Reactions of Co-ordinated Ligands. Part 38.[1] The Reactions of 1,2-Dienes, 1,3-Dienes, and Alkynes with the μ-Allylidene Complex $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$; Molecular Structures of $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\mu\text{-}\eta^3:\eta^3\text{-}CH_2C(CH_2)CHCHCMe_2\}Mo(CO)_2(\eta\text{-}C_5H_5)]$, $[Mo_2\{\mu\text{-}\eta^4\text{-}\overline{CMe_2CHCHCHC(Bu^t)C}O\}(CO)_2(\eta\text{-}C_5H_5)_2]$ and $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\mu\text{-}\eta^2:\eta^3\text{-}C(Me)C(Me)C(O)CHCHCMe_2\}Mo(CO)_2(\eta\text{-}C_5H_5)]$ *

Michael Green, Richard J. Mercer, A. Guy Orpen, Colin J. Schaverien, and Ian D. Williams
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS

Reaction of the μ-allylidene complex $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with propa-1,2-diene leads to cleavage of the metal–metal bond and formation of the bis-allylic complex $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\mu\text{-}\eta^3:\eta^3\text{-}CH_2C(CH_2)CHCHCMe_2\}Mo(CO)_2(\eta\text{-}C_5H_5)]$ identified by *X*-ray crystallography. In contrast, *trans*-penta-1,3-diene reacts *via* an alternative reaction path involving carbonyl 'insertion' to form $[Mo(CO)_2\{\eta^3\text{-}MeCH{=}CHCH{=}CHC(O)CH{\cdots}CH{\cdots}CMe_2\}(\eta\text{-}C_5H_5)]$. The corresponding reactions of alkynes have also been studied. The electronegatively substituted alkyne $MeO_2CC{\equiv}CCO_2Me$ forms $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}C(CO_2Me)C(CO_2Me)CHCH{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$, whereas but-2-yne leads to the crystallographically identified dinuclear species $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\mu\text{-}\eta^2:\eta^3\text{-}C(Me)C(Me)C(O)CHCHCMe_2\}Mo(CO)_2(\eta\text{-}C_5H_5)]$. Reaction with Bu^tC_2H or Pr^iC_2H leads to an unusual cyclisation reaction and the formation of $[Mo_2\{\mu\text{-}\eta^4\text{-}\overline{CMe_2CHCHCHC(R)C}O\}(CO)_2(\eta\text{-}C_5H_5)_2]$ (R = Bu^t or Pr^i). An *X*-ray crystallographic study of the Bu^t substituted complex established a dinuclear structure containing a $Mo_2(\eta\text{-}C_5H_5)_2$ core asymmetrically bridged by two carbonyl ligands and 2-t-butyl-6,6-dimethylcyclohexa-2,4-dienone. The Mo(1)–Mo(2) internuclear separation [2.524(1) Å] is consistent with the presence of a Mo≡Mo triple bond. The cyclohexa-2,4-dienone ligand is bonded asymmetrically to the Mo_2 core, and this is related to non-bonding interactions. The structures, bonding, and mechanisms of formation of these molecules are discussed.

It is thought[2,3] that μ-alkylidene species play an important role in the heterogeneous Fischer–Tropsch reduction of carbon monoxide, and as a result di- and tri-nuclear μ-alkylidene complexes have become the focus of attention in the belief that this could lead to a better understanding of the heterogeneous system and perhaps the development of homogeneous catalysts. In exploring the reaction chemistry of the related μ-allylidene species, and in particular complex $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (1),[1,4] it became clear that the allylidene fragment readily underwent thermally promoted hydrogen-shift processes, which could be explained by postulating the intermediacy of a co-ordinatively unsaturated μ-σ-vinylcarbene species. With a view to intercepting such intermediates the thermal reactions of (1) with 1,2-dienes, 1,3-dienes, and alkynes have been investigated. This paper describes the extension of our initial investigations, which were the subject of a preliminary publication.[5]

Results and Discussion

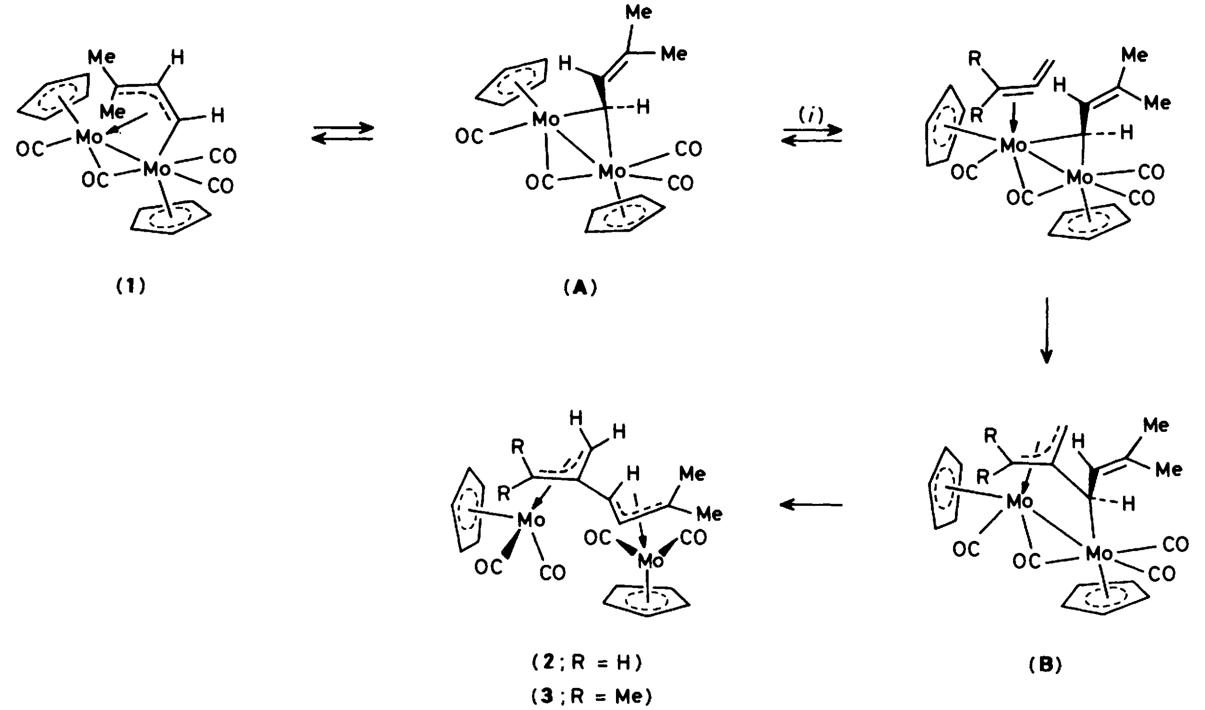
The red crystalline complex (1)[1] reacted smoothly at 50 °C in methylene chloride as solvent with propa-1,2-diene and 3-methylbuta-1,2-diene to afford respectively the air-stable yellow crystalline complexes (2) and (3) (see Scheme 1). Elemental analysis, m.s., i.r., and n.m.r. spectroscopy (see Experimental section) showed that these complexes were 1:1 adducts of the respective 1,2-diene and the μ-allylidene complex (1). Both the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra suggested that the reaction had resulted in the attachment of a $CHCHCMe_2$ fragment onto the central carbon atom of the 1,2-diene. Although such 'insertion' reactions of 1,2-dienes have been previously observed, and have been discussed from a theoretical standpoint,[6] the n.m.r. data did not unequivocally confirm the structures of (2) and (3). A single-crystal *X*-ray diffraction study of (2) established the solid-state structure illustrated in Figure 1; bond lengths and angles are listed in Table 1.

