Reactions of Co-ordinated Ligands. Part 37.[1] Synthesis and Structure of the Dimolybdenum μ-Allylidene Complex [Mo₂(μ-σ:η³-CHCHCMe₂)(CO)₄(η-C₅H₅)₂]; Formation and Crystal Structure of the Oxo-μ-allylidene Complex [Mo₂O(μ-σ:η³-CHCHCMe₂)(μ-CO)(CO)(η-C₅H₅)₂]. Thermal Rearrangement to Alkyne and 1,3-Diene Dimolybdenum Species and Structure of [Mo₃(μ₃-η⁴-CCHCMeCH)(CO)₄-(η-C₅H₅)₃]†

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Reaction of the unsaturated dinuclear complex [Mo₂(CO)₄(η-C₅H₅)₂] with 3,3-dimethylcyclopropene leads to ring opening and formation of the μ-allylidene complex [Mo₂(μ-σ,η³-CHCHCMe₂)(CO)₄-(η-C₅H₅)₂] (1), which has been structurally identified by X-ray crystallography. The molecule contains two molybdenum atoms singly bonded [Mo(1)–Mo(2) 3.1057(9) Å]. A CHCHCMe₂ fragment bonds σ to Mo(1) and as an allyl, η³, to Mo(2), *i.e.* as a dimethyl substituted μ-allylidene where the two olefinic protons of the original cyclopropene retain a relative *cis* configuration. The mechanism of formation of (1) is discussed in terms of a reaction at a dinuclear centre. In refluxing wet acetonitrile (1) is transformed into the mixed-valence μ-allylidene complex [Mo₂O(μ-σ,η³-CHCHCMe₂)(μ-CO)(CO)(η-C₅H₅)₂] (2). An X-ray crystal-structure determination shows that the oxygen ligand is co-ordinated to Mo(1) which is σ bonded to the μ-allylidene fragment; the Mo–Mo bond is reduced to 2.881(1) Å. In refluxing toluene–hexane (1) rearranges to form the alkyne complex [Mo₂(μ-PrⁱC₂H)(CO)₄(η-C₅H₅)₂] (3), an isoprene complex [Mo₂{CH₂CHC(Me)CH₂}-(CO)₂(η-C₅H₅)₂] (4), and a trinuclear complex [Mo₃(μ₃-η⁴-CCHCMeCH)(CO)₄(η-C₅H₅)₃] (5), the last being identified by X-ray crystallography. The molecule is a triangular array of three molybdenum atoms, which show typical Mo–Mo single bond separations. The μ-allylidene fragment present in (1) loses three hydrogen atoms in the formation of (5), generating a methyl substituted molybdacyclopentadiene. The mechanism of formation of (3), (4), and (5) is discussed.

Cyclopropenes undergo an interesting group of reactions with metal complexes where cleavage of a 2,3 carbon-to-carbon σ bond leads to the apparent formation of a vinylcarbene transition-metal intermediate.[2,3] An example is the observation[3] that 3,3-dimethylcyclopropene reacts with methyl acrylate, dimethyl-maleate or -fumarate in the presence of bis-(cyclo-octa-1,5-diene)nickel to form dimethylvinyl substituted cyclopropanes. It has been suggested[3,4] that in these reactions a vinylcarbene is captured by the electronegatively substituted olefin, however, in this system, and in related reactions, vinylcarbene complexes have not been isolated or positively identified as intermediates. We reasoned that if it was possible to promote 2,3 σ-bond cleavage of a cyclopropene at a suitable dinuclear metal centre then the presumed vinylcarbene intermediate might be intercepted as a stable μ-allylidene complex. For our initial study[5] we chose the co-ordinatively unsaturated dimolybdenum complex [Mo₂(CO)₄(η-C₅H₅)₂],[6,7] which was

known to react readily with alkynes,[6,8,9] allenes,[10] and diazoalkanes.[11]

Results and Discussion

An excess of 3,3-dimethylcyclopropene reacted slowly with [Mo₂(CO)₄(η-C₅H₅)₂] in toluene at room temperature to afford on column chromatography a red crystalline complex [Mo₂(μ-CHCHCMe₂)(CO)₄(η-C₅H₅)₂] (1) (54% yield), which was identified by elemental analysis, m.s., i.r., and n.m.r. spectroscopy as a 1:1 adduct. The i.r. spectrum of (1) showed bands corresponding to both terminal and bridging carbonyl ligands, and the ¹H n.m.r. spectrum contained resonances corresponding to two inequivalent η⁵-cyclopentadienyl ligands, two inequivalent methyl groups, and two doublet resonances at 5.91 and 10.93 p.p.m. each assignable to one proton. The latter high-field signal was characteristic of a Mo(μ-CHR)Mo system, an assignment supported by the appearance of a signal at 174.9 p.p.m. [¹J(CH) 140 Hz] in the ¹³C n.m.r. spectrum. These observations clearly suggested that 2,3-carbon bond cleavage of the 3,3-dimethylcyclopropene had occurred, and that the resultant dimethyl substituted C₃ fragment was stabilised by co-ordination to the two molybdenum centres.

In order to define the bonding mode of the ring-opened cyclopropene a single-crystal X-ray diffraction study was undertaken. This established the molecular structure shown in Figure 1, the selected bond lengths and interbond angles are given in Table 1. The molecule contains two molybdenum

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Table 1. Selected bond lengths (Å) and angles (°) for (1)

Mo(1)–Mo(2)	3.1057(9)	Mo(2)–C(21)	2.317(8)
Mo(1)–C(11)	2.323(7)	Mo(2)–C(22)	2.351(8)
Mo(1)–C(12)	2.361(6)	Mo(2)–C(23)	2.364(7)
Mo(1)–C(13)	2.391(7)	Mo(2)–C(24)	2.327(8)
Mo(1)–C(14)	2.390(7)	Mo(2)–C(25)	2.273(8)
Mo(1)–C(15)	2.344(7)	Mo(2)–C(201)	1.935(7)
Mo(1)–C(101)	1.948(7)	Mo(2)–C(202)	1.990(7)
Mo(1)–C(102)	1.948(7)	Mo(2)–C(1)	2.249(5)
Mo(1)–C(1)	2.126(6)	Mo(2)–C(2)	2.270(6)
Mo(1)···C(202)	2.473(7)	Mo(2)–C(3)	2.477(7)
C(11)–C(12)	1.392(11)	C(101)–O(101)	1.151(10)
C(12)–C(13)	1.393(11)	C(102)–O(102)	1.152(9)
C(13)–C(14)	1.396(11)	C(201)–O(201)	1.153(8)
C(14)–C(15)	1.418(13)	C(202)–O(202)	1.179(9)
C(15)–C(11)	1.400(13)	C(1)–C(2)	1.397(8)
C(21)–C(22)	1.374(15)	C(2)–C(3)	1.418(9)
C(22)–C(23)	1.370(12)	C(3)–C(31)	1.478(10)
C(23)–C(24)	1.376(15)	C(3)–C(32)	1.537(9)
C(24)–C(25)	1.406(16)	C(1)–H(1)	1.06(9)
C(25)–C(21)	1.414(17)	C(2)–H(2)	0.95(9)
Mo(2)–Mo(1)–C(1)	46.42(11)	Mo(1)–Mo(2)–C(1)	43.20(10)
Mo(2)–Mo(1)–C(101)	96.4(2)	Mo(1)–Mo(2)–C(2)	74.3(2)
Mo(2)–Mo(1)–C(102)	110.9(2)	Mo(1)–Mo(2)–C(3)	86.9(2)
Mo(2)–Mo(1)–cp(1)[a]	121.1(2)	Mo(1)–Mo(2)–C(201)	107.2(2)
C(1)–Mo(1)–C(101)	118.4(3)	Mo(1)–Mo(2)–C(202)	52.7(2)
C(1)–Mo(1)–C(102)	79.6(2)	Mo(1)–Mo(2)–cp(2)[b]	129.1(2)
C(1)–Mo(1)–cp(1)	117.3(3)	C(1)–Mo(2)–C(2)	36.0(2)
C(101)–Mo(1)–C(102)	74.2(3)	C(1)–Mo(2)–C(3)	64.0(2)
C(101)–Mo(1)–cp(1)	124.1(3)	C(1)–Mo(2)–C(201)	120.8(2)
C(102)–Mo(1)–cp(1)	120.8(3)	C(1)–Mo(2)–C(202)	95.9(2)
		C(1)–Mo(2)–cp(2)	117.2(2)
Mo(1)–C(101)–O(101)	175.3(8)	C(2)–Mo(2)–C(3)	34.4(2)
Mo(1)–C(102)–O(102)	178.1(6)	C(2)–Mo(2)–C(201)	99.4(3)
Mo(1)–C(1)–Mo(2)	90.4(2)	C(2)–Mo(2)–C(202)	122.0(3)
Mo(1)–C(1)–C(2)	139.5(5)	C(2)–Mo(2)–cp(2)	116.5(2)
Mo(2)–C(1)–C(2)	72.8(3)	C(3)–Mo(2)–C(201)	65.0(2)
C(1)–C(2)–Mo(2)	71.2(3)	C(3)–Mo(2)–C(202)	113.1(3)
C(1)–C(2)–C(3)	126.4(6)	C(3)–Mo(2)–cp(2)	131.6(3)
Mo(2)–C(2)–C(3)	80.8(4)	C(201)–Mo(2)–C(202)	78.2(3)
C(2)–C(3)–Mo(2)	64.8(3)	C(201)–Mo(2)–cp(2)	118.5(3)
C(2)–C(3)–C(31)	124.6(6)	C(202)–Mo(2)–cp(2)	114.8(3)
C(2)–C(3)–C(32)	115.5(6)		
Mo(2)–C(3)–C(31)	118.0(5)	Mo(1)···C(202)–O(202)	121.7(5)
Mo(2)–C(3)–C(32)	113.5(5)	Mo(2)–C(201)–O(201)	175.6(6)
C(31)–C(3)–C(32)	112.2(6)	Mo(2)–C(202)–O(202)	150.3(6)

