Synthesis and X-Ray Crystal Structure of the Dimolybdenum Acetaldehyde Complex $[Mo_2(\eta\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ *

Harry Adams, Neil A. Bailey, J. Trevor Gauntlett, Mark J. Winter and Simon Woodward
Department of Chemistry, The University, Sheffield S3 7HF, UK

The reaction of $[Mo(MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ **1** with $[C_7H_7][BF_4]$ gives the three organometallics $[Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ **2**, $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and $[Mo(CO)_2(\eta^3\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$, the first of which has been characterised by X-ray crystallography [monoclinic, space group $P2_1/c$, a = 8.265(4), b = 15.191(13), c = 13.511(9) Å, β = 97.89(5)°, R 0.0362 for 2104 independent reflections for which $I/\sigma(I) > 3.0$]. The molecule consists of two $Mo(CO)_2(\eta\text{-}C_5H_5)$ groups linked by a Mo–Mo bond [2.9670(8) Å] and bridged by an acetaldehyde ligand (η^2 through both C and O to one metal atom, σ through the oxygen to the second metal). The same three products arise in the reaction of **1** with $[Mo(CO)_3(\eta\text{-}C_7H_7)][BF_4]$, together with $[\{Mo(CO)_3(\eta^6\text{-}C_7H_7)\}_2]$. Addition of $LiBEt_3H$ to $[Mo_2(\mu\text{-}\eta^2\text{-}MeCO)(CO)_4(\eta\text{-}C_5H_5)_2]BF_4$ gives a high yield of **2**, as does the reaction of $HBF_4\cdot OEt_2$ with **1**. The reactions of complex **1** with any of $(CF_3CO)_2O$, $HC{\equiv}CCH_2Br$, $PhCH_2Br$, $[M(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ (M = Mo or W), CH_2Cl_2, $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ and $Fe_2(SO_4)_3$ lead to low yields of **2**. The tungsten complex $[W_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ is produced in low yield in the reaction of $Li[W(H)(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4\cdot OEt_2$.

In previous papers we addressed the reaction of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$[1] with $LiBEt_3H$.[2] This leads to the complexed acetaldehyde anion $[Mo(MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ **1** which is nucleophilic and reacts with MeI to form a Mo–Me bond. In the presence of donor ligands such as CO or PPh_3 the end result is evolution of MeCHO and formation of $[MoMe(CO)_2L(\eta\text{-}C_5H_5)]$ (L = CO or PPh_3). Other methylating agents ($MeSO_3F$ or $[Me_3O][BF_4]$) react at the aldehyde oxygen atom.[3] In this paper we address reactions of anion **1** whose common feature is the formation of a complex $[Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ **2**. Parts of this work are the subject of a preliminary communication.[4]

Results and Discussion

The reaction of $[Mo(MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ with $[C_7H_7][BF_4]$ proceeds over 3 h in tetrahydrofuran (thf) at ambient temperature to give three organometallic complexes characterised as $[Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ **2**, the known dimer $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[5] and the known η^3-tropyl $[Mo(CO)_2(\eta^3\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$.[6] The second two of these are well known and isolated in respective yields of 15 and 18%. Complex **2** is isolated in 20% yield and is fully spectroscopically characterised (see Experimental section). During chromatography on alumina it appears as a green-brown band but after crystallization is a very dark red, virtually black, crystalline solid. In addition to terminal stretching bands, the IR spectrum shows a relatively low ν_{CO} stretch at 1815 cm^{-1} in a position characteristic of semibridging carbonyls.[7] At −70 °C the ^{13}C NMR spectrum shows four carbonyl, two cyclopentadienyl, a methyl and a signal at δ 104.5 assigned to the aldehyde carbon. All four carbonyl and the two cyclopentadienyl signals are present in the room-temperature spectrum, indicating the structure is relatively static at ambient temperatures.

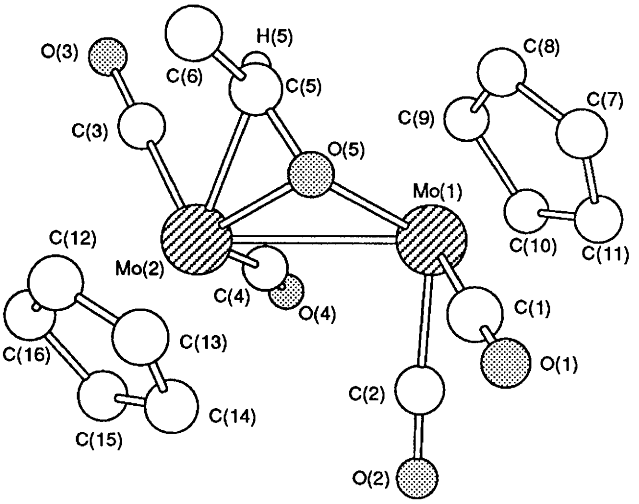


Fig. 1 Molecular geometry of $[Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2]$ **2** showing atom labelling