The reaction has resulted in the cleavage of the metal–metal bond, the Mo ··· Mo distance being 5.515(1) Å. The molecule is formally derived by insertion of propa-1,2-diene into the Mo–μ-C σ bond of (1) forming a C–C bond between the central carbon of the 1,2-diene and the bridging carbon atom of the μ-allylidene fragment. The bis-allyl ligand thus formed is bound *endo* η^3 to Mo(1) and *exo* η^3 to Mo(2), each molybdenum atom being further co-ordinated by a $\eta\text{-}C_5H_5$ and two carbonyl ligands. The propa-1,2-diene forms the *endo*-allyl fragment $CH_2CR'CH_2$ [R′ = $(CHCHCMe_2)Mo(CO)_2(\eta\text{-}C_5H_5)$] and shows unusual variation in Mo–C contact distances. In the majority of Mo^{II} η^3-allyl species Mo–C(central) is shorter than Mo–C(outer) [*cf.* complexes in refs. 7—14; Mo(2)–C distances in (2) and Mo–C in (6), see later], for the *endo* allyl in (2) the reverse is the case [Mo(1)–C(3) 2.290(3), Mo(1)–C(4) 2.325(3), Mo(1)–C(5) 2.318(3) Å; *cf.* Mo(2)–C(6) 2.356(2), Mo(2)–C(7) 2.238(3), Mo(2)–C(8) 2.428(2) Å]. On inspection of the established crystal structures it is clear that all Mo^{II} η^3-allyls

---

* μ-[5-Methyl-2-methylenehex-4-ene-1,3-diyl-$C^{1,2,2\alpha}$(Mo),C^{3-5}(Mo′)]-bis[dicarbonyl(η^5-cyclopentadienyl)molybdenum], μ-[4-t-butyl-6,6-dimethyl-5-oxocyclohex-3-ene-1,2-diyl-$C^{1,2}$(Mo),C^{2-4}(Mo′)]-di-μ-carbonyl-bis[(η^5-cyclopentadienyl)molybdenum](*Mo≡Mo*),and μ-[3,7-dimethyl-4-oxo-octa-2,6-diene-2,5-diyl-C^2(Mo),*O*(Mo),C^{5-7}(Mo′)]-bis[dicarbonyl(η^5-cyclopentadienyl)molybdenum] respectively.

Supplementary data available (No. SUP 56581, 8 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



(1)

(A)

(2; R = H)
(3; R = Me)

(B)

Scheme 1. (*i*) + 1,2-diene

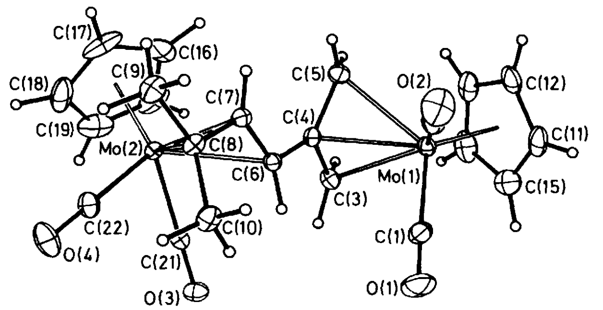


Figure 1. Molecular structure of (**2**) showing atom labelling scheme

having substituents at the central carbon adopt an *endo* conformation, as found in (**2**), while both *exo* and *endo* are observed for other substituent positions. For the *endo* allyls the Mo–C bond length variation is much less marked than for *exo* allyls. The preference for *endo* orientation of C(3)C(4)C(5) in (**2**) seems to be steric in origin since computer simulation of a plausible *exo* orientation [by rotation of 180° about the Mo–allyl bond and of 5° about the C(3)C(5) vector to bring Mo–C(4) to a typical value (2.270 Å)] leads to short C(6)–η-C_5H_5 contacts [C(6) ··· C(13) 3.313 Å]. Rotation about the C(3)C(5) axis in the *endo* orientation by 5° [giving Mo–C(4) 2.270 Å] leads to short C(6) ··· CO contacts [C(6) ··· C(1) 3.09, C(6) ··· C(2) 3.09 Å]. The propa-1,2-diene substitutes the C(6)–C(7)–C(8) allyl in the site *syn* to the central carbon substituent, the less sterically hindered site. As a consequence the hydrogens on C(6) and C(7) are *trans* in (**2**) having been *cis* in (**1**) and implying rotation about the C(6)–C(7) bond in the course of formation of (**2**). The C–C distances in the two η^3-allyl moieties lie in the usual range [1.405(5)—1.423(4) Å], while the bond linking them C(4)–C(6) [1.489(4) Å] is relatively short. This is presumably a consequence of some overlap between the π systems of the allyls, as is allowed by the small dihedral angle between them (9.2°). Retrospective analysis of the n.m.r. data (see Experimental section) confirmed that (**2**) adopts the same structure in solution, and also showed that (**3**) had an analogous structure as is shown in Scheme 1.

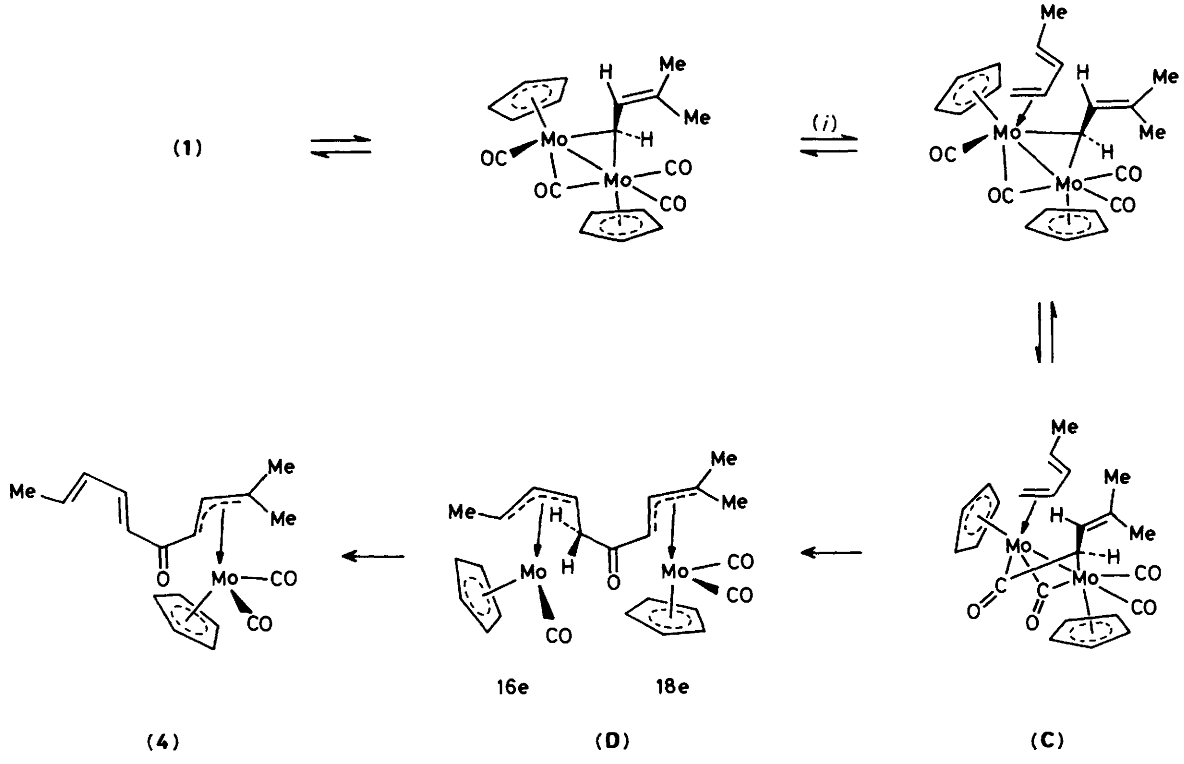
Related reactions of propa-1,2-diene with Pd^{II} halides,[15] $[Fe_2(CO)_9]$,[16] $[Fe_3(CO)_{12}]$,[17] $[Pd_2(\mu\text{-}Br)(\mu\text{-}C_5H_5)(PPr^i{}_3)_2]$,[18] and $[Ru_2(\mu\text{-}CO)\{\mu\text{-}C(O)C(Ph)C(Ph)\}(CO)(\eta\text{-}C_5H_5)_2]$[19] have been reported, where addition to the central carbon of the 1,2-diene occurs. In the case of the formation of (**2**) and (**3**) our previous study[1] of the rearrangements of the μ-allylidene complex (**1**) suggests that the thermally generated co-ordinatively unsaturated μ-vinylcarbene species (**A**) (Scheme 1) is captured by the 1,2-diene, which in the case of the 3-methylbuta-1,2-diene reaction would be expected to orientate itself *via* rotation about an axis passing through the metal and perpendicular to the 1,2-diene C–C bond, so as to place the substituted end of the 1,2-diene away from the two dimethyl groups of the μ-CHCHCMe$_2$ fragment. Migratory insertion of the μ-vinylalkylidene onto the central carbon of the co-ordinated 1,2-diene with retention[20] of the carbon configuration would then generate (**B**), where the dimethyl-substituted vinyl group is not co-ordinated. In order to allow the formation of the second η^3-allyl group the molybdenum–molybdenum bond then breaks in concert with the transformation of the μ-CO ligand to a terminal bonding mode. As is illustrated this sequence of reactions places the ligands in the correct position so as to achieve an *exo*- and *endo*-η^3-allyl conformation as was established by the crystallographic study.