[a] cp(1) is the centroid of the cyclopentadienyl ring C(11)—C(15); cp(1) has co-ordinates 0.0306, 0.0324, −0.1026. [b] cp(2) is the centroid of the cyclopentadienyl ring C(21)—C(25); cp(2) has co-ordinates 0.2910, −0.1108, −0.2097.

Figure 1. Molecular structure of (1) showing labelling scheme, methyl and cyclopentadienyl hydrogens have been omitted for clarity
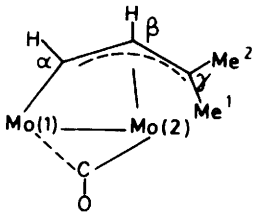

Scheme 1.

atoms at a distance appropriate[12,13] for a single bond [Mo(1)–Mo(2) 3.106(1) Å]. Each molybdenum carries a η^5-bonded cyclopentadienyl ligand, and whereas Mo(1) has two terminal carbonyl ligands, one of the two carbonyl ligands co-ordinated to Mo(2) is semi-bridging [Mo(1)···C(202) 2.473(7) Å]. Of the four possible extreme views of the bonding modes (A), (B), (C),[5] and (D)[14] (Scheme 1) for the fragment C(1)–C(2)–C(3) to the dimolybdenum centre, the structural evidence indicates that (B) is the best description, as further discussed below. This description views the ligand as binding σ to Mo(1) and as an allyl, η^3, to Mo(2), i.e. as a di-methyl substituted μ-allylidene moiety. Whereas (A) and (C) imply there to be twisting from planarity about C(1)–C(2) and C(2)–C(3) respectively (see Table 3, below), (B) implies Mo(1), C(1), C(2), and C(3), to be essentially coplanar, with C(1)–C(2) ≅ C(2)–C(3). Although formal oxidation states in

this complex may be of limited help σ:η^3, i.e. (B), leads to a Mo^{II}–Mo^{II}, d^4—d^4 assignment in (1). It is particularly noteworthy that the olefinic protons of 3,3-dimethylcyclo-propene remain mutually cis in (1). In contrast ring opening of 3,3-dimethylcyclopropene at a dirhenium centre has been observed[14] to lead to a trans arrangement in [Re₂(μ-CHCHCMe₂)(CO)₈].

When (1) is refluxed in acetonitrile containing water the two carbonyl groups co-ordinated to Mo(1) are replaced by an oxo ligand, resulting in the formation of the orange-red crystalline complex [Mo₂O(μ-CHCHCMe₂)(μ-CO)(CO)(η-C₅H₅)₂] (2). This complex was characterised by analysis, i.r. and n.m.r. spectroscopy. The i.r. spectrum showed carbonyl bands at 1 917 and 1 675 cm⁻¹ together with a band at 910 cm⁻¹, assigned to an Mo=O stretch. Examination of ^{1}H and ^{13}C n.m.r. spectra indicated the absence of co-ordinated acetonitrile and showed that the μ-allylidene fragment remained intact. To confirm this and to allow a structural comparison with (1) a single-crystal X-ray diffraction study of (2) was carried out. The molecular geometry of (2) is shown in Figure 2 and selected bond lengths and interbond angles are given in Table 2. For ease of comparison with (1), selected molecular parameters for (1) and (2) are collected in Table 3.

Replacement of two carbonyls by the oxo ligand has had remarkably minor effects on the gross geometry of the Mo₂(μ-CHCHCMe₂) framework (see Table 3). The most notable
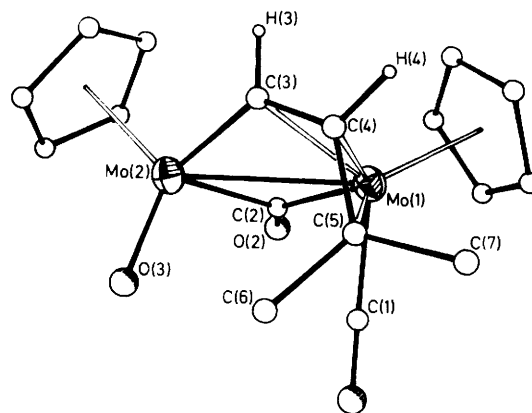
Table 2. Selected bond lengths (Å) and angles (°) for (2)

Mo(1)–Mo(2)	2.881(1)	Mo(1)–C(1)	1.963(4)	O(1)–C(1)	1.153(5)	O(2)–C(2)	1.205(4)
Mo(1)–C(2)	2.060(3)	Mo(1)–C(3)	2.267(3)	C(3)–H(3)	0.919(30)	C(3)–C(4)	1.426(4)
Mo(1)–C(4)	2.284(3)	Mo(1)–C(5)	2.492(3)	C(4)–H(4)	1.024(43)	C(4)–C(5)	1.420(4)
Mo(1)–C(10)	2.396(8)	Mo(1)–C(11)	2.374(10)	C(5)–C(6)	1.512(5)	C(5)–C(7)	1.522(5)
Mo(1)–C(12)	2.356(8)	Mo(1)–C(13)	2.300(7)	C(10)–C(11)	1.416(15)	C(10)–C(14)	1.427(15)
Mo(1)–C(14)	2.318(12)	Mo(1)–C(30)	2.368(12)	C(11)–C(12)	1.411(13)	C(12)–C(13)	1.403(13)
Mo(1)–C(31)	2.295(7)	Mo(1)–C(32)	2.292(8)	C(13)–C(14)	1.350(14)	C(30)–C(31)	1.370(15)
Mo(1)–C(33)	2.338(10)	Mo(1)–C(34)	2.328(10)	C(30)–C(34)	1.366(16)	C(31)–C(32)	1.382(12)
Mo(2)–O(3)	1.705(2)	Mo(2)–C(2)	2.161(3)	C(32)–C(33)	1.380(13)	C(33)–C(34)	1.422(17)
Mo(2)–C(3)	2.088(3)	Mo(2)–C(20)	2.426(4)	C(20)–C(21)	1.386(7)	C(20)–C(24)	1.379(6)
Mo(2)–C(21)	2.383(4)	Mo(2)–C(22)	2.363(5)	C(21)–C(22)	1.383(7)	C(22)–C(23)	1.384(7)
Mo(2)–C(23)	2.365(4)	Mo(2)–C(24)	2.434(4)	C(23)–C(24)	1.392(7)		

Mo(2)–Mo(1)–C(1)	87.7(1)	Mo(2)–Mo(1)–C(2)	48.4(1)	Mo(1)–C(2)–Mo(2)	86.0(1)	Mo(1)–C(2)–O(2)	140.3(3)
C(1)–Mo(1)–C(2)	80.0(1)	Mo(2)–Mo(1)–C(3)	46.0(1)	Mo(2)–C(2)–O(2)	133.6(2)	Mo(1)–C(3)–Mo(2)	82.7(1)
C(1)–Mo(1)–C(3)	114.0(1)	C(2)–Mo(1)–C(3)	91.3(1)	Mo(1)–C(3)–H(3)	117.0(19)	Mo(2)–C(3)–H(3)	116.5(20)
Mo(2)–Mo(1)–C(4)	76.6(1)	C(1)–Mo(1)–C(4)	103.0(1)	Mo(1)–C(3)–C(4)	72.4(2)	Mo(2)–C(3)–C(4)	133.1(2)
C(2)–Mo(1)–C(4)	125.0(1)	C(3)–Mo(1)–C(4)	36.5(1)	H(3)–C(3)–C(4)	110.2(20)	Mo(1)–C(4)–C(3)	71.1(2)
Mo(2)–Mo(1)–C(5)	85.4(1)	C(1)–Mo(1)–C(5)	70.3(1)	Mo(1)–C(4)–H(4)	111.7(24)	C(3)–C(4)–H(4)	119.9(23)
C(2)–Mo(1)–C(5)	125.9(1)	C(3)–Mo(1)–C(5)	63.4(1)	Mo(1)–C(4)–C(5)	80.9(2)	C(3)–C(4)–C(5)	123.6(3)
C(4)–Mo(1)–C(5)	34.2(1)	Mo(1)–Mo(2)–O(3)	106.6(1)	H(4)–C(4)–C(5)	115.7(23)	Mo(1)–C(5)–C(4)	64.8(2)
Mo(1)–Mo(2)–C(2)	45.5(1)	O(3)–Mo(2)–C(2)	103.7(1)	Mo(1)–C(5)–C(6)	119.2(2)	C(4)–C(5)–C(6)	121.3(3)
Mo(1)–Mo(2)–C(3)	51.3(1)	O(3)–Mo(2)–C(3)	117.7(1)	Mo(1)–C(5)–C(7)	113.1(2)	C(4)–C(5)–C(7)	117.6(3)
C(2)–Mo(2)–C(3)	93.7(1)	Mo(1)–C(1)–O(1)	117.9(3)				

