Formation of η^3-Bonded Lactone Complexes and Eight-membered Ring Metallacycles with Ketene Groups by the Insertion of Acetylenes into Carbon–Molybdenum and –Tungsten σ Bonds; Molecular and Crystal Structures of Carbonyl(η-cyclopentadienyl)(3—5-η-2,3-dihydro-3,4,5-trimethyl-2-oxo-3-furyl)(t-butyl isocyanide)molybdenum and Carbonyl(η-cyclopentadienyl)(3—4:5—6-η-2,3,4,5-tetramethyl-6-oxo-1-trifluoromethylhexa-1,3,5-trienyloxo)molybdenum

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Reaction of $[MR(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo, R = $COCF_3$, Me, or $PhCH_2$; M = W, R = $COCF_3$ or Me) with but-2-yne either thermally or on u.v. irradiation affords the crystalline vinylketone complexes $[M\{C(Me)\text{:}C(Me)\cdot C(R)O\}(CO)_2(\eta\text{-}C_5H_5)]$ (R = CF_3, Me, or $PhCH_2$). These complexes react with donor ligands such as $CNBu^t$, CNC_6H_{11}, CO, or PPh_3 to form η^3-allylic lactone complexes of the type $[M\{\eta^3\text{-}C(Me)\cdot C(Me)\cdot C(R)\cdot C(O)\cdot O\}(CO)(\eta\text{-}C_5H_5)L]$ (L = CO, $CNBu^t$, CNC_6H_{11}, or PPh_3). The complex where L = $CNBu^t$ and R = Me is structurally identified by single-crystal *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/a$ with four molecules in a unit cell of dimensions $a = 9.3013(15)$, $b = 22.161(6)$, $c = 9.353(3)$ Å, and $\beta = 102.76(2)°$. The mode of formation of this type of complex is discussed in detail. A further product obtained from the reaction of $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ with but-2-yne is the purple-red complex $[Mo\{C(O)\cdot(CMe)_4\cdot C(CF_3)\cdot O\}(CO)(\eta\text{-}C_5H_5)]$ crystallographically shown to contain an unusual eight-membered ring structure containing an η^2-ketenic group. Eight molecules crystallise in a unit cell of dimensions $a = 18.389(4)$, $b = 11.137(3)$, $c = 16.686(5)$ Å, $\beta = 92.55°$, and space group *P*2/*n*. The mechanism of formation of this and of a related tungsten complex is discussed. In addition, complexes are formed which are considered to be isostructural with the eight-membered ring species, except that the terminal carbon monoxide is replaced by an η^2-bonded but-2-yne molecule. Simple symmetry arguments are developed which refer the co-ordination geometries of both the lactone and the metallacycle complexes to different isomers of a monocapped trigonal prism.

It has been shown that γ-lactones are formed in the tetracarbonylnickel-catalysed reaction of acetylenes with carbon monoxide and alkyl, allyl, or aryl halides.[1,2] In this reaction acylnickel carbonyl species are probably first formed. Support for this idea derives from the observation [3,4] that acyl compounds $[Co\{C(O)R'\}(CO)_4]$ react with acetylenes to give η^3-bonded lactonyl complexes of the type $[Co\{C(R)\cdot C(R)\cdot C(R')\cdot O\cdot CO\}(CO)_3]$, and Heck [5] has suggested that the immediate precursor is a vinyl ketone complex. The latter species have been obtained [6] from *cis*-insertion reactions of acetylenes with methyl-, acetyl-, or phenyl-pentacarbonylmanganese. However, lactones are not formed from these molecules on reaction with ligands. Instead a competing reaction intervenes, and only η^5-pyranyl complexes have been obtained on further reaction with acetylenes. Although a number of studies have reported on the reaction of electronegatively substituted acetylenes with transition-metal complexes containing σ-bonded carbon atoms, in general rather different reaction paths are followed.[7,8] In the hope that it might be possible to identify firmly the individual steps in the γ-lactone-forming reaction, we have explored reactions of acetylenes with alkyl- and acyl-tricarbonyl(η-cyclopentadienyl)-molybdenum and -tungsten complexes, it having already been established [9,10] that carbonyl-insertion reactions readily occur with phosphorus ligands. A preliminary account of some aspects of this work has been published.[11]

RESULTS AND DISCUSSION

Column chromatography of the reaction mixture obtained on heating (60 °C) a hexane solution of tricarbonyl(η-cyclopentadienyl)(trifluoroacetyl)molybdenum and excess of but-2-yne afforded bright red air-sensitive crystals of the complex (1), for which the illustrated structure was assigned on the basis of elemental analysis, a mass spectrum, and i.r. and n.m.r. spectra. The i.r. spectrum showed, in addition to two terminal-carbonyl bands, a weaker band at 1 505 cm^{-1}, which is assigned by analogy with previous observations [6,12] to a ν(CO) stretch of a keto-group co-ordinated

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[3] W. Hübel, 'Organic Synthesis *via* Metal Carbonyls,' vol. 1, eds. I. Wender and P. Pino, Interscience, New York, 1968, p. 273.

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[5] R. F. Heck, 'Organotransition Metal Chemistry: A Mechanistic Approach,' Academic Press, New York, 1974, p. 248.

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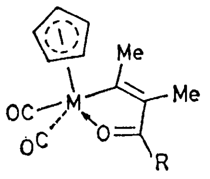
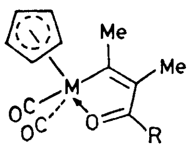
[12] D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1765.

to molybdenum *via* an oxygen lone pair. The ^{1}H n.m.r. spectrum showed a singlet at τ 4.66 due to the cyclopentadienyl protons, a singlet at τ 6.96 ascribed to a methyl group α to the molybdenum, and a quartet centred at τ 7.90 which is assigned to the methyl group adjacent to the carbon carrying a trifluoromethyl substituent. In agreement, the ^{19}F spectrum showed a single quartet at 67.7 p.p.m. with a coupling constant [J(HF) 2.0 Hz] identical to that observed in the ^{1}H n.m.r. spectrum.

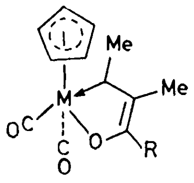


	M	R
(1)	Mo	CF_3
(2)	Mo	Me
(3)	Mo	$PhCH_2$
(4)	W	Me
(5)	W	CF_3

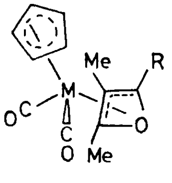
Similar thermal reactions of but-2-yne with methyl- or benzyl-tricarbonyl(η-cyclopentadienyl)molybdenum afforded red-orange crystals of (2) and bright red crystals of (3), respectively. Attempts to cause methyl- or trifluoroacetyl-tricarbonyl(η-cyclopentadienyl)tungsten to react thermally with but-2-yne failed. However, u.v. irradiation of hexane solutions of the reactants gave a good yield of the crystalline complex (4) and a low yield of (5). All these complexes showed in their i.r. and n.m.r. spectra the expected features for a vinyl ketone derivative isostructural with (1).



(*A*)



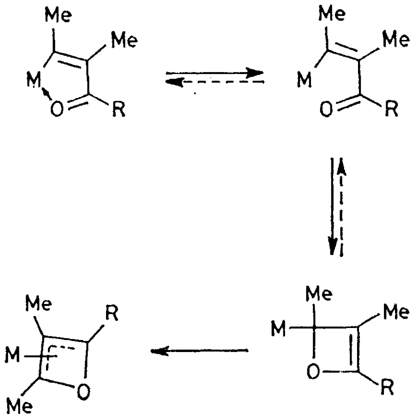
(*B*)



(*C*)

There are three alternative structures (*A*)—(*C*) for these complexes which merit comment. Structure (*A*) seems most probable and is assigned on the basis of the i.r. bands near 1 500 cm^{-1} attributable to a metal co-ordinated ketone group. In (*B*) a metal–oxygen σ bond is invoked and the carbon atom α to the metal atom has carbenoid character. On the experimental evidence available it is not possible to eliminate entirely a contribution of this form to the bonding. Structure (*C*) arises by assuming that an initially formed vinyl ketone complex (*A*) rearranges by dissociation of the co-ordinated keto-group to give a 4-oxabutadienylmetal species, which then, *via* a conrotatory ring closure of the kind that has been postulated [13] in palladium chemistry, forms the four-membered η^3-oxacyclobutenyl ring system (Scheme 1). The occurrence in the ^{1}H n.m.r. spectrum of (2) of three distinct methyl environments strongly suggests, however, that such a bonding mode is not involved.

In the formation of (1) from a trifluoroacetylmolybdenum species the acyl group is already formed. Hence the reaction with the but-2-yne probably involves capture of a 16-electron species formed by dissociation of a carbon monoxide molecule *cis* to the trifluoroacetyl group. A similar sequence is likely to be involved in the initial reaction of diphenylacetylene with [MoCl(CO)$_3$-(η-C$_5$H$_5$)]. In the latter case, dissociation of a further carbon monoxide occurs to give [14] [MoCl(CO)(PhC$_2$Ph)-(η-C$_5$H$_5$)], whereas with the CF$_3$COMo system the acyl group undergoes a competitive migration onto the co-ordinated but-2-yne to form (1). Although related migrations of acyl groups from a metal onto co-ordinated olefins,[15] 1,3-dienes,[16] and acetylenes [6] have been reported, we have little understanding of these interesting reactions. One plausible reaction path would involve a concerted migration, which from the standpoint of the symmetry of the orbitals involved would be an allowed process.[17]



Scheme 1

In the reactions leading to the formation of (2) and (3) an acyl group must first be formed. In general terms this does not present a problem since it is known that

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[13] P. M. Maitlis, *Accounts Chem. Res.*, 1976, **9**, 93.

[14] J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 706; J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2531.

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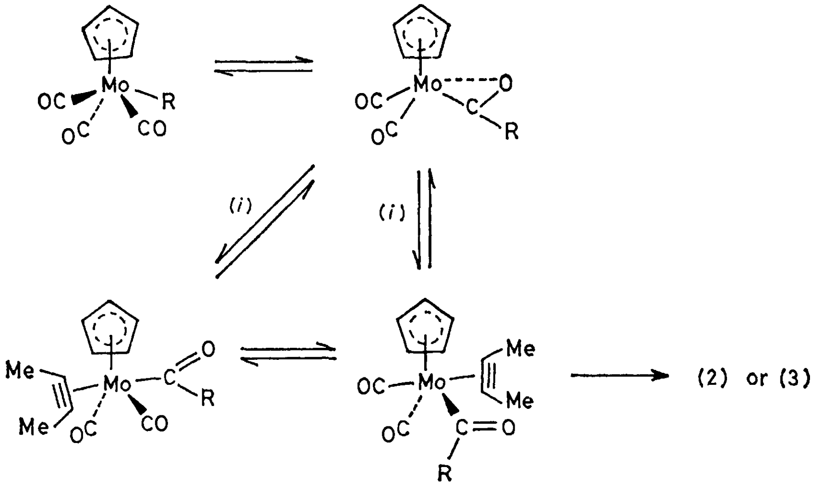
[16] M. Green and R. I. Hancock, *J. Chem. Soc.* (*A*), 1968, 109.

[17] R. G. Pearson, *Chem. in Britain*, 1976, **12**, 160.