The 1,3-diene *trans*-penta-1,3-diene also reacts thermally with $[Mo_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**) forming an orange-yellow crystalline complex (**4**); however, elemental analysis and m.s. suggested the molecule was mononuclear, and in addition the i.r. spectrum showed bands corresponding to the presence of terminal carbonyl ligands and a α,β-unsaturated ketone. Examination of the $^{13}C\text{-}\{^1H\}$ n.m.r. and partially ^1H-decoupled ^{13}C spectra showed signals corresponding to three methyl groups, two co-ordinated CH=C groups, four

Table 1. Bond lengths (Å) and angles (°) for (**2**)

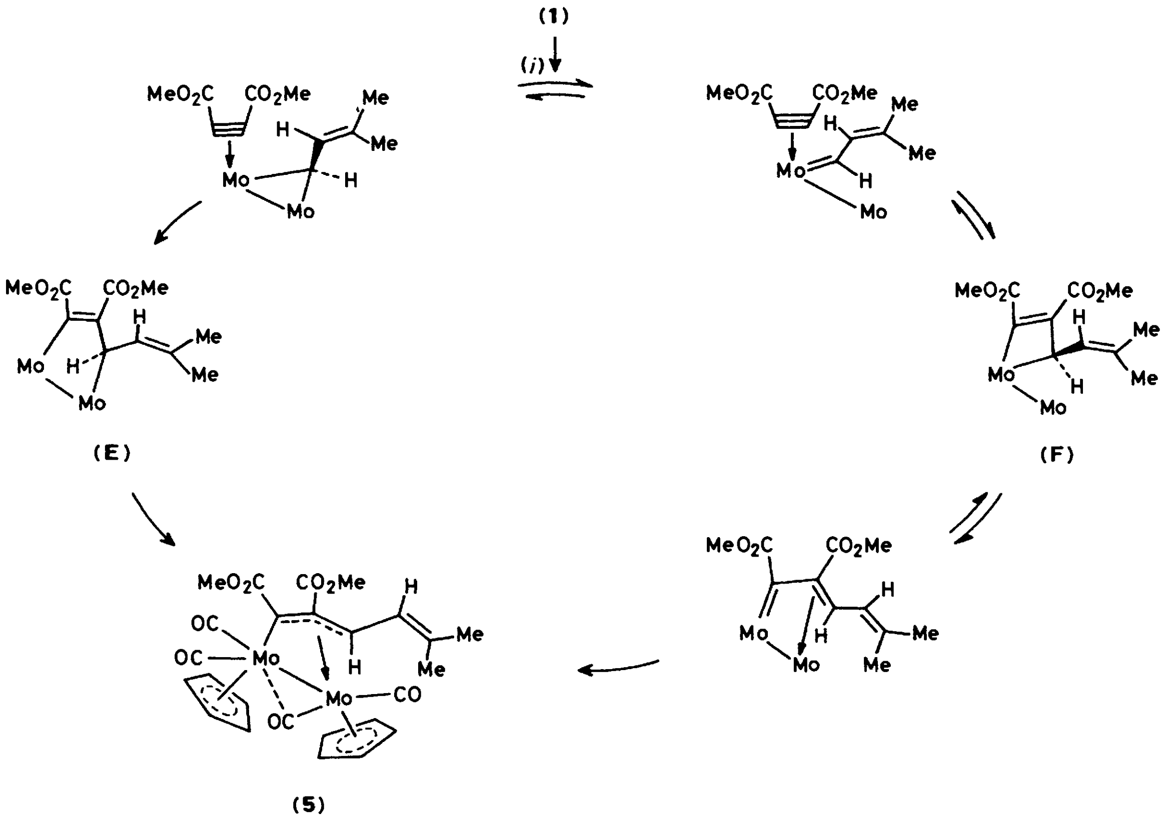
Mo(1)–C(1)	1.952(4)	Mo(1)–C(2)	1.969(3)	C(3)–H(3a)	0.959(32)	C(3)–H(3b)	0.947(35)
Mo(1)–C(3)	2.290(3)	Mo(1)–C(4)	2.325(3)	C(3)–C(4)	1.414(4)	C(4)–C(5)	1.405(5)
Mo(1)–C(5)	2.318(3)	Mo(1)–C(11)	2.302(4)	C(4)–C(6)	1.489(4)	C(5)–H(5a)	0.954(29)
Mo(1)–C(12)	2.318(4)	Mo(1)–C(13)	2.381(5)	C(5)–H(5b)	0.959(32)	C(6)–H(6)	0.964(26)
Mo(1)–C(14)	2.392(5)	Mo(1)–C(15)	2.325(4)	C(6)–C(7)	1.423(4)	C(7)–H(7)	0.903(26)
Mo(2)–C(6)	2.356(2)	Mo(2)–C(7)	2.238(3)	C(7)–C(8)	1.410(4)	C(8)–C(9)	1.517(4)
Mo(2)–C(8)	2.428(2)	Mo(2)–C(16)	2.365(4)	C(8)–C(10)	1.517(4)	C(11)–C(12)	1.406(6)
Mo(2)–C(17)	2.370(3)	Mo(2)–C(18)	2.336(4)	C(11)–C(15)	1.404(6)	C(12)–C(13)	1.392(5)
Mo(2)–C(19)	2.318(4)	Mo(2)–C(20)	2.340(3)	C(13)–C(14)	1.367(7)	C(14)–C(15)	1.424(6)
Mo(2)–C(21)	1.936(3)	Mo(2)–C(22)	1.948(4)	C(16)–C(17)	1.394(7)	C(16)–C(20)	1.369(7)
O(1)–C(1)	1.152(5)	O(2)–C(2)	1.141(4)	C(17)–C(18)	1.367(8)	C(18)–C(19)	1.355(8)
O(3)–C(21)	1.165(4)	O(4)–C(22)	1.156(5)	C(19)–C(20)	1.331(7)		

