyl ligands of **1** have become linked in **4** to form a second fulvalene ligand. The Mo–Mo distance is 3.1428(4) Å, which is slightly longer than one might expect for a Mo–Mo single bond from the sum of the covalent radii (3.12 Å), but significantly shorter than the Mo–Mo distances of 3.235(1) and 3.371(1) Å in $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$[13] and $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(CO)_6]$.[8] We also note that in two bis(fulvalene) systems in which no metal–metal bond is present the distance is significantly longer. In $[Fe_2(C_{10}H_8)_2]$ a distance of 3.984(4) Å[14] has been observed while in the analogous nickel complex

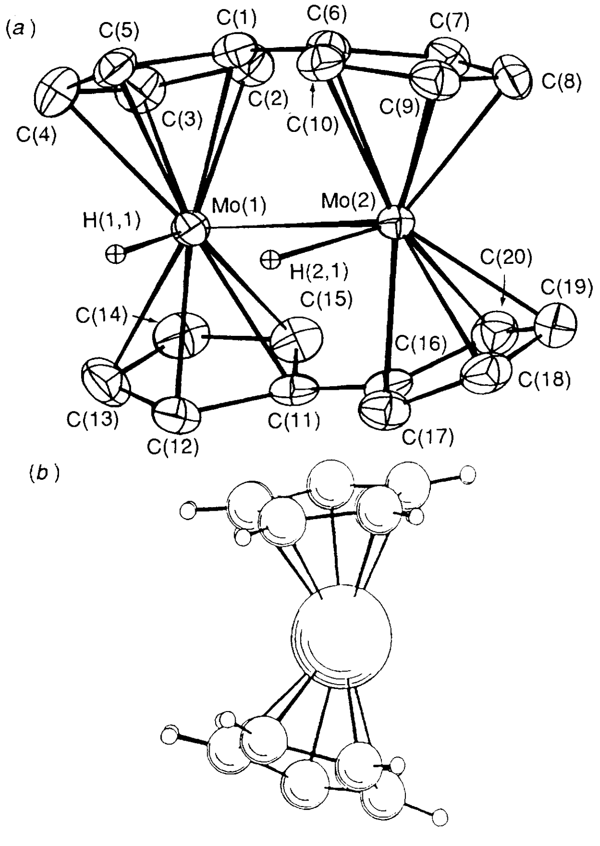


Fig. 2 Molecular structure of compound **4** viewed perpendicular to the Mo–Mo axis (*a*) and along the Mo–Mo axis (*b*)

the distance is 4.163(1) Å.[15] Thus the Mo–Mo distance must reflect a compromise between the metal–metal interaction and the geometrical requirements of the fulvalene ligands. The two fulvalene ligands of **4** are very similar. In contrast with compound **2**, in **4** the fulvalene rings are non-planar and show substantial twisting around the bridging C–C bond: the dihedral angle between the C(1)–C(5) and C(6)–C(10) planes is 22.2°, and between the C(11)–C(15) and C(16)–C(20) planes it is 22.7°. It should be noted that a similar distortion of the fulvalene planarity has been observed for $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(CO)_6]$ (the corresponding dihedral angle 15.3°) and other fulvalene dimetal systems.[8] This is a direct consequence of the drawing together of the two cyclopentadienyl ligands and linking them in a fulvalene unit. Each five-membered ring is planar to within experimental error and, as was noted for **2**, shows C–C bond distances consistent with delocalization over the framework. The Fu(centroid)–Mo–Fu(centroid) angles are 150.9 and 151.7° respectively. These angles are comparable with the value of 149.9° observed for **2**.

Fig. 2(*b*) presents the molecule of **4** as viewed along the Mo–Mo vector. This shows that the fulvalene ligands are canted 'sideways' in an arrangement reminiscent of bent metallocenes. A similar distortion occurs in $[V_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2(MeCN)_2][PF_6]_2$. Supporting evidence for the presence of the hydride ligands comes from the infrared spectrum which shows a weak band at 1829 cm^{-1}. This is in the normal region for ν(Mo–H) and may be compared with the metal–hydride vibrations observed in **2**.