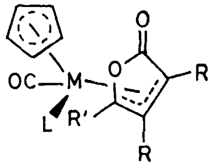
both phosphines and arsines react with $[\mathrm{MoR(CO)_3(\eta\text{-}C_5H_5)}]$ complexes (R = Me, Et, or $\mathrm{PhCH_2}$) to form substituted acyl species.[9] In the formation of the vinyl ketone complexes it is therefore reasonable to propose initial formation of an η^2-bonded acetylene complex *via* a side-bonded acyl species, this being followed by migration of the newly formed acyl group onto the co-ordinated acetylene (Scheme 2). A difficulty arises in considering the stereochemistry of the initial step, it having been observed that phosphines and arsines give the *trans*-substituted acyl complexes. However, it has not so far been possible to decide whether this stereochemistry arises under thermodynamically or kinetically controlled conditions, and in the case of the postulated η^2-acetylene species it is at present not possible to estimate the magnitude of the barrier to intramolecular[18] *cis–trans* interconversion. Thus, this aspect of the mode of formation of the vinyl ketone complexes remains unclear.



SCHEME 2 (*i*) $\mathrm{MeC_2Me}$

As previously mentioned, Booth and Hargreaves,[6] in studying the related reaction of phenylacetylene with carbon-to-manganese σ-bonded complexes, were unable to effect the conversion of a vinyl ketone complex into an η^3-allylic lactone species. It was, therefore, of importance to examine the reactivity of complexes (1)—(5) towards donor ligands. Treatment of a diethyl ether solution of (2) at room temperature with an excess of t-butyl isocyanide resulted in an immediate reaction with formation of the yellow crystalline complex (6). Elemental analysis and spectroscopy suggested that the sought-for conversion to a lactone complex had in fact been achieved. In particular, the i.r. spectrum showed bands at 2 096, 1 888, and 1 726 $\mathrm{cm^{-1}}$, which can be ascribed respectively to a terminal bonded isocyanide, a terminal carbonyl, and a γ-lactone carbonyl stretch. The ^{1}H n.m.r. spectrum showed singlets due to an η-cyclopentadienyl group, a co-ordinated t-butyl isocyanide, and three methyl-group environments. In order to confirm this important structural feature a single-crystal *X*-ray diffraction study was undertaken.

Complex (6) crystallises as discrete, neutral, monomeric molecules with no imposed symmetry. The atomic numbering scheme is given in Figure 1. Table 1 lists the interatomic distances (uncorrected for thermal effects) that do not involve hydrogen atoms,* and Table 2 selected interbond angles. The geometry of the molybdenum co-ordination [formally seven-co-ordinate, with the allyl function C(5)C(6)C(7) occupying two, and the cyclopentadienyl ligand three, co-ordination sites] displays the C_s symmetry possessed by all three dominant seven-co-ordinate forms, the pentagonal bipyramid (1 : 5 : 1), the capped octahedron (1 : 3 : 3), and the capped trigonal prism (1 : 4 : 2). In (6) the central mirror is defined by atoms C(05), Mo, and C(6). With respect to this plane, the planes defined by the cyclopentadienyl ring and by the allyl group lie in perpendicular (⊥) orientations. The neutral donor ligands,



(6) M = Mo, R = R′ = Me, L = CNBu^t
(7) M = Mo, R = Me, R′ = $\mathrm{CF_3}$, L = CO
(8) M = Mo, R = Me, R′ = $\mathrm{CF_3}$, L = CNBu^t
(9) M = Mo, R = Me, R′ = $\mathrm{CF_3}$, L = $\mathrm{CNC_6H_{11}}$
(10) M = Mo, R = R′ = Me, L = $\mathrm{PPh_3}$
(11) M = W, R = R′ = Me, L = CNBu^t
(12) M = Mo, R = $\mathrm{SiMe_3}$, R′ = Me, L = CO
(13) M = W, R = Me, R′ = $\mathrm{CF_3}$, L = CO

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* All the hydrogen-atom data (positional and thermal parameters, distances, and angles) appear as Appendix A of Supplementary Publication No. SUP 22228 (40 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[18] J. W. Faller, A. S. Anderson, and C. C. Chen, *J. Organometallic Chem.*, 1969, **17**, P7.

CO and $CNBu^t$, are related by the mirror. Assuming that the symmetrical orientation of the cyclopentadienyl ring reflects a symmetrical disposition of the three Mo *fac*-orbitals, the precise geometry at the molybdenum may be deduced since, (*a*) the cyclopentadienyl function must occupy a triangulated face of the co-ordination polyhedron *through which passes a plane of symmetry*, (*b*) the carbonyl and isocyanide ligands must be disposed about the plane of symmetry, and (*c*) the allyl group must occupy two adjacent sites.

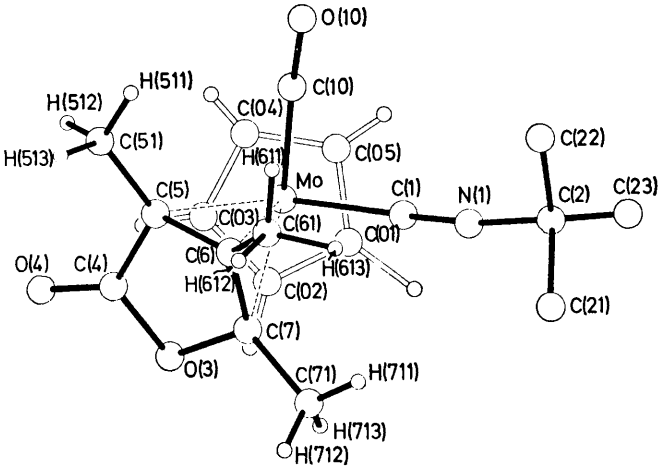

FIGURE 1 The molecular structure of $[Mo\{\eta^3\text{-}C(Me)\cdot C(Me)\cdot C(Me)\cdot C(O)\cdot O\}(CO)(\eta\text{-}C_5H_5)(CNBu^t)]$ (6) viewed perpendicular to the cyclopentadienyl ring. Hydrogen atoms of the C_5H_5 ring carry the same number as the carbon to which they are bound

TABLE 1

Interatomic distances (Å) not involving hydrogen atoms for complex (6) *

Mo–C(01)	2.334(8)	C(1)–N(1)	1.153(7)
Mo–C(02)	2.372(9)	N(1)–C(2)	1.475(8)
Mo–C(03)	2.361(8)	C(2)–C(21)	1.539(15)
Mo–C(04)	2.304(10)	C(2)–C(22)	1.532(15)
Mo–C(05)	2.297(9)	C(2)–C(23)	1.523(11)
Mo–C(1)	2.053(5)	C(10)–O(10)	1.153(10)
Mo–C(10)	1.955(8)	O(3)–C(4)	1.377(10)
Mo–C(5)	2.353(7)	C(4)–O(4)	1.204(9)
Mo–C(6)	2.243(6)	C(4)–C(5)	1.459(11)
Mo–C(7)	2.284(6)	C(5)–C(51)	1.510(14)
C(01)–C(02)	1.379(11)	C(5)–C(6)	1.434(9)
C(02)–C(03)	1.374(14)	C(6)–C(61)	1.510(10)
C(03)–C(04)	1.413(15)	C(6)–C(7)	1.409(9)
C(04)–C(05)	1.406(12)	C(7)–C(71)	1.502(10)
C(05)–C(01)	1.407(12)	C(7)–O(3)	1.431(7)

* Estimated standard deviations are given in parentheses throughout this paper.

Figure 2[(*i*)—(*ix*)] shows the various geometrical isomers of the major seven-co-ordinate polyhedra which obey criterion (*a*) above. The donor ligands are then positioned with due regard to rule (*b*), and the remaining sites examined. In the one possible pentagonal-bipyramidal isomer (*i*) the residual sites are adjacent, but lead to an allyl group in the parallel (||) conformation. For the capped octahedron a similar result follows for (*ii*) and (*iii*), whilst (*iv*) and (*v*) can be dismissed through non-adjacency of the allyl positions. This is also the

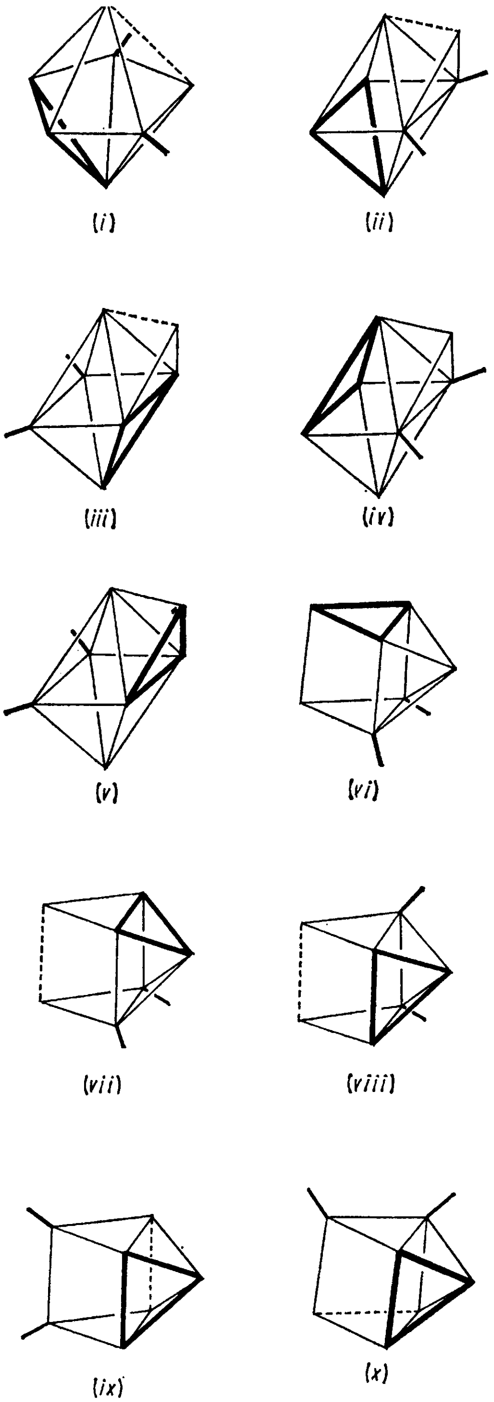

FIGURE 2 Geometrical isomers (*i*)—(*ix*) for a seven-co-ordinate molecule $[ML_2(\eta^3\text{-allyl})(\eta\text{-}C_5H_5)]$. The cyclopentadienyl ligand is represented by the thick triangle and the allyl group by the broken line. The conformation of the allyl group with respect to the molecular mirror plane is parallel (||) for (*i*)—(*iii*) and (*vii*), and perpendicular (⊥) for (*viii*) and (*ix*). Conformation (*x*) shows the only possible isomer of a molecule $[ML_2(\eta^4\text{-butadienyl})(\eta\text{-}C_5H_5)]$ [see discussion of complex (14) in the text]. The broken line again represents the open-chain η-ligand

situation for the first capped trigonal-prismatic possibility (*vi*). Isomer (*vii*) again gives rise to a parallel allylic function.