**Table 3.** Comparison of molecular parameters for (1) and (2); bond lengths in Å, angles in °

	(1)	(2)
Mo(1)–Mo(2)	3.1057(9)	2.881(1)
Mo(1)–C(α)	2.126(6)	2.088(3)
Mo(2)–C(α)	2.249(5)	2.267(3)
Mo(2)–C(β)	2.270(6)	2.284(3)
Mo(2)–C(γ)	2.477(7)	2.492(3)
C(α)–C(β)	1.397(8)	1.426(4)
C(β)–C(γ)	1.418(9)	1.420(4)
Mo(1)–C	2.473(7)	2.161(3)
Mo(2)–C	1.990(7)	2.060(3)
C–O	1.179(9)	1.205(3)
Mo(1)–C(α)–Mo(2)	90.4(2)	82.7(1)
Mo(1)–C(α)–C(β)	139.5(5)	133.1(2)
C(α)–C(β)–C(γ)	126.4(6)	123.6(3)
Mo(2)–C–O	150.3(6)	140.3(3)

Torsion angles

Mo(1)–C$_\alpha$–C$_\beta$–C$_\gamma$	6.9	−3.3
C$_\alpha$–C$_\beta$–C$_\gamma$–Me^1	−49.6	−50.2
C$_\alpha$–C$_\beta$–C$_\gamma$–Me^2	163.5	164.5

Figure 2. Molecular structure of (2) showing labelling scheme, methyl and cyclopentadienyl hydrogens have been omitted for clarity

effects are in the Mo(1)–Mo(2) distance [reduced by 0.225 to 2.881(1) Å] and in the bridging carbonyl, which is now much more nearly symmetrical [Mo(2)–C(2) 2.161(3) Å] and more severely bent at CO [Mo(1)–C(2)–O(2) 140.3(3)°] with weaker C–O (Table 3)]. The short molybdenum–oxo bond [Mo(2)–O(3) 1.705(2) Å] implies strong π donation from oxygen to molybdenum. Thus, although Mo(2) is formally a 16e, Mo^{IV} centre [if O(3) is viewed as a 4e, O^{2-}, donor] a combination of

oxo π donation and μ-CO π acceptance may lead to effective co-ordinative saturation. The reduced Mo–Mo distance is probably a consequence of delocalising electrons in $d\pi$ type orbitals (i.e. M–M non- or anti-bonding) on Mo(1) in (1) to the oxo and μ-CO ligands in (2), as well as reducing steric pressure thus allowing closer approach of the metal atoms {cf. shorter Mo–Mo bonds in d^3–d^3, Mo^{III}–Mo^{III} Mo$_2$L$_6$[15,16] species than in d^5—d^5, Mo^I–Mo^I [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$].[6] Other changes in lengths and angles in the Mo$_2$(μ-CHCHCMe$_2$) unit are subtle (Table 3), and may be taken to indicate a marginally greater contribution of mode (D) (metalla-diene) to the bonding in (2) as compared with (1). The general pattern of Mo–C and C–C bond lengths in the Mo$_2$(μ-CHCHCMe$_2$) fragment is similar to those observed[17-20] in a range of dinuclear species containing μ-allylidenes and related ligands.

Finally we note that (2) is the first mixed-valence μ-allylidene (formally Mo^{IV}–Mo^{II}) complex. In light of this its reactivity was examined towards alkynes, but it was found to be much less reactive than (1) despite formal unsaturation at Mo(2), as discussed above. It is interesting to note that it is the
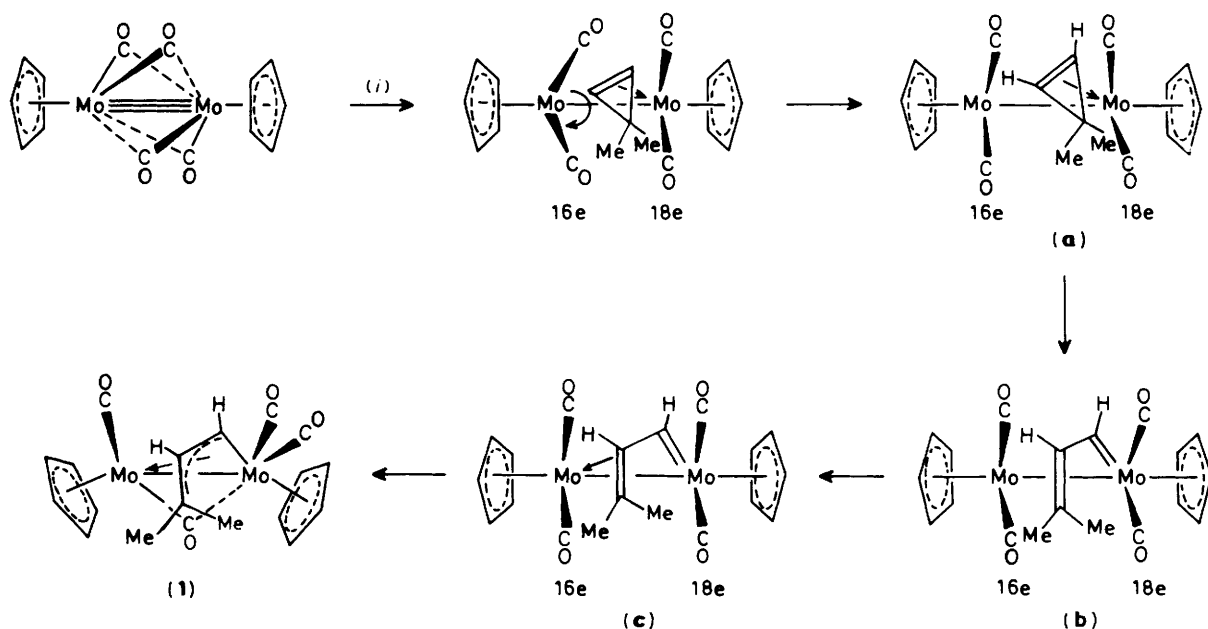
Scheme 2. (*i*) + 3,3-dimethylcyclopropene

molybdenum to which the μ-allylidene is σ bonded which is activated towards attack by a water molecule.[21]

The formation of the μ-allylidene complex (1) from 3,3-dimethylcyclopropene and [Mo₂(CO)₄(η-C₅H₅)₂] is particularly interesting since this formally unsaturated dinuclear complex is reported[10] to be unreactive towards mono-olefins. Moreover, this reaction represents a new synthetic route to a dinuclear μ-allylidene complex, a type of molecule in which there is currently[11,17–22] considerable interest. Although there is evidence[23] that cyclopropenes on thermolysis undergo 2,3 σ-bond cleavage to form a biradical, which could be converted to a vinylcarbene, these are high-temperature reactions, and it is clear that the formation of the dimolybdenum μ-allylidene (1) involves a metal mediated process. An insight into this reaction was provided by a recent[7] theoretical study of the complexes [M₂(CO)₄(η-C₅H₅)₂] (M = Cr, Mo, or W). This showed that there are suitable acceptor orbitals on each molybdenum centre, which would allow for the initial interaction of the 3,3-dimethylcyclopropene with one metal on one side of the [Mo₂(CO)₄(η-C₅H₅)₂] molecule (Scheme 2). In order to utilise the full acceptor capability of the dinuclear fragment a Mo(CO)₂(η-C₅H₅) group must rotate. This, of course, disrupts semi-bridging to the carbonyl ligands, however, and as is illustrated in Scheme 2 a vinylcarbene generated by ring-opening at one metal centre can now be captured by co-ordination to the second unsaturated (16 electron) molybdenum centre, the resultant dinuclear species (a) collapsing to form (1). These latter steps (Scheme 2) involve an apparent rotational movement of the two methyl substituents with a concomitant slippage so that one of the original two alkene carbons becomes doubly bonded to the molybdenum. In this reaction the two alkene hydrogens remain in a relative *cis* configuration suggesting that if the intermediate (b) (Scheme 2) is formed, it is rapidly configurationally stabilised by co-ordination of the double bond to the second molybdenum centre. The resultant bridged system (c) then adopts a more stable arrangement by formation of a semibridging carbonyl.

