Reactions of Co-ordinated Ligands. Part 28.[1] The Reaction of Nucleophilic Reagents with the Cationic Bis(acetylene) Molybdenum Complexes $[Mo(CO)(RC_2R')_2(\eta\text{-}C_5H_5)][BF_4]$; *X*-Ray Crystal Structures of $[Mo\{C(Me)=C(Me)C(O)C(Me)=CHMe\}(CO)_2(\eta\text{-}C_5H_5)]$ and $[Mo\{\eta^3{:}\eta^2\text{-}HBu^tC\overset{\cdots}{-}CH\overset{\cdots}{-}C{-}O{-}C(O)C(Bu^t)=CH\}(CO)(\eta\text{-}C_5H_5)]$ *

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Reaction of $[Mo(CO)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ with lithium dimethylcuprate affords $[Mo(CO)(\eta^2\text{-}MeC_2Me)(\sigma\text{-}CMe{=}CMe_2)(\eta\text{-}C_5H_5)]$, whereas reaction with $K[BHBu^s_3]$ followed by treatment with CO gives $[Mo\{C(Me)=C(Me)C(O)C(Me)=CHMe\}(CO)_2(\eta\text{-}C_5H_5)]$, which has been identified by *X*-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$, in a unit cell with $a = 6.495(3)$, $b = 16.902(9)$, $c = 14.002(7)$ Å, $\beta = 97.62(4)°$. The structure has been refined to $R = 0.025$ ($R' = 0.024$) for 2 136 reflections (293 K) to $2\theta < 55°$ (Mo-K_α *X*-radiation). The molybdenum atom is co-ordinated by an $\eta\text{-}C_5H_5$ ligand, two terminal linear carbonyl ligands, and a bidentate ligand derived from one CO, two but-2-yne molecules, and a hydride ligand. Reaction of CO with $[Mo(CO)(\eta^2\text{-}MeC_2Me)(\sigma\text{-}CMe{=}CMe_2)(\eta\text{-}C_5H_5)]$ affords an analogous complex. A similar reaction between $K[BHBu^s_3]$ and $[Mo(CO)(\eta^2\text{-}EtC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ gives two analogous isomeric complexes, both isomers containing the vinyl group, $C(Me)=CHEt$. In contrast $[Mo(CO)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$ affords the lactone complex $[Mo\{\eta^3{:}\eta^2\text{-}HBu^tC\overset{\cdots}{-}CH\overset{\cdots}{-}C{-}O{-}C(O)C(Bu^t)=CH\}(CO)(\eta\text{-}C_5H_5)]$ characterised by *X*-ray crystallography. Crystals are monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, in a unit cell with $a = 11.935(7)$, $b = 11.673(9)$, $c = 13.674(9)$ Å, $\beta = 105.93(5)°$. The structure has been refined to $R = 0.053$ ($R' = 0.052$) for 2 526 reflections (230 K) to $2\theta \leqslant 50°$ (Mo-K_α *X*-radiation). The molybdenum atom is bound to an η-cyclopentadienyl ligand and a linear terminal CO. The remainder of the co-ordination sphere is taken up by an $\eta^3{:}\eta^2$ vinyl-substituted, unsaturated γ-lactone derived from one hydride, two carbonyls, and two Bu^tC_2H ligands. The structures of these complexes and the mechanism of their formation are discussed.

We have previously described [2] the synthesis of the cationic molybdenum acetylene complexes $[Mo(CO)(RC_2R')_2(\eta\text{-}C_5H_5)][BF_4]$ and $[MoLL'(RC_2R')(\eta\text{-}C_5H_5)][BF_4]$ [$L = L' = P(OMe)_3$; $L = PEt_3$, $L' = CO$], in which the acetylene donates more than two electrons to the central metal atom. In studying the reactions of the monoacetylene cations with hydride anion sources we observed that, depending on the acetylene substituent, η^3-allyl,[1] σ-vinyl,[1] or η^2-vinyl [3] complexes are formed. In this paper we report on the reaction of nucleophilic reagents with bis(acetylene)carbonyl cations where there is now the possibility of the acetylenes coupling with the co-ordinated carbon monoxide.

Results and Discussion

Reaction of $[Mo(CO)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ with lithium dimethylcuprate at −78 °C in tetrahydrofuran (thf) afforded an air-sensitive purple solid (1) in 70% yield. The i.r. spectrum of (1) showed a single carbonyl band at 1 912 cm^{-1}, and the ^1H n.m.r. spectrum exhibited five methyl signals and a singlet of intensity 5 H for the $\eta\text{-}C_5H_5$ ligand. Two of the methyl resonances, at 2.71 and 2.64 p.p.m., appeared as quartets and this is consistent with the retention of an η^2-bonded but-2-yne ligand. These signals reversibly coalesced on raising the temperature to 100 °C giving $\Delta G_{T_c}^{\ddagger}$ for rotation of the acetylene of 83 ± 2 kJ mol^{-1}, a value very similar to that reported [4] for $[W(CO)(\eta^2\text{-}HC_2H)(Me)(\eta\text{-}C_5H_5)]$. The other three methyl signals in the ^1H spectrum of (1) were complex multiplets, and this suggested that a $\sigma\text{-}CMe{=}CMe_2$ ligand had been formed giving the formulation of (1) as $[Mo(CO)(\eta^2\text{-}MeC_2Me)(\sigma\text{-}CMe{=}CMe_2)(\eta\text{-}C_5H_5)]$. This was confirmed by the $^{13}C\text{-}\{^1H\}$ spectrum, which showed resonances for the vinylic carbons at 153.1 and 131.5 p.p.m., which are assigned respectively to the vinylic β- and α-carbon atoms, by analogy with the related σ-vinylic species [1,5] $[Mo\{P(OMe)_3\}_3\{\sigma\text{-}(E)\text{-}CH{=}CHBu^t\}(\eta\text{-}C_5H_5)]$. The two but-2-yne contact carbons resonated at 188.1 and 185.9 p.p.m., in the region typical [2] for acetylenes acting as four-electron donors, the $\eta\text{-}C_5H_5$ ring at 94.1 p.p.m., and the five methyl carbons in the anticipated region between 32 and 17 p.p.m. The spectrum was completed by the singlet of the carbonyl carbon at 242.1 p.p.m.

The recent report [6] that the 18e system $[Fe(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$ reacts with lithium dimethylcuprate to give $[Fe(\sigma\text{-}CMe{=}CMe_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ could be interpreted as suggesting that (1) is formed by direct nucleophilic attack on the co-ordinated but-2-yne. However, the acetylene in the iron system can function only as a 2e donor, whereas the but-2-yne ligands present in the complex $[M(CO)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$[2] can donate more than two

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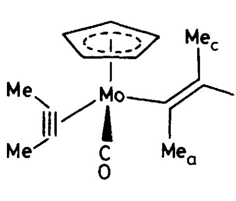
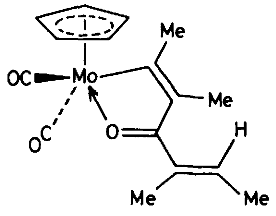
* Dicarbonyl(η-cyclopentadienyl)(1,2,4-trimethyl-3-oxo-hexa-1,4-dien-1-yl-C^1,*O*)molybdenum(II) and [1—3-η : 3′—4′-η-(3′-t-butyl-2′-oxo-furan-5′-yl)-3-t-butylallyl]carbonyl(η-cyclopentadienyl)molybdenum(II).

Supplementary data available (No. SUP 23609, 38 pp.): bond lengths and angles involving hydrogen atoms, hydrogen atom co-ordinates, observed and calculated structure factors, thermal paramers. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



(1)



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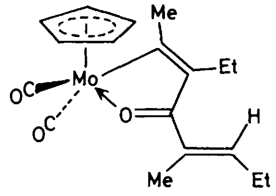

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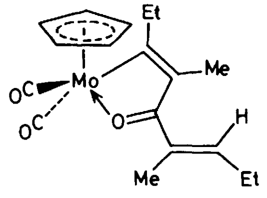

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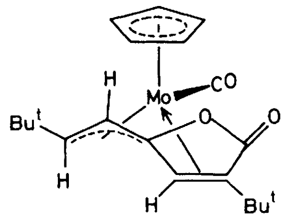

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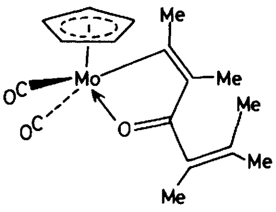