The molecular structure of **2**, as determined by X-ray crystallography, is shown in Fig. 1 and its parameters listed in Tables 1 and 2. The structure consists of two $Mo(CO)_2(\eta\text{-}C_5H_5)$ units linked by the Mo–Mo bond and bridged by an acetaldehyde ligand. The aldehyde is σ bonded (*via* the oxygen) to Mo(1) and η^2 (*via* the C=O) to Mo(2). The bridged Mo–Mo bond is shorter than the unsupported bond in $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (3.235 Å)[8] and close to that in bridged Mo–Mo complexes such as $[Mo_2(CO)_4(\mu\text{-}Me_3SiCCSiMe_3)(\eta\text{-}C_5H_5)_2]$ (Mo–Mo 2.953 Å)[9] and $[Mo_2(CO)_4(\mu\text{-}CH_2{=}C{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (Mo–Mo 3.117 Å).[10] The aldehyde C=O (1.354 Å) distance is lengthened relative to free aldehydes (typically 1.22 Å). The plane of the aldehyde is twisted by 68.3° relative to the bridge plane Mo(1),Mo(2),O(5) through the bridging oxygen atom but is more perpendicular (87.2°) to the plane defined by Mo(1), Mo(2) and C(5). One of the carbonyl ligands is semibridging and is somewhat bent [Mo(2)–C(4)–O(4) 166.3°]

---

* μ-Acetaldehyde-1κC^1,1:2$\kappa^2 O$-bis[dicarbonyl(η-cyclopentadienyl)-molybdenum] (*Mo–Mo*).

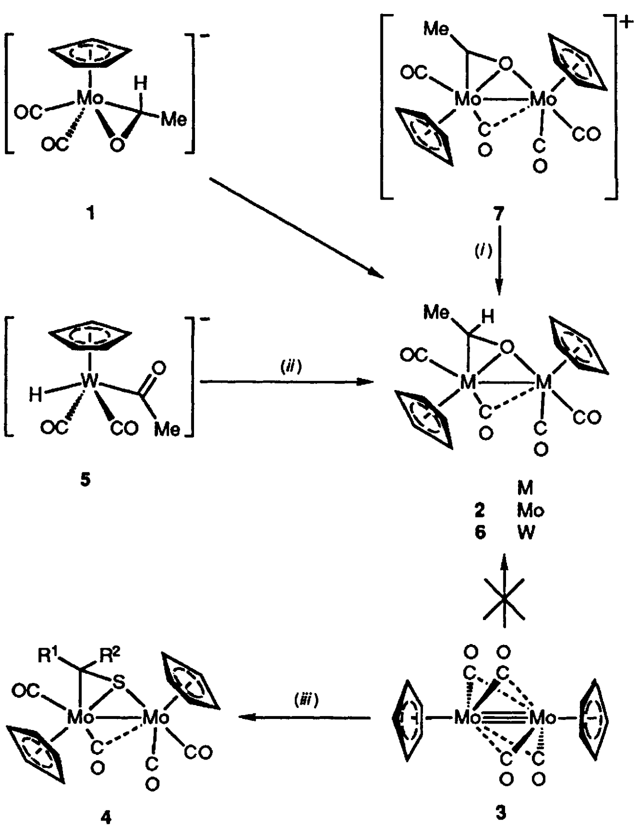
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atom coordinates for $[Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ **2**

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.159 26(7)	0.099 77(4)	0.142 62(4)
Mo(2)	0.297 30(7)	−0.032 35(4)	0.292 63(4)
O(1)	−0.214 6(7)	0.073 0(4)	0.105 8(5)
O(2)	0.008 5(10)	0.189 2(5)	0.314 6(5)
O(3)	0.664 1(7)	−0.064 9(5)	0.281 0(6)
O(4)	0.444 5(10)	0.151 4(4)	0.340 1(5)
O(5)	0.180 5(5)	−0.039 3(3)	0.147 4(3)
C(1)	−0.073 7(9)	0.079 0(5)	0.119 0(5)
C(2)	0.067 5(11)	0.155 1(5)	0.252 8(6)
C(3)	0.526 6(9)	−0.051 5(5)	0.286 0(6)
C(4)	0.380 7(11)	0.086 3(6)	0.310 6(6)
C(5)	0.325 0(9)	−0.079 2(5)	0.140 4(6)
C(6)	0.318 6(11)	−0.175 4(5)	0.117 9(7)
C(7)	0.164 5(10)	0.150 8(6)	−0.019 6(6)
C(8)	0.320 6(10)	0.113 6(5)	0.009 2(6)
C(9)	0.402 6(10)	0.157 4(6)	0.091 3(7)
C(10)	0.298 8(13)	0.225 7(5)	0.114 2(7)
C(11)	0.154 6(12)	0.222 6(5)	0.045 0(7)
C(12)	0.215 4(13)	−0.158 7(7)	0.372 4(7)
C(13)	0.075 7(11)	−0.114 6(7)	0.339 6(7)
C(14)	0.079 1(12)	−0.036 6(7)	0.386 9(7)
C(15)	0.228 6(17)	−0.030 4(8)	0.453 7(7)
C(16)	0.312 9(12)	−0.110 1(9)	0.441 6(7)