TABLE 2

Selected interbond angles (°) for complex (6)

C(01)–Mo–C(02)	34.1(3)	C(05)–Mo–C(01)	35.4(3)
C(02)–Mo–C(03)	33.8(3)	C(5)–Mo–C(6)	36.3(2)
C(03)–Mo–C(04)	35.2(4)	C(6)–Mo–C(7)	36.3(2)
C(04)–Mo–C(05)	35.6(3)	C(1)–Mo–C(10)	80.3(3)
Mo–C(10)–O(10)	175.6(7)		
C(05)–C(01)–C(02)	108.1(7)	C(03)–C(04)–C(05)	107.5(8)
C(01)–C(02)–C(03)	109.4(8)	C(04)–C(05)–C(01)	107.2(7)
C(02)–C(03)–C(04)	107.8(8)		
Mo–C(1)–N(1)	178.0(6)	N(1)–C(2)–C(23)	107.4(6)
C(1)–N(1)–C(2)	169.5(7)	C(21)–C(2)–C(22)	110.1(8)
N(1)–C(2)–C(21)	106.8(7)	C(21)–C(2)–C(23)	113.2(8)
N(1)–C(2)–C(22)	106.2(6)	C(22)–C(2)–C(23)	112.7(9)
C(7)–O(3)–C(4)	104.8(5)	C(5)–C(6)–C(61)	128.3(6)
O(3)–C(4)–O(4)	120.9(8)	C(5)–C(6)–C(7)	102.5(5)
O(3)–C(4)–C(5)	108.9(5)	C(61)–C(6)–C(7)	127.5(5)
O(4)–C(4)–C(5)	130.1(8)	C(6)–C(7)–C(71)	128.0(6)
C(4)–C(5)–C(51)	119.6(7)	C(6)–C(7)–O(3)	110.7(5)
C(4)–C(5)–C(6)	106.4(6)	C(71)–C(7)–O(3)	110.9(5)
C(51)–C(5)–C(6)	124.7(9)		

Isomers (*viii*) and (*ix*) are acceptable but distinct. In (*viii*) the carbonyl and isocyanide ligands occupy positions on the capped face, whereas in (*ix*) they do not, and our ignorance of the precise orientation of the three metal orbitals used to bind the cyclopentadienyl group prohibits conclusive distinction to be made. Possible use of the measured angle between the C_5 ring and the Mo–C(1) and Mo–C(10) lines, 61.5 and 62.4° respectively, could be unreliable since the five-membered ring is slightly tilted (see later). One feature that may favour (*viii*), however, is our calculation of the idealised L–M–L angles in (*viii*) and (*ix*) from shape parameters determined for an idealised capped trigonal-prismatic geometry obtained[19] for a hard-sphere model using a value of 6.0 as the exponent in the potential $E = \sum_{i \neq j} r_{ij}^{-n}$. For (*viii*) the angle is 80.9°, and for (*ix*) 73.4°. The observed value (Table 2) is 80.3(3)°.

We therefore tentatively suggest that the co-ordination geometry in (6) may be effectively represented by the monocapped trigonal-prismatic * isomer (*viii*). Introduction of an asymmetrical allyl group and the use of dissimilar donor ligands, as is the case for complex (6), further produces four geometrical variations of (*viii*).

Distances and angles within the MoCO and $MoCNCMe_3$ fragments are unexceptional for a molybdenum(II) complex of this co-ordination number. Thus the Mo–C(10) separation [1.955(8) Å] agrees well with the majority of such dimensions sampled from the literature.[20-28] Similarly, the Mo–C(1) distance [2.053(5) Å] may be set against reported values of 2.05(1) Å in *trans*-$[(\eta\text{-}C_5H_5)(CO)_2(CNMe)MoMo(CO)_3(\eta\text{-}C_5H_5)]$,[24] 2.04(3) and 2.07(3) Å for the non-capped site in $[MoI(CNBu^t)_6]^+$,[29] and 2.051(7) Å for the similar position in $[Mo(CNBu^t)_7]^{2+}$.[30] The distance Mo–C(1) is significantly longer than Mo–C(10), but as Cotton and his co-workers[24] have pointed out this does not necessarily imply differing degrees of back donation from molybdenum to the CO and $CNBu^t$ ligands.

There is no statistically significant variation in either C–C distances or C–C–C angles around the cyclopentadienyl ring, which is accordingly a regular planar pentagon. Table 3, which lists the equations of, deviations from, and angles between various best (least-squares) molecular planes, shows the molybdenum atom to be *ca.* 2.01 Å above the ring, which is quite normal.

TABLE 3

Molecular planes for complex (6). The equation of the least-squares plane is given by $Px + Qy + Rz = S$, where *x*, *y*, and *z* are the atomic fractional co-ordinates (Å) (Table 7). Atomic deviations (Å) are given in square brackets

	P	*Q*	*R*	*S*
Plane A: C(01)—C(05)				
	−5.005	1.595	8.772	−0.772
[C(01) 0.002, C(02) 0.000, C(03) −0.001, C(04) 0.003, C(05) −0.003, Mo 2.007]				
Plane B: C(5)C(6)C(7)				
	−7.329	13.583	2.850	3.113
[Mo −2.034, C(51) 0.220, C(61) 0.292, C(71) 0.267]				
Plane C: C(5)C(4)O(3)C(7)				
	−6.783	9.822	6.262	3.278
[C(5) 0.005, C(4) −0.008, O(3) 0.008, C(7) −0.005, O(4) −0.045, C(6) 0.368]				

Dihedral angles (°): A–B 54.7; B–C 24.5

The bond distances (Table 1), and to a lesser extent the bond angles (Table 2), however, clearly demonstrate a distorted metal–ligand interaction which could either be interpreted in terms of a slip of the molybdenum atom of *ca.* 0.09 Å along the co-ordination mirror plane, roughly

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* It would of course be much simpler to adopt a tetragonal base–trigonal base (4 : 3) description, but such an arrangement can furnish no clear explanation for the asymmetric $M\text{–}C_5H_5$ interaction often observed in $[M(W)(X)(Y)(Z)(\eta\text{-}C_5H_5)]$ structures.

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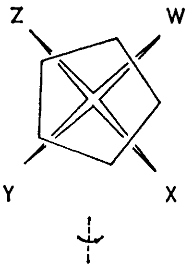
[27] J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 6610.

[28] M. R. Churchill and S. W.-Y Chang, *Inorg. Chem.*, 1975, **14**, 98.

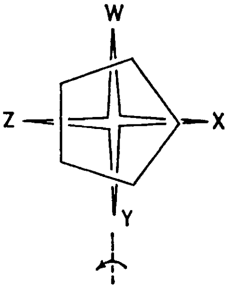
[29] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.

[30] D. L. Lewis and S. J. Lippard, *J. Amer. Chem. Soc.*, 1975, **97**, 2697.

towards C(05), or in terms of a tilt of the cyclopentadienyl ligand of *ca*. 2.6° about an axis perpendicular to this mirror. The direction of tilt is schematically given by (I) below. Rotation of the C_5H_5 group in a similar sense has been noted by Baird and Dahl[31] for [Nb(CO)$_4$(η-C_5H_5)] and [{Mo(CO)$_3$(η-C_5H_5)}$_2$], complexes in which the relative orientation of the remaining four co-ordination sites is also as shown in (I). The alternative arrangement is (II), where the vacant sites are rotated through 45° in the plane of the paper. Several [Mo(W)(X)(Y)(Z)(η-C_5H_5)] complexes have this configuration (see, for example, Table 7 of ref. 20), showing a tilting in the opposite sense. Clearly the *direction* of tilt could be rationalised in terms of intramolecular interligand steric effects. The *origin* of the distortion more probably lies in the unequal bonding capabilities of the capping and non-capping sites in the polyhedron.



(I)



(II)

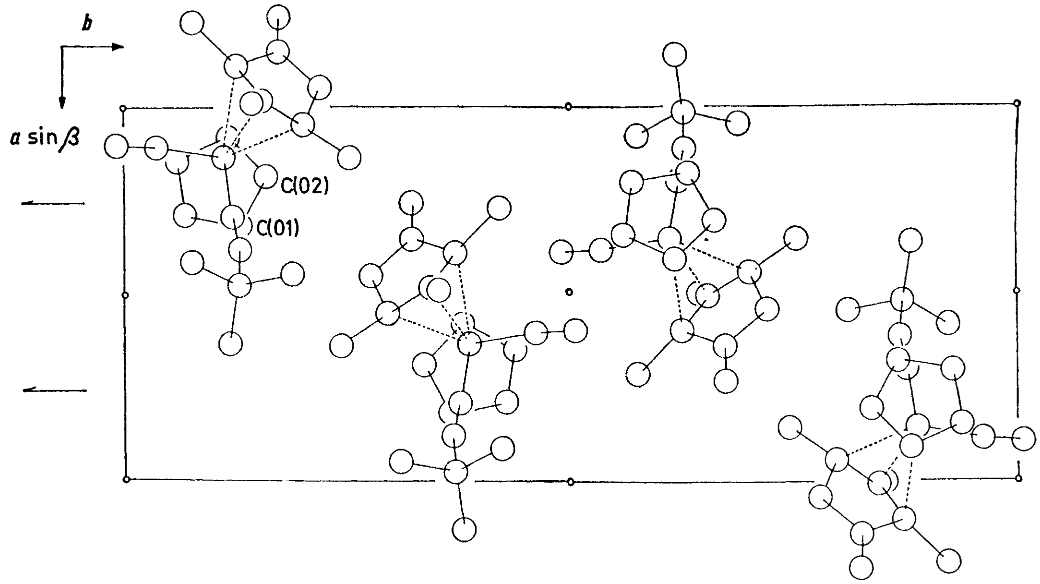


FIGURE 3 Packing diagram for complex (6), as viewed along the crystallographic *c* axis, with only the minimum number of symmetry elements required shown for clarity and hydrogen atoms omitted

Metal co-ordination is completed by the lactone ring O(3)·C(4)·C(5)·C(6)·C(7), acting as an η^3-allyl ligand through C(5), C(6), and C(7). All the three Mo–C distances are significantly different. As anticipated,[22,32–36] the central carbon remains nearest to molybdenum even though the lactone ring adopts an envelope conformation with a fold of some 25° along the line C(5) · · · C(7) away from the molybdenum atom. The C(5)C(4)O(3)C(7) moiety is closely planar (Table 3). Somewhat surprisingly,[37] although C(5)–C(6) is marginally significantly longer than C(6)–C(7), within the allyl group it is atom C(5) which is furthest from the molybdenum atom. There are few interligand non-bonded contacts, and none of any severity. Figure 3 shows one unit cell of the crystal structure, as seen along the *c* axis, looking towards the origin.

Column chromatography of the reaction mixture, which had yielded as the principal product (1), gave a second fraction which on recrystallisation afforded in low yield yellow crystals of (7). This complex is formed in high yield by reaction (60 °C) of (1) with carbon monoxide (10 atm).* The i.r. spectrum of (7) showed strong bands at 2 000 and 1 945 cm^{-1} [ν(CO)], and in addition a band at 1 755 cm^{-1} characteristic of the lactone system. In agreement, the ^{1}H and ^{19}F n.m.r. spectra showed the expected features for a complex essentially isostructural with (6), *i.e.* an η^3-allyl lactone system. Similar reactions between (1) and t-butyl or cyclohexyl isocyanide, or between (2) and triphenylphosphine afforded respectively

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* Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

[31] H. W. Baird and L. F. Dahl, unpublished work. See R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

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[34] E. M. Holt, S. L. Holt, and K. J. Watson, *J.C.S. Dalton*, 1973, 2444.