The formation of the second fulvalene unit in compound **4** is quite unexpected. Although a number of bis(fulvalene) species have been reported, they have always been synthesized by metathesis of the metal halide with the $NaC_{10}H_8$ or $LiC_{10}H_8$. In particular, Smart and Curtis[16] have described the reaction between dimolybdenum tetraacetate and the fulvalenide anion to give dark red crystals which were proposed to be the bis(fulvalene) dimolybdenum compound $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2]$. The dark red compound is diamagnetic and in the absence of crystals suitable for X-ray diffraction, the structure shown in Fig. 3 was proposed. They did not report a band assignable to ν(Mo–H) and this together with the apparent difference of solubility compared to that of **4** suggests that the two compounds are different.

Any mechanism for the formation of **4** requires the removal of one equivalent of dihydrogen, presumably by hydrogenation of ethylene as has been discussed above for the formation of **3**. A likely key intermediate is the co-ordinatively unsaturated alkyl hydride shown in Fig. 4. We note that when the reaction is carried out under 10 atm of ethylene we have no evidence for the formation of **4**, suggesting that in the presence of significant amounts of ethylene, this intermediate is efficiently scavanged to give **3**. On the other hand, in the absence of an incoming ligand, reductive elimination of ethane occurs generating two co-ordinatively unsaturated metal centres. Sequential oxidative addition of a C–H bond of each of the two η-cyclopentadienyl ligands to the alternate molybdenum centres would give an intermediate with two $\mu\text{-}\sigma:\eta^5\text{-}C_5H_4$ ligands and two terminal hydride ligands. Reductive coupling of the two cyclopentadienyl ligands from this intermediate would then give **4**.

No reaction was observed between compound **1** and cyclohexene, cyclopentene, 2,3-dimethylbut-2-ene, or *tert*-butylethylene. Over a period of six months only slow decomposition was observed in the case of 2,3-dimethylbut-2-ene to give a sludgy brown precipitate. Our failure to observe reactions between **1** and the other olefins may be attributable to steric factors. We may view the dimolybdenum unit as being embedded in a fairly rigid 'tetracyclopentadienyl' cavity which restricts the more bulky substituted olefins from gaining access to the metal–metal bond.

Heating a toluene solution of **1** with but-2-yne at 120 °C for a period of 4 d gave a deep orange solution. Slow cooling of the solution gave a mixture of orange plates **5** and a black powder **6**.

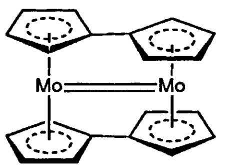


Fig. 3 The bis(fulvalene) complex proposed by Smart and Curtis[16]

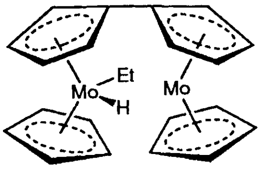


Fig. 4 The intermediate proposed to account for the formation of **4**

The two materials could not be separated by recrystallization and samples for elemental analysis were prepared by manual separation. The microanalysis of the orange crystals, **5**, is consistent with the stoichiometry $C_{28}H_{24}Mo_2$. The ^1H NMR spectrum shows the typical AA′BB′ pattern for the fulvalene ligand and a singlet for the methyl group, suggesting that the molecule contains two planes of symmetry or an inversion centre. The infrared spectrum shows a sharp peak at 1829 cm^{-1}, consistent with a side-bound alkyne. The ^{13}C chemical shift of the peak due to the quaternary 'acetylenic' carbons is at δ 117. Both the chemical shift and stretching frequency are in the range expected for a side-bound alkyne acting as a two-electron donor and the values are very similar to those reported for the mononuclear molybdenum but-2-yne complex $[Mo(\eta\text{-}C_5H_5)_2(MeC{\equiv}CMe)]$, prepared by photolysis of $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ in the presence of alkyne.[17] Thus, the data suggest the orange crystals to be $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(MeC{\equiv}CMe)_2]$ **5**, the but-2-yne analogue of compound **3** above. Since both metal centres are co-ordinatively saturated we would expect a structure in an *anti* conformation.