C(1)–Mo(1)–C(2)	77.1(2)	C(1)–Mo(1)–C(3)	81.4(1)	Mo(1)–C(4)–C(6)	120.2(2)	C(3)–C(4)–C(6)	120.2(3)
C(2)–Mo(1)–C(3)	119.5(1)	C(1)–Mo(1)–C(4)	88.3(1)	C(5)–C(4)–C(6)	124.1(2)	Mo(1)–C(5)–C(4)	72.6(2)
C(2)–Mo(1)–C(4)	87.6(1)	C(3)–Mo(1)–C(4)	35.7(1)	Mo(1)–C(5)–H(5a)	103.2(15)	C(4)–C(5)–H(5a)	118.9(18)
C(1)–Mo(1)–C(5)	120.3(1)	C(2)–Mo(1)–C(5)	81.9(1)	Mo(1)–C(5)–H(5b)	123.3(18)	C(4)–C(5)–H(5b)	121.7(25)
C(3)–Mo(1)–C(5)	62.3(1)	C(4)–Mo(1)–C(5)	35.2(1)	H(5a)–C(5)–H(5b)	111.0(28)	Mo(2)–C(6)–C(4)	114.2(1)
C(6)–Mo(2)–C(8)	62.0(1)	C(6)–Mo(2)–C(7)	36.0(1)	Mo(2)–C(6)–H(6)	107.2(15)	C(4)–C(6)–H(6)	112.7(15)
C(6)–Mo(2)–C(21)	72.5(1)	C(7)–Mo(2)–C(8)	34.9(1)	Mo(2)–C(6)–C(7)	67.5(1)	C(4)–C(6)–C(7)	123.5(3)
C(8)–Mo(2)–C(21)	102.1(1)	C(7)–Mo(2)–C(21)	102.9(1)	H(6)–C(6)–C(7)	120.5(14)	Mo(2)–C(7)–C(6)	76.5(1)
C(21)–Mo(2)–C(22)	79.7(1)	Mo(1)–C(1)–O(1)	117.0(3)	Mo(2)–C(7)–H(7)	107.3(13)	C(6)–C(7)–H(7)	119.7(15)
Mo(1)–C(2)–O(2)	177.5(4)	Mo(1)–C(3)–H(3a)	118.4(14)	Mo(2)–C(7)–C(8)	80.0(2)	C(6)–C(7)–C(8)	120.9(3)
Mo(1)–C(3)–H(3b)	100.9(19)	H(3a)–C(3)–H(3b)	118.3(26)	H(7)–C(7)–C(8)	118.9(15)	Mo(2)–C(8)–C(7)	66.2(1)
Mo(1)–C(3)–C(4)	73.5(2)	H(3a)–C(3)–C(4)	118.7(17)	Mo(2)–C(8)–C(9)	116.2(2)	C(7)–C(8)–C(9)	117.9(3)
H(3b)–C(3)–C(4)	117.4(20)	Mo(1)–C(4)–C(3)	70.8(2)	Mo(2)–C(8)–C(10)	115.2(2)	C(7)–C(8)–C(10)	120.8(2)
Mo(1)–C(4)–C(5)	72.1(2)	C(3)–C(4)–C(5)	115.3(3)	Mo(2)–C(21)–O(3)	178.9(2)	Mo(2)–C(22)–O(4)	177.7(3)



Scheme 2. (*i*) + *trans*-penta-1,3-diene

unco-ordinated CH=C groups, an organic carbonyl carbon, a quaternary carbon as well as two terminal carbonyls, and a cyclopentadienyl group which are consistent with η^3-allylic structure illustrated in Scheme 2. This structural formulation was further supported by the ^{1}H spectrum, which showed resonances corresponding to a dimethyl-substituted η^3-allylic fragment carrying an acyldienyl group. Clearly the formation of (**4**) is related to the 1,2-diene reactions, but a carbonyl 'insertion' reaction is intervening. In a similar manner to the 1,2-diene reactions it is likely that the thermally generated μ-vinylcarbene intermediate is captured by the *trans*-penta-1,3-diene *via* co-ordination of the 1,3-diene by the unsubstituted double bond



Scheme 3. (*i*) + $C_2(CO_2Me)_2$

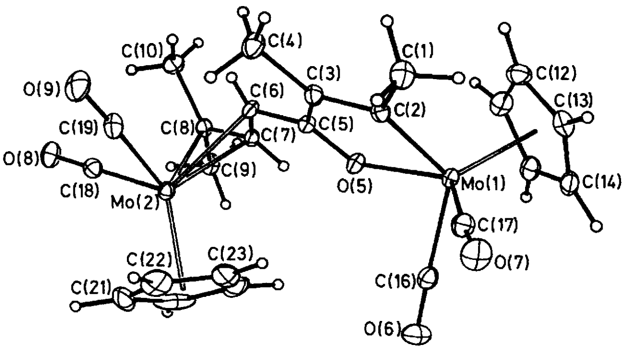


Figure 2. Molecular structure of (**6**) showing atom labelling scheme

(Scheme 2). However, migratory insertion of the μ-vinylcarbene onto co-ordinated carbon monoxide intercepts the intermediate resulting in the formation of the illustrated bridging acyl system (**C**) (Scheme 2). Since it is known that acyl groups bonded to Mo[21] and Mn[22] can migrate onto a co-ordinated 1,3-diene, rearrangement of (**C**) into (**D**) is then a plausible next step; cleavage of the metal–metal bond generating the 16-electron molybdenum centre needed for a β-elimination reaction which leads to (**4**). In the 1,3-diene reaction it is evident that competitive CO 'insertion' is preferred to alkyl migration of the μ-vinylcarbene onto the co-ordinated diene. This is in contrast with the 1,2-diene reactions where CO 'insertion' does not intervene.