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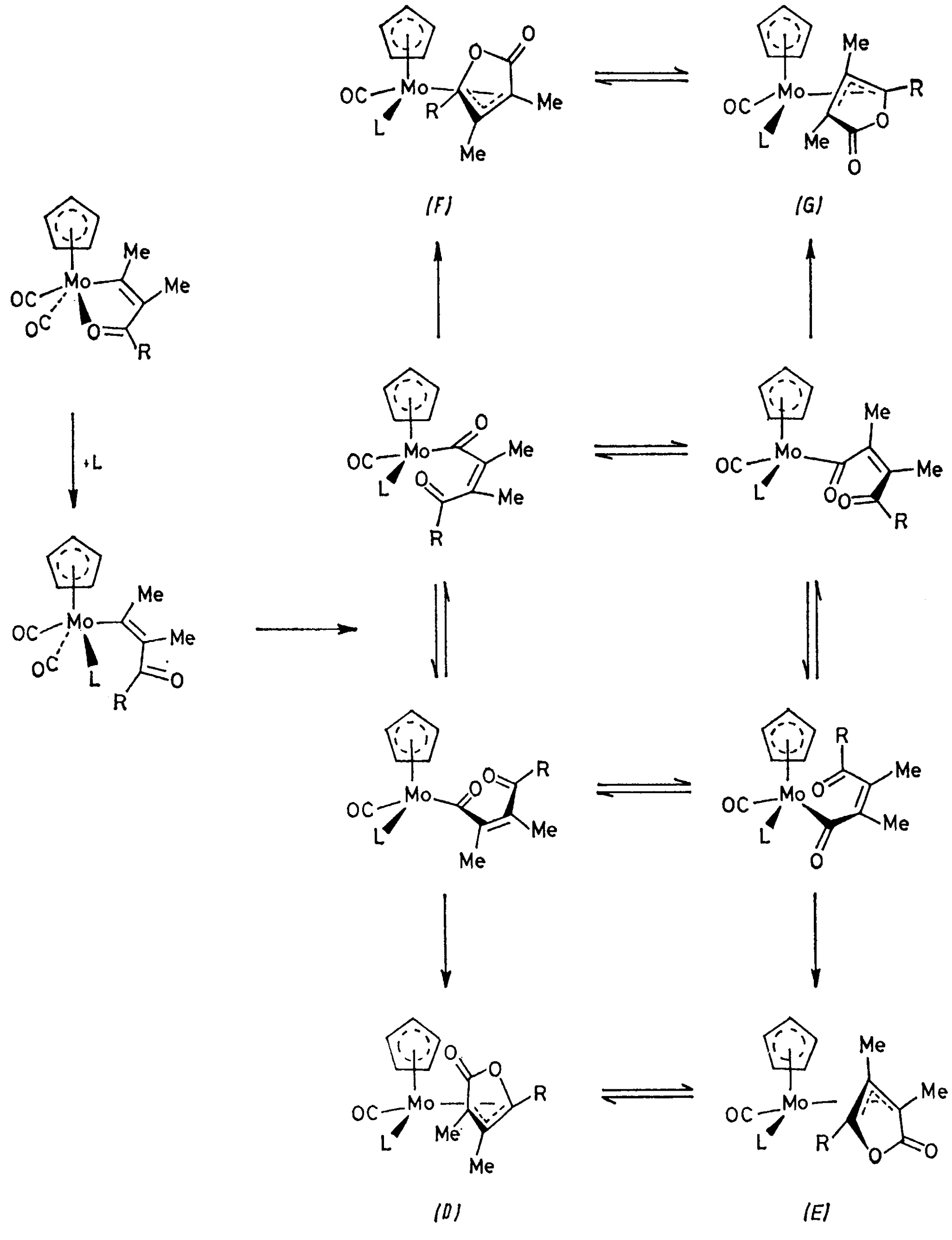
[36] C. K. Prout and G. V. Rees, *Acta Cryst.*, 1974, **B30**, 2251.

[37] R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.

the analogous lactone complexes (8), (9), and (10), which were all obtained in high yield as crystalline materials. The corresponding reactions with the tungsten complexes required more forcing conditions, and in refluxing diethyl ether (4) reacted with CNBu^t to give yellow crystals of (11) in low yield. Further examples of η^3-allylic lactone complex formation were observed in the reaction of $[\text{MoMe(CO)}_3(\eta\text{-C}_5\text{H}_5)]$ with $\text{Me}_3\text{SiC}_2\text{SiMe}_3$, and of $[\text{W(COCF}_3)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ with but-2-yne, under u.v. irradiation, forming the crystalline complexes (12) and (13) respectively. Of course, in the latter two examples the stepwise nature of their formation was not demonstrated.



Scheme 3

A plausible reaction path for the formation of, for example, complex (6) is illustrated in Scheme 3 (R = Me; L = CNBu^t). The reasonable assumption is made that in the reaction of (2) with CNBu^t the keto-group of the vinyl ketone ligand dissociates, the resulting co-ordination site being occupied by the incoming isocyanide. Although no detailed studies have been made on the stereochemistry of the insertion of carbon monoxide into transition-metal σ-bonded vinyl complexes,[38] it is likely that the next step involves migration of the vinyl system onto a *cis*-terminally bonded carbon monoxide. As is shown in Scheme 3, the resulting species can adopt

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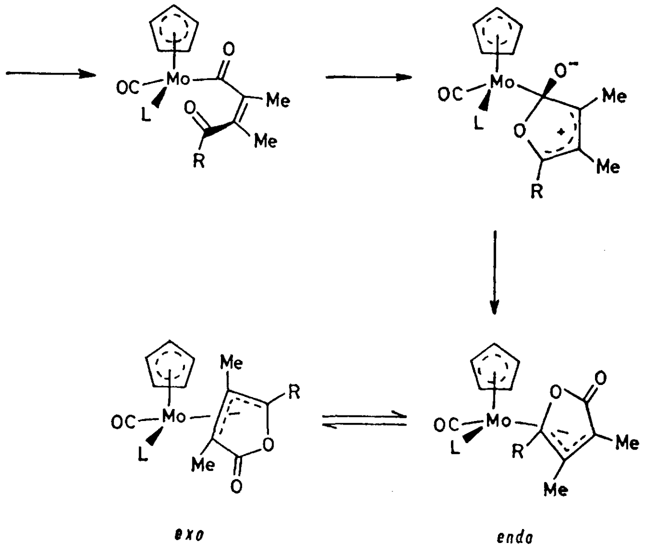
[38] F. Calderazzo, *Angew. Chem. Internat. Edn.*, 1977, **16**, 299.

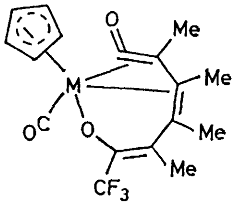
four (disregarding enantiomeric pairs) discrete conformations arising from the relative orientation of the acyl group with respect to the cyclopentadienyl ligand, and to the position of the vinyl chain in relationship to the substituting ligand L. Collapse of these intermediates can then lead to the formation of η^3-allylic lactone complexes with *four* different stereochemistries (*D*)—(*G*). These are related pairwise, *i.e.* *endo*-(*D*) $\rightleftharpoons$ *exo*-(*E*) and *endo*-(*F*) $\rightleftharpoons$ *exo*-(*G*), by a simple rotation of the η^3-allyl group about an axis perpendicular to the plane of the allyl group and through the molybdenum. Thus, complex (6) has the *endo* structure (*F*; R = Me, L = CNBu^t), which could arise directly or by initial formation of *exo*-(*E*) followed by rotation. It seems likely that the same conformation is adopted in solution as in the solid state. Examination of the ^{1}H and ^{19}F n.m.r. spectra of these L-substituted lactone complexes showed the presence of a second isomer (1 : 10, ratio temperature invariant), suggesting that the reaction is only 90% stereoselective.



SCHEME 4

It is suggested that the mode of collapse of the acyl vinyl species involves nucleophilic [15] attack by the lone pair of the oxygen of the terminal RC(O) group on the acyl carbon adjacent to the molybdenum. Such a process requires an essentially coplanar transition state, and the inspection of molecular models suggests that this can be readily achieved as shown in Scheme 4. The final step in the formation of the lactone system involves charge collapse, and a 1,2 shift of the [Mo(CO)L(η-C$_5$H$_5$)] group to an electron-deficient carbon atom.

A third product, which was obtained in low yield from the reaction of [Mo(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] with but-2-yne, is the purple-red crystalline complex (14), showing in the i.r. spectrum strong bands at 1 993 and 1 675 cm^{-1}. The ^{1}H n.m.r. spectrum showed singlets at τ 4.94 (η-C$_5$H$_5$), 7.80 (Me), 8.12 (Me), and 8.38 (Me), and a quartet at τ 8.05 assigned to the fourth methyl group adjacent to a trifluoromethyl group. The presence in the spectrum of four methyl environments suggested that two molecules of but-2-yne had been incorporated into (14). The ^{19}F n.m.r. spectrum showed a quartet [*J*(HF) 2.0 Hz] at 65.2 p.p.m. Since the spectroscopic data did not unequivocally establish the structure of (14), a single-crystal *X*-ray diffraction study was undertaken.



(14) M = Mo
(15) M = W

Two independent molecules, (A) and (B), of complex (14) crystallise in the asymmetric fraction of the unit cell. A view of molecule (A) perpendicular to the cyclopentadienyl ring, and demonstrating the atomic numbering scheme adopted, is presented in Figure 4. An equivalent plot of molecule (B) is practically superimposable on this Figure, save for the orientation of the fluorine atoms of the CF$_3$ groups, approximately staggered with respect to the C(6)–C(61) bond; for consistency the atom *trans* to F(61A) is numbered F(61B) and so on. Intermolecular distances (uncorrected for thermal effects) and important interbond angles for the two independent molecules are compared in Tables 4 and 5, respectively. In only two cases [Mo–C(2), $\Delta = 4.0\sigma$; C(02)–C(03), $\Delta = 4.3\sigma$] are corresponding parameters different by more than three times the greater individual standard deviation, and the following discussion accordingly employs average values.

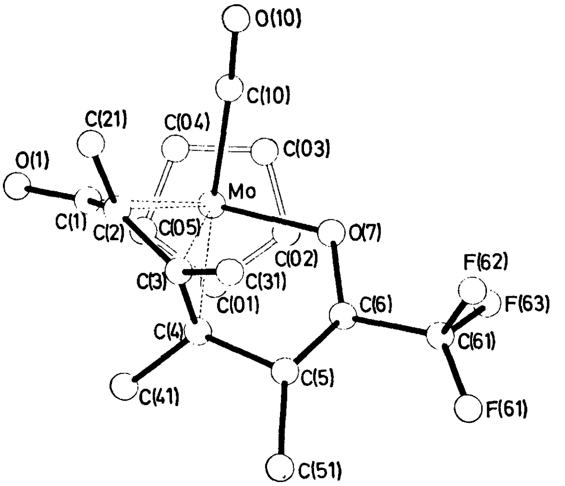


FIGURE 4 The molecular structure of [Mo{C(O)·(CMe)$_4$·C(CF$_3$)·O}(CO)(η-C$_5$H$_5$)] (14)

The co-ordination number for molybdenum is again seven, the disposition of atoms C(10) and O(7) with respect to the atoms of the cyclopentadienyl ring suggesting the presence of a co-ordination mirror plane through C(04), Mo, and the midpoint of the C(01)–C(02) bond. In contrast to (6), the σ-bonded atoms are thus on the *same* side of the mirror and, further, the local plane of the η^4-group [C(1)C(2)C(3)C(4)] is in a || conformation.

We have again assumed that the symmetry of the C_5 ring follows from the symmetry of the molybdenum orbitals, and have examined the possibility of assigning a precise co-ordination geometry. The task is greatly simplified since all the polytopes with more than one vertex lying in the mirror plane are immediately excluded. In fact, only one isomer [Figure 2(*x*)], again based on the monocapped trigonal prism, is possible. This differs from the possibilities (*viii*) and (*ix*) deduced for (6) only in the disposition of adjacent paired sites, and consequently demands the alternative (||) orientation for the η-edge-bonded ligand.