Purification of the black material, **6**, was difficult, the contaminant being **5**. Elemental analysis obtained on a sample separated manually from **5** under the microscope was consistent with the stoichiometry $C_{24}H_{24}Mo_2$. The ^1H NMR spectrum of compound **6** is more complex than for **5**. The singlet at δ 4.31 may be assigned to the cyclopentadienyl protons. Since only one peak is observed this implies that the two metal centres must be equivalent. Selective decoupling experiments show that the four multiplets between δ 4.96 and 2.82 form an ABCD spin system for the fulvalene ligand. Thus the two sides of the fulvalene must be inequivalent. However, the singlet at δ 1.62 implies that the two methyl groups of the but-2-yne unit are equivalent. The ^{13}C NMR spectrum mirrors the ^1H spectrum exactly, with one peak for the cyclopentadienyl ligands, four for the fulvalene ligand and one for the methyl group. We therefore tentatively propose a structure for **6** in which a but-2-yne molecule bridges the two metals $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(\mu\text{-}MeC{\equiv}CMe)]$. The geometry of the $Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2$ core in this structure proposed for **6** might be expected to be similar to that found in **4**.

Bridging alkyne complexes are well known and fall into two classes.[18] Complexes in which the alkyne lies perpendicular to the metal–metal vector are comparatively common. The 'parallel' alkyne complexes, of which this would be an example, are more unusual. Takats and co-workers[19] have reported $[Os_2(CO)_8(\mu\text{-}HC{\equiv}CH)]$. We note that Cuenca and Royo[20] have recently proposed a related parallel alkyne-bridged zirconocene system $[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}HC{\equiv}CR)Cl_2]$ (R = H or Ph).

When a solution of **1** in toluene was heated for 10 d with an excess of hex-3-yne a red solution was obtained from which dark-red, air-sensitive needles of **7** were isolated. Elemental analysis was consistent with the stoichiometry $C_{32}H_{46}Mo_2$. The ^1H NMR spectrum of the complex shows the expected pattern of a singlet for the η-C_5H_5 ring and two AA′BB′ multiplets which suggests a symmetrical molecule with a fulvalene bridge. In addition, a complex twelve line multiplet and a triplet observed to higher field may be assigned to co-ordinated hex-3-yne units. This suggests that the methylene protons of the hex-3-yne are diastereotopic and that the resonance therefore consists of an AA′BB′ system coupled to the X_3X_3' system of the methyl groups. The ^{13}C-{^1H} NMR spectrum of complex **7** shows only two peaks in the cyclopentadienyl region as opposed to the expected three. Selective irradiation of the proton frequencies of the fulvalene protons suggests that the fulvalene ^{13}C chemical shifts are degenerate. The singlet assigned to the alkyne carbon atoms appears at δ 123, which is in the range normally found for an alkyne acting as a two-electron donor. These observations suggest that the structure of **7** would be analogous to those of **2** and **5**.

We have no evidence for the formation of a μ-hex-3-yne complex analogous to **6**. This may reflect the increased steric demand placed on such a structure by the ethyl groups in this system. The increase of steric factors is also reflected by the fact that the reaction of **1** with hex-3-yne occurs much more slowly than with but-2-yne.