An alternative to the suggested concerted ring-opening step is an oxidative insertion reaction resulting in the formation of a molybdacyclobutene (Scheme 3). The vinylcarbene intermediate
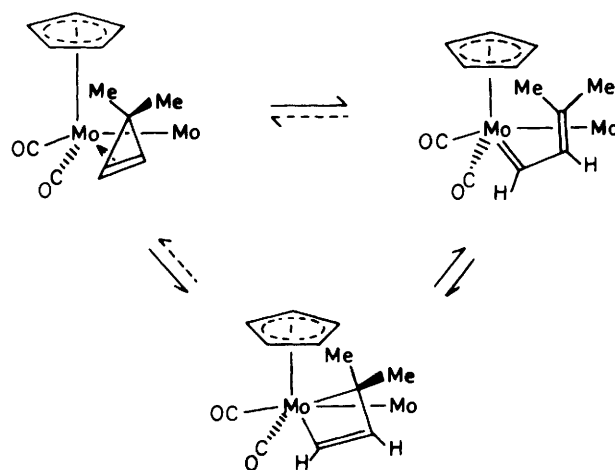

Scheme 3. Some ligands omitted for clarity

(b) is then generated by a ring-opening reaction, which maintains the *cis* formation of the two hydrogen substituents. This could occur either *via* a conrotatory process if the cyclobutene is not co-ordinated to the second molybdenum centre, or by a disrotatory process if co-ordination had already occurred. Obviously, in the first mentioned concerted process rotational opening of the cyclopropene could also in principle occur in either of two rotational directions.

The μ-allylidene complex (1) is stable in refluxing dry acetonitrile, the oxo complex (2) only being formed on addition of water. However, in dry refluxing toluene–hexane (1:1), (1) undergoes unusual rearrangement reactions which result[24] in the formation of three new complexes. They were separated by column chromatography, the major product (3) being isolated as red crystals. Complex (3) was identified by analysis, m.s., i.r., and n.m.r. spectroscopy as the transversely bridged 3-methylbut-1-yne complex [Mo₂(μ-Pr^{i}C₂H)(CO)₄(η-C₅H₅)₂], a type of molecule previously well documented.[6,8,9] In agreement with earlier observations the room temperature ¹H n.m.r.

spectrum displayed equivalent cyclopentadienyl resonances, the ^{13}C n.m.r. two CO environments, and there was also no diastereotopic splitting of the isopropyl methyl groups, although these signals were slightly broadened ($\Delta v_{\frac{1}{2}}$ 8 Hz). This is consistent with the type of fluxional process previously discussed by Cotton and co-workers.[8]

The second product (4) was obtained as green crystals. Analysis, m.s., i.r., and n.m.r. spectroscopy suggested that the complex had the molecular formula $[Mo_2\{CH_2CHC(Me)CH_2\}-(CO)_2(\eta\text{-}C_5H_5)_2]$. The presence of co-ordinated isoprene was supported by the observation that carbon monoxide (1 atm, room temperature) rapidly reacted with (4) to give $[Mo_2-(CO)_6(\eta\text{-}C_5H_5)_2]$ and isoprene, the latter being identified by m.s., and gas chromatography. A related complex $[Mo_2(cis\text{-}CH_2CHCHCHMe)(CO)_2(\eta\text{-}C_5H_5)_2]$ [(I) in Scheme 4] has previously been obtained[25] as black crystals in very low yield (2%) by reacting a mixture of cis- and trans-penta-1,3-diene with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in refluxing octane. As is shown in Scheme 4 it was suggested that the cis-penta-1,3-diene is symmetrically bonded relative to the Mo $\cdots$ Mo vector, a type of bonding which has been identified by X-ray crystallography in the dirhodium complex (III) (Scheme 4) $[Rh_2(\mu\text{-}CO)(\mu\text{-}C_6H_8)(\eta^5\text{-}C_9H_7)_2]$.[26] Such a bonding mode might be adopted by the isoprene complex (4) [structure (II) in Scheme 4], however, there is an alternative way in which a 1,3-diene fragment can bond to $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2]$, and this is illustrated by the 2-t-butyl-6,6-dimethylcyclohexa-2,4-dienone-dimolybdenum complex (IV) (Scheme 4) where the 1,3-diene unit is partially rotated [22.3° in (IV)] relative to the

(I, R = H, R' = Me)

(II, R = Me, R' = H)

(III)

(IV)
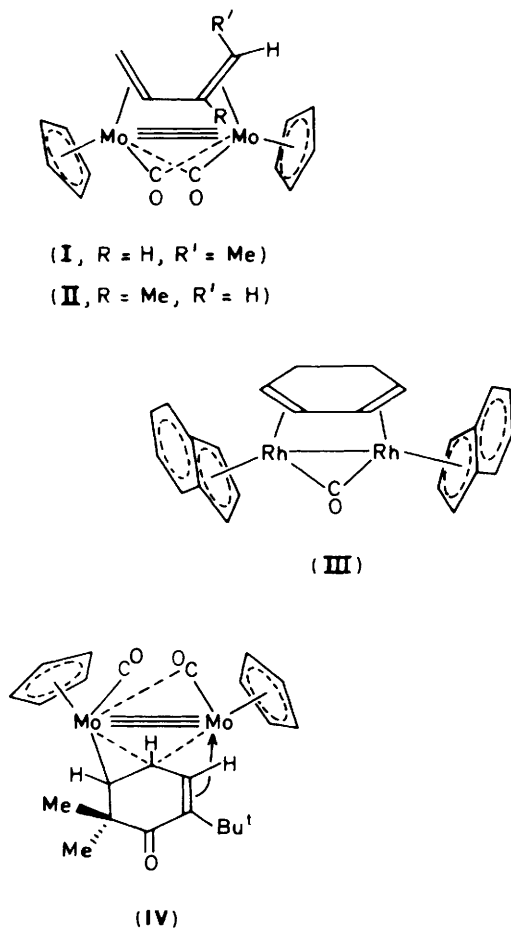
Scheme 4.

Mo $\cdots$ Mo vector.[27] A choice between these two possibilities for (4) must await an X-ray crystallographic study.

The third product of the thermolysis reaction was obtained as dark green-black crystals, (5), examination of the n.m.r. data suggesting that the molecule was trinuclear. This was confirmed by single-crystal X-ray crystallography, which established the structure shown in Figure 3, selected bond lengths and interbond angles being listed in Table 4.

The molecule consists of a triangular framework of three molybdenum atoms, which show typical molybdenum–molybdenum single bond separations [Mo(1)–Mo(2) 2.929(1), Mo(1)–Mo(3) 3.079(1), and Mo(2)–Mo(3) 3.049(1) Å]. Each molybdenum carries an η^5-cyclopentadienyl ligand, Mo(1) and Mo(2) being co-ordinated by one carbonyl, whereas Mo(3) has two bonded carbonyl ligands. The original μ-allylidene fragment present in the parent molecule (1) has lost three hydrogen atoms, one from the bridging carbon [C(5) in (5)] and two from a methyl group [C(9) in (5)], resulting in the formation of a methyl substituted molybdacyclopentadiene unit incorporating Mo(1) which is η^4-bonded to Mo(2) and metallated by Mo(3) at the carbon atom C(5), α to Mo(1). Thus, C(5) asymmetrically bridges the Mo_3 triangle in a manner reminiscent of the μ_3-carbon in the complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCH_2)(CO)_9]$[28] [C(5)–Mo(3) 2.048(4), C(5)–Mo(1) 2.079(4), and C(5)–Mo(2) 2.200(4) Å]. The C–C and Mo–C distances in the 'metallacyclopentadiene' ring indicate there to be essentially delocalised multiple bonding present [C(5)–C(6) 1.405(6), C(6)–C(7) 1.435(6), C(7)–C(9) 1.403(7), and Mo(1)–C(9) 2.151(4) Å]. The carbonyl ligands show varying degrees of non-linearity which correlate with the degree of interaction with neighbouring metal atoms [hence Mo(1)–C(1)–O(1) 178.0(4), Mo(2)–C(2)–O(2) 163.1(4), Mo(3)–C(3)–O(3) 171.6(4), Mo(3)–C(4)–O(4) 164.6(4)°, C(1) $\cdots$ Mo(3) 3.643, C(2) $\cdots$ Mo(1) 2.864, C(3) $\cdots$ Mo(2) 3.015, and C(4) $\cdots$ Mo(1) 2.929 Å].