The idealised C(10)–Mo–O(7) angle, again calculated from shape parameters of a hard-sphere model, is 76.1° and represents relatively poor agreement with that observed (87.2°). O(7), however, is constrained by a cyclic system whose effect could be to widen the electronically preferred angle. The molybdenum atom in (14) is fractionally closer to the plane of the cyclopentadienyl ring than in (6) (see Table 4 or the molecular planes of Table 6), which once more is unevenly bonded whilst maintaining the central mirror. Average slip and tilt values are 0.09 Å and 2.7° respectively. The mean Mo–CO distance, although *ca.* 4σ longer than in (6), is nevertheless within the range given by a literature survey.[20–28]

TABLE 4

Interatomic distances (Å) for complex (14)

	Molecule	
	(A)	(B)
Mo–C(01)	2.363(16)	2.361(16)
Mo–C(02)	2.334(14)	2.338(15)
Mo–C(03)	2.310(15)	2.306(16)
Mo–C(04)	2.260(15)	2.266(16)
Mo–C(05)	2.311(15)	2.313(13)
Mo–C(1)	2.087(13)	2.076(11)
Mo–C(2)	2.473(12)	2.425(11)
Mo–C(3)	2.434(12)	2.439(12)
Mo–C(4)	2.288(11)	2.303(10)
Mo–O(7)	2.107(10)	2.127(8)
Mo–C(10)	1.989(12)	2.003(13)
C(10)–O(10)	1.161(17)	1.158(18)
C(01)–C(02)	1.376(22)	1.431(22)
C(02)–C(03)	1.455(21)	1.360(22)
C(03)–C(04)	1.420(22)	1.428(22)
C(04)–C(05)	1.446(23)	1.418(24)
C(05)–C(01)	1.425(22)	1.414(22)
C(1)–O(1)	1.218(17)	1.209(15)
C(1)–C(2)	1.470(19)	1.476(16)
C(2)–C(21)	1.529(22)	1.533(20)
C(2)–C(3)	1.402(18)	1.381(17)
C(3)–C(31)	1.527(23)	1.513(20)
C(3)–C(4)	1.446(19)	1.477(16)
C(4)–C(41)	1.531(20)	1.533(16)
C(4)–C(5)	1.511(20)	1.497(16)
C(5)–C(51)	1.516(23)	1.509(18)
C(5)–C(6)	1.373(21)	1.365(17)
C(6)–C(61)	1.510(25)	1.485(22)
C(61)–F(61)	1.25(3)	1.28(3)
C(61)–F(62)	1.35(3)	1.32(3)
C(61)–F(62)	1.28(3)	1.27(2)
C(6)–O(7)	1.323(17)	1.326(15)

TABLE 5

Selected interbond angles (°) for complex (14)

	Molecule	
	(A)	(B)
C(01)–Mo–C(02)	34.1(5)	35.5(5)
C(02)–Mo–C(03)	36.5(5)	34.1(5)
C(03)–Mo–C(04)	36.2(6)	36.4(5)
C(04)–Mo–C(05)	36.9(6)	36.1(6)
C(05)–Mo–C(01)	35.5(5)	35.2(5)
C(1)–Mo–C(2)	36.4(5)	37.3(4)
C(2)–Mo–C(3)	33.2(4)	33.0(4)
C(3)–Mo–C(4)	35.5(5)	36.1(4)
C(10)–Mo–O(7)	86.8(4)	87.5(4)
C(05)–C(01)–C(02)	110.0(13)	107.4(14)
C(01)–C(02)–C(03)	109.5(13)	108.7(14)
C(02)–C(03)–C(04)	105.1(13)	109.1(14)
C(03)–C(04)–C(05)	110.0(14)	107.1(14)
C(04)–C(05)–C(01)	105.4(13)	107.7(13)
Mo–C(10)–O(10)	175.7(11)	174.2(11)
O(1)–C(1)–C(2)	131.0(12)	130.5(11)
C(1)–C(2)–C(21)	118.7(11)	117.1(11)
C(1)–C(2)–C(3)	114.9(11)	116.5(10)
C(21)–C(2)–C(3)	125.5(13)	126.1(11)
C(2)–C(3)–C(31)	118.7(13)	119.3(11)
C(2)–C(3)–C(4)	119.6(12)	120.2(10)
C(31)–C(3)–C(4)	121.6(12)	120.3(11)
C(3)–C(4)–C(41)	118.1(12)	117.0(10)
C(3)–C(4)–C(5)	115.3(12)	114.7(9)
C(41)–C(4)–C(5)	116.1(11)	117.7(9)
C(4)–C(5)–C(51)	119.6(12)	120.6(10)
C(4)–C(5)–C(6)	111.5(12)	112.5(10)
C(51)–C(5)–C(6)	128.6(14)	126.9(11)
C(5)–C(6)–C(61)	124.8(14)	124.1(12)
C(5)–C(6)–O(7)	122.8(13)	122.9(11)
C(61)–C(6)–O(7)	112.4(13)	113.0(12)
C(6)–C(61)–F(61)	120.7(17)	115.6(17)
C(6)–C(61)–F(62)	108.6(18)	110.8(16)
C(6)–C(61)–F(63)	113.5(17)	119.5(16)
F(61)–C(61)–F(62)	99.9(18)	104.6(18)
F(61)–C(61)–F(63)	116.9(19)	108.5(17)
F(62)–C(61)–F(63)	90.8(18)	95.1(17)
C(6)–O(7)–Mo	114.4(8)	113.9(7)

Molybdenum co-ordination is completed by an η^4-bonded fragment C(1)—C(4) itself linked through the localised double bond [C(5)–C(6)] to O(7), thus completing an eight-membered metallacycle. In a preliminary communication [11] we described the binding of the η^4 function as comprising a σ bond [Mo–C(1)] and an η^3-allylic link which showed a pronounced distortion towards η^2 [C(2)=C(3)]–σ[C(4)] localisation.[37] Whilst this formalism satisfactorily rationalises the C–C bond lengths from C(1) through C(4), it also requires an eight-co-ordinate (Mo^{IV}) geometry, at variance with our arguments presented above.

The arrangement corresponds, of course, to the valence-bond description of a co-ordinated butadiene. In molecular-orbital (m.o.) terms, the C–C bond sequence [C(1)–C(2) $\approx$ C(3)–C(4) $>$ C(2)–C(3)] is regarded as a consequence of substantial back donation from the (formally seven-co-ordinate) metal to the lowest-lying unfilled π m.o. (*a'* local symmetry) of the butadiene. C(1)O(1) is formally a ketenic- and not a ketonic-carbonyl group, a thesis consistent with the magnitude

(130.8°) of the O(1)–C(1)–C(2) angle. In the related (ketonic) complex $[\overline{\mathrm{Mo\{C(O)\cdot CH_2\cdot CH_2\cdot N}}\mathrm{H\}(CO)_2(\eta\text{-}C_5H_5)]}$ the equivalent angle is *ca.* 120°.[39] A full complement of torsion angles around the eight-membered metallacycle is given in Table 6. Most dramatic are the twists about C(1)–C(2) (−46.7), C(3)–C(4) (+164.9), C(4)–C(5) (−124.3), and O(7)–Mo (+77.0°). The crystal packing is seen in Figure 5, a view along the *b* axis, looking towards the origin. The most important non-bonded contacts are intramolecular, between C(51A) and F(61A) [2.93(2) Å], and C(51B) and F(63B) [2.99(2) Å].

TABLE 6

Molecular planes for complex (14) defined as in Table 3

Plane	*P*	*Q*	*R*	*S*
Plane (1A): C(01A)—C(05A)	5.207	−5.283	13.685	5.572
[C(01A) −0.012, C(02A) 0.011, C(03A) −0.006, C(04A) −0.001, C(05A) 0.008, Mo(A) 1.971]				
Plane (2A): C(1A, 2A, 3A, 4A)	16.372	−4.447	−4.305	2.475
[C(1A) −0.028, C(2A) 0.056, C(3A) −0.058, C(4A) 0.030, Mo(A) −1.655, O(1A) 0.584, C(21A) 0.015, C(31A) −0.317, C(41A) 1.308, C(5A) −0.611]				
Plane (3A): C(4A)C(5A)C(6A)O(7A)C(51A)C(61A)	3.786	−6.158	13.305	8.101
[C(4A) 0.053, C(5A) −0.037, C(6A) 0.005, O(7A) −0.042, C(51A) −0.020, C(61A) 0.041, Mo(A) −0.799]				
Plane (1B): C(01B)—C(05B)	13.500	6.952	−4.998	4.853
[C(01B) 0.005, C(02B) −0.011, C(03B) 0.012, C(04B) −0.008, C(05B) 0.002, Mo(B) −1.980]				
Plane (2B): C(1B, 2B, 3B, 4B)	6.421	−5.061	13.402	1.958
[C(1B) −0.017, C(2B) 0.035, C(3B) −0.036, C(4B) 0.018, Mo(B) −1.647, O(1B) 0.616, C(21B) 0.031, C(31B) −0.263, C(41B) 1.301, C(5B) −0.662]				
Plane (3B): C(4B)C(5B)C(6B)O(7B)C(51B)C(61B)	12.196	7.769	−5.011	2.236
[C(4B) −0.111, C(5B) −0.004, C(6B) 0.012, O(7B) 0.119, C(51B) 0.094, C(61B) −0.110, Mo(B) 0.845]				

Dihedral angles (°):

(1A)–(2A)	75.0	(1A)–(3A)	6.5	(2A)–(3A)	76.8
(1B)–(2B)	75.7	(1B)–(3B)	5.9	(2B)–(3B)	72.1

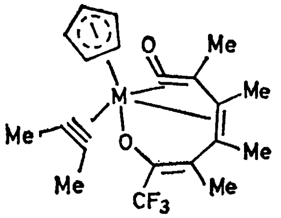
Torsion angles (°) around the metallacycle:*

	Molecule	
	(A)	(B)
O(7)–Mo–C(1)–C(2)	+9.5	+8.2
Mo–C(1)–C(2)–C(3)	−45.2	−48.2
C(1)–C(2)–C(3)–C(4)	−12.5	−7.8
C(2)–C(3)–C(4)–C(5)	+157.5	+172.2
C(3)–C(4)–C(5)–C(6)	−123.3	−125.2
C(4)–C(5)–C(6)–O(7)	−8.0	−9.1
C(5)–C(6)–O(7)–Mo	−18.8	−17.7
C(6)–O(7)–Mo–C(1)	+76.1	+77.8

* Sign convention as defined in W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

The formation of the eight-membered ring complexes (14) and (15) presumably involves replacement of the co-ordination site occupied by the keto-group of the vinyl ketone complexes (1) and (5) by η^2-bonded but-2-yne (Scheme 5). The vinyl ketone chain then migrates on to the co-ordinated acetylene rather than on to the carbon monoxide. At this point, formation of a pyranyl complex might have occurred; however, a competitive migration onto co-ordinated CO intervenes. The final step in the formation of (14) and (15) involves a remarkable electronic rearrangement, in which a metal-to-oxygen σ bond is formed and a co-ordinated ketene results. There is no precedent for such a reaction.

In contrast to the thermal reaction of $[\mathrm{Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)}]$ with but-2-yne, the reaction under u.v. irradiation yields orange crystals of complex (16). The i.r. spectrum of (16) does not show a terminal carbonyl band, but has bands at 1 945w and 1 660s cm^{-1} which are assigned respectively to $\nu_{\max.}$(C≡C) and $\nu_{\max.}$(C=O) stretches. The relatively high frequency of the acetylenic stretch implies weak back bonding from the metal to a η^2-bonded but-2-yne. The ^{1}H n.m.r. spectrum has singlets at τ 5.10 (η-C_5H_5), 7.80 (Me), 7.90 (Me), and 8.19 (Me), and a quartet at τ 8.12 assigned to a Me group adjacent to a CF_3 group. Another singlet of twice the intensity of the other methyl groups at τ 8.72 may be assigned to the two methyl groups of the co-ordinated acetylene. The ^{19}F n.m.r. spectrum shows a single quartet at 65.4 p.p.m. These observations suggest the illustrated structure for (16). A fourth chromatographic fraction from the reaction of $[\mathrm{W(COCF_3)(CO)_3(\eta\text{-}C_5H_5)}]$ with but-2-yne gave orange crystals of (17), which showed spectroscopic properties similar to (16) and is therefore assigned an analogous structure.