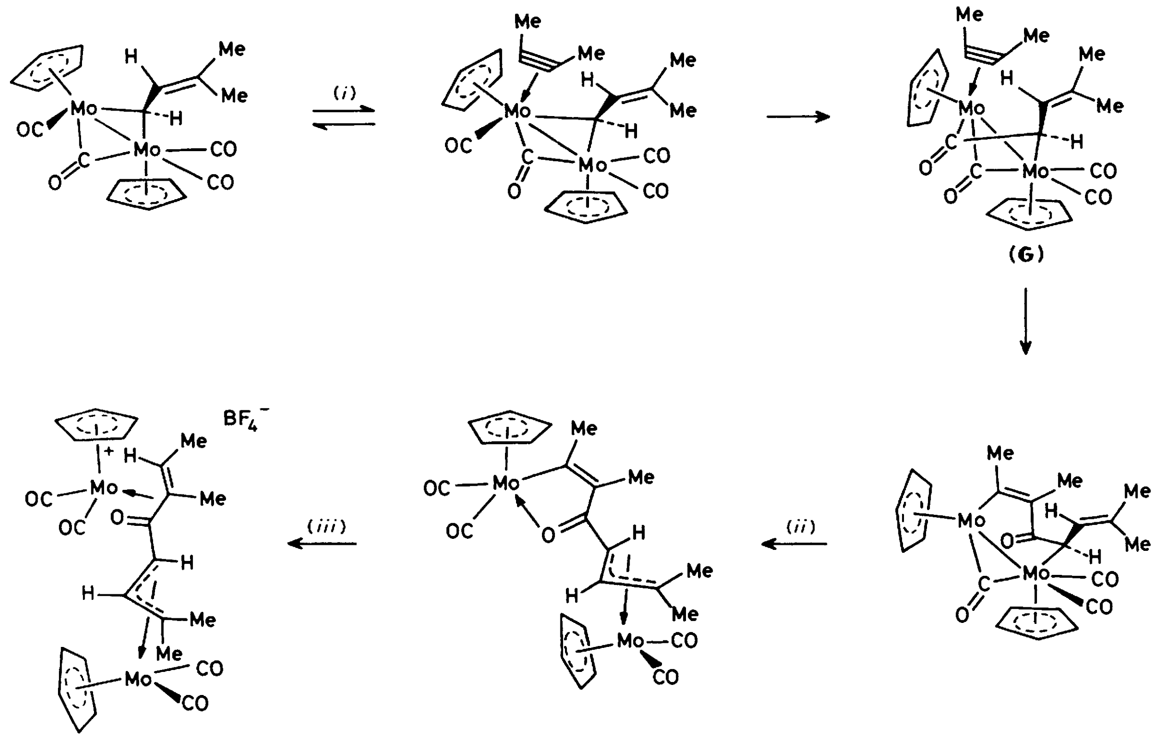
In the case of the corresponding reactions of alkynes competition between reaction pathways is controlled by the nature of the alkyne substituents. Thermal reaction (50 °C) of (**1**) with the electronegatively substituted alkyne $MeO_2CC{\equiv}CCO_2Me$ afforded a moderate yield of a single red crystalline complex (**5**). Elemental analysis and m.s. showed that (**5**) was a 1 : 1 adduct of the reactants. The absence of a characteristic low-field signal in the ^1H n.m.r. spectrum indicated that the original μ-$CHCHCMe_2$ ligand was no longer directly attached to a molybdenum atom. The ^1H spectrum displayed inequivalent η^5-C_5H_5 resonances at 5.28 and 5.19 p.p.m., and the former μ-allylidene methine hydrogens now resonated at 2.80 and 5.2 p.p.m. [*J*(HH) 12 Hz]. The magnitude of the coupling constant indicated that these hydrogens were mutually *trans*. These observations together with the ^{13}C-$\{^1H\}$ n.m.r. data suggested that (**5**) is a vinyl substituted μ-allylidene as is shown in Scheme 3. This type of reaction has been observed previously in Fe_2,[23] Ru_2,[24] and W_2[25] chemistry. The formation of (**5**) can be explained if it is assumed that an unsaturated μ-vinylcarbene complex is again intercepted by a molecule of $MeO_2CC{\equiv}CCO_2Me$. However, unlike the related 1,3-diene reaction a carbonyl 'insertion' reaction does not occur, instead the alkyne formally inserts into a bridging saturated carbon σ bond.

There are two distinct pathways by which this could be achieved. The first involves migration of the μ-vinylcarbene with retention of configuration onto the co-ordinated $MeO_2CC{\equiv}CCO_2Me$ to give (**E**) (Scheme 3). Although such reactions, *i.e.* migration of alkyl groups onto co-ordinated alkynes, are relatively rare,[26,27] it is possible that co-ordination of the developing vinyl group onto the second molybdenum centre provides assistance for the reaction. Alternatively, the μ-vinylcarbene could transform into a vinylcarbene terminally bonded to the molybdenum atom carrying the co-ordinated $MeO_2CC{\equiv}CCO_2Me$. Molybdenacyclobutene (**F**) formation followed by ring-opening could then access a 1,3-diene substituted

Table 2. Bond lengths (Å) and angles (°) for (**6**)

Mo(1)–O(5)	2.132(3)	Mo(1)–C(2)	2.158(4)	C(2)–C(1)	1.521(5)	C(2)–C(3)	1.378(6)
Mo(1)–C(11)	2.404(5)	Mo(1)–C(12)	2.371(5)	C(3)–C(4)	1.530(6)	C(3)–C(5)	1.420(5)
Mo(1)–C(13)	2.318(4)	Mo(1)–C(14)	2.293(5)	C(5)–C(6)	1.481(6)	C(6)–H(6)	0.742(35)
Mo(1)–C(15)	2.356(4)	Mo(1)–C(16)	2.008(5)	C(6)–C(7)	1.409(5)	C(7)–H(7)	0.896(37)
Mo(1)–C(17)	1.969(5)	Mo(2)–C(6)	2.349(4)	C(7)–C(8)	1.411(6)	C(8)–C(9)	1.515(5)
Mo(2)–C(7)	2.239(4)	Mo(2)–C(8)	2.463(4)	C(8)–C(10)	1.510(7)	C(11)–C(12)	1.405(6)
Mo(2)–C(18)	1.971(4)	Mo(2)–C(19)	1.954(4)	C(11)–C(15)	1.416(7)	C(12)–C(13)	1.413(8)
Mo(2)–C(20)	2.337(7)	Mo(2)–C(21)	2.318(7)	C(13)–C(14)	1.411(6)	C(14)–C(15)	1.433(7)
Mo(2)–C(22)	2.357(7)	Mo(2)–C(23)	2.263(7)	C(20)–C(21)	1.437(9)	C(20)–C(24)	1.398(9)
Mo(2)–C(24)	2.364(6)	O(5)–C(5)	1.286(4)	C(21)–C(22)	1.349(9)	C(22)–C(23)	1.347(9)
O(6)–C(16)	1.152(6)	O(7)–C(17)	1.149(6)	C(23)–C(24)	1.353(8)		
O(8)–C(18)	1.151(6)	O(9)–C(19)	1.165(5)				

O(5)–Mo(1)–C(2)	73.6(1)	O(5)–Mo(1)–C(16)	80.2(2)	C(2)–C(3)–C(5)	113.9(3)	C(4)–C(3)–C(5)	121.5(4)
C(2)–Mo(1)–C(16)	122.6(2)	C(16)–Mo(1)–C(17)	79.9(2)	O(5)–C(5)–C(3)	117.2(4)	O(5)–C(5)–C(6)	117.8(3)
O(5)–Mo(1)–C(17)	126.7(1)	C(2)–Mo(1)–C(17)	76.7(2)	C(3)–C(5)–C(6)	125.0(3)	Mo(2)–C(6)–C(5)	117.1(3)
C(6)–Mo(2)–C(7)	35.7(1)	C(6)–Mo(2)–C(8)	62.3(1)	Mo(2)–C(6)–H(6)	105.5(26)	C(5)–C(6)–H(6)	112.4(25)
C(7)–Mo(2)–C(8)	34.5(1)	C(6)–Mo(2)–C(18)	118.4(2)	Mo(2)–C(6)–C(7)	67.9(2)	C(5)–C(6)–C(7)	120.2(3)
C(7)–Mo(2)–C(18)	103.7(2)	C(8)–Mo(2)–C(18)	69.5(2)	H(6)–C(6)–C(7)	123.6(26)	Mo(2)–C(7)–C(6)	76.4(2)
C(6)–Mo(2)–C(19)	79.3(2)	C(7)–Mo(2)–C(19)	108.0(2)	Mo(2)–C(7)–H(7)	109.4(24)	C(6)–C(7)–H(7)	117.6(22)
C(8)–Mo(2)–C(19)	104.7(2)	C(18)–Mo(2)–C(19)	78.2(2)	Mo(2)–C(7)–C(8)	81.4(2)	C(6)–C(7)–C(8)	124.0(3)
Mo(1)–O(5)–C(5)	118.8(2)	Mo(1)–C(2)–C(1)	124.9(3)	H(7)–C(7)–C(8)	118.2(22)	Mo(2)–C(8)–C(7)	64.0(2)
Mo(1)–C(2)–C(3)	116.1(3)	C(1)–C(2)–C(3)	118.7(4)	Mo(2)–C(8)–C(9)	115.2(3)	C(7)–C(8)–C(9)	117.7(4)
C(2)–C(3)–C(4)	124.6(3)			Mo(2)–C(8)–C(10)	115.7(3)	C(7)–C(8)–C(10)	121.0(3)



(**G**)

(**7**)

(**6**)

Scheme 4. (*i*) +MeC$_2$Me; (*ii*) +CO; (*iii*) HBF$_4$·Et$_2$O

terminally bonded carbene, which transforms *via* carbon monoxide migration into (**5**). In principle this is a viable alternative reaction pathway since there is evidence[28–31] in dinuclear chemistry that μ-carbene ligands can readily transform into terminally-bonded carbenes. In addition the terminally bonded vinylcarbene could also be captured by a 1,2-diene thus providing an alternative explanation for the formation of (**2**) and (**3**). However, an objection to the idea that these reactions are taking place with a terminally-bonded carbene species is that it does not accommodate the apparent competitive formation of the carbonyl 'insertion' product (**4**) obtained in the 1,3-diene reaction. This difficulty was further underlined when the reactions of (**1**) with other alkynes were explored.