The reactions leading to the formation of (3), (4), and (5) clearly involve hydrogen-shift processes, and although a great deal is known about such reactions at a one metal centre,[29] little work has been reported on rearrangement reactions of organic ligands co-ordinated to two metal centres.[30,31] Of special interest is the formation of (3) where it would appear that activation of a vinylic C–H bond is an important step. Although such reactions are of potential importance in relation to the
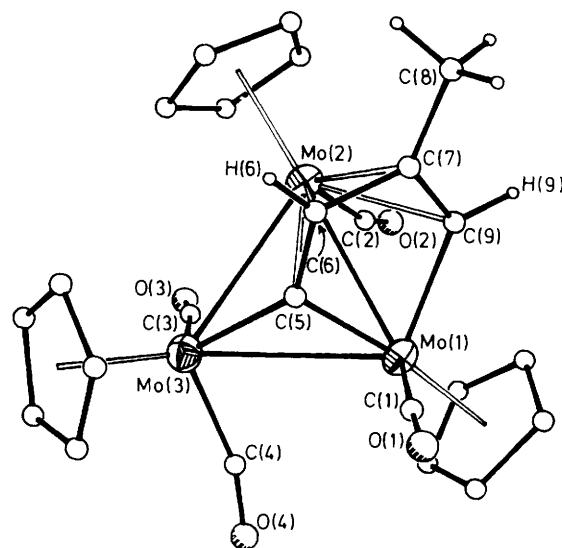

Figure 3. Molecular structure of (5) showing labelling scheme, methyl and cyclopentadienyl hydrogens have been omitted for clarity

Table 4. Selected bond lengths (Å) and angles (°) for (5)

Mo(1)-Mo(2)	2.929(1)	Mo(1)-Mo(3)	3.079(1)	Mo(3)-C(35)	2.346(6)	O(1)-C(1)	1.154(5)
Mo(1)-C(1)	1.942(4)	Mo(1)-C(5)	2.079(4)	O(2)-C(2)	1.159(6)	O(3)-C(3)	1.164(6)
Mo(1)-C(9)	2.151(4)	Mo(1)-C(11)	2.367(7)	O(4)-C(4)	1.181(7)	C(5)-C(6)	1.405(6)
Mo(1)-C(12)	2.383(6)	Mo(1)-C(13)	2.313(9)	C(6)-H(6)	0.934(47)	C(6)-C(7)	1.435(6)
Mo(1)-C(14)	2.275(7)	Mo(1)-C(15)	2.302(6)	C(7)-C(8)	1.504(7)	C(7)-C(9)	1.403(7)
Mo(2)-Mo(3)	3.049(1)	Mo(2)-C(2)	1.954(5)	C(9)-H(9)	1.004(42)	C(11)-C(12)	1.314(10)
Mo(2)-C(5)	2.200(4)	Mo(2)-C(6)	2.263(4)	C(11)-C(15)	1.365(8)	C(12)-C(13)	1.332(12)
Mo(2)-C(7)	2.346(4)	Mo(2)-C(9)	2.361(4)	C(13)-C(14)	1.403(10)	C(14)-C(15)	1.411(11)
Mo(2)-C(21)	2.350(6)	Mo(2)-C(22)	2.322(5)	C(21)-C(22)	1.392(9)	C(21)-C(25)	1.386(8)
Mo(2)-C(23)	2.305(5)	Mo(2)-C(24)	2.304(4)	C(22)-C(23)	1.395(9)	C(23)-C(24)	1.420(8)
Mo(2)-C(25)	2.358(5)	Mo(3)-C(3)	1.969(5)	C(24)-C(25)	1.408(8)	C(31)-C(32)	1.384(8)
Mo(3)-C(4)	1.937(5)	Mo(3)-C(5)	2.048(4)	C(31)-C(35)	1.410(8)	C(32)-C(33)	1.411(7)
Mo(3)-C(31)	2.363(5)	Mo(3)-C(32)	2.338(5)	C(33)-C(34)	1.409(7)	C(34)-C(35)	1.388(7)
Mo(3)-C(33)	2.315(5)	Mo(3)-C(34)	2.326(5)				