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for $[Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2]$ **2**

Mo(1)–Mo(2)	2.967 0(8)	Mo(2)–C(3)	1.932(8)
Mo(1)–C(1)	1.934(7)	Mo(2)–C(4)	1.933(9)
Mo(1)–C(2)	1.951(9)	Mo(2)–C(12)	2.345(10)
Mo(1)–C(7)	2.331(8)	Mo(2)–C(13)	2.374(10)
Mo(1)–C(8)	2.395(8)	Mo(2)–C(14)	2.347(10)
Mo(1)–C(9)	2.382(9)	Mo(2)–C(15)	2.324(12)
Mo(1)–C(10)	2.293(10)	Mo(2)–C(16)	2.322(11)
Mo(1)–C(11)	2.282(9)	Mo(2)–O(5)	2.068(4)
Mo(1)–O(5)	2.120(4)	Mo(2)–C(5)	2.218(7)
Mo(1) ··· C(4)	2.721(9)	C(5)–C(6)	1.493(11)
O(5)–C(5)	1.354(8)		
Mo(2)–Mo(1)–O(5)	44.18(12)	Mo(1)–Mo(2)–O(5)	45.60(12)
Mo(2)–Mo(1)–C(1)	106.46(21)	Mo(1)–Mo(2)–C(3)	110.99(24)
Mo(2)–Mo(1)–C(2)	85.61(25)	Mo(1)–Mo(2)–C(4)	63.40(25)
O(5)–Mo(1)–C(1)	85.34(24)	O(5)–Mo(2)–C(3)	106.36(26)
O(5)–Mo(1)–C(2)	116.44(27)	O(5)–Mo(2)–C(4)	106.19(28)
C(1)–Mo(1)–C(2)	73.4(3)	C(3)–Mo(2)–C(4)	79.1(3)
Mo(1)–C(1)–O(1)	175.1(6)	Mo(1)–Mo(2)–C(5)	70.26(19)
Mo(1)–C(2)–O(2)	177.1(8)	O(5)–Mo(2)–C(5)	36.63(22)
Mo(2)–C(3)–O(3)	178.5(7)	C(3)–Mo(2)–C(5)	71.45(30)
Mo(2)–C(4)–O(4)	166.3(8)	C(4)–Mo(2)–C(5)	109.6(3)
Mo(1)–O(5)–Mo(2)	90.22(17)	Mo(2)–C(5)–O(5)	65.6(3)
Mo(1)–O(5)–C(5)	120.9(4)	Mo(2)–C(5)–C(6)	119.9(5)
Mo(2)–O(5)–C(5)	77.7(4)	O(5)–C(5)–C(6)	116.5(6)



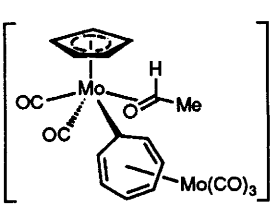
Scheme 1 (*i*) $LiBEt_3H$; (*ii*) $HBF_4{\cdot}OEt_2$; (*iii*) $R^1R^2C{=}S$

with the C(4) ··· Mo(1) distance relatively short (2.721 Å). Semibridging carbonyl groups of this type are well known in $[M_2(CO)_4(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ (M = Mo or W; L = four-electron bridging donor ligand, typically alkyne).[11] The closely planar cyclopentadienyl groups are slightly asymmetrically bonded to their molybdenum atoms in a manner consistent with the π-bonding nature of the *trans* ligands. Thus the carbon atoms most nearly *trans* to the carbonyl groups are more remote from molybdenum.

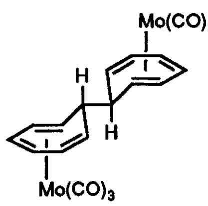
Many small molecules such as CO, phosphines, alkynes, isonitriles, *etc*., react by addition across the Mo≡Mo bond of $[\{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2\}]$ **3**.[12] It might be expected that acetaldehyde would react with $[\{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2\}]$ **3**, since **2** is a formal addition product of MeCHO across the Mo≡Mo bond of **3**. In the event, such an addition does not take place, even in the presence of large excesses of acetaldehyde. However, a number of thioketones,[13] thioesters, thiolactones[14] and dithioesters[15] *are* known to add across the Mo≡Mo bond (Scheme 1). As examples, thiocamphor (1,7,7- trimethylbicyclo-[2.2.1]heptane-2-thione) adds to $[\{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2\}]$ **3** to form **4**. The nature of the Mo_2CS central core is clearly very similar to that of the Mo_2CO core of **2**. A number of related complexes are also known. Although aldehydes have not apparently been reported bridging two molybdenum atoms, a number of complexes are known in which aldehydes bridge two other metals in manners reminiscent of **2**, although the formal representations of these species do not include metal–metal bonds.[16]