Table 3. Bond lengths (Å) and angles (°) for **(9)**·CH_2Cl_2

Mo(1)–Mo(2)	2.524(1)	Mo(1)–C(1)	1.951(4)	C(6)–C(5)	1.533(8)	C(6)–C(7)	1.559(8)
Mo(1)–C(7)	2.396(4)	Mo(1)–C(8)	2.222(4)	C(7)–C(8)	1.439(5)	C(7)–C(14)	1.498(6)
Mo(1)–C(9)	2.530(4)	Mo(1)–C(15)	2.300(8)	C(8)–H(8)	1.011(35)	C(8)–C(9)	1.428(7)
Mo(1)–C(16)	2.318(11)	Mo(1)–C(17)	2.405(9)	C(9)–H(9)	0.930(47)	C(9)–C(10)	1.420(6)
Mo(1)–C(18)	2.394(12)	Mo(1)–C(19)	2.311(10)	C(10)–H(10)	0.966(77)	C(10)–C(11)	1.527(6)
Mo(2)–C(1)	2.335(5)	Mo(2)–C(2)	1.918(6)	C(11)–C(12)	1.527(7)	C(11)–C(13)	1.542(7)
Mo(2)–C(9)	2.535(4)	Mo(2)–C(10)	2.233(5)	C(11)–C(14)	1.542(8)	C(15)–C(16)	1.428(13)
Mo(2)–C(20)	2.391(9)	Mo(2)–C(21)	2.347(9)	C(15)–C(19)	1.332(17)	C(16)–C(17)	1.382(17)
Mo(2)–C(22)	2.305(9)	Mo(2)–C(23)	2.298(7)	C(17)–C(18)	1.358(14)	C(18)–C(19)	1.367(12)
Mo(2)–C(24)	2.369(6)	Cl(1)–C	1.734(9)	C(20)–C(21)	1.394(10)	C(20)–C(24)	1.402(11)
Cl(2)–C	1.733(10)	O(1)–C(1)	1.178(5)	C(21)–C(22)	1.437(12)	C(22)–C(23)	1.408(10)
O(2)–C(2)	1.152(8)	O(3)–C(14)	1.208(4)	C(23)–C(24)	1.411(10)		
C(6)–C(3)	1.537(8)	C(6)–C(4)	1.542(8)				
Mo(2)–Mo(1)–C(1)	61.3(2)	Mo(2)–Mo(1)–C(7)	98.9(1)	C(6)–C(7)–C(14)	115.1(3)	C(8)–C(7)–C(14)	116.2(4)
C(1)–Mo(1)–C(7)	86.1(1)	Mo(2)–Mo(1)–C(8)	92.3(1)	Mo(1)–C(8)–C(7)	78.6(2)	Mo(1)–C(8)–H(8)	110.3(22)
C(1)–Mo(1)–C(8)	113.9(1)	C(7)–Mo(1)–C(8)	36.1(1)	C(7)–C(8)–H(8)	119.8(22)	Mo(1)–C(8)–C(9)	84.8(3)
Mo(2)–Mo(1)–C(9)	60.2(1)	C(1)–Mo(1)–C(9)	103.6(2)	C(7)–C(8)–C(9)	119.3(3)	H(8)–C(8)–C(9)	120.8(22)
C(7)–Mo(1)–C(9)	60.2(1)	C(8)–Mo(1)–C(9)	34.2(2)	Mo(1)–C(9)–Mo(2)	59.8(1)	Mo(1)–C(9)–C(8)	61.0(2)
Mo(1)–Mo(2)–C(2)	71.9(3)	Mo(1)–Mo(2)–C(1)	47.2(1)	Mo(2)–C(9)–C(8)	117.1(3)	Mo(1)–C(9)–H(9)	107.8(35)
Mo(1)–Mo(2)–C(9)	60.0(1)	C(1)–Mo(2)–C(2)	112.6(3)	Mo(2)–C(9)–H(9)	101.8(33)	C(8)–C(9)–H(9)	114.6(38)
C(2)–Mo(2)–C(9)	75.1(2)	C(1)–Mo(2)–C(9)	93.2(1)	Mo(1)–C(9)–C(10)	108.4(3)	Mo(2)–C(9)–C(10)	61.3(3)
C(1)–Mo(2)–C(10)	99.4(2)	Mo(1)–Mo(2)–C(10)	86.6(1)	C(8)–C(9)–C(10)	123.6(3)	H(9)–C(9)–C(10)	120.8(38)
C(9)–Mo(2)–C(10)	33.9(2)	C(2)–Mo(2)–C(10)	103.3(2)	Mo(2)–C(10)–C(9)	84.8(3)	Mo(2)–C(10)–H(10)	115.1(46)
Cl(1)–C–Cl(2)	113.3(4)	Mo(1)–C(1)–Mo(2)	71.5(1)	C(9)–C(10)–H(10)	115.2(35)	Mo(2)–C(10)–C(11)	117.8(3)
Mo(1)–C(1)–O(1)	163.2(5)	Mo(2)–C(1)–O(1)	125.2(4)	C(9)–C(10)–C(11)	114.3(4)	H(10)–C(10)–C(11)	108.3(39)
Mo(2)–C(2)–O(2)	168.4(7)	C(3)–C(6)–C(7)	112.1(5)	C(10)–C(11)–C(12)	112.8(5)	C(10)–C(11)–C(13)	107.5(4)
C(4)–C(6)–C(7)	108.1(5)	C(5)–C(6)–C(7)	113.0(4)	C(10)–C(11)–C(14)	110.4(4)	C(12)–C(11)–C(14)	109.8(4)
Mo(1)–C(7)–C(6)	124.9(3)	Mo(1)–C(7)–C(8)	65.3(2)	C(13)–C(11)–C(14)	107.6(5)	O(3)–C(14)–C(7)	122.4(4)
C(6)–C(7)–C(8)	120.0(3)	Mo(1)–C(7)–C(14)	105.9(3)	O(3)–C(14)–C(11)	119.4(4)	C(7)–C(14)–C(11)	117.5(3)