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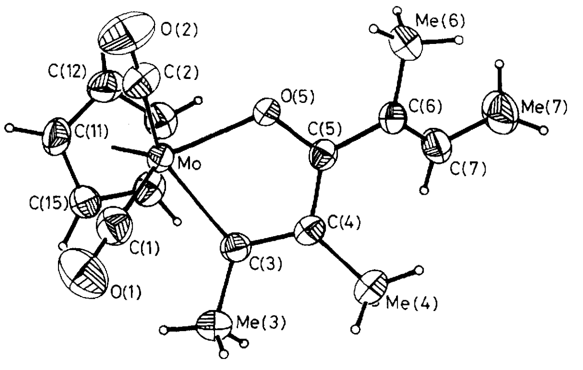
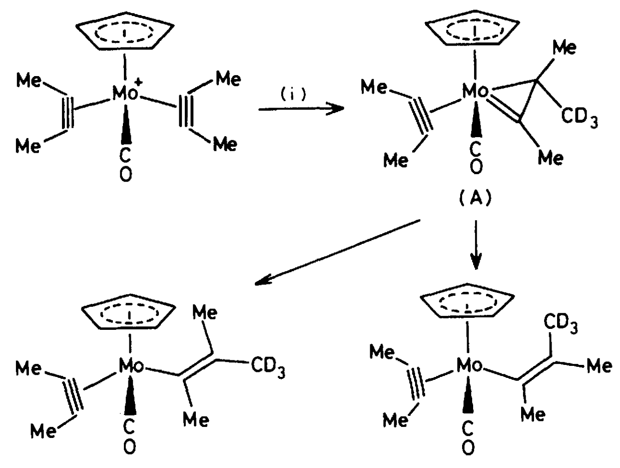


Figure 1. Molecular structure of (2) viewed perpendicular to the metallacycle plane and showing the labelling scheme; ellipsoids are drawn to enclose 50% probability density and hydrogen atoms are drawn as spheres of arbitrary radius



Scheme 1. (*i*) Li[Cu(CD$_3$)$_2$]

electrons to the formally 16e molybdenum atom. Thus an alternative pathway to (1) could involve direct nucleophilic attack at the metal centre with a ' switch ' in bonding mode of the but-2-yne to accommodate the incoming methyl ligand, followed by a *cis* migration of the methyl group from the metal onto the co-ordinated but-2-yne. In an attempt to distinguish between these two reaction paths Li[Cu(CD$_3$)$_2$] was reacted with [Mo(CO)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$]. Examination of the ^{1}H n.m.r. spectrum of the product revealed that the reaction was not stereospecific, the CD$_3$ group being incorporated equally into the ' inside ' (Me$_c$) and ' outside ' (Me$_b$) sites.

This observation is not consistent with either direct attack at the but-2-yne to give an σ-vinyl or initial attack at the metal centre. However, it may be explained if an η^2-vinyl bonded intermediate (A) (Scheme 1), of a type we have previously reported,[3] is formed, the remaining co-ordinated but-2-yne functioning as a 2e donor. Then a ' switch ' in the bonding mode of the but-2-yne [η^2-(2e) to η^2-(4e)] would promote a change [η^2-(3e) to σ-(1e)] in the way the vinyl fragment is bonded to the metal. As shown, such a process could give either the *E* or the *Z* isomer.* Alternatively, an interchange *via* a polytopal rearrangement[7] of the sites occupied in (A) by the Me and CD$_3$ groups attached to the saturated carbon could occur prior to bond breaking.

We believe that the more likely pathway to the η^2-vinyl complex (A) is *via* direct attack by the organocuprate on the least hindered side of the $\pi_\perp$ orbital[8] of the co-ordinated but-2-yne as illustrated. Alternatively, access could be gained to the η^2-vinyl intermediate by transformation of a σ-vinyl [σ-(1e) to η^2-(3e)] formed by migration of a methyl group from molybdenum onto a co-ordinated but-2-yne. However, we think this is unlikely because all attempts[9] to promote such a reaction with complexes containing methyl groups and acetylenes bonded to a molybdenum in a relative *cis* configuration have been unsuccessful.

The reaction of [Mo(CO)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] with K[BHBu$^s_3$] was next examined. Although a rapid reaction occurred in thf at −78 °C giving a purple solution, attempts to isolate a stable crystalline complex were unsuccessful. However, the i.r. spectrum of the reaction mixture showed an intense absorption at 1 912 cm^{-1}, similar to that observed in the spectrum of (1). Since Alt and Schwarzle[4] had reported that [W(CO)(η^2-HC$_2$H)(Me)(η-C$_5$H$_5$)] readily reacted with carbon monoxide affording a stable five-membered metallacyclic compound, carbon monoxide was bubbled through the reaction mixture containing the unstable purple species. This resulted in an immediate colour change from purple to red, purification by column chromatography gave red needles of (2) (ν_{CO} 1 973 and 1 890 cm^{-1}) in 55% yield.

The structure of (2) was not readily discernible from the spectroscopic data hence a single-crystal *X*-ray diffraction study was undertaken. The complex crystallised as discrete molecules with no severe intermolecular contacts. A perspective view of a single molecule, together with the atomic numbering scheme adopted is given in Figure 1. Table 1 lists the interatomic distances and Table 2 important interbond angles.

The molybdenum atom is co-ordinated by an η-C$_5$H$_5$

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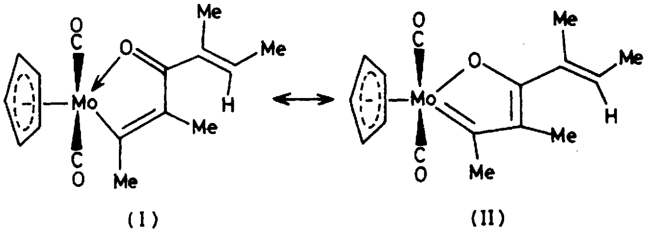
* It should be noted that direct *E*/*Z* isomerisation of the vinyl group present in (1) is excluded by the retention (n.m.r. time-scale) of the stereochemical identity of the ' outside ' (Me$_b$) and ' inside ' (Me$_c$) methyl environments.

Table 1. Bond lengths (Å) for (2)

Mo–C(1)	1.939(2)	Mo–C(2)	2.008(4)
Mo–C(3)	2.142(3)	Mo–O(5)	2.110(3)
Mo–C(11)	2.298(4)	Mo–C(12)	2.358(4)
Mo–C(13)	2.386(4)	Mo–C(14)	2.347(4)
Mo–C(15)	2.293(4)	C(1)–O(1)	1.161(3)
C(2)–O(2)	1.137(5)	C(3)–Me(3)	1.509(5)
C(3)–C(4)	1.380(4)	C(4)–Me(4)	1.517(5)
C(4)–C(5)	1.416(4)	C(5)–C(6)	1.480(4)
O(5)–C(5)	1.292(4)	C(6)–Me(6)	1.516(5)
C(6)–C(7)	1.326(5)	C(7)–Me(7)	1.505(6)
C(11)–C(12)	1.418(5)	C(11)–C(15)	1.410(5)
C(12)–C(13)	1.406(5)	C(13)–C(14)	1.395(5)
C(14)–C(15)	1.415(5)		

moiety, two terminal linear carbonyl ligands, and a bidentate ligand derived from the condensation of one CO, two but-2-yne molecules, and a hydride ligand within the co-ordination sphere. Two canonical forms, which can be invoked to explain qualitatively the bonding within this five-membered metallacycle, are shown in Scheme 2. As might be expected, the ring



(I) (II)

Scheme 2.

formed by Mo, C(3), C(4), C(5), and O(5) is close to planar [r.m.s. deviation from the plane is 0.027 Å, mean torsion angle around the ring is 4.7(5)° *] reflecting the conjugated nature of these canonical forms (I) and (II). Consideration of the C–C bond lengths within the ring indicates a slight preference for canonical form (I) over (II), as indicated by the fact that C(4)–C(5) [1.416(4) Å] is longer than C(3)–C(4) [1.380(4) Å]. However, both these lengths are notably longer than the C(6)–C(7) distance [1.326(5) Å], which reflects a full C=C double bond. The C(5)–O(5) distance [1.292(4) Å] falls between the C=O double bond and C–O single bond distances found in (5) [1.201(10) and 1.408(8) (mean) Å, respectively, see below] in accord with the effects to be expected in this bond in both (I) and (II). The contribution of (II) is notable both in the relative shortness of Mo–C(3) (2.142(3) Å, *cf.* Mo–C(sp^2) 2.243(3) Å in [Mo{P(OMe)$_3$}$_3$(σ-CH=CHBu^t)(η-C_5H_5)]^1) and the length of the Mo–C(2) bond *transoid* to this interaction [2.008(4) Å, *cf.* Mo–C(1) 1.939(2) *transoid* to the donor O(5)]. Canonical form (II) really reflects the ability of the ring to delocalise metal electron density into π* acceptor orbitals, thereby reducing the C(3)–C(4) bond order and increasing the Mo–C(3) bond order. Although the orientation of the π-acceptor orbitals on C(3) is at *ca.* 90° to the optimum for overlap with the π-donor orbitals of a ML$_3$(η-C_5H_5) fragment as deduced from extended Hückel molecular orbital calculations,^{10} there is no large electronic energy distinction between these orientations.