(16) M = Mo
(17) M = W

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer at 100 and 94.1 MHz, respectively, and ^{19}F shifts are relative to CCl_3F (0.0 p.p.m.). Infrared spectra were obtained using a Perkin-Elmer 257 spectrophotometer. Molecular weights were determined by mass spectroscopy using an A.E.I. MS902 instrument operating at 70 eV. All the reactions were carried out in Schlenk tubes under an atmosphere of oxygen-free nitrogen, or in tubes fitted with Westef high-pressure stopcocks so that they could be attached to vacuum systems.

Reaction of But-2-yne.—With $[\mathrm{Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)}]$. But-2-yne (0.54 g, 10 mmol) was condensed (−196 °C) into a tube (100 cm^3) containing $[\mathrm{Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)}]$ (0.50 g, 1.6 mmol) dissolved in hexane (20 cm^3). The tube

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[39] G. A. Jones and L. J. Guggenberger, *Acta Cryst.*, 1975, **B31**, 900.

and contents were heated (60 °C) for 24 h affording a red solution. The volatile material was removed *in vacuo* and the residue chromatographed on a Florisil packed column (50 × 1 cm). Elution with hexane gave a bright red fraction, which on crystallisation (−20 °C) from hexane yielded bright red *crystals* of $[\overline{\mathrm{Mo}\{\mathrm{C(Me)}{:}\mathrm{C(Me)}{\cdot}\mathrm{C(CF_3)}{:}\mathrm{O}}\}$-

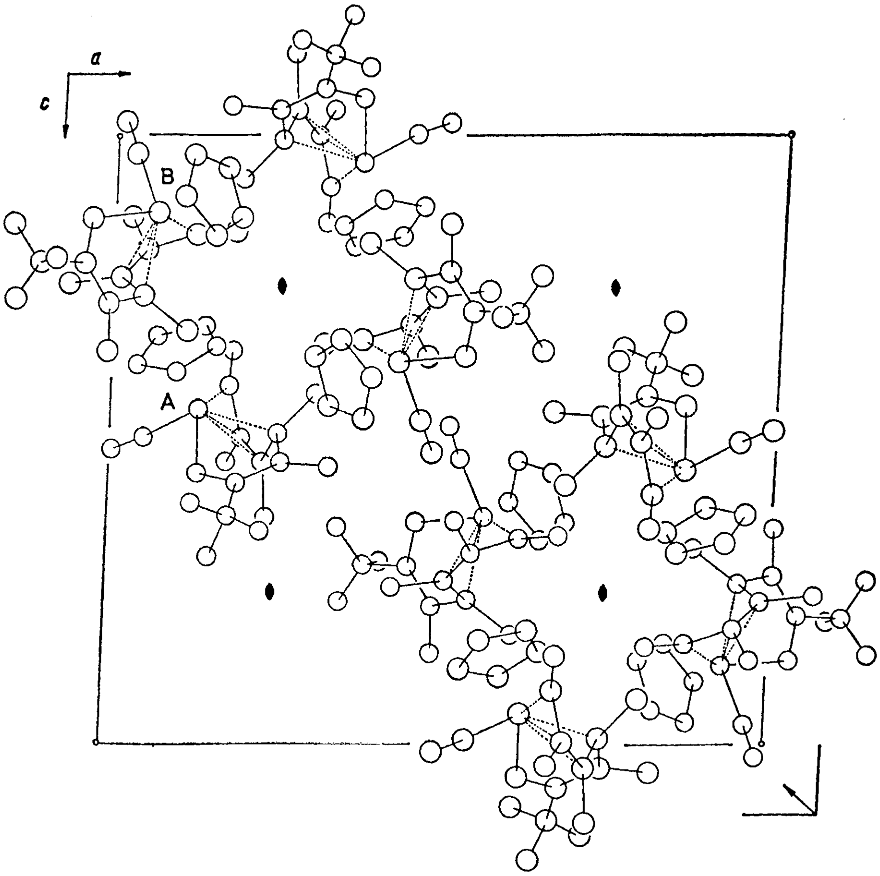
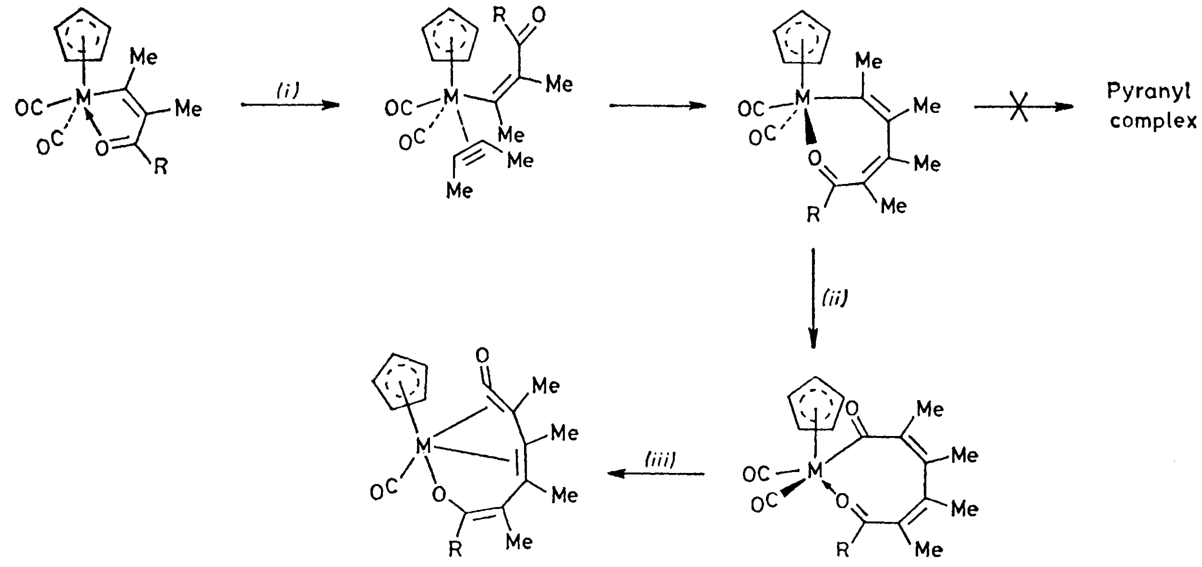


Figure 5 The contents of one unit cell of (14), viewed along the *b* axis towards the origin



(14) M = Mo, R = CF$_3$
(15) M = W, R = CF$_3$

Scheme 5 (*i*) MeC$_2$Me; (*ii*) CO; (*iii*) −CO

(CO)$_2$(η-C$_5$H$_5$)] (1) (0.20 g, 40%), m.p. 82—83 °C (decomp.) (Found: C, 42.9; H, 3.1%; *M* 368. C$_{13}$H$_{11}$F$_3$MoO$_3$ requires C, 42.4; H, 3.0%; *M*, 368), $\nu_{max.}$ in cyclohexane at 2 000vs, 1 915vs (CO), and 1 505w cm^{-1} (C=O). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 4.66 (s, 5 H, C$_5$H$_5$), 6.96 (s, 3 H, CMe), and 7.90 [q, 3 H, CMe, *J*(HF) 2.0 Hz]; ^{19}F in (CD$_3$)$_2$CO, 67.7 p.p.m. [q, 3 F, CF$_3$, *J*(HF) 2.0 Hz]. Elution with diethyl ether gave a yellow fraction which on recrystallisation (−20 °C) from hexane afforded yellow *crystals* of [Mo{C(CF$_3$)·C(Me)·C(Me)·C(O)·O}(CO)$_2$(η-C$_5$H$_5$)] (7) (0.10 g, 20%), m.p. 150—151 °C (decomp.) (Found: C, 42.4; H, 2.9%; *M* 396. C$_{14}$H$_{11}$F$_3$MoO$_4$ requires C, 42.4; H, 2.8%; *M* 396), $\nu_{max.}$ in CCl$_4$ at 2 000vs, 1 945vs (CO), and 1 755s cm^{-1} (C=O). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 4.56 (s, 5 H, C$_5$H$_5$), 7.44 (s, 3 H, CMe), and 8.10 (s, 3 H, CMe); ^{19}F in (CD$_3$)$_2$CO, 64.2 p.p.m. (s, 3 F, CF$_3$). This complex was obtained in higher yield (50%) by the reaction (10 atm, 60 °C, 24 h) of complex (1) with carbon monoxide. Further elution with diethyl ether gave a purple band. Recrystallisation (−20 °C) from diethyl ether–hexane yielded purple-red *crystals* of [Mo{C(O)·(CMe)$_4$·C(CF$_3$)·O}(CO)(η-C$_5$H$_5$)] (14) (0.05 g, 10%), m.p. 148—149 °C (decomp.) (Found: C, 48.6; H, 4.3. C$_{17}$H$_{17}$F$_3$MoO$_3$ requires C, 48.4; H, 4.0%), $\nu_{max.}$ in CCl$_4$ at 1 993vs (CO) and 1 675s cm^{-1} (C=O). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 4.94 (s, 5 H, C$_5$H$_5$), 7.80 (s, 3 H, CMe), 8.05 [q, 3 H, CMe, *J*(HF) 2.0 Hz], 8.12 (s, 3 H, CMe), and 8.38 (s, 3 H, CMe); ^{19}F in CDCl$_3$, 65.2 p.p.m. [q, 3 F, CF$_3$, *J*(HF) 2.0 Hz].

In contrast, when [Mo(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] (0.25 g, 0.74 mmol) and but-2-yne (10 mmol) in hexane (25 cm^3) were irradiated (Hanovia 250-W u.v. lamp) an orange solution was obtained. Filtration, followed by reduction of the volume *in vacuo*, and cooling (−20 °C) gave orange *crystals* of [Mo{C(O)·(CMe)$_4$·C(CF$_3$)·O}(MeC$_2$Me)(η-C$_5$H$_5$)] (16) (0.17 g, 50%), m.p. 139—140 °C (Found: C, 53.6; H, 5.3. C$_{20}$H$_{23}$F$_3$MoO$_2$ requires C, 53.6; H, 5.1%), $\nu_{max.}$ in CHCl$_3$ at 1 945m (C=C), 1 660s, and 1 635s cm^{-1} (C=O). The mass spectrum showed a strong peak at *m/e* 394 (*P* − C$_2$Me$_2$). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 5.10 (s, 5 H, C$_5$H$_5$), 7.80 (s, 3 H, CMe), 7.90 (s, 3 H, CMe), 8.12 [q, 3 H, CMe, *J*(HF) 2.5 Hz], 8.19 (s, 3 H, CMe), and 8.72 (s, 6 H, CMe); ^{19}F in (CF$_3$)$_2$CO, 65.4 p.p.m. [q, 3 F, CF$_3$, *J*(HF) 2.5 Hz].

With [MoMe(CO)$_3$(η-C$_5$H$_5$)]. A solution of [MoMe(CO)$_3$(η-C$_5$H$_5$)] (0.30 g, 1.14 mmol) and but-2-yne (10 mmol) in hexane (30 cm^3) contained in a tube (100 cm^3) was heated (60 °C) for 48 h. The resulting red solution was filtered, the volume of the solvent reduced, and cooling (−20 °C) gave orange-red *crystals* of [Mo{C(Me)⁚C(Me)·C(Me)⁚O}(CO)$_2$(η-C$_5$H$_5$)] (2) (0.20 g, 60%), m.p. 158—159 °C (Found: C, 49.3; H, 4.5; O, 15.5%; *M* 314. C$_{13}$H$_{14}$MoO$_3$ requires C, 49.7; H, 4.5; O, 15.3%; *M* 314), $\nu_{max.}$ in CCl$_4$ at 1 970vs, 1 878vs (CO), and 1 514m cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 4.76 (s, 5, H, C$_5$H$_5$), 7.16 (s, 3 H, Me), 7.72 (s, 3 H, Me), and 8.07 (s, 3 H, Me).