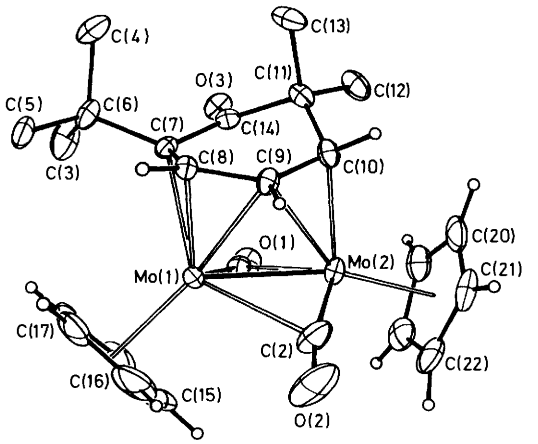


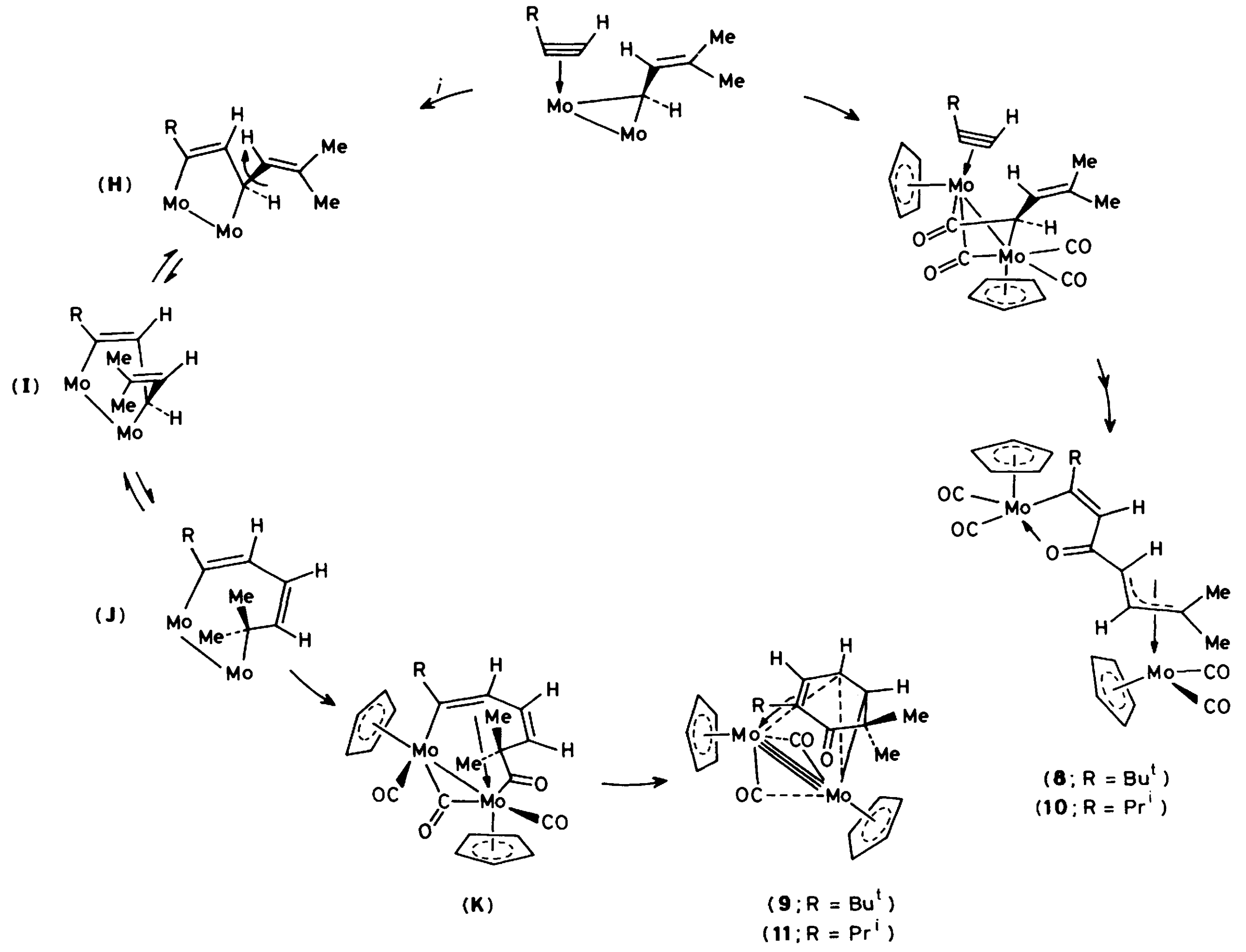
Figure 3. Molecular structure of **(9)** showing atom labelling scheme

Treatment of **(1)** with an excess of but-2-yne gave on chromatographic work-up a red crystalline complex **(6)**, which could not be positively identified by i.r. and n.m.r. spectroscopy. A single-crystal *X*-ray diffraction study was therefore carried out resulting in the establishment of the structure shown in Figure 2, bond lengths and angles being listed in Table 2.

The Mo–Mo bond present in **(1)** is broken on formation of **(6)** [Mo(1) ··· Mo(2) 5.809(2) Å]. Each molybdenum carries an η-C_5H_5 and two carbonyl ligands, the two molybdenum centres being linked by an organic ligand derived from the CHCHCMe$_2$ ligand, one carbon monoxide and one but-2-yne molecule, which acts as an η^2-vinylketone to Mo(1), and as an *exo*-η^3-allyl ligand to Mo(2). The molecular parameters of the vinylketone ligand, which is bonded in a *syn* position of the *exo* η^3-allyl, are similar to those reported for related structurally characterised species. In particular the Mo(1)–C(2) distance of 2.158(4) Å lies between that expected for molybdenum to carbon single and double bonds indicating a contribution from an oxyalkylidene canonical form as discussed[13] for $[\overline{\text{Mo}\{\text{CMeCMeC(CMe=CHMe)O}}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$. The two hydrogen substituents at C(6) and C(7), which adopt a relative *cis* configuration in the μ-allylidene ligand of **(1)**, have a relative *trans* geometry in the allyl fragment of **(6)**. In **(6)** the central allyl carbon atom C(7) is more tightly bonded to the molybdenum than the two outer carbons C(6) and C(8) [Mo(2)–C(6) 2.349(4), Mo(2)–C(7) 2.239(4), Mo(2)–C(8) 2.463(4) Å]. As discussed above this is typical of Mo^{II} *exo*-η^3-allyl species, as in **(2)** the doubly methyl substituted carbon [C(8)] has the longest Mo–C contact distance. The C(5)–C(6) bond which links the vinylketone and allyl moieties is relatively short [1.481(6) Å] indicating some delocalisation of the π systems of the two parts of the ligand, the dihedral angle between the C(6)C(7)C(8) and C(2)C(3)C(5)O(5) planes is 3.6° [Mo(1) lies 0.07 Å from the latter plane]. As in **(2)**, the large allyl substituent in **(6)** formed by formal insertion into the M–μ-C σ bond of **(1)** occupies the sterically undemanding *syn* site.

It is also interesting that protonation ($HBF_4{\cdot}Et_2O$) of **(6)** affords an orange crystalline complex **(7)**, which on the basis of elemental analysis, i.r., and n.m.r. is assigned the structure illustrated in Scheme 4. The proton has selectively attacked the α-carbon atom of the vinylketone ligand rather than the η^3-allyl system thus generating a cationic η^4-vinylketone complex.

If we assume that as in the reaction with $MeO_2CC{\equiv}CCO_2Me$ an unsaturated μ-vinylcarbene intermediate is captured by an alkyne, then the formation of **(6)** can be explained if the μ-vinylcarbene competitively migrates onto CO rather than onto co-ordinated but-2-yne. The resultant intermediate [**(G)** in Scheme 4] carries an acyl group and a but-2-yne both bonded to one molybdenum centre, and is set up to form the vinylketone ligand



Scheme 5. Ligands omitted for clarity

by migration of the acyl onto the but-2-yne. Simple reaction with one molecule of carbon monoxide and metal–metal bond cleavage then affords (**6**) with the correct stereochemistry.

The corresponding reactions of (**1**) with the unsymmetrical alkynes 3,3-dimethylbut-1-yne and 3-methylbut-1-yne are also interesting and serve to underline the delicate balance of the factors controlling access to the different reaction pathways available to these systems. Reactions with 3,3-dimethylbut-1-yne afforded two products (**8**) and (**9**), which were readily separated by column chromatography. Examination of the i.r., ^{1}H and ^{13}C n.m.r. spectra (see Experimental section) showed that the red crystalline complex (**8**) was an analogue of (**6**), where the sterically demanding Bu^t group preferentially resides on the α-carbon atom of the vinylketone fragment. The second compound (**9**) eluted from the column was obtained as green crystals, and showed i.r. bands at 1 803, 1 705, and 1 595 cm^{-1}, which are different from those exhibited by (**6**) and (**8**). The ^{1}H spectrum showed, as well as methyl and Bu^t singlets, inequivalent cyclopentadienyl resonances, and multiplets at 4.13, 4.33, and 5.20 p.p.m. forming an ABX spin system [^4J(AX) -0.75, ^3J(AB) 7.25, ^3J(BX) 6.31 Hz] reminiscent of an allylic type group possessing three adjacent methine units. The structure of (**9**) was not readily discernible from the spectroscopic data, therefore, it was subjected to an *X*-ray crystal-structure determination. The structure is shown in Figure 3, and bond lengths and angles are listed in Table 3.