The mechanisms of formation of the complexes are clearly of interest. A plausible mechanism for the formation of $[Mo(CO)_2(\eta^3\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ involves nucleophilic attack of the anion **1** at $[C_7H_7]^+$ to form an σ-C_7H_7 intermediate $[Mo(\sigma\text{-}C_7H_7)(MeCHO)(CO)_2(\eta\text{-}C_5H_5)]$. This loses MeCHO as the η^3-allyl interaction is formed. The origin of $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ is far less clear, but is clearly complex. Complex **2** would arise by electron transfer to $[C_7H_7]^+$ followed by dimerisation of two resulting $Mo(MeCHO)(CO)_2(\eta\text{-}C_5H_5)$ units with loss of MeCHO. It is assumed that this process will result in some ditropyl, but no attempt was made to detect this compound.

Electron transfer from complex **1** to other oxidants also occurs. For instance, the reaction of ferrocenium cation with **1** leads to **2** in 11% yield, together with some $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and ferrocene. The reaction of solid $Fe_2(SO_4)_3$ with **1** in thf leads to **2** (10%) together with some $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$. The latter is isolable as $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ by addition of MeI, although a lesser quantity of $[MoI(CO)_3(\eta\text{-}C_5H_5)]$ also results. A very reasonable yield of **2** is obtained through the reaction of **1** with $HBF_4{\cdot}OEt_2$. Addition of $HBF_4{\cdot}OEt_2$ to a solution of **1** gives a reaction mixture containing MeCHO (GLC analysis). The isolated organometallic products isolated are $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and a 57% yield of **2**. This



8



9

reaction needs to be worked up promptly, isolated yields fall sharply if the reaction mixture is left stirring. During chromatography of the reaction mixture a yellow material is also evident. This yellow band turns to pink [{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] during elution under air, suggesting that the yellow material is probably [MoH(CO)$_3$(η-C$_5$H$_5$)], although this is not confirmed. A moderate yield of **2** (31%) is also obtained if the thf solvent is removed from the reaction producing **1** and replaced with CH_2Cl_2. This is probably a consequence of traces of acid in the CH_2Cl_2 when used as supplied.

We recently described the formation of the anion [WH(COMe)(CO)$_2$(η-C$_5$H$_5$)]$^-$ **5** by treatment of [WMe(CO)$_3$(η-C$_5$H$_5$)] with LiBEt$_3$H.[17] Its reaction with HBF$_4$·OEt$_2$ leads to a low yield of complex **6**, the tungsten analogue of **2**. Insufficient quantities of this compound were obtained for a ^{13}C NMR spectrum but the other spectroscopic data (see Experimental section) are clearly closely related. No complex **6** is observed in the reaction of **5** with [Fe(η-C$_5$H$_5$)$_2$][PF$_6$], the only observed organometallic products of this reaction being ferrocene and a little [WMe(CO)$_3$(η-C$_5$H$_5$)].

The μ-acetyl complex **7** is known.[18] It is made by the reaction of [Mo(CO)$_3$(FBF$_3$)(η-C$_5$H$_5$)] with [MoMe(CO)$_3$(η-C$_5$H$_5$)]. Addition of LiBEt$_3$H to a suspension of **7** in thf represents a rational synthesis of **2**. This approach is successful and the yield of **2** is 59%. Very small amounts of [{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] are also isolated.

The reaction of [M(CO)$_3$(η-C$_5$H$_5$)][BF$_4$] (M = Mo or W) with **1** also leads to moderate quantities of **2**. In the former case [{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] is also formed, in the latter a mixture of [{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$], [{W(CO)$_3$(η-C$_5$H$_5$)}$_2$] and [(η-C$_5$H$_5$)(OC)$_3$Mo–W(CO)$_3$(η-C$_5$H$_5$)] also arises. In both cases, quantities of [MoMe(CO)$_3$(η-C$_5$H$_5$)] are seen. This material was not present in the original solution of **1**. This reflects a tendency of the cations [M(CO)$_3$(η-C$_5$H$_5$)]BF$_4$ (M = Mo or W) to abstract hydride from **1** in pathways competing with the formation of **2**. The result of such an abstraction is the intermediate [Mo(COMe)(CO)$_3$(η-C$_5$H$_5$)] which decarbonylates rapidly to form [MoMe(CO)$_3$(η-C$_5$H$_5$)].