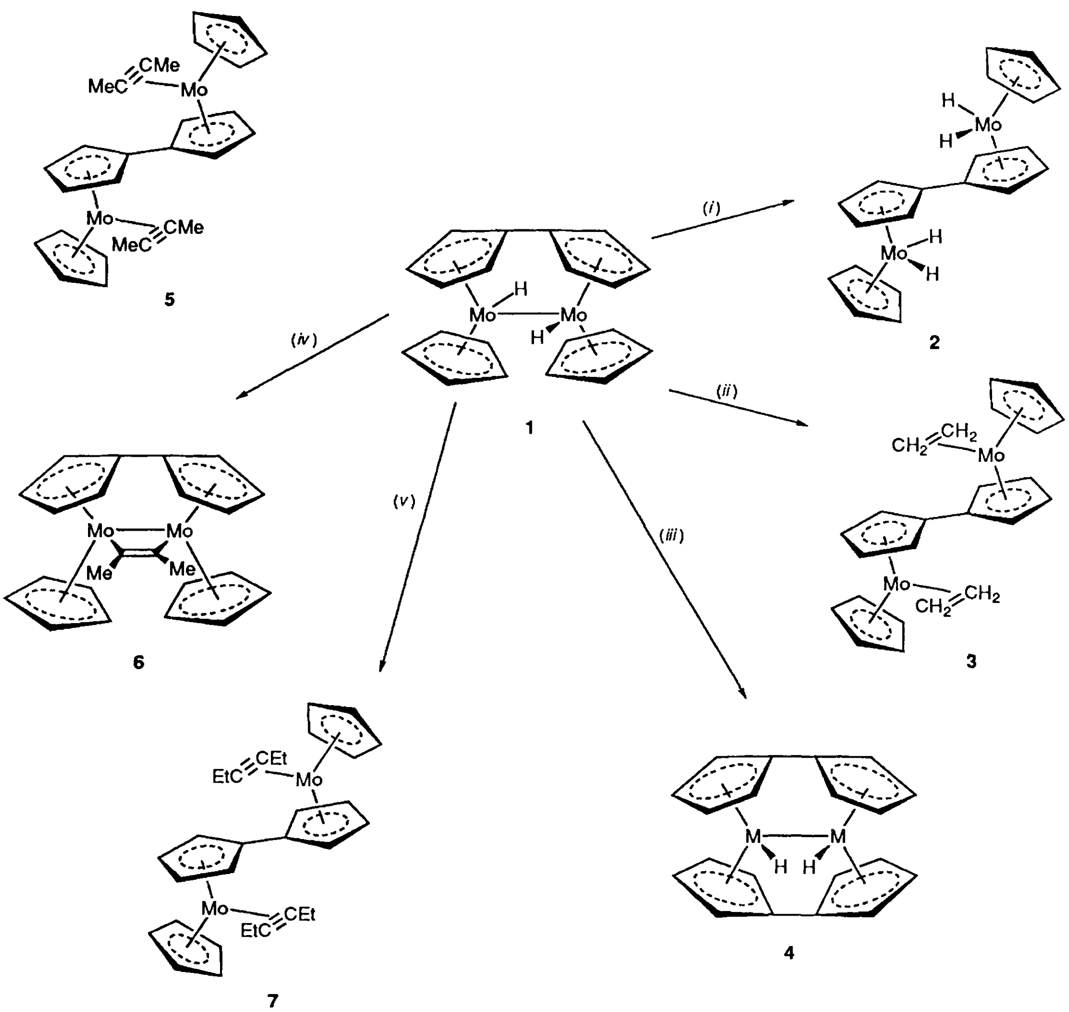
Reaction of **1** with acetylene, phenylacetylene, and with dimethylacetylene dicarboxylate gave deep red products which proved to be intractable. Investigations of the reactions of **1** with diazo compounds are in progress.

In conclusion, the reactions and structures proposed for the new compounds are given in Scheme 1.

Experimental

General Techniques.—All preparations and manipulations were performed using standard Schlenk line and dry-box techniques under an atmosphere of dinitrogen which had been purified by passage through a column containing BASF BTS catalyst and 4 Å molecules sieves. Reactions requiring gaseous reagents were carried out in custom-built reactors of the Fischer-Porter type. All solvents (except acetone) were pre-dried over 5 Å molecular sieves and refluxed over appropriate drying agents {sodium (toluene), potassium–benzophenone (tetrahydrofuran), Na–K alloy [light petroleum (b.p. 40–60 °C), pentane, diethyl ether], P_2O_5 (CH_2Cl_2), calcium hydride (acetonitrile), potassium carbonate (acetone)} and distilled under an atmosphere of dinitrogen before use. Deuteriated solvents (Aldrich) for NMR spectroscopy were stored under nitrogen over molecular sieves in a Young's ampoule and transferred in the dry-box using Pasteur pipettes. Celite 545 (Fluka) was stored in the oven (80 °C) before use. All reagents were obtained from commercial sources and used without further purification.