With [Mo(CH$_2$Ph)(CO)$_3$(η-C$_5$H$_5$)]. Similarly, reaction (60 °C, 69 h) of [Mo(CH$_2$Ph)(CO)$_3$(η-C$_5$H$_5$)] (0.25 g, 0.74 mmol) with but-2-yne (10 mmol) gave bright red *crystals* of [Mo{C(Me)⁚C(Me)·C(CH$_2$Ph)⁚O}(CO)$_2$(η-C$_5$H$_5$)] (3) (0.06 g, 20%), m.p. 145—146 °C (decomp.) (Found: C, 59.0; H, 4.6%; *M* 390. C$_{19}$H$_{18}$MoO$_3$ requires C, 58.5; H, 4.6%; *M* 390), $\nu_{max.}$ in CCl$_4$ at 1 972vs, 1 885vs (CO), and 1 498m cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 2.84 (m, 5 H, C$_6$H$_5$), 4.78 (s, 5 H, C$_5$H$_5$), 6.10 (s, 2 H, C$_6$H$_5$C*H*$_2$), 7.16 (s, 3 H, CMe), and 8.10 (s, 3 H, CMe).

With [WMe(CO)$_3$(η-C$_5$H$_5$)]. Ultraviolet irradiation (24 h) of a solution of [WMe(CO)$_3$(η-C$_5$H$_5$)] (0.50 g, 1.44 mmol) and but-2-yne (10 mmol) in hexane (15 cm^3) gave bright red *crystals* of [W{C(Me)⁚C(Me)·C(Me)⁚O}(CO)$_2$(η-C$_5$H$_5$)] (4) (0.50 g, 80%), m.p. 172—173 °C (Found: C, 38.6; H, 3.7%; *M* 402. C$_{13}$H$_{14}$O$_3$W requires C, 38.8; H, 3.5%; *M* 402), $\nu_{max.}$ in CCl$_4$ at 1 958vs, 1 857vs (CO), and 1 470m cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 4.55 (s, 5 H, C$_5$H$_5$), 7.00 (s, 3 H, CMe), 7.64 (s, 3 H, CMe), and 8.00 (s, 3 H, CMe).

With [W(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)]. The reaction mixture from a similar u.v. irradiation (48 h) of a solution of [W(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] (0.50 g, 1.2 mmol) and but-2-yne (10 mmol) in hexane (20 cm^3) was chromatographed on Florisil. Elution with diethyl ether–hexane gave a bright red fraction which on recrystallisation (−20 °C) from hexane yielded red *crystals* of [W{C(Me)⁚C(Me)·C(CF$_3$)⁚O}(CO)$_2$(η-C$_5$H$_5$)] (5) (0.01 g, 2%), m.p. 125—126 °C (Found: C, 34.0; H, 2.7. C$_{13}$H$_{11}$F$_3$O$_3$W requires C, 34.2; H, 2.4%), $\nu_{max.}$ in hexane at 1 987s, 1 900s (CO), and 1 450m cm^{-1} (C=O). Elution with diethyl ether then gave a yellow band, which on recrystallisation from diethyl ether–hexane gave yellow *crystals* of [W{C(CF$_3$)·C(Me)·C(Me)·C(O)·O}(CO)$_2$(η-C$_5$H$_5$)] (13) (0.015 g, 2%), m.p. 168—169 °C (Found: C, 34.5; H, 2.2%: *M* 484. C$_{14}$H$_{11}$F$_3$O$_4$W requires C, 34.0; H, 2.2%; *M* 484), $\nu_{max.}$ in CCl$_4$ at 2 015vs, 1 950vs (CO), and 1 765s cm^{-1} (C=O). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 4.50 (s, 5 H, C$_5$H$_5$), 7.16 (s, 3 H, CMe), and 7.70 (s, 3 H, CMe); ^{19}F in (CD$_3$)$_2$CO, 65.0 p.p.m. (s, 3 F, CF$_3$). Further elution with diethyl ether gave a purple band which on recrystallisation (−20 °C) from diethyl ether gave purple-red *crystals* of [W{C(O)·(CMe)$_4$·C(CF$_3$)·O}(CO)(η-C$_5$H$_5$)] (15) (0.008 g, 1%), m.p. 170—171 °C, $\nu_{max.}$ in CCl$_4$ at 1 968s (CO) and 1 640m cm^{-1} (C=O). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 4.72 (s, 5 H, C$_5$H$_5$), 7.70 (s, 3 H, CMe), 7.80 [q, 3 H, CMe, *J*(HF) 1.5 Hz], 8.00 (s, 3 H, CMe), and 8.12 (s, 3 H, CMe); ^{19}F in CDCl$_3$, 63.3 p.p.m. [q, 3 F, CF$_3$, *J*(HF) 1.5 Hz]. Finally a yellow-orange band was eluted with diethyl ether. Recrystallisation (−78 °C) from diethyl ether–hexane gave orange *crystals* of [W{C(O)·(CMe)$_4$·C(CF$_3$)·O}(MeC$_2$Me)(η-C$_5$H$_5$)] (17) (0.10 g, 20%), m.p. 182—183 °C (decomp.) (Found: C, 44.6; H, 4.6%; *M* 536. C$_{20}$H$_{23}$F$_3$O$_2$W requires C, 44.8; H, 4.3%; *M* 536), $\nu_{max.}$ in CHCl$_3$ at 1 875m (C≡C) and 1 635s cm^{-1} (C=O). N.m.r. spectra: ^{1}H in CDCl$_3$, τ 4.84 (s, 5 H, C$_5$H$_5$), 7.66 (s, 6 H, CMe), 7.96 (s, 3 H, CMe), 8.10 [q, 3 H, CMe, *J*(HF) 2.5 Hz], 8.64 (s, 3 H, CMe), and 8.74 (s, 3 H, CMe); ^{19}F in CDCl$_3$, 61.8 p.p.m. [q, 3 F, CF$_3$, *J*(HF) 2.5 Hz].

Reaction of [MoMe(CO)$_3$(η-C$_5$H$_5$)] *with Bis*(*trimethylsilyl*)-*acetylene*.—Ultraviolet irradiation (5 d) of a solution of [MoMe(CO)$_3$(η-C$_5$H$_5$)] (0.50 g, 1.8 mmol) and C$_2$(SiMe$_3$)$_2$ (0.36 g, 2.0 mmol) in hexane (30 cm^3) gave an orange solution. Chromatography on Florisil and elution with diethyl ether gave a yellow band, which on crystallisation (−78 °C) from diethyl ether–hexane gave yellow *crystals* of [Mo{C(Me)·C(SiMe$_3$)·C(SiMe$_3$)·C(O)·O}(CO)$_2$(η-C$_5$H$_5$)] (12) (0.05 g, 10%), m.p. 155—156 °C (Found: C, 47.4; H, 5.7%;

M 458. $C_{18}H_{26}MoO_4Si_2$ requires C, 47.2; H, 5.7%, *M* 458), $\nu_{max.}$ in CCl_4 at 1 972vs, 1 910vs (CO), and 1 716s cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 4.70 (s, 5 H, C_5H_5), 7.70 (s, 3 H, CMe), 9.53 (s, 9 H, Me_3Si), and 9.57 (s, 9 H, Me_3Si).

η^3-Lactonyl Complex-forming Reactions.—Complex (2) *with t-butyl isocyanide.* An excess of $CNBu^t$ (0.2 cm^3) was added (room temperature) to a stirred solution of complex (2) (0.15 g, 0.48 mmol) in diethyl ether (15 cm^3). An immediate colour change occurred. The yellow solution was filtered, reduced in volume, and cooled affording yellow *crystals* of [Mo{C(Me)·C(Me)·C(Me)·C(O)·O}(CO)(η-C_5H_5)($CNBu^t$)] (6) (0.32 g, 80%), m.p. 108—110 °C (decomp.) (Found: C, 54.6; H, 5.8; N, 3.6%; *M* 397. $C_{18}H_{23}MoNO_3$ requires C, 54.4; H, 5.8; N, 3.6%; *M* 397), $\nu_{max.}$ in CCl_4 at 2 096vs, 2 055s (NC), 1 888vs (CO), and 1 726vs cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 4.87 (s, 5 H, C_5H_5), 7.72 (s, 3 H, CMe), 7.95 (s, 3 H, CMe), 8.14 (s, 3 H, CMe), and 8.50 (s, 9H, $CNBu^t$).

Complex (1) *with t-butyl isocyanide.* Similarly, reaction of (1) (0.10 g, 0.27 mmol) with $CNBu^t$ (0.2 cm^3) in diethyl ether (10 cm^3) gave yellow *crystals* of [Mo{C(CF_3)·C(Me)·C(Me)·C(O)·O}(CO)(η-C_5H_5)($CNBu^t$)] (8) (0.40 g, 90%), m.p. 130—132 °C (decomp.) (Found: C, 47.9; H, 4.7; N, 3.3. $C_{18}H_{20}F_3MoNO_3$ requires C, 47.9; H, 4.4; N, 3.1%), $\nu_{max.}$ in CCl_4 at 2 120s (NC), 1 930vs (CO), and 1 740vs cm^{-1} (C=O). N.m.r. spectra corresponding to two isomers (10 : 1): ^1H in $CDCl_3$, τ 4.76 (s, 5 H, C_5H_5), 7.54 (s, 3 H, CMe), 8.16, 8.28 (s, 3 H, CMe), 8.46, and 8.50 (s, 9 H, $CNBu^t$); ^{19}F in $(CD_3)_2CO$, 62.6 and 64.2 p.p.m. (s, 3 F, CF_3).

Complex (1) *with cyclohexyl isocyanide.* In the same way reaction of (1) (0.10 g, 0.27 mmol) with CNC_6H_{11} (0.5 g, 5.0 mmol) gave from diethyl ether–hexane pale yellow *crystals* of [Mo{C(CF_3)·C(Me)·C(Me)·C(O)·O}(CO)(η-C_5H_5)(CNC_6H_{11})] (9) (0.35 g, 70%), m.p. 58—60 °C (decomp.) (Found: C, 50.2; H, 4.4; N, 3.0%; *M* 477. $C_{20}H_{22}F_3MoNO_3$ requires C, 50.3; H, 4.6; N, 2.8%; *M* 477), $\nu_{max.}$ in CCl_4 at 2 122s (NC), 1 928vs (CO), and 1 740vs cm^{-1} (C=O). N.m.r. spectra corresponding to two isomers (10 : 1): ^1H in $CDCl_3$, τ 4.66, 4.74 (s, 5 H, C_5H_5), 7.54, 7.55 (s, 3 H, CMe), 8.28 (s, 3 H, CMe), and 8.36 (m, 11 H, $C_6H_{11}NC$); ^{19}F in $(CD_3)_2CO$, 62.7 and 64.2 p.p.m. (s, 3 F, CF_3).