Mo(2)-Mo(1)-Mo(3)	60.9(1)	Mo(2)-Mo(1)-C(1)	113.4(1)	Mo(1)-Mo(3)-C(5)	42.1(1)	Mo(2)-Mo(3)-C(5)	46.1(1)
Mo(3)-Mo(1)-C(1)	90.1(1)	Mo(2)-Mo(1)-C(5)	48.5(1)	C(3)-Mo(3)-C(5)	112.5(2)	C(4)-Mo(3)-C(5)	103.9(2)
Mo(3)-Mo(1)-C(5)	41.4(1)	C(1)-Mo(1)-C(5)	69.5(2)	Mo(1)-C(1)-O(1)	178.0(4)	Mo(2)-C(2)-O(2)	163.1(4)
Mo(2)-Mo(1)-C(9)	52.7(1)	Mo(3)-Mo(1)-C(9)	107.7(1)	Mo(3)-C(3)-O(3)	171.6(4)	Mo(3)-C(4)-O(4)	164.6(4)
C(1)-Mo(1)-C(9)	91.5(2)	C(5)-Mo(1)-C(9)	72.8(2)	Mo(1)-C(5)-Mo(2)	86.4(1)	Mo(1)-C(5)-Mo(3)	96.5(2)
Mo(1)-Mo(2)-Mo(3)	62.0(1)	Mo(1)-Mo(2)-C(2)	68.5(1)	Mo(2)-C(5)-Mo(3)	91.7(1)	Mo(1)-C(5)-C(6)	120.6(3)
Mo(3)-Mo(2)-C(2)	99.6(2)	Mo(1)-Mo(2)-C(5)	45.1(1)	Mo(2)-C(5)-C(6)	74.1(2)	Mo(3)-C(5)-C(6)	138.5(3)
Mo(3)-Mo(2)-C(5)	42.2(1)	C(2)-Mo(2)-C(5)	111.9(2)	Mo(2)-C(6)-C(5)	69.2(2)	Mo(2)-C(6)-H(6)	118.0(24)
Mo(1)-Mo(2)-C(6)	70.5(1)	Mo(3)-Mo(2)-C(6)	73.4(1)	C(5)-C(6)-H(6)	125.4(27)	Mo(2)-C(6)-C(7)	75.0(2)
C(2)-Mo(2)-C(6)	136.2(2)	C(5)-Mo(2)-C(6)	36.7(2)	C(5)-C(6)-C(7)	113.4(4)	H(6)-C(6)-C(7)	120.8(27)
Mo(1)-Mo(2)-C(7)	70.7(1)	Mo(3)-Mo(2)-C(7)	104.9(1)	Mo(2)-C(7)-C(6)	68.8(2)	Mo(2)-C(7)-C(8)	127.1(3)
C(2)-Mo(2)-C(7)	113.3(2)	C(5)-Mo(2)-C(7)	62.9(1)	C(6)-C(7)-C(8)	122.9(4)	Mo(2)-C(7)-C(9)	73.3(2)
C(6)-Mo(2)-C(7)	36.2(2)	Mo(1)-Mo(2)-C(9)	46.5(1)	C(6)-C(7)-C(9)	111.6(4)	C(8)-C(7)-C(9)	125.5(4)
Mo(3)-Mo(2)-C(9)	103.0(1)	C(2)-Mo(2)-C(9)	79.8(2)	Mo(1)-C(9)-Mo(2)	80.8(1)	Mo(1)-C(9)-C(7)	119.3(3)
C(5)-Mo(2)-C(9)	66.7(1)	C(6)-Mo(2)-C(9)	61.0(2)	Mo(2)-C(9)-C(7)	72.1(2)	Mo(1)-C(9)-H(9)	125.4(25)
C(7)-Mo(2)-C(9)	34.7(2)	Mo(1)-Mo(3)-Mo(2)	57.1(1)	Mo(2)-C(9)-H(9)	121.2(21)	C(7)-C(9)-H(9)	115.1(25)
Mo(1)-Mo(3)-C(3)	89.5(1)	Mo(2)-Mo(3)-C(3)	70.1(1)				
Mo(1)-Mo(3)-C(4)	67.0(1)	Mo(2)-Mo(3)-C(4)	118.1(1)				
C(3)-Mo(3)-C(4)	85.7(2)						
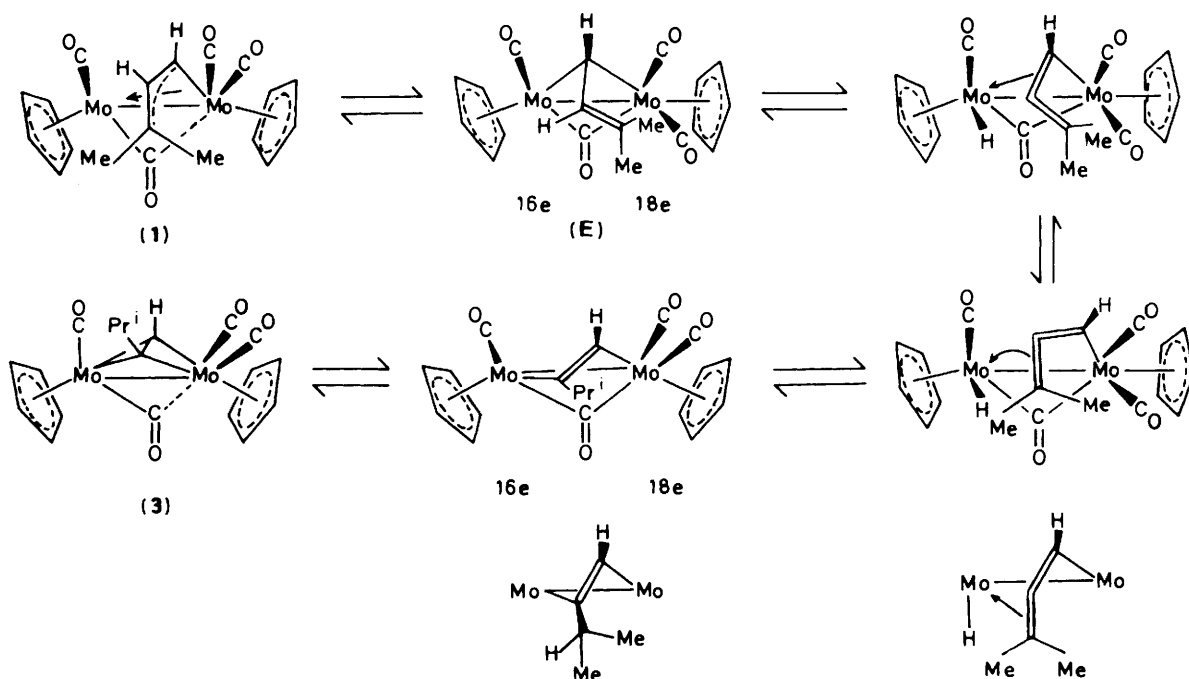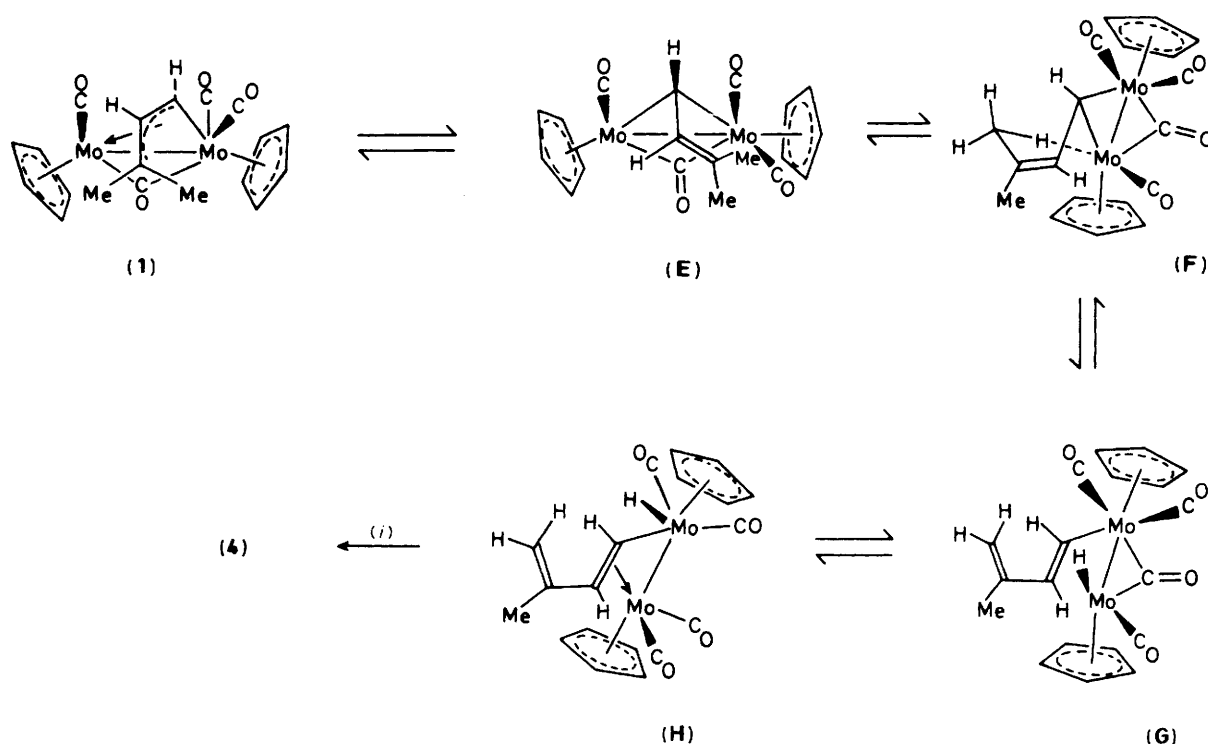
Scheme 5.

Scheme 6. (i) $-2CO$

activation of alkenes and 1,3-dienes, they have received little attention. Recent studies included vinyl hydrogen activation of ethylene at dirhodium[32] and dirhenium[33] centres, and of hexatriene in a dicobalt[34] system. In the rearrangement of (1) into (3) a likely first step is the reversible transformation of the μ-allylidene into (E), a μ-σ-vinylcarbene, thus creating a vacant co-ordination site at one of the molybdenum centres [(1) to (E) in Scheme 5]. An agostic CHMo interaction could then lead to a β-hydrogen elimination reaction and formation of a bent μ-σ:η²-bonded allenyl ligand. The allenyl ligand has available an orthogonal π system, and a rotational movement about the Mo–CH=C=CMe₂ single bond would allow this to interact with the second molybdenum centre, thus alligning the carbon–carbon double bond with the Mo–H bond, which is a geometrical prerequisite for an 'insertion' reaction. As is shown in Scheme 5 this insertion reaction generates an isopropyl group of a co-ordinated 3-methylbut-1-yne, which straddles the Mo · · · Mo vector. The species, which is generated, is a partially rotated transversely bridged alkyne complex, and a rotational movement would afford (3).

The formation of the isoprene complex (4) can be understood in terms of a δ-hydrogen abstraction reaction. If the μ-vinylcarbene complex (E) (Scheme 6) has a finite lifetime then rotation can occur about a carbon–carbon bond allowing access to the boat-shaped conformational isomer (F). Hydrogen transfer to the unsaturated molybdenum centre with concomitant cleavage of a Mo–C σ bond affords the σ-dienyl species (G). A switch in the bonding mode of the bridging carbonyl to a terminal carbonyl then allows transfer of the terminal Mo–H to the molybdenum atom carrying the σ-dienyl ligand. The resultant complex (H) can then collapse to (4) via a reductive elimination reaction and loss of carbon monoxide. It is important to recognise that in this reaction sequence and in the one leading to the formation of the alkyne complex (3) the presence of two metal centres is necessary.

The formation of the trinuclear complex (5) is clearly far more

complicated and at the present time all that can be said is that a dehydrogenation reaction is involved and that Mo–Mo bond scission and intermolecular stages are necessary.

Experimental

All experiments were carried out in Schlenk tubes under an atmosphere of dry, oxygen-free nitrogen, using freshly distilled solvents. The ¹H and ¹³C n.m.r. spectra were recorded on JEOL FX 90 Q or FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise indicated, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference; SiMe₄ for ¹³C and ¹H. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. 3,3-Dimethylcyclopropene[35] was prepared by the published procedure.