Sodium cyclopentadienide was prepared by titration of sodium dissolved in liquid ammonia with freshly cracked cyclopentadiene and recrystallized from tetrahydrofuran–light petroleum. Dimolybdenum tetraacetate was prepared in 65% yield by the method of Cotton[21] using acetic acid dehydrated by refluxing with acetic anhydride. Compound **1** was synthesized by a modification of the method of Sharp *et al.*[15] from dimolybdenum tetraacetate and sodium cyclopentadienide directly in hot toluene.



Scheme 1 Reactions of compound **1**. (*i*) H_2, 10 atm, 100 °C, toluene, 12 h; (*ii*) C_2H_4, 10 atm, 100 °C, toluene, 12 h; (*iii*) C_2H_4, 1 atm, 100 °C, toluene, 16 h; (*iv*) but-2-yne, 4 d, toluene, 120 °C; (*v*) hex-3-yne, 10 d, toluene, 120 °C

Table 4 Crystallographic data and experimental conditions for $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_4]$ **2** and $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$ **4**

Compound	**2**	4
Formula	$C_{20}H_{22}Mo_2$	$C_{20}H_{18}Mo_2$
M	454.27	450.24
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	5.982(4)	9.219(2)
b/Å	7.591(2)	13.614(3)
c/Å	9.997(2)	11.669(2)
α/°	70.38(3)	90
β/°	85.56(4)	96.68(1)
γ/°	68.44(3)	90
U/Å^3	397.13	1454.7
Z	1	4
D_c/g cm^{-3}	1.90	2.06
F(000)	226	888
Radiation	Mo-Kα	Mo-Kα
λ/Å	0.710 69	0.710 69
μ/cm^{-1}	15.36	16.77
Crystal size/mm	0.20 × 0.30 × 0.60	0.15 × 0.38 × 0.40
θ_{max}/°	27.5	30
Scan mode	ω–2θ	ω–2θ
Scan width	1 + 0.35 tan θ	1 + 0.35 tan θ
Total data collected	2125	4172
No. of observations	1733 (> 3σ)	3297 (> 5σ)
No. of parameters	145	272
Weighting coefficients	9.43, −5.18, 7.58	12.20, −1.86, 10.30
Final residuals *R* (*R*′)*	0.0184 (0.0209)	0.0368 (0.0428)
T/°C	22	22
Max., min peaks in final difference map/ e Å^{-3}	0.56, −0.69	0.84, −0.95

* $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{\frac{1}{2}}$.

Table 5 Fractional coordinates for compound **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.220 30(2)	0.808 83(1)	0.269 16(1)
C(1)	0.469 1(3)	0.515 2(2)	0.426 5(2)
C(2)	0.595 9(3)	0.580 3(2)	0.302 4(2)
C(3)	0.485 8(3)	0.574 3(2)	0.182 3(2)
C(4)	0.292 6(4)	0.506 7(3)	0.231 5(2)
C(5)	0.282 3(3)	0.470 6(2)	0.379 6(2)
C(6)	0.013 9(4)	1.117 6(3)	0.300 4(2)
C(7)	0.006 7(3)	1.148 2(2)	0.154 1(2)
C(8)	0.246 4(3)	1.095 7(2)	0.109 5(2)
C(9)	0.401 5(3)	1.032 1(2)	0.231 7(2)
C(10)	0.256 6(4)	1.043 8(3)	0.350 8(2)
H(2)	0.729(4)	0.615(3)	0.303(2)
H(3)	0.539(5)	0.604(4)	0.090(3)
H(4)	0.185(6)	0.486(4)	0.177(3)
H(5)	0.179(4)	0.416(4)	0.442(3)
H(6)	−0.128(5)	1.143(4)	0.356(3)
H(7)	−0.136(5)	1.198(4)	0.095(3)
H(8)	0.291(5)	1.101(4)	0.016(3)
H(9)	0.562(5)	0.994(4)	0.239(3)
H(10)	0.306(5)	1.014(4)	0.434(3)
H(1,1)	0.016(6)	0.790(5)	0.378(3)
H(1,2)	0.013(6)	0.837(5)	0.167(3)