Very small amounts of complex **2** are also formed in the reactions of **1** with (CF$_3$CO)$_2$O, HC≡CCH$_2$Br, PhCH$_2$Br or [Mo(CO)$_3$(η^7-C$_7$H$_7$)][BF$_4$]. In the last case, substantial quantities of [Mo(CO)$_3$(η^3-C$_7$H$_7$)(η-C$_5$H$_5$)] are formed. This would arise from an intermediate structure **8** from which the Mo(CO)$_3$ fragment is lost as the η^3-tropyl interaction is formed. A further product is [{Mo(CO)$_3$}$_2$(η^6,η$'^6$-C$_{14}$H$_{14}$)] **9** (14%) previously identified in the reaction of [Mo(CO)$_3$(η^7-C$_7$H$_7$)]$^+$ with **1**.[19]

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer calibrated using the absorption of polystyrene film at 1601.4 cm^{-1} or on a Perkin-Elmer FT1710 instrument linked to a 3600 data station. Proton NMR spectra were recorded using JEOL PFT-100 (100.00 MHz), Bruker WP-80SY (80.13 MHz), AM-250 (250.13 MHz), WH-400 (400.13 MHz) and Perkin-Elmer R34 (200 MHz) instruments, carbon-13 NMR spectra using JEOL PFT-100 (25.15 MHz), Bruker AM-250 (62.88 MHz) and WH-400 (100.13 MHz) instruments. Mass spectra were recorded using Kratos MS 25 [electron impact and gas chromatography (GC)–mass spectrometry] or MS 80 (chemical ionisation and fast atom bombardment) instruments. All reactions were performed under nitrogen or argon atmospheres generally in Schlenk glassware dried by heating under vacuum. Solvents were used as supplied, except thf which was distilled from sodium–benzophenone immediately prior to use and light petroleum (fraction boiling at 40–60 °C throughout) which was distilled from LiAlH$_4$. Alumina was Brockmann activity I deactivated with water (5% w/w) to activity II or supplied as Brockmann activity II. The reagent LiBEt$_3$H (Aldrich 'Super Hydride') was used as supplied. The compounds [MoMe(CO)$_3$(η-C$_5$H$_5$)],[20] Li[Mo(MeCHO)(CO)$_2$(η-C$_5$H$_5$)], **1**, Li[WH(COMe)(CO)$_2$(η-C$_5$H$_5$)],[17] [Mo$_2$(μ-η^2-MeCO)(CO)$_4$(η-C$_5$H$_5$)$_2$][BF$_4$],[18] [Fe(η-C$_5$H$_5$)$_2$][PF$_6$],[21] [C$_7$H$_7$][BF$_4$][22] and [Mo(CO)$_3$(η^7-C$_7$H$_7$)][BF$_4$][20] were synthesised according to literature procedures.

Reactions of [Mo(MeCHO)(CO)$_2$(η-C$_5$H$_5$)]$^-$ **1**.—*With* [C$_7$H$_7$][BF$_4$]. Solid [C$_7$H$_7$][BF$_4$] (0.50 g, 2.81 mmol) was added to a solution of complex **1** (1.9 mmol in thf) at ambient temperature. The solution darkened to red-brown as the solid dissolved (30 min). After filtration of the reaction mixture through an alumina plug, the solvent was removed under reduced pressure and the resulting brown material chromatographed on alumina (25 × 3 cm) using light petroleum–dichloromethane (7:1 increasing to 4:1). Elution gave orange [Mo(CO)$_2$(η^3-C$_7$H$_7$)(η-C$_5$H$_5$)] (0.088 g, 18%), pink [{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] (0.085 g, 15%), and black [Mo$_2$(μ-η^2-MeCHO)(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.093 g, 20%).

[Mo$_2$(μ-η^2-MeCHO)(CO)$_4$(η-C$_5$H$_5$)$_2$] **2**: m.p., decomp. without melting, too dark to observe (Found: C, 40.1; H, 2.9%; M^+, 478. C$_{16}$H$_{14}$Mo$_2$O$_5$ requires C, 40.2; H, 3.0%; M 478); ν_{CO}/cm^{-1} (light petroleum) 1959m, 1932s, 1871s and 1833m; ^{1}H NMR, δ(400 MHz, CDCl$_3$) 5.53 (5 H, s, C$_5$H$_5$), 5.22 (5 H, s, C$_5$H$_5$), 2.16 [1 H, q, J(HH) = 5, CH] and 1.86 [3 H, d, J(HH) = 5 Hz, Me]; ^{13}C NMR (63 MHz, C$_6$D$_5$CD$_3$, −70 °C) 253.2 (CO), 247.9 (CO), 229.2 (CO), 227.8 (CO), 104.5 (Me*C*HO), 98.2 (C$_5$H$_5$), 96.0 (C$_5$H$_5$) and 30.0 (Me).

With [Mo(CO)$_3$(η^7-C$_7$H$_7$)][BF$_4$]. Solid [Mo(CO)$_3$(η-C$_7$H$_7$)][BF$_4$] (0.54 g, 1.5 mmol) was added to a solution of complex **1** (1.15 mmol in thf). The solution darkened from the original orange-brown instantly but was left to stir (18 h). Removal of solvent under reduced pressure resulted in a brown solid. Chromatography on alumina (30 × 3 cm) eluting with light petroleum–dichloromethane (7:1 changing to 4:1) gave orange [Mo(CO)$_2$(η^3-C$_7$H$_7$)(η-C$_5$H$_5$)] (0.17 g, 47%) followed by black [Mo$_2$(μ-η^2-MeCHO)(CO)$_4$(η-C$_5$H$_5$)$_2$] **2** (0.005 g, 1%). Further extraction of the brown solid into CH$_2$Cl$_2$ followed by filtration through a short alumina plug resulted in a red solution containing [{Mo(CO)$_3$}$_2$(η^6,η$'^6$-C$_{14}$H$_{14}$)] **9** isolated in 14% yield (0.055 g) by crystallisation from light petroleum–dichloromethane. A similar ratio of products was isolated when the reaction was carried out under a carbon monoxide atmosphere.