The increased Mo–C(3) bond order is reflected in the low-field chemical shift (261.0 p.p.m.) observed for C(3). It is apparent from the long C(5)–C(6) bond length [1.480(4) Å, which is appropriate for a C(sp^2)–C(sp^2) single bond] and the large dihedral angle between the vinyl [C(6), Me(6), C(7), H(7), Me(7)] and metallacyclic planes [41.0(5)°] that the delocalised π system in the ring does not interact significantly with the localised C=C double bond in the vinyl substituent. Related C_3OM, near-planar unsaturated metallacycles showing similar bonding patterns have been characterised for mononuclear ^{11} (M = Fe, Ru, or Co) and dinuclear species ^{12} (M = Ru). We note in passing that the isolobal mapping replacing Mo(CO)$_2$(η-C_5H_5) by CH gives a description of the molecule in form (II) as a substituted metallafuran, but fails to identify canonical form (I). With the establishment of the structure of (2) the ^{1}H and ^{13}C-{^{1}H} spectra were interpreted as detailed in the Experimental section.

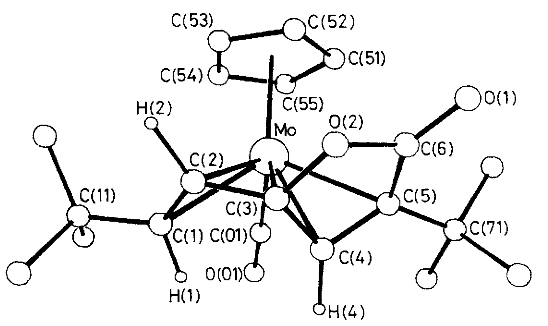


Figure 2. Molecular structure of (5) showing the labelling scheme; atoms are drawn as spheres of arbitrary radius

In order to explore the selectivity of this reaction the cations [Mo(CO)(η^2-EtC$_2$Me)$_2$(η-C_5H_5)][BF$_4$] and [Mo(CO)(η^2-Bu^{t}C$_2$H)$_2$(η-C_5H_5)][BF$_4$] containing unsymmetrical acetylenes were treated with K[BHBu$^s_3$] in the presence of carbon monoxide. Chromatographic work-up of the reaction of the pent-2-yne complex followed by recrystallisation from hexane yielded an orange powder, which analysed satisfactorily and gave mass spectral data consistent with the expected analogue of (2). However, ^{1}H and ^{13}C-{^{1}H} n.m.r. data revealed the presence of two isomers (3) and (4) [ratio 3 : 2, respectively]. The isomers differed in that the major product (3) exhibited a low-field methyl singlet in its ^{1}H spectrum at 2.98 p.p.m. corresponding to a methyl group bound to a carbenoid carbon [*cf.* 2.88 p.p.m. for Me$_a$ in complex (2)], whereas, the corresponding signal for (4) was at 2.04 p.p.m. [*cf.* 1.98 p.p.m. for Me$_b$ in (2)]. Thus complex (3) bears a methyl group on the α-carbon and (4) a methyl group on the β-carbon of the five-membered ring, both systems containing an identical pent-2-enyl fragment.

The cation [Mo(CO)(η^2-Bu^{t}C$_2$H)$_2$(η-C_5H_5)][BF$_4$] reacted similarly with K[BHBu$^s_3$] at low temperature to give a purple solution. Bubbling CO through this thf solution resulted in a rapid change in colour to orange, which on work-up afforded orange crystals of (5). The spectroscopic data recorded for (5) were inconsistent with its formulation as an analogue of (2), (3), and (4); the solution i.r. spectrum showed only a single terminal carbonyl band at 1 918 cm^{-1}, and an additional carbonyl stretch at 1 766 cm^{-1}.

A single-crystal *X*-ray diffraction study established the molecular structure illustrated in Figure 2, bond lengths and angles are given in Tables 3 and 4. The molybdenum atom is bound to an η^5-cyclopentadienyl ligand and to a linear, terminal CO, both of which show typical geometries [Mo–C(01) 1.953(6), Mo–C(C_5H_5 ring) 2.300(8)—2.378(9) Å, Mo–C(01)–O 178.2(6)°, C_5H_5 planar within experimental

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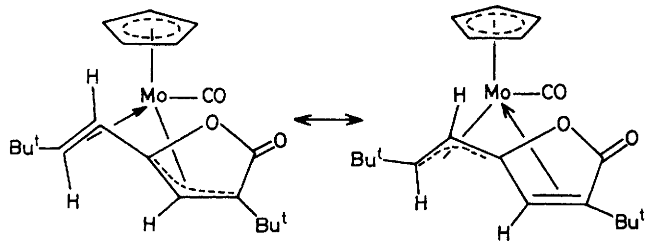
* The estimated standard deviation in the last significant digit is given in parentheses here and throughout this paper.

Table 2. Interbond angles (°) for (2)

C(1)–Mo–C(2)	80.7(1)	C(1)–Mo–C(3)	74.7(1)	C(13)–Mo–C(15)	58.2(1)	C(14)–Mo–C(15)	35.5(1)
C(2)–Mo–C(3)	123.9(1)	C(1)–Mo–O(5)	122.9(1)	Mo–C(1)–O(1)	176.5(1)	Mo–C(2)–O(2)	178.1(3)
C(2)–Mo–O(5)	79.2(1)	C(3)–Mo–O(5)	73.8(1)	Mo–C(3)–Me(3)	124.6(2)	Mo–C(3)–C(4)	116.5(2)
C(1)–Mo–C(11)	96.1(2)	C(2)–Mo–C(11)	96.7(1)	Me(3)–C(3)–C(4)	118.6(3)	C(3)–C(4)–Me(4)	123.4(3)
C(3)–Mo–C(11)	135.0(1)	O(5)–Mo–C(11)	138.9(1)	C(3)–C(4)–C(5)	113.2(3)	Me(4)–C(4)–C(5)	123.3(3)
C(1)–Mo–C(12)	130.0(1)	C(2)–Mo–C(12)	91.7(1)	C(4)–C(5)–O(5)	116.9(3)	C(4)–C(5)–C(6)	127.8(3)
C(3)–Mo–C(12)	141.8(1)	O(5)–Mo–C(12)	103.5(1)	O(5)–C(5)–C(6)	115.2(2)	Mo–O(5)–C(5)	119.1(2)
C(11)–Mo–C(12)	35.4(1)	C(1)–Mo–C(13)	147.1(1)	C(5)–C(6)–Me(6)	116.0(3)	C(5)–C(6)–C(7)	120.5(3)
C(2)–Mo–C(13)	119.2(1)	C(3)–Mo–C(13)	108.0(1)	Me(6)–C(6)–C(7)	123.3(3)	C(6)–C(7)–Me(7)	126.6(3)
O(5)–Mo–C(13)	88.0(1)	C(11)–Mo–C(13)	58.1(1)	Mo–C(11)–C(12)	74.6(2)	Mo–C(11)–C(15)	71.9(2)
C(12)–Mo–C(13)	34.5(1)	C(1)–Mo–C(14)	116.9(1)	C(12)–C(11)–C(15)	108.0(3)	Mo–C(12)–C(11)	70.0(2)
C(2)–Mo–C(14)	149.6(1)	C(3)–Mo–C(14)	85.9(1)	Mo–C(12)–C(13)	73.8(2)	C(11)–C(12)–C(13)	107.4(3)
O(5)–Mo–C(14)	106.8(1)	C(11)–Mo–C(14)	58.8(1)	Mo–C(13)–C(12)	71.7(2)	Mo–C(13)–C(14)	71.3(2)
C(12)–Mo–C(14)	57.9(1)	C(13)–Mo–C(14)	34.3(1)	C(12)–C(13)–C(14)	108.8(3)	Mo–C(14)–C(13)	74.4(2)
C(1)–Mo–C(15)	89.0(1)	C(2)–Mo–C(15)	130.1(1)	Mo–C(14)–C(15)	70.1(2)	C(13)–C(14)–C(15)	108.2(3)
C(3)–Mo–C(15)	99.3(1)	O(5)–Mo–C(15)	142.2(1)	Mo–C(15)–C(11)	72.3(2)	Mo–C(15)–C(14)	74.4(2)
C(11)–Mo–C(15)	35.8(1)	C(12)–Mo–C(15)	58.9(1)	C(11)–C(15)–C(14)	107.6(3)		

error]. The remainder of the co-ordination sphere is taken up by an η^3:η^2 vinyl-substituted, unsaturated γ-lactone derived from one hydride, two carbonyl, and two Bu^{t}C$_2$H ligands. The bonding of the η^5-lactone moiety to the molybdenum may be represented by a variety of canonical forms of which (III) and (IV) in Scheme 3 represent the major contributors. Both (III) and (IV) may be viewed as vinyl-substituted allyl ligands such that in (III) the allyl fragment is formed by C(3), C(4), and C(5), and the vinyl by C(1) and C(2) and their respective substituents. These 'allyl' fragments are then *endo* and *exo* respectively with respect to the η-C$_5$H$_5$ ligand.



(III) (IV)

Scheme 3.