The ^1H and ^{13}C NMR spectra in solution were obtained on Bruker AM-300 and AM-500 spectrometers at 300, 75.48 and 500 MHz respectively. All spectra were calibrated internally relative to residual solvent (^1H) and solvent (^{13}C) resonances respectively, and are reported relative to tetramethylsilane; high-frequency shifts are reported as being positive. Infrared spectra were recorded on either Mattson Polaris or Perkin Elmer 1510 FTIR spectrometer. Electron-impact ionization mass spectra were recorded either on an AEI MS 302 mass spectrometer updated with a MSS data handling system or by the SERC Mass Spectrometry Centre at the University College of Swansea. Elemental analyses were carried out by the Microanalytical Services of the Inorganic Chemistry Laboratory, Oxford.

Crystal Structure Determinations.—Crystals of compounds **2** and **4** were sealed under nitrogen in Lindemann capillaries. Crystallographic data were collected on an Enraf-Nonius CAD-4 diffractometer. Details are reported in Tables 4–6. The structures were solved using Patterson and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms (Chebushev weighting scheme). Hydrogen atoms attached to carbon were placed in calculated positions (C–H = 0.96 Å), whereas hydrogen atoms attached to molybdenum were located in the difference Fourier maps. All hydrogen atoms were refined isotropically. Corrections for Lorentz, polarization and extinction effects as well as empirical correction for absorption[22] were applied. Anomalous-dispersion contributions were included in the calculated structure factors.

Crystallographic calculations were carried out using the CRYSTALS suite of programs[23] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Preparation of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_4]$ **2**.—Compound **1** (500 mg, 1.1 mmol) in a Fischer-Porter bottle was suspended in toluene (20 cm^3) and pressurized to 10 atm with hydrogen. After stirring for 12 h at 100 °C, the solution was allowed to cool to room temperature (r.t.) over a period of 3 h. The resulting yellow block-like crystals were filtered off, washed with light petroleum (b.p. 40–60 °C) and dried *in vacuo* to yield analytically pure $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2H_4]$. Yield: 310 mg (60%).

Preparation of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(C_2H_4)_2]$ **3**.—Compound **1** (500 mg, 1.1 mmol) in a Fischer-Porter bottle was suspended in toluene (20 cm^3) and pressurized with 10 atm of ethylene. After stirring for 12 h at 100 °C the solution was allowed to cool to r.t. over a period of 3 h. Deep red crystals of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(C_2H_4)_2]$ were isolated by decantation of the mother-liquor, washed with light petroleum (b.p. 40–60 °C), and dried *in vacuo*. Yield: 250 mg (46%). Analytically pure samples of **3** were obtained by recrystallization from hot toluene.

Preparation of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$ **4**.—Compound **1** (200 mg, 0.44 mmol) in a Young's ampoule was suspended in toluene (20 cm^3). The flask was evacuated and back-filled with ethylene to a pressure of 1 atm. After stirring for 16 h at 100 °C the solution had turned red and a dark crystalline material had precipitated. The hot solvent was decanted off and the residue was extracted with boiling toluene until the washings were colourless. The residue was dried *in vacuo* yielding analytically pure $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)_2H_2]$. Yield: 120 mg (60.5%).

Preparation of $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(MeC{\equiv}CMe)_2]$ **5** *and* $[Mo_2(\mu\text{-}\eta:\eta\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2(\mu\text{-}MeC{\equiv}CMe)]$ **6**.—Compound **1** (200 mg, 0.44 mmol) was suspended in light petroleum (b.p. 40–60 °C, 30 cm^3) in a Young's ampoule. But-2-yne (Aldrich) (1 cm^3) was introduced into the flask by vapour transfer. The flask was kept *in vacuo* at 120 °C for 5 d by which time the dark green crystals had dissolved giving an orange-brown solution. This was transferred quickly into a Schlenk flask and allowed to cool to r.t. Thin orange plates and a black powder were seen to form on the glass wall. The solution was cooled to −80 °C for 12 h. The solvent was decanted at low temperature, the crystals were washed with cold light petroleum (b.p. 40–60 °C) and dried *in vacuo*. A total of 150 mg of material