With (CF$_3$CO)$_2$O. An instant colour change to dark brown resulted on addition of (CF$_3$CO)$_2$O (0.2 cm^3, 1.5 mmol) to a solution of complex **1** (1.0 mmol in thf, 60 cm^3). The reaction mixture was filtered through short alumina and Florisil plugs. Chromatography on alumina (10 × 2 cm) eluting with light petroleum–dichloromethane (7:1 changing to 4:1) afforded [{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] (0.005 g, 2%) and [Mo$_3$(μ-η^2-MeCHO)(CO)$_4$(η-C$_5$H$_5$)$_2$] **2** (0.048 g, 20%).

With HC≡CCH$_2$Br. Prop-2-ynyl bromide (0.2 cm^3, 80% w/w in toluene, 1.9 mmol) was added to a solution of complex **1** (1.0 mmol in thf, 40 cm^3) at −70 °C and the solution allowed to warm to ambient temperature. The solvent was removed under reduced pressure and the resulting brown solid dissolved in CH$_2$Cl$_2$ (10 cm^3) and filtered through Kieselguhr. Removal of solvent under reduced pressure and extraction of the resulting brown gum into light petroleum (3 × 20 cm^3) gave a green solution from which black crystals of [Mo$_2$(μ-η^2-MeCHO)(CO)$_4$(η-C$_5$H$_5$)$_2$] **2** (0.012 g, 5%) separated on cooling.

With $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$. A solution of $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ (0.83 g, 2.5 mmol in 40 cm^3 thf) was added dropwise to a solution of complex **1** (2.5 mmol in thf, 40 cm^3) at ambient temperature. The solution darkened to red-brown (4 h). Removal of solvent under reduced pressure resulted in a dark brown solid. Chromatography on alumina (20 × 3 cm) under nitrogen in the absence of light, eluting with light petroleum–dichloromethane (4:1 changing to 3:1), provided yellow $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$ (0.088 g, 14%) followed by pink $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]$ (0.080 g, 13%) and black $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ (0.121 g, 20%).

With $[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$. A solution of $[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ (0.59 g, 1.4 mmol in 40 cm^3 thf) was added to a solution of complex **1** (1.4 mmol in thf, 35 cm^3) at ambient temperature and the solution stirred (2 h) during which time it darkened to red-brown. The solvent was removed under reduced pressure. Chromatography on alumina (15 × 3 cm) under nitrogen, eluting with light petroleum–dichloromethane (4:1), gave yellow $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$ (0.035 g, 13%), a pink mixture (0.11 g total) containing $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]$, $[\mathrm{MoW(CO)_6(\eta\text{-}C_5H_5)_2}]$ and $[\{\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}\}_2]$, and black $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ (0.064 g, 19%).

With $[\mathrm{Fe(\eta\text{-}C_5H_5)_2}][\mathrm{PF_6}]$. Solid $[\mathrm{Fe(\eta\text{-}C_5H_5)_2}][\mathrm{PF_6}]$ (0.84 g, 2.6 mmol) was added to a solution of complex **1** (1.7 mmol in thf, 80 cm^3). The solution was stirred (2 h) during which time the solid dissolved and the solution darkened to red-brown. After removal of solvent under reduced pressure, chromatography on alumina (15 × 3 cm) under nitrogen and eluting with light petroleum–dichloromethane (4:1) gave orange ferrocene (0.142 g, 34%), pink $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]$ (0.008 g, 2%) and black $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ **2** (0.045 g, 11%).

With $\mathrm{Fe_2(SO_4)_3}$. A solution of complex **1** (1.0 mmol in thf, 50 cm^3) was treated at ambient temperature with solid $\mathrm{Fe_2(SO_4)_3}$ (0.4 g, 1.0 mmol) and the solution stirred (3 h) during which time the solid dissolved. The IR spectrum of the reaction mixture contained bands assigned to the anion $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}]^-$. This was converted into $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$ by addition of MeI (0.18 cm^3, 0.4 g, 2.8 mmol) followed by stirring (40 h). The cloudy brown solution was filtered through alumina (6 × 1 cm) and the solvent removed under reduced pressure. Extraction into light petroleum–dichloromethane (7:1 v/v 3 × 10 cm^3) followed by chromatography on alumina (15 × 3 cm) resulted in yellow, orange and green bands. Eluting with light petroleum–dichloromethane (4:1 v/v) gave yellow $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$ (0.048 g, 19%), orange $[\mathrm{MoI(CO)_3(\eta\text{-}C_5H_5)}]$ (0.015 g, 4%), and black $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ **2** (0.024 g, 10%).