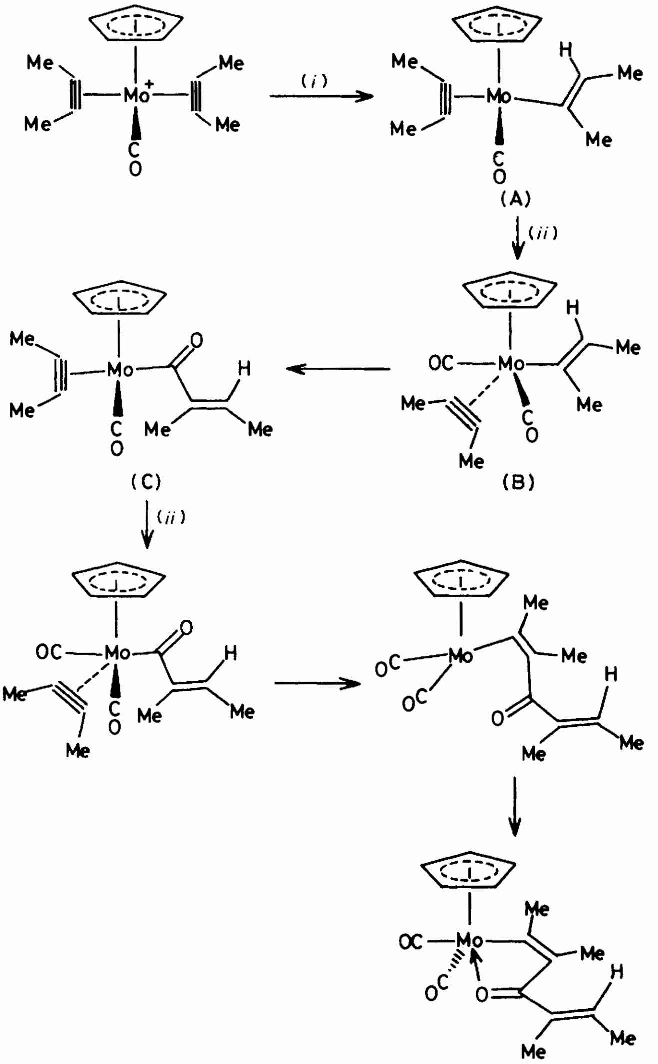
The complex [Mo{η^3-C(O)–O–C(Me)$\cdots$C(Me)$\cdots$C(Me)}-(CO)(CNBu^t)(η-C$_5$H$_5$)],[13] a related γ-lactone, shows an *endo* configuration for the allylic portion of the lactone ring. A comparison of the geometries of the η^3-lactone in the latter complex and the η^5-lactone in (5) is instructive. The η^3-lactone complex shows Mo–C(allyl) contact distances of 2.353(7), 2.243(6), and 2.284(6) Å, reflecting the normal tendency of the central allyl carbon to be closest to the metal in addition to some asymmetry caused by the inequivalent carbonyl and isocyanide ligands. In contrast, the three contact carbons of the lactone ring in (5) show Mo–C distances of 2.386(8), 2.204(8) and 2.204(7) Å for C(5), C(4), and C(3), respectively, and Mo–C(2) 2.284(7) and Mo–C(1) 2.384(7) Å. These lengths reflect a 'slippage' of the lactone ring in order better to accommodate the co-ordination of the vinyl moiety to the molybdenum atom. Although a realistic picture of the bonding of the vinyl-lactone (5) must include components of (III) and (IV) (Scheme 3) some geometric features indicate a preponderance of (IV). Firstly, the longest C–C bond length in the C(1)—C(5) chain is C(3)–C(4) 1.454(9) Å [*cf.* C(1)–C(2) 1.410(9), C(2)–C(3) 1.377(11), and C(4)–C(5) 1.412(11) Å]. Secondly, the torsion angles about the C(1)–C(2), C(2)–C(3), C(3)–C(4), and C(4)–C(5) bonds clearly indicate that largest distortions from planarity within the chain occur at the C(3)–C(4) bond in accord with form (IV) being the major contributor to the observed geometries [torsion angles are C(11)–C(1)–C(2)–C(3) 0.5(7), C(1)–C(2)–C(3)–C(4) 7.3(11), C(1)–C(2)–C(3)–O(2) 15.2(7), C(2)–C(3)–C(4)–C(5) 49.8(8), O(2)–C(3)–C(4)–C(5) 30.1(8), C(3)–C(4)–C(5)–C(6) 24.5(8), and C(3)–C(4)–C(5)–C(71) 11.7(7)°].

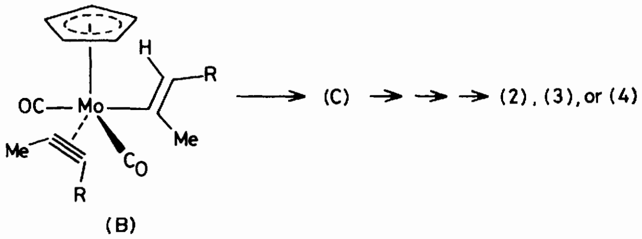
Table 3. Bond lengths (Å) for (5)

Mo–C(51)	2.378(9)	Mo–C(52)	2.336(8)
Mo–C(53)	2.300(8)	Mo–C(54)	2.332(9)
Mo–C(55)	2.360(8)	Mo–C(1)	2.384(7)
Mo–C(2)	2.284(7)	Mo–C(3)	2.204(7)
Mo–C(4)	2.204(8)	Mo–C(5)	2.386(8)
Mo–C(01)	1.953(6)	C(51)–C(52)	1.402(10)
C(51)–C(55)	1.403(11)	C(52)–C(53)	1.396(12)
C(53)–C(54)	1.412(10)	C(54)–C(55)	1.393(12)
C(1)–C(2)	1.410(9)	C(1)–C(11)	1.533(10)
C(2)–C(3)	1.377(11)	C(3)–C(4)	1.454(9)
C(3)–O(2)	1.417(8)	C(4)–C(5)	1.412(11)
C(5)–C(6)	1.518(9)	C(5)–C(71)	1.520(10)
C(6)–O(1)	1.201(10)	C(11)–C(12)	1.502(10)
C(11)–C(13)	1.529(11)	C(11)–C(14)	1.538(12)
C(71)–C(72)	1.537(10)	C(71)–C(73)	1.521(13)
C(71)–C(74)	1.545(14)	C(01)–O(01)	1.160(8)
O(2)–C(6)	1.399(9)		

A change in the reaction conditions and of the source of 'H$^-$' in these reactions was next examined. Treatment of [Mo(CO)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] with NaBH$_4$ in thf at room temperature in the presence of carbon monoxide led to the formation of the lemon complex [Mo(CO)$_2${*anti*-η^3-CH$_2\cdots$CH$\cdots$C(Me)H}(η-C$_5$H$_5$)] (6), a similar reaction with the pent-2-yne cation affording [Mo(CO)$_2${*syn,anti*-η^3-C(Me)H$\cdots$CH$\cdots$C(Me)H}(η-C$_5$H$_5$)] (7). These compounds were fully characterised by elemental analysis, i.r., mass and n.m.r. spectroscopy as detailed in the Experimental section.

The formation of the complexes (2)—(5) can be understood if it is assumed that the initial product of the reaction of the bis(acetylene) carbonyl-substituted cations with [BHBu$^s{}_3$]$^-$ is a σ-vinyl complex (A) (Scheme 4), isostructural with (1). As illustrated, the reacting carbon monoxide can be accommodated at the molybdenum centre by a change in the bonding mode of the remaining co-ordinated but-2-yne ligand allowing





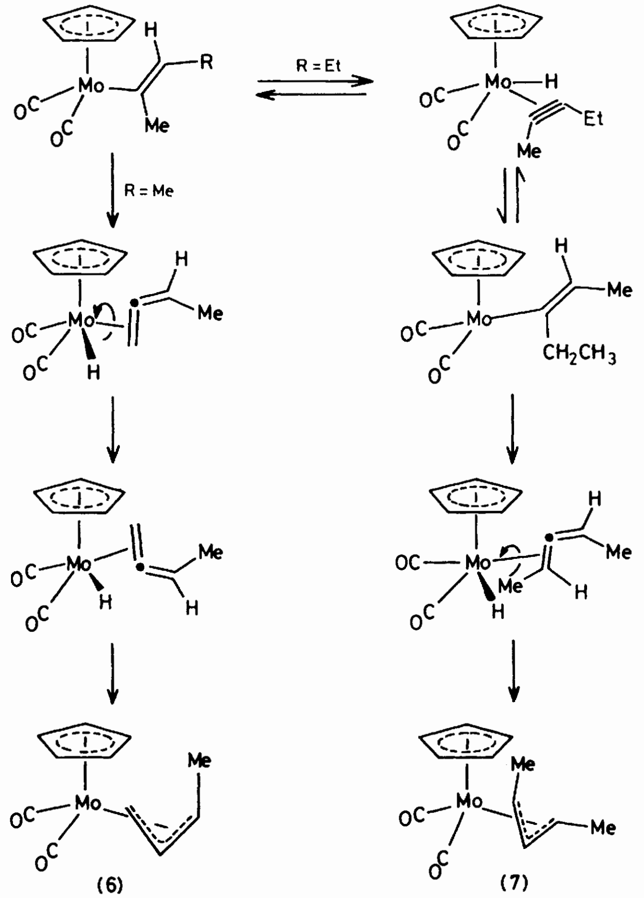
Scheme 4. (*i*) K[BHBu$^s_3$]; (*ii*) CO

formation of (B). Then, promoted by a ' switch ' back to the 4e bonding mode, the but-2-enyl fragment migrates from the metal onto co-ordinated carbon monoxide to give (C). A repeat of this bond ' switch ' sequence and reaction with more CO affords, *via* migration of the acyl fragment onto a 2e donor but-2-yne, a 16e complex, which would then be expected to collapse to (2).