Preparation of [Mo₂(μ-σ:η³-CHCHCMe₂)(CO)₄(η-C₅H₅)₂] (1).—Aliquots (0.2 cm³) of 3,3-dimethylcyclopropene were added at 4-d intervals to a stirred solution of [Mo₂(CO)₄(η-C₅H₅)₂] (4.0 g, 9.22 mmol) in toluene (150 cm³). The extent of the reaction was monitored by i.r. spectroscopy, the product precipitating as a red powder. After 20 d (1.0 cm³ of 3,3-dimethylcyclopropene) at room temperature the volatile material was removed *in vacuo* and the residue dissolved in CH₂Cl₂ (10 cm³) and chromatographed on an alumina packed column (30 × 4 cm). Elution with diethyl ether afforded [Mo₂(CO)₄(η-C₅H₅)₂] and [Mo₂(CO)₆(η-C₅H₅)₂]. Further elution with CH₂Cl₂ afforded a red band, which was collected and re-crystallised (−10 °C) from CH₂Cl₂–hexane to give red *crystals* of (1) (2.2 g, 54%) (Found: C, 45.4, H, 3.6. C₁₉H₁₈Mo₂O₄ requires C, 45.4; H, 3.6%); νmax. at 1 945vs, 1 905s, 1 847s, 1 771m cm⁻¹ (CH₂Cl₂). N.m.r.: ¹H (CD₂Cl₂), δ 10.93 [d, 1 H, μ-CH, ³J(HH) 9.8], 5.91 [d, 1 H, μ-CHCHCMe₂, ³J(HH) 9.8], 5.38 (s, 5 H, C₅H₅), 5.16 (s, 5 H, C₅H₅), 1.71 (s, 3 H, Me), 1.10 (s, 3 H, Me); ¹³C-{¹H} (CD₂Cl₂), δ 249.7 (CO), 242.8 (CO), 242.7

Table 5. Structure analyses of (1), (2), and (5)

	(1)	(2)	(5)
Formula	$C_{19}H_{18}Mo_2O_4$	$C_{17}H_{18}Mo_2O_3$	$C_{24}H_{20}Mo_3O_4$
M	502.2	462.2	660.1
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$	$P2_1/n$
$a/\text{Å}$	17.304(12)	7.473(1)	8.066(1)
$b/\text{Å}$	7.832(8)	12.123(2)	17.557(5)
$c/\text{Å}$	14.417(10)	18.073(3)	15.754(5)
$\beta/°$	113.61(6)	92.87(2)	101.35(2)
$U/\text{Å}^3$	1 790(2)	1 635.4(5)	2 187(1)
Z	4	4	4
$D_c/\text{g cm}^{-3}$	1.86	1.88	2.00
$F(000)$ (electrons)	992	912	1 288
$\mu(\text{Mo-}K_\alpha)/\text{cm}^{-1}$	14.0	15.1	16.8
Approx. crystal size (mm)	$0.5 \times 0.3 \times 0.2$	$0.5 \times 0.45 \times 0.15$	$0.4 \times 0.28 \times 0.10$
Method of data collection	θ—2θ	Wyckoff(ω)	Wyckoff(ω)
Scan species/° min^{-1}	$\geqslant 2.4$	3.9—19.5	2.9—29.3
Scan width/°	$2.4 + 0.7 \tan \theta$	1.0	1.0
Diffractometer	CAD-4	Nicolet P3m	Nicolet P3m
2θ range/°	3—52	3—55	3—50
No. of unique data	3 510	3 221	2 969
No. of observed data	3 165	3 055	2 888
Criterion for observed $[I > n\sigma(I)]$	$n = 1$	$n = 2$	$n = 2$
No. of parameters refined	238	260	291
Final R^a	0.061	0.025	0.026
R'^a	0.095	0.030	0.031
g^b	0.005 65	0.000 31	0.000 20
Largest final difference electron-density features/e Å^{-3}	± 0.46	± 0.50	± 0.58

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$. ^{b} $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ from counting statistics, g chosen to minimise variations of R' with $|F_o|$.

Table 6. Atomic co-ordinates of refined atoms for (1) ($\times 10^5$ Mo; $\times 10^4$ C, O; $\times 10^3$ H)

Atom	x	y	z
Mo(1)	4 899(3)	15 465(6)	−21 703(4)
Mo(2)	20 544(3)	7 605(6)	−26 421(4)
C(11)	−381(5)	962(12)	−1 333(6)
C(12)	356(5)	1 641(10)	−605(5)
C(13)	1 019(5)	521(11)	−466(5)
C(14)	709(6)	−891(10)	−1 098(6)
C(15)	−170(6)	−613(12)	−1 627(6)
C(21)	3 288(6)	−515(14)	−2 559(11)
C(22)	2 683(6)	−1 769(12)	−2 881(8)
C(23)	2 393(5)	−2 115(9)	−2 146(7)
C(24)	2 815(7)	−1 081(15)	−1 326(8)
C(25)	3 372(6)	−57(12)	−1 575(10)
C(101)	587(5)	4 014(9)	−2 252(6)
O(101)	585(5)	5 479(8)	−2 218(7)
C(102)	−465(4)	2 248(8)	−3 389(5)
O(102)	−1 040(3)	2 683(8)	−4 093(4)
C(201)	2 403(4)	2 891(9)	−3 036(5)
O(201)	2 659(4)	4 153(6)	−3 215(5)
C(202)	1 991(4)	2 360(10)	−1 603(5)
O(202)	2 325(4)	3 256(10)	−897(5)
C(1)	687(3)	2(8)	−3 269(4)
C(2)	916(4)	175(8)	−4 090(4)
C(3)	1 193(4)	1 692(9)	−4 397(5)
C(31)	759(5)	3 357(10)	−4 545(6)
C(32)	1 637(6)	1 443(12)	−5 123(6)
H(1)	59(6)	−130(11)	−312(7)
H(2)	94(6)	−80(11)	−447(7)

(CO), 242.2 (CO), 174.9 [μ-CH, ^{1}H coupled spectrum, ^1J(CH) 140], 99.2 (CMe$_2$), 96.1 (C$_5$H$_5$), 94.9 [μ-CHCHCMe$_2$, ^{1}H coupled spectrum, ^1J(CH) 151], 93.1 (C$_5$H$_5$), 33.0 (Me), and 22.2 p.p.m. (Me).

Reaction of (1) *with Aqueous Acetonitrile.*—A solution of (1) (0.2 g, 0.4 mmol) in freshly distilled MeCN (100 cm^3), to which distilled H$_2$O (0.2 cm^3, 11 mmol) was added, was heated under reflux. After 4 h the solvent was removed *in vacuo* and the residue chromatographed on alumina. Elution with CH$_2$Cl$_2$–diethyl ether (1:1) afforded unreacted (1) (0.02 g). Further elution with CH$_2$Cl$_2$–MeCN (4:1) gave an orange-red band which was collected and recrystallised (−20 °C) from CH$_2$Cl$_2$-hexane to give orange-red *crystals* of [Mo$_2$O(μ-σ:η^3-CHCHCMe$_2$)(μ-CO)(CO)(η-C$_5$H$_5$)$_2$] (2) (0.07 g, 42%) (Found: C, 44.0; H, 4.0. C$_{17}$H$_{18}$Mo$_2$O$_3$ requires C, 44.2; H, 3.9%); ν$_{max.}$ at 1 917s, 1 675m, 910 (MoO) cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), δ 8.43 [d, 1 H, μ-CH, ^3J(HH) 9.5], 5.98 [d, 1 H, μ-CHCH*C*Me$_2$, ^3J(HH) 9.5], 5.67 (s, 5 H, C$_5$H$_5$), 5.04 (s, 5 H, C$_5$H$_5$), 1.86 (s, 3 H, Me), 1.30 (s, 3 H, Me); ^{13}C-{^{1}H} (CD$_2$Cl$_2$, −80 °C), δ 292.7 (CO), 231.2 (CO), 169.7 (μ-CH), 101.6 (C$_5$H$_5$), 94.5 (*C*Me$_2$), 94.0 (μ-CHCHCMe$_2$), 93.5 (C$_5$H$_5$), 33.2 (Me), and 21.6 p.p.m. (Me).

Thermolysis of (1).—A solution of (1) (0.3 g, 0.6 mmol) in toluene–hexane (1:1) (50 cm^3) was heated under reflux. After 4 h the volatile material was removed *in vacuo*, and the residue dissolved in CH$_2$Cl$_2$ and chromatographed on alumina (15 × 2 cm). Elution with hexane afforded a deep red band, which was collected and recrystallised (−78 °C) from hexane–diethyl ether (2:1) to give red *crystals* of [Mo$_2$(μ-Pr^{i}C$_2$H)(CO)$_4$(η-C$_5$H$_5$)$_2$] (3) (0.12 g, 40%) (Found: C, 44.9; H, 3.6. C$_{19}$H$_{18}$Mo$_2$O$_4$ requires C, 45.4; H, 3.6%); ν$_{max.}$ at 1 977s, 1 953(sh), 1 901vs, 1 825s cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), δ 6.04 [d, 1 H, CH, ^4J(HH) 0.7], 5.28 (s, 10 H, C$_5$H$_5$), 2.65 [septet, 1 H, C*H*Me$_2$, ^3J(HH) 6.6], 0.95 [d, 6 H, CH*Me*$_2$, ^3J(HH) 6.6]; ^{13}C-{^{1}H} (CDCl$_3$), δ 233.2 (CO), 226.5 (CO), 91.0 (C$_5$H$_5$), 85.1 (μ-CH), 65.3 (μ-CCHMe$_2$), 31.9 (*C*HMe$_2$), and 25.8 p.p.m. (Me).