With $\mathrm{HBF_4{\cdot}OEt_2}$. A solution of complex **1** (0.42 mmol in thf, 20 cm^3) was mixed with $\mathrm{HBF_4{\cdot}OEt_2}$ (0.22 g, 1.36 mmol) and the solution stirred (5 min). Gas–liquid chromatography showed the presence of MeCHO. Prompt filtration of the red-brown solution through alumina (4 × 1 cm) and removal of solvent under reduced pressure gave a dark brown solid. This was extracted into light petroleum–dichloromethane (7:1 v/v, 10 cm^3) and chromatographed on alumina (5 × 2 cm) under nitrogen using the same solvent. This gave yellow, pink and green bands. The yellow band slowly turned pink on the column. The fractions collected were pink $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]$ (0.01 g, 10%) and black $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ **2** (0.058 g, 57%).

Dissolution of $[\mathrm{Mo(CO)_2(MeCHO)(\eta\text{-}C_5H_5)}]^-$ **1** *in* $\mathrm{CH_2Cl_2}$.—The solvent was removed from a solution of complex **1** prepared from $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$ (0.26 g, 1.0 mmol) and $\mathrm{LiBEt_3H}$ (1.2 cm^3, 1.2 mmol). The resulting brown gum was dissolved in deoxygenated, reagent-grade dichloromethane. Removal of the solvent followed by extraction into light petroleum–dichloromethane (7:1 v/v, 100 cm^3) and filtration through alumina (10 × 2 cm) resulted in a faint pink and a green band. The former was discarded and the second gave black $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ **2** (0.05 g, 31%).

Reaction of $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCO)(CO)_4(\eta\text{-}C_5H_5)_2}][\mathrm{BF_4}]$ **7** *and* $\mathrm{LiBEt_3H}$.—A suspension of the cationic complex $[\mathrm{Mo_2(\mu\text{-}\eta^2\text{-}MeCO)(CO)_4(\eta\text{-}C_5H_5)_2}][\mathrm{BF_4}]$ **7** (0.1 g, 0.18 mmol) in thf (20 cm^3) was cooled to 0 °C and $\mathrm{LiBEt_3H}$ (0.25 cm^3, 1 mol dm^{-3} solution in thf, 0.25 mmol) added dropwise over 5 min. The solution darkened slowly to green-black as the solid dissolved. Filtration of the reaction mixture through an alumina plug followed by chromatography on alumina (12 × 2 cm) resolved pink and green fractions, the latter being eluted by light petroleum–dichloromethane (2:1). The pink band contained a little $[\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]$ and the green band contained complex **2** (0.051 g, 59%).

Reaction between $\mathrm{Li[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]}$ *and* $\mathrm{HBF_4{\cdot}OEt_2}$.—A solution of the salt $\mathrm{Li[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]}$ (0.57 mmol in thf, 15 cm^3) was cooled (−90 °C) and a standard diethyl ether solution of $\mathrm{HBF_4{\cdot}OEt_2}$ (1.0 cm^3, 0.46 mmol) added over 15 min. The reaction mixture turned dark orange and was allowed to warm to room temperature (1 h) during which time it turned black. The solvent was removed and the residue extracted with diethyl ether (2 × 25 cm^3). Filtration through an alumina plug and crystallisation afforded $[\mathrm{W_2(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ **6** as brown microcrystals (0.016 g, 5%), m.p. 108–110 °C (decomp.) (Found: C, 29.4; H, 1.9%; M^+, 654. $\mathrm{C_{16}H_{14}O_5W_2}$ requires C, 29.4; H, 2.2%; M, 654); ν_{CO}/cm^{-1} ($\mathrm{CH_2Cl_2}$) 1953w, 1913s and 1834m, NMR($\mathrm{CDCl_3}$): ^{1}H (250.13 MHz), δ 5.74 (5 H, s, η-$\mathrm{C_5H_5}$), 5.49 (5 H, s, η-$\mathrm{C_5H_5}$), 2.10 [1 H, q, ^3J(HH) = 5 Hz, CH] and 1.97 (3 H, d, Me); ^{13}C (100.61 MHz), δ 101.0 (CH), 96.7 (η-$\mathrm{C_5H_5}$), 93.5 (η-$\mathrm{C_5H_5}$) and 29.8 (Me). An inadequate signal-to-noise ratio prevented assignment of the carbonyl signals.