Corroborative evidence for this suggestion was obtained by treating a solution of (1) with carbon monoxide at −78 °C. A rapid reaction occurred and work-up by column chromatography gave a good yield of the orange crystalline complex (8), which was characterised as the methyl-substituted analogue of (2) by elemental analysis, i.r., mass and n.m.r. spectroscopy.

An interesting aspect of this reaction sequence is that in the formation of the isomeric complexes (3) and (4) from the pent-2-yne complex the intermediate [Mo(σ-CMe=CHEt)(CO)(η^2-MeC$_2$Et)(η-C$_5$H$_5$)] is formed regioselectively, whereas the step involving migration of the acyl fragment COCMe=CHEt from the molybdenum onto the co-ordinated pent-2-yne is not selective. A further point is that migration of the vinyl group from Mo to CO proceeds with retention of configuration.

As is shown in Scheme 5 the formation at room temperature of the η^3-allyl complexes (6) and (7) can be understood in terms of an alternative reaction path becoming available by dissociative loss of an acetylene molecule from the intermediate (B), which leads to the formation of a 16e dicarbonyl(vinyl) complex. Then by a process, which we have previously discussed,[1] β-hydrogen elimination to form a hydrido(allene) intermediate followed by rotation and ' insertion ' affords the η^3-allyl complex (6) from the but-2-yne system.



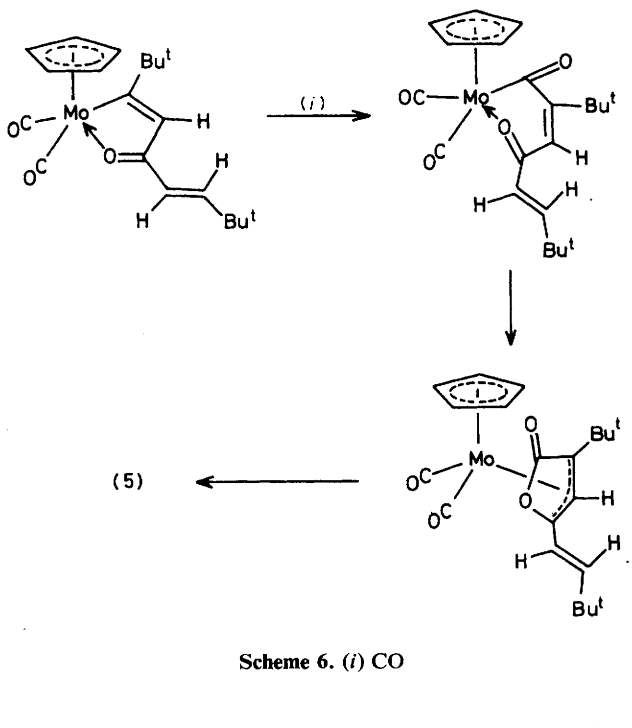
Scheme 5.

An extension of this mechanism to the formation of (7) from the pent-2-yne-substituted cation requires that the 16e species [Mo(σ-CMe=CHEt)(CO)$_2$(η-C$_5$H$_5$)] rapidly fragments to the hydrido-complex [MoH(η^2-MeC$_2$Et)(CO)$_2$(η-C$_5$H$_5$)]. Then rotation of the acetylene followed by its ' insertion ' allows formation of [Mo(σ-CEt=CHMe)(CO)$_2$(η-C$_5$H$_5$)], which can rearrange as shown (Scheme 5) to form the *syn*,*anti*-substituted 1,3-dimethylallyl complex (7).

Although the lactone complex (5) formed from the 3,3-dimethylbut-1-yne complex appears complex, its formation can be understood in terms of a sequence of reactions analogous to those involved in the production of (2). As is shown in

Table 4. Interbond angles (°) for (5)

C(51)–Mo–C(52)	34.6(2)	C(51)–Mo–C(53)	57.9(3)	C(5)–Mo–C(01)	93.1(3)	Mo–C(51)–C(52)	71.1(5)
C(52)–Mo–C(53)	35.0(3)	C(51)–Mo–C(54)	57.9(3)	Mo–C(51)–C(55)	72.1(5)	C(52)–C(51)–C(55)	107.3(7)
C(52)–Mo–C(54)	58.5(3)	C(53)–Mo–C(54)	35.5(3)	Mo–C(52)–C(51)	74.4(5)	Mo–C(52)–C(53)	71.1(5)
C(51)–Mo–C(55)	34.4(3)	C(52)–Mo–C(55)	57.5(2)	C(51)–C(52)–C(53)	108.0(6)	Mo–C(53)–C(52)	73.9(5)
C(53)–Mo–C(55)	57.7(3)	C(54)–Mo–C(55)	34.5(3)	Mo–C(53)–C(54)	73.5(5)	C(52)–C(53)–C(54)	108.7(7)
C(51)–Mo–C(1)	157.0(3)	C(52)–Mo–C(1)	125.9(3)	Mo–C(54)–C(53)	71.0(5)	Mo–C(54)–C(55)	73.8(5)
C(53)–Mo–C(1)	99.2(3)	C(54)–Mo–C(1)	103.6(3)	C(53)–C(54)–C(55)	106.7(7)	Mo–C(55)–C(51)	73.5(5)
C(55)–Mo–C(1)	135.1(3)	C(51)–Mo–C(2)	134.3(2)	Mo–C(55)–C(54)	71.6(5)	C(51)–C(55)–C(54)	109.4(6)
C(52)–Mo–C(2)	100.1(3)	C(53)–Mo–C(2)	88.5(3)	Mo–C(1)–C(2)	68.6(4)	Mo–C(1)–C(11)	128.3(5)
C(54)–Mo–C(2)	112.6(3)	C(55)–Mo–C(2)	145.4(3)	C(2)–C(1)–C(11)	124.7(6)	Mo–C(2)–C(1)	76.4(4)
C(1)–Mo–C(2)	35.1(2)	C(51)–Mo–C(3)	122.7(3)	Mo–C(2)–C(3)	69.0(4)	C(1)–C(2)–C(3)	116.3(6)
C(52)–Mo–C(3)	99.9(3)	C(53)–Mo–C(3)	108.9(3)	Mo–C(3)–C(2)	75.3(4)	Mo–C(3)–C(4)	70.7(4)
C(54)–Mo–C(3)	142.3(2)	C(55)–Mo–C(3)	156.4(3)	C(2)–C(3)–C(4)	123.1(6)	Mo–C(3)–O(2)	108.7(5)
C(1)–Mo–C(3)	62.0(3)	C(2)–Mo–C(3)	35.7(3)	C(2)–C(3)–O(2)	124.0(6)	C(4)–C(3)–O(2)	109.7(6)
C(51)–Mo–C(4)	123.7(3)	C(52)–Mo–C(4)	123.5(3)	Mo–C(4)–C(3)	70.8(4)	Mo–C(4)–C(5)	79.3(5)
C(53)–Mo–C(4)	146.0(3)	C(54)–Mo–C(4)	178.0(3)	C(3)–C(4)–C(5)	103.2(6)	Mo–C(5)–C(4)	65.1(4)
C(55)–Mo–C(4)	146.0(3)	C(1)–Mo–C(4)	75.1(3)	Mo–C(5)–C(6)	97.9(5)	C(4)–C(5)–C(6)	105.6(5)
C(2)–Mo–C(4)	67.4(3)	C(3)–Mo–C(4)	38.5(2)	Mo–C(5)–C(71)	131.6(5)	C(4)–C(5)–C(71)	127.0(7)
C(51)–Mo–C(5)	88.3(3)	C(52)–Mo–C(5)	97.2(3)	C(6)–C(5)–C(71)	117.3(6)	C(5)–C(6)–O(1)	132.5(7)
C(53)–Mo–C(5)	131.2(3)	C(54)–Mo–C(5)	145.9(3)	C(5)–C(6)–O(2)	108.0(6)	O(1)–C(6)–O(2)	119.4(6)
C(55)–Mo–C(5)	113.5(3)	C(1)–Mo–C(5)	110.3(3)	C(1)–C(11)–C(12)	109.0(6)	C(1)–C(11)–C(13)	113.1(6)
C(2)–Mo–C(5)	93.9(3)	C(3)–Mo–C(5)	58.4(2)	C(12)–C(11)–C(13)	110.3(8)	C(1)–C(11)–C(14)	107.3(7)
C(4)–Mo–C(5)	35.5(3)	C(51)–Mo–C(01)	115.6(3)	C(12)–C(11)–C(14)	108.8(6)	C(13)–C(11)–C(14)	108.2(6)
C(52)–Mo–C(01)	147.5(3)	C(53)–Mo–C(01)	131.4(3)	C(5)–C(71)–C(72)	110.7(6)	C(5)–C(71)–C(73)	111.9(7)
C(54)–Mo–C(01)	97.3(3)	C(55)–Mo–C(01)	90.1(3)	C(72)–C(71)–C(73)	107.8(5)	C(5)–C(71)–C(74)	107.7(6)
C(1)–Mo–C(01)	78.0(3)	C(2)–Mo–C(01)	109.9(3)	C(72)–C(71)–C(74)	108.8(7)	C(73)–C(71)–C(74)	110.0(7)
C(3)–Mo–C(01)	111.7(3)	C(4)–Mo–C(01)	80.9(3)	Mo–C(01)–O(01)	178.2(6)	C(3)–O(2)–C(6)	105.2(5)