TABLE 7

Final atomic co-ordinates (fractional $\times$ 10^5 for Mo; $\times$ 10^4 for C, N, and O) of the non-hydrogen atoms for complex (6)

Atom	*x*	*y*	*z*
Mo	13 828(5)	11 131(2)	19 943(5)
C(01)	3 205(9)	1 329(4)	709(8)
C(02)	1 947(10)	1 609(4)	−62(8)
C(03)	893(10)	1 181(5)	−587(9)
C(04)	1 499(11)	609(5)	−133(10)
C(05)	2 948(9)	703(4)	671(9)
C(1)	2 968(6)	1 234(3)	3 884(7)
N(1)	3 837(6)	1 289(3)	4 964(6)
C(2)	4 776(7)	1 284(4)	6 458(7)
C(21)	4 523(13)	1 889(5)	7 173(11)
C(22)	4 222(13)	762(6)	7 264(11)
C(23)	6 361(9)	1 197(7)	6 312(10)
C(10)	1 103(8)	371(3)	3 030(9)
O(10)	1 031(9)	−76(3)	3 642(9)
O(3)	−457(6)	2 207(2)	1 290(5)
C(4)	−1 449(8)	1 741(4)	923(8)
O(4)	−2 395(8)	1 757(4)	−187(7)
C(5)	−1 106(7)	1 274(3)	2 047(9)
C(51)	−2 249(11)	803(6)	2 156(18)
C(6)	−117(6)	1 542(3)	3 277(7)
C(61)	−59(9)	1 450(4)	4 888(8)
C(7)	515(7)	2 017(3)	2 621(6)
C(71)	1 415(11)	2 537(4)	3 363(10)

TABLE 8

Atomic positional parameters (fractional co-ordinates, $\times$ 10^5 for Mo; $\times$ 10^4 for C, O, and F) for complex (14)

Atom	*x*	*y*	*z*
(*a*) Molecule (A)			
Mo	13 212(5)	−13 328(8)	44 953(6)
C(01)	1 587(8)	70(14)	3 486(9)
C(02)	1 002(8)	493(12)	3 889(9)
C(03)	397(8)	−341(14)	3 785(10)
C(04)	665(9)	−1 294(15)	3 318(9)
C(05)	1 413(9)	−1 063(14)	3 130(9)
C(10)	504(7)	−2 255(10)	4 937(7)
O(10)	13(6)	−2 812(11)	5 145(7)
C(1)	1 779(6)	−2 938(12)	4 114(8)
O(1)	1 824(6)	−3 583(10)	3 529(6)
C(2)	1 998(6)	−3 139(10)	4 962(9)
C(21)	1 763(10)	−4 302(16)	5 364(11)
C(3)	2 305(6)	−2 140(12)	5 359(8)
C(31)	2 382(10)	−2 158(17)	6 274(11)
C(4)	2 518(6)	−1 106(12)	4 900(8)
C(41)	3 083(8)	−1 286(14)	4 263(9)
C(5)	2 565(8)	63(13)	5 360(8)
C(51)	3 291(10)	704(16)	5 463(11)
C(6)	1 919(8)	332(13)	5 700(9)
C(61)	1 801(11)	1 386(18)	6 249(12)
F(61)	2 328(9)	1 997(15)	6 518(9)
F(62)	1 546(13)	973(22)	6 940(14)
H(63)	1 206(10)	1 945(18)	6 092(11)
O(7)	1 315(5)	−290(8)	5 548(6)
(*b*) Molecule (B)			
Mo	7 051(5)	36 897(9)	12 873(6)
C(01)	1 525(9)	5 234(14)	1 679(10)
C(02)	1 053(9)	5 669(14)	1 039(9)
C(03)	1 163(8)	5 007(15)	371(9)
C(04)	1 688(8)	4 095(14)	561(11)
C(05)	1 917(7)	4 253(13)	1 377(10)
C(10)	301(6)	2 770(12)	337(8)
O(10)	123(7)	2 189(11)	−213(7)
C(1)	1 240(6)	2 131(10)	1 659(7)
O(1)	1 808(6)	1 586(9)	1 653(6)
C(2)	514(6)	1 748(10)	1 901(8)
C(21)	230(9)	540(15)	1 578(10)
C(3)	129(6)	2 563(11)	2 340(7)
C(31)	−670(9)	2 339(15)	2 468(10)
C(4)	480(6)	3 682(10)	2 634(6)
C(41)	1 135(7)	3 551(11)	3 228(7)
C(5)	−32(6)	4 703(10)	2 758(7)
C(51)	−35(8)	5 346(13)	3 554(8)
C(6)	−455(7)	4 955(11)	2 086(7)
C(61)	−1 089(10)	5 782(17)	2 070(11)
F(61)	−1 460(8)	5 889(14)	2 693(9)
F(62)	−1 528(11)	5 692(19)	1 458(12)
F(63)	−872(12)	6 915(20)	2 066(13)
O(7)	−346(4)	4 462(8)	1 378(5)

Complex (2) *with triphenylphosphine.* A solution of complex (2) (0.10 g, 0.3 mmol) and triphenylphosphine (0.10 g, 0.4 mmol) in dichloromethane (20 cm^3) was allowed to stand at room temperature for 7 d. The resulting yellow solution was filtered, the volume of the solvent reduced and hexane added, and cooling (−20 °C) gave yellow *crystals* of [Mo{C(Me)·C(Me)·C(Me)·C(O)·O}(CO)(η-C_5H_5)(PPh_3)] (10) (0.19 g, 30%), m.p. 150—151 °C (decomp.) (Found: C, 65.3; H, 5.3%; *M* 576. $C_{31}H_{29}MoO_3P$ requires C, 64.6; H, 5.0%; *M* 576), $\nu_{max.}$ in CCl_4 at 1 842 (CO) and 1 725s cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 2.44 (m, 15 H, C$_6$H$_5$P), 5.18, 5.20 (s, 5 H, C$_5$H$_5$), 8.18 (s, 3 H, CMe), 8.52, 8.53 (s, 3 H, CMe), and 8.58 (s, 3 H, CMe); two isomers (1 : 10).

Complex (4) *with t-butyl isocyanide.* A solution of (4) (0.10 g, 0.25 mmol) and CNBu^t (0.2 cm^3) in diethyl ether (10 cm^3) was heated under reflux (4 d). The yellow solution was filtered, hexane added, and cooling (−20 °C) gave yellow *crystals* of $[\mathrm{W}\{\overline{\mathrm{C(Me)\cdot C(Me)\cdot C(Me)\cdot C(O)\cdot O}}\}(\mathrm{CO})(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CNBu^t})]$ (11) (0.10 g, 20%), m.p. 115—116 °C (decomp.) (Found: C, 44.6; H, 4.8; N, 3.0%; *M* 485. C$_{18}$H$_{23}$NO$_3$W requires C, 44.5; H, 4.7; N, 2.9%; *M* 485), $\nu_{\max.}$ in CCl$_4$ at 2 095s (NC), 1 890s (CO), and 1 720s cm^{-1} (C=O). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 4.76 (s, 5 H, C$_5$H$_5$), 7.34 (s, 3 H, CMe), 8.00 (s, 3 H, CMe), 8.12 (s, 3 H, CMe), and 8.47 (s, 9 H, CNBu^t).

Molecular-structure Determinations.—The single-crystal analyses of complexes (6) and (14) followed similar lines and are therefore described for (6) only, data in parentheses representing differences in respect of (14). A single crystal, *ca.* 0.15 × 0.125 × 0.05 mm (0.075 × 0.07 × 0.05 mm) was mounted on a glass fibre with epoxy-resin adhesive, and unit-cell and space groups determined *via* Weissenberg (Cu) and precession (Mo) *X*-ray photography.

On transference to a Syntex $P2_1$ four-circle diffractometer, accurate setting was achieved *via* the automatic centering of 15 high-angle reflections. The unit cell was chosen by inspection [40] and the orientation matrix calculated. For data collection, $2.9 \leqslant 2\theta \leqslant 55.0°$ (60.0°) using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha1}$ 0.709 26, $\lambda_{\alpha2}$ 0.713 54 Å) at *ca.* 295 K. Peaks were scanned (θ—2θ in 96 steps) from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$ at rates between 0.042 5 and 0.483 3° s^{-1}, dependent on an initial 2-s peak count in which 150 and 1 500 counts were taken as critical limits. The intensities of three check reflections (whose scattering vectors were as nearly mutually orthogonal as possible) were remonitored once every 28 (43) reflections, but subsequent analysis [41] of their net counts as individual functions of time implied no significant crystal decomposition or movement, or machine instability, over the *ca.* 129 h (222 h) *X*-ray exposure. Of 4 338 (8 047) independent reflections measured ($0 + k + l$, $+ h + k \pm l$), 3 412 (5 228) had $I \geqslant 1.0\ \sigma(I)$ and were retained for structure solution and refinement. No absorption correction was applied.

Crystal data. (6), C$_{18}$H$_{23}$MoNO$_3$, $M = 397.3$, Monoclinic, $a = 9.301\ 3(15)$, $b = 22.161(6)$, $c = 9.353(3)$ Å, $\beta = 102.76(2)°$, $U = 1\ 880.2(9)$ Å^3, $D_m = 1.39$ (flotation), $Z = 4$, $D_c = 1.402$ g cm^{-3}, $F(000) = 832$, μ(Mo-$K_{\bar\alpha}$) = 7.0 cm^{-1}, space group $P2_1/a$ (alternative setting of $P2_1/c$, C_{2h}^5, no. 14) from systematic absences.

(14), C$_{17}$H$_{17}$F$_3$MoO$_3$, $M = 424.3$, Monoclinic, $a = 18.389(4)$, $b = 11.137(3)$, $c = 16.686(5)$ Å, $\beta = 92.55(2)°$, $U = 3\ 413.7(16)$ Å^3, $D_m = 1.63$ (flotation), $Z = 8$, $D_c = 1.651$ g cm^{-3}, $F(000) = 1\ 696$, μ(Mo-$K_{\bar\alpha}$) = 8.9 cm^{-1}, space group Pn (alternative to Pc, C_s^2, no. 7) or $P2/n$ (alternative setting of $P2/c$, C_{2h}^4, no. 13) from systematic absence.

The structures were solved *via* Patterson (Mo atoms) and difference Fourier (C, N, O, and F) techniques. For (14) the preponderance of vectors on the U0W level implied the centrosymmetric space group $P2/n$, and nothing occurred under subsequent refinement to suggest otherwise. In the solution of both structures all the atoms of the heterocyclic organic ligands were treated as carbon until identified by chemical logic and supported by examination of post-refinement temperature factors and internuclear distances. F_o moduli were weighted according to $w^{-1} = xy$ with $x = F_o/a$ if $F_o > a$, $x = 1$ if $F_o \leqslant a$, $y = b/\sin\theta$ if $\sin\theta < b$, and $y = 1$ if $\sin\theta > b$, in which a and b took values of 50.0 and 0.25 respectively.

For (6), hydrogen atoms of the two organic rings were located *via* ΔF maps computed with only those data for which $(\sin\theta)/\lambda \leqslant 0.5$. In the final stages of refinement all the non-hydrogen atoms were allowed anisotropic thermal motion and, with the 265 variables divided between two blocks, least-squares refinement converged at R 0.058, R' 0.070. For (14), hydrogen atoms were not located, and only those atoms directly bonded to a metal were refined anisotropically. Using four least-squares blocks, ultimate residuals of R 0.103, R' 0.127 were recorded, at a data : variable ratio better than 16.5 : 1.

Final difference syntheses for both sets of data revealed nothing more than the relatively high noise usually associated with a low $I : \sigma(I)$ criterion. The scattering factors of refs. 42 (Mo and F), 43 (C, N, and O), and 44 (H) were taken, all the non-hydrogen sets being adjusted [45] for both components of anomalous dispersion. For (6) Table 7 lists the derived atomic co-ordinates, Appendix B thermal parameters, and Appendix C the structure factors. Equivalent data for (14) are in Table 8 and Appendices D and E. All the calculations employed programs of the ' *X*-RAY '72 ' package,[46] implemented on the University of London CDC 7600 computer.

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