Further elution with diethyl ether gave a green band which

Table 7. Atomic co-ordinates (× 10⁴) for (2)

Atom	x	y	z
Mo(1)	6 740(1)	3 281(1)	6 201(1)
Mo(2)	4 274(1)	2 650(1)	7 300(1)
O(1)	3 896(5)	2 506(3)	4 992(2)
O(2)	3 594(3)	4 862(2)	6 454(2)
O(3)	2 693(3)	1 836(2)	6 861(1)
C(1)	4 952(5)	2 772(3)	5 444(2)
C(2)	4 486(4)	4 046(3)	6 566(2)
C(3)	6 957(4)	2 203(2)	7 226(2)
C(4)	7 921(4)	1 671(2)	6 665(2)
C(5)	7 102(4)	1 263(3)	5 994(2)
C(6)	5 472(5)	524(3)	5 994(2)
C(7)	8 317(5)	997(3)	5 367(2)
C(10)ᵃ	9 786(10)	3 789(8)	6 020(7)
C(11)ᵃ	9 106(13)	4 508(9)	6 556(6)
C(12)ᵃ	7 648(11)	5 141(6)	6 268(6)
C(13)ᵃ	7 467(10)	4 810(6)	5 524(4)
C(14)ᵃ	8 680(16)	4 027(9)	5 373(6)
C(30)ᵇ	7 885(17)	4 455(10)	5 290(7)
C(31)ᵇ	7 365(11)	5 067(6)	5 879(5)
C(32)ᵇ	8 380(11)	4 823(6)	6 518(5)
C(33)ᵇ	9 616(13)	4 039(9)	6 330(7)
C(34)ᵇ	9 244(12)	3 799(9)	5 568(7)
C(20)	5 128(6)	2 766(4)	8 611(2)
C(21)	3 417(8)	2 324(4)	8 534(2)
C(22)	2 309(6)	3 137(5)	8 231(2)
C(23)	3 328(7)	4 062(4)	8 095(2)
C(24)	5 076(6)	3 836(4)	8 352(2)

ᵃ Occupancy 0.518(12). ᵇ Occupancy 0.482(12).

Table 8. Atomic co-ordinates (× 10⁴) for (5)

Atom	x	y	z
Mo(1)	1 870(1)	1 309(1)	1 088(1)
Mo(2)	1 863(1)	1 150(1)	2 939(1)
Mo(3)	1 052(1)	2 709(1)	2 108(1)
O(1)	− 1 705(4)	1 359(2)	− 70(2)
O(2)	5 554(4)	870(3)	2 768(3)
O(3)	4 758(5)	2 790(2)	3 162(3)
O(4)	2 539(6)	3 302(2)	567(3)
C(1)	− 383(6)	1 349(3)	373(3)
C(2)	4 124(7)	1 000(3)	2 696(3)
C(3)	3 386(6)	2 699(3)	2 777(3)
C(4)	2 052(6)	2 975(3)	1 126(3)
C(5)	111(5)	1 636(2)	1 822(2)
C(6)	− 822(5)	1 086(3)	2 176(3)
C(7)	− 167(5)	329(3)	2 151(3)
C(8)	− 962(7)	− 353(3)	2 491(3)
C(9)	1 236(6)	310(2)	1 749(3)
C(11)	3 964(7)	1 737(4)	338(4)
C(12)	4 684(7)	1 188(5)	848(4)
C(13)	3 865(11)	533(4)	654(6)
C(14)	2 531(8)	661(4)	− 50(4)
C(15)	2 630(8)	1 443(5)	− 238(3)
C(21)	693(7)	1 183(4)	4 192(3)
C(22)	1 518(8)	489(3)	4 169(3)
C(23)	3 239(8)	629(3)	4 229(3)
C(24)	3 471(7)	1 431(3)	4 280(3)
C(25)	1 879(7)	1 763(3)	4 272(3)
C(31)	− 1 816(6)	3 063(3)	1 970(4)
C(32)	− 993(7)	3 636(3)	1 612(3)
C(33)	236(7)	3 955(3)	2 280(3)
C(34)	152(7)	3 564(3)	3 051(3)
C(35)	− 1 099(7)	3 012(3)	2 860(4)

was recrystallised (− 20 °C) from hexane–diethyl ether to give dark green crystals of [Mo₂{CH₂CHC(Me)CH₂}(CO)₂(η-C₅H₅)₂] (4) (Found: C, 45.3; H, 4.1. C₁₇H₁₈Mo₂O₂ requires C, 45.7; H, 4.0%); $v_{max.}$ at 1 777m, 1 745m cm⁻¹ (CH₂Cl₂). N.m.r.: ¹H (CDCl₃), δ 5.14 (s, 5 H, C₅H₅), 5.05 (s, 5 H, C₅H₅), 4.34 [dd,

1 H, H³, ³J(H³H⁴) 7.33, ³J(H³H⁵) 10.8], 2.99 [dd, 1 H, H², ²J(H¹H²) 3.3, ⁴J(H²H³) 0.74], 2.19 [dd, 1 H, H⁴, ³J(H⁴H³) 7.33, ²J(H⁴H⁵) 4.4], 2.04 (s, 3 H, Me), 0.48 [dd, 1 H, H⁵, ³J(H⁵H³) 10.8, ²J(H⁵H⁴) 4.4], 0.16 [d, 1 H, H¹, ²J(H¹H²) 3.3]; ¹³C-{¹H} (CD₂Cl₂), δ 268.1 (CO), 266.4 (CO), 97.6 (CMe), 93.6 (C₅H₅), 92.8 (C₅H₅), 57.4 (CH), 33.9 (CH₂), 30.8 (Me), and 28.8 p.p.m. (CH₂).
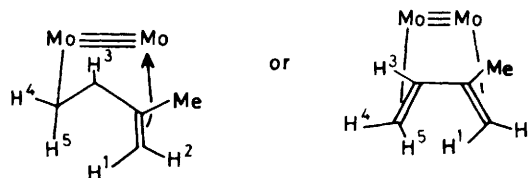
Finally, elution with hexane–CH₂Cl₂ (3:1) afforded a green band, which on recrystallisation (− 20 °C) from hexane–CH₂Cl₂ gave dark green-black crystals of [Mo₃(μ₃-η⁴-CCHCMeCH)(CO)₄(η-C₅H₅)₃] (5) (0.02 g, 5%) (Found: C, 43.7; H, 3.1. C₂₄H₂₀Mo₃O₄ requires C, 43.6; H, 3.0%); $v_{max.}$ at 1 881vs, 1 799m cm⁻¹ (CH₂Cl₂). N.m.r.: ¹H (CD₂Cl₂), δ 6.49 [d, 1 H, CH, ⁴J(HH) 2.3], 5.78 [d, 1 H, CH, ⁴J(HH) 2.3], 5.10 (s, 5 H, C₅H₅), 4.95 (s, 5 H, C₅H₅), 4.89 (s, 5 H, C₅H₅), and 1.92 p.p.m. (s, 3 H, Me).

Crystal Structure Determinations and Structure Refinements.—Table 5 gives experimental and refinement details for the structure determinations of (1), (2), and (5). All diffraction measurements were made at room temperature using graphite-monochromated Mo-K_α X-radiation (λ = 0.710 69 Å). Structure solution was by conventional heavy-atom (Patterson and difference Fourier) methods and refinement by least-squares [full matrix for (1) and blocked cascade for (2) and (5)]. All non-hydrogen atoms were assigned anisotropic vibrational parameters. All hydrogen atoms were held in idealised geometries [C–H = 1.08 for (1) and 0.96 Å for (2) and (5)] except for H(1) and H(2) in (1), H(3) and H(4) in (2), and H(6) and H(9) in (5) which were directly located from difference electron-density synthesis and refined without positional constraints. All hydrogens were assigned fixed isotropic vibrational parameters [$U_{iso.}$ = 0.06 and 0.07 Å² for cyclopentadienyl and methyl hydrogens in (1), $U_{iso.}$ = ca. 1.2 × $U_{iso.}$ for the attached carbon atoms in (2) and (5)] except for H(3) and H(5) in (2) and H(6) and H(9) in (5) which had freely refined $U_{iso.}$.* No absorption corrections were applied, but for (2) an isotropic extinction correction was applied such that F_c(corrected) = $F_c[1.0 + 0.002xF^2/\sin 2\theta]^{-\frac{1}{4}}$, where x refined to 0.002 52(8). In (2) the cyclopentadienyl ligand attached to Mo(1) was disordered between two sites [C(10)—(14) and C(30)—(34)] with occupancies 0.518(12) and 0.482(12) respectively. All calculations were made with programs written by G. M. Sheldrick [SHELX-76 on the ULCC CDC 7600 for (1), and SHELXTL on the Nicolet R3m/E system for (2) and (5)]. Complex neutral-atom scattering factors were used throughout, taken from ref. 36. Tables 6, 7, and 8 list the final non-hydrogen atomic co-ordinates for (1), (2), and (5) respectively.

* The isotropic thermal parameter exponent has the form $-8\pi^2 U_{iso.}(\sin^2\theta/\lambda^2)$.

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