Scheme 6. (*i*) CO

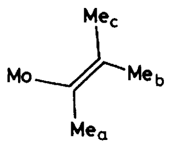
Scheme 6, a CO-promoted migration of the kind we have previously observed[13] in the reaction of Bu^{t}NC with [Mo{C(Me)=CMeC(O)Me}(CO)$_2$(η-C$_5$H$_5$)] leads to complex (5) and in a similar manner to that observed with the reaction of the pent-2-yne complex, *i.e.* formation of (3) and (4), there is a difference in regioselectivity of the reactions which generate the Mo{σ-(*E*)-CH=CHBu^t} and Mo–C(Bu^t)=CHCO– systems.

An important question remaining and related to this latter point is what controls the regioselectivity and stereochemistry of the formation of the vinyl group Mo{σ-(*E*)–CH=CHBu^t}. Earlier we suggested that the reaction of lithium dimethylcuprate with [Mo(CO)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] involves direct attack by the nucleophile on the $\pi_\perp$ orbital of the co-ordinated acetylene giving an η^2-vinyl complex, and clearly a similar pathway could be followed in the reaction of the molybdenum cations with BHBu$^s{}_3{}^-$ and BH$_4{}^-$. However, this is a complex mechanistic problem as we have previously commented,[1] and we defer discussion of this problem to a subsequent paper.

Experimental

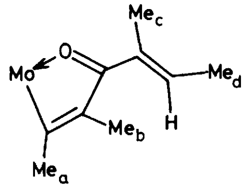
The spectral data were recorded as previously described.[1]

Reactions of [Mo(CO)(MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$].—(*a*) *With lithium dimethylcuprate.* A freshly prepared solution of lithium dimethylcuprate (2.5 mmol) in diethyl ether (20 cm^3) was added dropwise with stirring to a suspension (−78 °C) of [Mo(CO)(MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.8 g, 2 mmol) in thf (20 cm^3). When the addition was complete the stirred reaction mixture was allowed to warm to −40 °C when a deep purple solution was formed. The reaction mixture was filtered through a cold (−40 °C) alumina packed column (10 × 4 cm) using diethyl ether to remove the purple product. The solvents were removed (0 °C) by evaporation under a flow of oxygen-free nitrogen. The residue was extracted with pentane, and cooled (−78 °C) to give purple *crystals* of (1) (0.5 g, 77%) (Found: C, 57.5; H, 6.9%; *M*, 312. C$_{15}$H$_{20}$MoO requires C, 57.9; H, 6.5%; *M*, 312); ν_{CO} 1 912s cm^{-1} (hexane). N.m.r. ^{1}H (C$_6$D$_6$) (q = quartet), δ 4.90 (s, 5 H, C$_5$H$_5$), 2.71 [q, 3 H, MeC≡C, ^5J(HH)

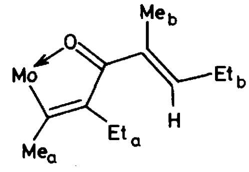


0.7], 2.64 [q, 3 H, MeC≡C, ^5J(HH) 0.7], 1.99 [qq, 3 H, $\mathrm{Me_c}$, $^4J(\mathrm{H_bH_c})$ 0.4, $^5J(\mathrm{H_cH_a})$ 1.3], 1.76 [qq, 3 H, $\mathrm{Me_b}$, $^4J(\mathrm{H_bH_c})$ 0.4, $^5J(\mathrm{H_bH_a})$ 0.85], 1.68 [qq, 3 H, $\mathrm{Me_a}$, $^5J(\mathrm{H_cH_a})$ 1.3, $^5J(\mathrm{H_bH_a})$ 0.85 Hz]; ^{13}C-{^{1}H} (C_6D_6), δ 242.1 (s, CO), 188.1 (s, Me*C*≡C), 185.9 (s, Me*C*≡C), 153.1 [s, C(Me)=*C*$\mathrm{Me_2}$], 131.5 [s, *C*(Me)=$\mathrm{CMe_2}$], 94.1 (s, C_5H_5), 32.1 (s, *Me*C≡C), 30.0 (s, *Me*C≡C), 20.9 [s, C(Me)=CMe_2], 19.7 [s, C(Me)=CMe_2], and 17.1 p.p.m. [s, C(*Me*)=$\mathrm{CMe_2}$]. The mass spectrum also showed a peak at *m/e* 284 (*P* − CO).

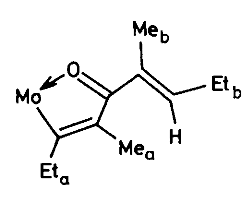
(*b*) *With* K[$\mathrm{BHBu^s_3}$] *in the presence of carbon monoxide*. A suspension of [Mo(CO)($\mathrm{MeC_2Me}$)$_2$(η-C_5H_5)][BF_4] (1.0 g, 2.6 mmol) in thf (20 cm^3) was cooled to −78 °C. One equivalent of K[$\mathrm{BHBu^s_3}$] (2.6 cm^3 of 1 mol dm^{-3} solution in thf) was added dropwise with stirring over 1 min, resulting in the formation of a deep purple solution (ν_{CO} 1 912 cm^{-1}). After 5 min at −78 °C, carbon monoxide was bubbled through the solution causing an immediate change in colour from purple to red. The reaction mixture was then allowed to warm to room temperature. The volatile material was removed *in vacuo*, the residue extracted with diethyl ether, and the extracts filtered through a Kieselguhr plug. The solvent was removed and the hexane-soluble material chromatographed on an alumina packed column (10 × 4 cm). Elution with diethyl ether–hexane (1 : 4) afforded an orange-red band, which was collected. Recrystallisation (−30 °C) from hexane gave red *needles* of (2) (0.6 g, 55%) (Found: C, 54.5; H, 5.5%; *M*, 354. $C_{16}H_{18}MoO_3$ requires C, 54.3; H, 5.1%; *M*, 354); ν_{CO} 1 973s and 1 890s cm^{-1} (hexane). N.m.r. ^{1}H (C_6D_6), δ 5.68 [qq, 1 H, C*H*($\mathrm{Me_d}$), ^3J(HH) 6.9, ^4J(HH) 1.4], 4.76 (s, 5 H, C_5H_5), 2.88 (s, 3 H, $\mathrm{Me_a}$), 1.98 (s, 3 H, $\mathrm{Me_b}$), 1.80 (m, 3 H, $\mathrm{Me_c}$), 1.46 [d of m, 3 H, $\mathrm{Me_d}$, ^3J(HH) 6.9 Hz]; ^{13}C-{^{1}H} (C_6D_6), δ 261.0 [s, *C*($\mathrm{Me_a}$)], 248.7 (s, br, 2CO), 199.0 (s, C=O), 136.0 [s, *C*($\mathrm{Me_b}$)], 134.3 [s, *C*($\mathrm{Me_c}$)], 129.0 [s, *C*H($\mathrm{Me_d}$)], 93.2 (s, C_5H_5), 34.6 (s, $\mathrm{Me_a}$), 15.1 (s, $\mathrm{Me_b}$), 14.2 (s, $\mathrm{Me_c}$), and 13.6 p.p.m. (s, $\mathrm{Me_d}$). The mass spectrum also showed peaks at *m/e* 326 (*P* − CO) and 298 (*P* − 2CO).



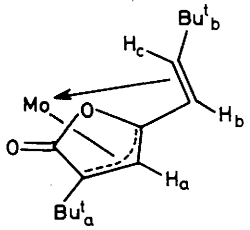
An identical procedure was used to obtain (60%) an isomeric mixture of (3) and (4) (Found: C, 57.0; H, 6.1; *M*, 382. $C_{18}H_{22}MoO_3$ requires C, 56.6; H, 5.8%; *M* 382); ν_{CO} 1 977s, 1 897s, and 1 896s cm^{-1} (hexane). N.m.r. (3) ^{1}H (C_6D_6), δ 5.64 [tq, 1 H, C*H*($\mathrm{Et_b}$), ^3J(HH) 7.0, ^4J(HH) 1.5], 4.76 (s, 5 H, C_5H_5), 2.98 (s, 3 H, $\mathrm{Me_a}$), 2.54 [q, 2 H, (C*H*$_2$CH$_3$)$_a$, ^3J(HH) 7.0], 1.98 [q, 2 H, (C*H*$_2$CH$_3$)$_b$, ^3J(HH) 7.0], 1.84 (m, 3 H, $\mathrm{Me_b}$), 1.04 [t, 3 H, (CH$_2$C*H*$_3$)$_a$, ^3J(HH) 7 0], 0.84 [t, 3 H, (CH$_2$C*H*$_3$)$_b$, ^3J(HH) 7.0 Hz].