X-Ray Crystal Structure of $[\mathrm{Mo(\mu\text{-}\eta^2\text{-}MeCHO)(CO)_4(\eta\text{-}C_5H_5)_2}]$ **2**.—*Crystal data.* $\mathrm{C_{16}H_{14}Mo_2O_5}$, $M = 478.08$, crystallises from light petroleum as thick red plates, crystal dimensions 0.6 × 0.2 × 0.35 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 8.265(4)$, $b = 15.191(13)$, $c = 13.511(9)$ Å, $\beta = 97.89(5)°$, $U = 1680.2(20)$ Å^3, $Z = 4$, $D_c = 1.890$ g cm^{-3}, Mo-Kα radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-Kα) = 14.77 cm^{-1}, $F(000) = 936$.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet *R*3*m* diffractometer by the ω-scan method. The 2104 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions [C–H 0.97 Å, C–C–H(methyl) 111°]; their contributions were included in structure-factor calculations ($B = 7.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0362 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of molybdenum. Table 2 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from those published.[23] Unit weights were used throughout the refinement; computer programs form part of the Sheffield X-ray system.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

J. T. G. and S. W. are pleased to be recipients of SERC research studentships. We are grateful to the Royal Society and to the SERC for generous support.

References

1 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.

2 J. T. Gauntlett, B. F. Taylor and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1985, 1815; J. T. Gauntlett, B. F. Taylor and M. J. Winter, *J. Chem. Soc., Chem. Commun.*, 1984, 420; J. T. Gauntlett and M. J. Winter, *Polyhedron*, 1986, **5**, 451.

3 H. Adams, N. A. Bailey, J. T. Gauntlett, I. M. Harkin, M. J. Winter and S. Woodward, *J. Chem. Soc., Dalton Trans.*, 1991, 1117.

4 H. Adams, N. A. Bailey, J. T. Gauntlett and M. J. Winter, *J. Chem. Soc., Chem. Commun.*, 1984, 1360.

5 R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 99.

6 J. W. Faller, *Inorg. Chem.*, 1969, **8**, 767; M. A. Bennett, R. Bramley and R. Watt, *J. Am. Chem. Soc.*, 1969, **91**, 3089.

7 R. J. Klingler, W. M. Butler and M. D. Curtis, *J. Am. Chem. Soc.*, 1978, **100**, 5034.

8 R. D. Adams, D. M. Collins and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086.

9 J. A. Beck, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 195.

10 W. I. Bailey, M. H. Chisholm, F. A. Cotton, C. A. Murillo and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 802.

11 W. I. Bailey, F. A. Cotton, J. D. Jamerson and J. R. Kolb, *J. Organomet. Chem.*, 1976, **121**, C23; W. I. Bailey, D. M. Collins and F. A. Cotton, *J. Organomet. Chem.*, 1977, **135**, C55.

12 F. A. Cotton and R. A. Walton, in *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982; M. J. Winter, *Adv. Organomet. Chem.*, 1989, **29**, 101.

13 H. Alper, N. D. Silavwe, G. I. Birnbaum and F. R. Ahmed, *J. Am. Chem. Soc.*, 1979, **101**, 6582.

14 H. Alper, F. W. B. Einstein, R. Nagai, J.-F. Petrignani and A. C. Willis, *Organometallics*, 1983, **2**, 1291.

15 H. Alper, F. W. B. Einstein, F. W. Hartstock and A. C. Willis, *J. Am. Chem. Soc.*, 1985, **107**, 173; *Organometallics*, 1986, **5**, 9.

16 G. Erker, K. Kropp, K. Kruger and A.-P. Chiang, *Chem. Ber.*, 1982, **115**, 2447; G. Fachinetti, C. Floriani, A. Roselli and C. Pucci, *J. Chem. Soc., Chem. Commun.*, 1978, 269; S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 1983, **105**, 1690; G. Fachinetti, C. Biran, C. Floriani, A. C. Villa and C. Guastini, *Inorg. Chem.*, 1978, **17**, 2995; J. A. Marsella, J. C. Huffman and K. G. Caulton, *ACS Symp. Ser.*, 1981, **152**, 35; K. Kropp, V. Skibbe, G. Erker and C. Krüger, *J. Am. Chem. Soc.*, 1983, **105**, 3353; B. D. Martin, S. A. Matchett, J. R. Norton and O. P. Anderson, *J. Am. Chem. Soc.*, 1985, **107**, 7952; G. Erker, U. Dorf, P. Czisch and J. L. Petersen, *Organometallics*, 1986, **668**, 5; G. Erker, U. Hoffmann, R. Zwetler, P. Betz and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 630.

17 J. T. Gauntlett, B. E. Mann, M. J. Winter and S. Woodward, *J. Organomet. Chem.*, 1988, **342**, C5; *J. Chem. Soc., Dalton Trans.*, 1991, 1427.

18 K.-H. Sunkel, K. Schloter, W. Beck, K. Ackermann and U. Schubert, *J. Organomet. Chem.*, 1983, **241**, 333; S. J. LaCroce and A. R. Cutler, *J. Am. Chem. Soc.*, 1982, **104**, 2312.

19 H. Adams, N. A. Bailey, D. G. Willett and M. J. Winter, *J. Organomet. Chem.*, 1987, **333**, 61.

20 *Organometallic Syntheses, Transition Metal Chemistry*, eds. R. B. King and J. J. Eisch, Academic Press, New York and London, 1965, vol. 1.

21 J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, 1980, **102**, 1009.

22 H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, 1957, **79**, 4557.

23 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 18*th March* 1991; *Paper* 1/01299A