Table 6 Fractional coordinates for compound **4**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.134 02(3)	0.133 79(2)	0.351 47(2)
Mo(2)	0.362 49(3)	0.302 23(2)	0.414 68(2)
C(1)	0.033 5(3)	0.285 2(2)	0.308 1(3)
C(2)	0.028 1(4)	0.227 7(3)	0.205 9(3)
C(3)	−0.063 4(4)	0.145 3(3)	0.219 5(3)
C(4)	−0.113 9(4)	0.150 8(3)	0.330 4(4)
C(5)	−0.055 0(3)	0.236 6(3)	0.384 7(3)
C(6)	0.139 3(3)	0.362 4(2)	0.338 3(3)
C(7)	0.247 9(4)	0.390 5(3)	0.266 8(3)
C(8)	0.350 2(4)	0.451 9(3)	0.332 9(3)
C(9)	0.306 5(4)	0.462 2(3)	0.446 7(3)
C(10)	0.175 9(4)	0.406 0(3)	0.449 0(3)
C(11)	0.369 1(4)	0.074 6(2)	0.370 0(3)
C(12)	0.289 6(4)	0.021 8(3)	0.448 7(3)
C(13)	0.171 9(5)	−0.029 8(3)	0.384 6(4)
C(14)	0.179 3(4)	−0.008 3(3)	0.265 2(4)
C(15)	0.299 5(4)	0.055 9(3)	0.256 3(3)
C(16)	0.473 2(3)	0.152 8(2)	0.398 6(3)
C(17)	0.521 6(4)	0.190 7(3)	0.510 1(3)
C(18)	0.596 4(4)	0.279 9(3)	0.499 5(4)
C(19)	0.595 9(4)	0.298 1(3)	0.378 5(4)
C(20)	0.519 5(4)	0.219 1(3)	0.315 8(3)
H(2)	0.074(5)	0.250(3)	0.141(4)
H(3)	−0.088(6)	0.090(5)	0.174(5)
H(4)	−0.180(5)	0.118(4)	0.364(4)
H(5)	−0.072(4)	0.267(3)	0.461(4)
H(7)	0.252(5)	0.374(3)	0.190(4)
H(8)	0.429(4)	0.479(3)	0.307(3)
H(9)	0.360(5)	0.501(3)	0.503(4)
H(10)	0.121(6)	0.400(4)	0.515(5)
H(12)	0.315(4)	0.018(3)	0.523(4)
H(13)	0.097(5)	−0.070(3)	0.417(4)
H(14)	0.107(5)	−0.037(3)	0.205(4)
H(15)	0.333(5)	0.085(4)	0.190(4)
H(17)	0.501(5)	0.162(4)	0.583(4)
H(18)	0.645(5)	0.310(3)	0.564(4)
H(19)	0.637(6)	0.346(5)	0.338(5)
H(20)	0.507(5)	0.204(3)	0.240(5)
H(2,1)	0.299(9)	0.260(6)	0.540(7)
H(1,1)	0.119(5)	0.141(3)	0.493(4)

was obtained. Attempts to separate the two compounds by recrystallization and by chromatography were unsuccessful so the black powder and the orange crystals were separated manually for the purpose of obtaining elemental analyses.

Preparation of [Mo$_2$(μ-η : η-C$_{10}$H$_8$)(η^5-C$_5$H$_5$)$_2$(EtC≡CEt)$_2$] 7.—Compound **1** (200 mg, 0.44 mmol) was suspended in light petroleum (b.p. 40–60 °C, 30 cm^3) in a Young's ampoule. Hex-2-yne (Aldrich) (1 cm^3) was introduced into the flask which was kept under vacuum at 120 °C for 10 d. The crystals of **1** gradually dissolved giving an orange-brown solution. The solution was cooled to r.t. and the solvent removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40–60 °C) and the extract was filtered. The volume of the filtrate was reduced to approximately 15 cm^3 and cooled to −80 °C for 16 h. Dark red air-sensitive needles separated which were washed with cold light petroleum (b.p. 40–60 °C). Yield: 180 mg (67%).

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