N.m.r. (4) ^{1}H (C_6D_6), δ 5.64 [tq, 1 H, C*H*($\mathrm{Et_b}$), ^3J(HH) 7.0, ^4J(HH) 1.5], 4.82 (s, 5 H, C_5H_5), 3.38 [q, 2 H, (C*H*$_2$CH$_3$)$_a$, ^3J(HH) 7.0], 2.44 [quintet, 2 H, (C*H*$_2$CH$_3$)$_b$, ^3J(HH) 7.0], 2.04 (s, 3 H, $\mathrm{Me_a}$), 1.84 (m, 3 H, $\mathrm{Me_b}$), 1.26 [t, 3 H, (CH$_2$C*H*$_3$)$_a$, ^3J(HH) 7.0], and 1.02 p.p.m. [t, 3 H, (CH$_2$C*H*$_3$)$_b$, ^3J(HH) 7.0 Hz]. The mass spectrum of the mixture showed additional peaks at *m/e* 354 (*P* − CO) and 326 (*P* − 2CO).

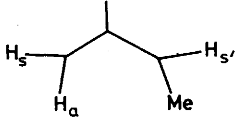


Similarly, reaction of [Mo(CO)($\mathrm{HC_2Bu^t}$)$_2$(η-C_5H_5)][BF_4] (0.5 g, 1.1 mmol) with a slight excess of K[$\mathrm{BHBu^s_3}$] (1.5 cm^3 of 1 mol dm^{-3} solution in thf) gave orange *crystals* of (5) (0.2 g, 45%) (Found: C, 58.7; H, 6.7; *M*, 410. $C_{20}H_{26}MoO_3$ requires C, 58.5; H, 6.4%; *M*, 410); ν_{CO} 1 918s and 1 766 cm^{-1} (hexane).



N.m.r. ^{1}H (C_6D_6), δ 5.17 [d, 1 H, $\mathrm{H_b}$, ^3J(HH) 9.0], 4.99 (s, 5 H, C_5H_5), 4.14 (s, 1 H, $\mathrm{H_a}$), 1.79 [d, 1 H, $\mathrm{H_c}$, ^3J(HH) 9.0 Hz], 1.28 (s, 9 H, $\mathrm{Bu^t_a}$), 0.80 (s, 9 H, $\mathrm{Bu^t_b}$); ^{13}C-{^{1}H} (C_6D_6), δ 235.6 (s, CO), 171.1 (s, C=O), 111.0 (s, C−O), 93.8 (s, C_5H_5), 85.8 (s, $\mathrm{CH_a}$), 79.3 (s, $\mathrm{CH_b}$), 72.2 (s, $\mathrm{CH_c}$), 70.5 (s, *C*$\mathrm{Bu^t_a}$), 33.6 [s, (*C*Me$_3$)$_a$], 32.8 [s, (*C*Me$_3$)$_b$], 31.9 [s, (C*Me*$_3$)$_a$], and 30.0 p.p.m. [s, (C*Me*$_3$)$_b$]. The mass spectrum showed a peak at *m/e* 382 (*P* − CO).

Reaction of [Mo(CO)($\mathrm{MeC_2Me}$)$_2$(η-C_5H_5)][BF_4] *with* $NaBH_4$ *at Room Temperature in the Presence of Carbon Monoxide*.— A stream of carbon monoxide was bubbled through a stirred (room temperature) suspension of [Mo(CO)($\mathrm{MeC_2Me}$)$_2$(η-C_5H_5)][BF_4] (1.0 g, 2.6 mmol) in thf (20 cm^3) for 5 min. Maintaining the flow of carbon monoxide, sodium tetrahydroborate (0.2 g, 5.2 mmol) was added. Over 1 h of stirring the starting material dissolved with the formation of a primrose-yellow solution. The solvent was removed *in vacuo*, the residue extracted with hexane, and chromatographed on alumina (10 × 4 cm). Elution with diethyl ether–hexane (1 : 4) gave a yellow band, which was collected. Recrystallisation (−30 °C) from hexane gave yellow *crystals* of (6) (0.4 g, 55%) (Found: C, 48.9; H, 4.6%; *M*, 272. $C_{11}H_{12}MoO_2$ requires C, 48.6; H, 4.4%; *M*, 272); ν_{CO} 1 952s and 1 880s cm^{-1} (hexane).



N.m.r. ^{1}H ([$^2H_8$]toluene), δ 4.38 (s, 5 H, C_5H_5), 3.46 [m, 1 H, $\mathrm{H_{s'}}$, $J(\mathrm{H_{s'}H_c})$ 8.0], 3.32 (m, 1 H, $\mathrm{H_c}$), 2.42 [ddd, 1 H, $\mathrm{H_s}$, $J(\mathrm{H_sH_c})$ 7.1, $J(\mathrm{H_sH_a})$ 2.5, $J(\mathrm{H_sH_{s'}})$ 1.7], 1.30 [dd, 1 H, $\mathrm{H_a}$, $J(\mathrm{H_aH_c})$ 10.6, $J(\mathrm{H_aH_s})$ 2.5], 1.02 [d, 3 H, Me, ^3J(HH) 6.4 Hz]; ^{13}C-{^{1}H}

Table 5. Atomic positional parameters (fractional co-ordinates) for (2)

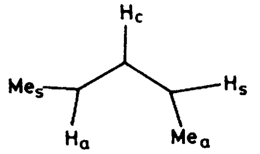
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.203 02(4)	0.114 28(2)	0.142 84(2)	O(5)	0.044 1(4)	0.023 17(11)	0.205 68(13)
C(1)	0.466 7(6)	0.156 7(2)	0.202 3(3)	C(6)	−0.162 8(5)	−0.025 4(2)	0.317 4(3)
O(1)	0.620 4(4)	0.185 9(2)	0.236 8(2)	Me(6)	−0.114 8(7)	−0.110 0(2)	0.291 7(3)
C(2)	0.386 3(6)	0.021 3(2)	0.124 7(3)	C(7)	−0.330 1(6)	−0.005 1(2)	0.356 6(3)
O(2)	0.493 4(5)	−0.030 0(2)	0.112 9(2)	Me(7)	−0.499 0(7)	−0.059 5(3)	0.380 8(4)
C(3)	0.145 7(5)	0.157 5(2)	0.280 7(2)	C(11)	0.214 0(7)	0.170 2(2)	−0.006 0(3)
Me(3)	0.193 2(7)	0.240 5(2)	0.316 9(3)	C(12)	0.057 0(6)	0.111 4(3)	−0.020 6(3)
C(4)	0.041 2(5)	0.107 3(2)	0.335 3(2)	C(13)	−0.103 7(6)	0.134 7(2)	0.031 5(3)
Me(4)	−0.008 8(7)	0.127 9(3)	0.435 1(3)	C(14)	−0.048 7(6)	0.206 1(2)	0.078 0(3)
C(5)	−0.021 9(5)	0.035 8(2)	0.287 4(2)	C(15)	0.148 7(6)	0.228 7(2)	0.055 1(3)

Table 6. Atomic positional parameters (fractional co-ordinates) for (5)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.266 17(4)	0.409 60 (5)	0.654 65(4)	C(11)	0.191 0(6)	0.115 3(6)	0.648 2(6)
C(51)	0.341 6(7)	0.546 4(8)	0.560 5(7)	C(12)	0.312 7(7)	0.076 2(8)	0.700 2(8)
C(52)	0.236 9(6)	0.502 3(8)	0.498 3(6)	C(13)	0.167 7(9)	0.106 3(8)	0.532 8(7)
C(53)	0.252 6(7)	0.385 4(7)	0.484 9(6)	C(14)	0.104 1(8)	0.037 0(8)	0.680 8(7)
C(54)	0.367 7(7)	0.355 5(8)	0.538 6(6)	C(71)	0.280 7(6)	0.652 0(7)	0.818 2(6)
C(55)	0.420 9(6)	0.455 2(8)	0.584 9(6)	C(72)	0.376 3(7)	0.592 1(8)	0.901 0(6)
C(1)	0.173 9(6)	0.236 8(7)	0.684 1(6)	C(73)	0.339 6(9)	0.738 3(9)	0.765 3(8)
C(2)	0.092 2(6)	0.316 4(7)	0.628 4(6)	C(74)	0.197 2(8)	0.714 3(9)	0.869 2(8)
C(3)	0.089 0(6)	0.421 3(7)	0.673 8(6)	C(01)	0.377 4(6)	0.350 0(7)	0.776 7(6)
C(4)	0.173 2(6)	0.455 7(7)	0.767 7(6)	O(01)	0.443 5(5)	0.311 9(5)	0.847 9(4)
C(5)	0.209 5(6)	0.564 9(6)	0.744 1(6)	O(1)	0.088 2(6)	0.703 8(5)	0.621 2(5)
C(6)	0.110 2(7)	0.610 2(7)	0.658 0(7)	O(2)	0.033 5(4)	0.519 6(5)	0.621 3(4)

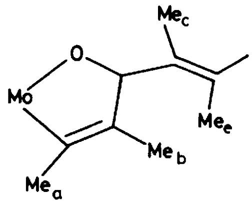
($CDCl_3$), δ 91.5 (s, C_5H_5), 66.2 [s, C(central)], 57.6 [s, C(saturated)], 35.0 [s, C(unsaturated)], and 14.6 p.p.m. (s, Me). The mass spectrum showed additional peaks at *m*/*e* 244 (*P* − CO) and 216 (*P* − 2CO).

A similar reaction between $[Mo(CO)(MeC_2Et)_2(\eta\text{-}C_5H_5)][BF_4]$ (0.4 g, 1.0 mmol) and $NaBH_4$ (0.1 g, 3.0 mmol) gave yellow *crystals* of (7) (0.15 g, 54%) (Found: C, 50.3; H, 5.1%; *M*, 286. $C_{12}H_{14}MoO_2$ requires C, 50.4; H, 4.9%; *M*, 286); ν_{CO} 1 951s and 1 877s cm^{-1} (hexane). N.m.r. ^1H (C_6D_6), δ 4.63



(s, 5 H, C_5H_5), 3.48 [dd, 1 H, H_c, $J(H_cH_a)$ 9.6, $J(H_cH_s)$ 7.9], 3.14 (m, 1 H, H_s), 2.10 (m, 1 H, H_a), 1.56 [d, 3 H, Me_s, $^3J(Me_sH_a)$ 6.2], 1.06 [d, 3 H, Me_a, $^3J(Me_aH_s)$ 6.2 Hz]; $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 92.1 (s, C_5H_5), 69.2 [s, C(central)], 60.0 (s, *C*HMe_s), 48.2 (s, *C*HMe_a), 20.8 (s, Me_s), and 15.5 p.p.m. (s, Me_a). The mass spectrum showed peaks at *m*/*e* 258 (*P* − CO) and 230 (*P* − 2CO).

Reaction of Complex (1) *with Carbon Monoxide.*—A freshly prepared solution of lithium dimethylcuprate (2.5 mmol) in diethyl ether (20 cm^3) was added dropwise with stirring to a suspension (−78 °C) of $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (0.8 g, 2 mmol) in thf (20 cm^3). When the addition was complete the stirred reaction mixture was allowed to warm to *ca.* −40 °C when a deep purple solution was formed. After 5 min at −40 °C the reaction mixture was again cooled to −78 °C, and carbon monoxide was bubbled through the solution for 1 min. This resulted in an immediate colour change to red. The reaction mixture was allowed to warm to room temperature and the volatiles were removed *in vacuo*. The oily residue was extracted into diethyl ether and filtered through a Kieselguhr plug to remove polar material. The solvent was removed *in vacuo*, and the hexane-soluble material chromatographed on an alumina packed column (4 × 10 cm). Elution with diethyl ether–hexane (1 : 4) afforded an orange band, which was collected. Recrystallisation (−30 °C) from hexane yielded (8) as an orange powder (0.40 g, 42%) (Found: C, 55.9; H, 5.9%; *M*, 368. $C_{17}H_{20}MoO_3$ requires C, 55.4; H, 5.5%; *M*, 368); ν_{CO} 1 975s and 1 886s cm^{-1} (hexane). N.m.r. ^1H



(C_6D_6), δ 4.77 (s, 5 H, C_5H_5), 2.89 (s, 3 H, Me_a), 1.86 (s, 3 H, Me_b), 1.75 (br s, 3 H, Me_c), 1.67 (m, 3 H, Me_e), and 1.47 p.p.m. (m, 3 H, Me_d). The mass spectrum showed peaks at *m*/*e* 340 (*P* − CO) and 312 (*P* − 2CO).

Molecular Structure Determinations.—*Data collection and reduction.* A small single crystal of (2) (approximate dimensions 0.45 × 0.08 × 0.05 mm) was mounted in a thin-walled glass capillary under nitrogen for data collection on a Nicolet P3m diffractometer. The lattice periodicity, Laue symmetry, and crystal quality were checked by oscillation photography, and the space group determined by inspection of the integrated intensities of reflections (0*k*0) and (*h*0*l*). The orientation matrix and unit-cell dimensions were obtained by least-squares fit to the diffractometer setting angles for 15 strong reflections with 20 < 2θ < 27°. A full quadrant of intensity data in the range $3 < 2\theta < 55°$ were collected at 293 K by variable-speed θ—2θ scans; where the scan widths were $2.4° + \Delta_{\alpha_1\alpha_2}$ in 2θ and scan speed varied between 1.0 and 29.3° min^{-1} based on a 2-s prescan of the reflection. The intensities of two reflections measured after every 40 data showed no change over the period of data collection, and were constant within $\pm 2\%$. The total of 2 645 data collected yielded 2 222 unique reflections after averaging of duplicate measurements and symmetry related reflections and detection of systematic absences; of these, 2 136 with $F^2 > 2\sigma(F^2)$ were used in structure solution and refinement after application of Lorentz and polarization corrections.

Crystal data for (2). $C_{16}H_{18}MoO_3$, $M = 354$, Monoclinic, space group $P2_1/n$ (no. 14), $a = 6.495(3)$, $b = 16.902(9)$, $c = 14.002(7)$ Å, $\beta = 97.62(4)°$, $U = 1\,523(1)$ Å^3, $Z = 4$, $D_c = 1.544$ g cm^{-3}, $F(000) = 720$, μ(Mo-K_α) = 8.43 cm^{-1}, $\lambda = 0.710\,69$ Å.

The space group and approximate unit-cell dimensions of complex (5) were derived from oscillation and Weissenberg photographs. A small crystal of (5) was mounted in a thin-walled glass capillary under nitrogen for data collection on a Nicolet P3m diffractometer. All diffraction measurements were made with the crystal cooled to 230 K using the Nicolet LT-1 low-temperature facility. Cell dimensions were determined as for (2), and a full quadrant of intensity data in the range $3 < 2\theta < 50°$ was collected as above, except that scan speeds varied between 2.0 and 29.30° min^{-1}. Two reflections remeasured after every 50 data showed a smooth decrease in intensity of *ca.* 5% over the period of data collection; other reflection intensities were corrected accordingly. The total of 3 570 data collected yielded 2 526 unique reflections, after averaging of duplicate measurements and symmetry related reflections and deletion of systematic absences; of these, 2 257 with $F^2 > 2\sigma(F^2)$ were used in structure solution and refinement after application of Lorentz and polarisation corrections.

Crystal data for (5). $C_{20}H_{26}O_3Mo$, $M = 410$, Monoclinic, space group $P2_1/c$ (no. 14), $a = 11.935(7)$, $b = 11.673(9)$, $c = 13.674(9)$ Å, $\beta = 105.93(5)°$, $U = 1\,832(2)$ Å^3, $Z = 4$, $D_c = 1.487$ g cm^{-3}, $F(000) = 848$, μ(Mo-K_α) = 7.11 cm^{-1}, $\lambda = 0.710\,69$ Å.

Structure solution and refinement. The structures of (2) and (5) were solved by conventional heavy-atom methods (Patterson and difference-Fourier). All non-hydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were located from difference-Fourier maps. For (2) all hydrogen atoms were constrained to idealised geometries with C–H bond lengths fixed at 0.96 Å, and isotropic thermal parameters allowed to refine freely. For (5) atoms H(1), H(2), and H(4) were allowed to refine without positional constraints, the remaining hydrogen atoms being constrained as for (2); all hydrogen atom isotropic thermal parameters were fixed at *ca.* 1.2 times the value of the equivalent thermal parameter of their respective carbon atom. Refinement of parameters was by blocked-cascade full-matrix least squares methods with data weighted according to $w = [\{\sigma^2(F^2)/4F^2\} + gF^2]^{-1}$ where $g = 0.0002$ for (2) and 0.0008 for (5), these values being chosen to give no significant variation of $\Sigma w(F_o - |F_c|)^2$ with $|F_o|$. Refinement of (2) converged to give final agreement indices [*] $R = 0.025$, $R' = 0.024$, and ' goodness of fit ' $S = 1.15$, the corresponding values for (5) at convergence of refinement were $R = 0.053$, $R' = 0.052$, $S = 1.64$. All crystallographic calculations were carried out with the SHELXTL program package on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors of ref. 14 were used for all atoms. Final positional parameters for (2) and (5) are given in Tables 5 and 6, respectively.

Acknowledgements

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[*] $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w(F_o - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, N_o = number of observations, N_v = number of varied parameters.