The molecule consists of a $Mo_2(\eta\text{-}C_5H_5)_2$ core asymmetrically bridged by two carbonyl ligands and 2-t-butyl-6,6-dimethylcyclohexa-2,4-dienone. The Mo(1)–Mo(2) [2.524(1) Å] internuclear separation is consistent with the presence of a formal metal–metal triple bond.[32] Both of the carbonyl ligands show a degree of semi-bridging character displaying significant deviation from linearity [Mo(1)–C(1)–O(1) 163.2(5), Mo(2)–C(2)–O(2) 168.4(7)°], the distances to the metals being highly asymmetric [Mo(1)–C(1) 1.951(4), Mo(2)–C(1) 2.335(5), Mo(1)–C(2) 2.754(5), and Mo(2)–C(2) 1.918(6) Å]. The cyclohexa-2,4-dienone ligand is also bonded asymmetrically to the Mo_2 core. In contrast with the molecule $[Rh_2(\mu\text{-}CO)(\mu\text{-}C_6H_8)(\eta^5\text{-}C_9H_7)_2]$[33] where the metal atoms each bond to just two of the diene carbons such that two distinct metal–alkene interactions may be identified, in (**9**) one of the diene carbon atoms C(9) is equidistant from Mo(1) and Mo(2) [at 2.530(4) and 2.535(4) Å] and is formally five-co-ordinate. Considerable delocalisation is found over the four-carbon 1,3-diene unit, as the C–C bond lengths show little variation [C(7)–C(8) 1.439(5), C(8)–C(9) 1.428(7), and C(9)–C(10) 1.420(6) Å]. The greater share of the metal diene bonding involves Mo(1), which is bound to C(7) and C(8) at distances of 2.396(4) and 2.222(4) Å respectively. Mo(2) is bonded to C(10) at a distance of 2.233(5) Å.

The origin of the asymmetry in the diene bonding is possibly a result of non-bonding interactions. The bulky Bu^t substituent on C(7) may prevent the attainment of the diene geometry observed in the Rh$_2$ complex, in which the central C–C bond lies parallel to the metal–metal vector. In **(9)**, this orientation would lead to interactions between the hydrogen atoms on C(5) of the Bu^t group and C(17) of the cyclopentadienyl ring bound to Mo(1). In order to avoid this non-bonding interaction the central C(8)–C(9) bond of the diene is rotated by 19.4° relative to the Mo–Mo vector in a plane parallel to the metals. The effect of this is to 'tip' the diene towards Mo(1) and away from Mo(2). Computer simulation of this distortion indicates that it is accompanied by slippage of the diene parallel to the Mo(1)–Mo(2) vector towards Mo(1). Thus rotating the diene to bring C(8)–C(9) parallel to Mo(1)–Mo(2) leads to Mo(1) ··· C(9) 2.64 but Mo(2) ··· C(8) 3.37 Å; the importance of the steric factors outlined above is emphasised by the short Bu^t ··· (η-C$_5$H$_5$) contacts generated by this movement [C(18) ··· C(3) 2.91, C(17) ··· C(5) 3.17 Å, *cf.* 3.66 and 3.54 Å in the actual structure]. The diene shows some small deviations from planarity, with the C(7)–C(8)–C(9)–C(10) torsion angle 19.8°: deviations from the least-squares plane through the contact carbons are C(7) −0.038, C(8) +0.081, C(9) −0.084, C(10) + 0.041, Mo(1) −2.124, Mo(2) −2.187, C(14) + 0.107, O(3) −0.043, and C(11) + 0.674 Å. Thus, the ketone function lies close to the diene plane allowing some overlap of their π systems [C(7)–C(14) 1.498(6), *cf.* C(11)–C(14) 1.542(8) Å].

The corresponding reaction of **(1)** with 3-methylbut-1-yne gave two products **(10)** and **(11)**, which were identified by comparison of the i.r. and n.m.r. parameters (see Experimental section) as analogues of **(8)** and **(9)** respectively.

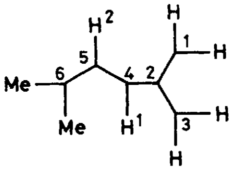
The formation of **(8)** and **(10)** can be understood in terms of the reaction pathway outlined for the formation of **(6)**. However, the cyclisation reaction, which leads to **(9)** and **(11)**, is clearly more complex. If we assume that the initial step is the same as postulated for the formation of **(5)**, *i.e.* co-ordination of the alkyne onto a μ-σ-vinylcarbene followed by migratory insertion, then access can be gained to the intermediate **(H)** (Scheme 5), where the bulky Bu^t or Pr^i substituent is preferentially orientated away from the CH=CMe$_2$ group of the μ-vinylcarbene. In the case of the bis(carboxymethoxy) system the corresponding intermediate collapses to form **(5)**, however, if **(H)** has sufficient lifetime to allow rotation about the carbon–carbon single bond then the required *all-cis* stereochemistry of the CH–CH–CH fragment can be achieved in **(I)**, and a simple σ-π-σ rearrangement of the allyl group gives the dimetallacycloheptadiene **(J)**. Migration of the dimethylvinyl substituted carbon onto a co-ordinated carbon monoxide then leads to formation of the acyl complex **(K)** where there would be expected to be sufficient conformational flexibility in the C$_6$ chain to allow co-ordination of the Mo–C(R)=CH vinyl group onto the molybdenum centre carrying the acyl substituent. It is known[21,22] that acyl groups readily migrate onto co-ordinated alkenes, and therefore, the ring-closure step **(K)** to **(9)** or **(11)** can be seen as an example of this type of reaction, rather than as a dinuclear reductive-elimination reaction.[34]

Thus, in summary the reactions of **(1)** with 1,2-dienes, 1,3-dienes, and alkynes can all be explained in terms of an initial capture of a μ-σ-vinylcarbene Mo$_2$ species, which can then undergo competitive migratory 'insertion' either onto the co-ordinated unsaturated organic molecule or onto carbon monoxide. As was mentioned when discussing the formation of **(5)** an alternative pathway involves transformation of the μ-σ-vinylcarbene into a terminally bonded vinylcarbene, which reacts with co-ordinated alkyne to form a molybdacyclobutene. This same postulate can be extended to explain the formation of **(9)** and **(11)**, but not **(8)** and **(10)**. Whilst it is possible that different pathways are followed with changing organic reactants, application of Occam's razor[35] would favour the unified mechanism.

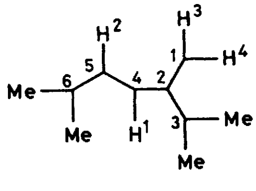
Experimental

All experiments were carried out in glass tubes fitted with a Young's tap or in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvent. The ^{1}H and ^{13}C n.m.r. spectra were recorded on JEOL FX 90 Q or FX 200 spectrometers, as appropriate. Data are given for room-temperature measurements unless otherwise indicated, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference; SiMe$_4$ for ^{13}C and ^{1}H. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer.

Reaction of [Mo(μ-σ:η^3-CHCHCMe$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] **(1)** *with (a) Propa-*1,2-*diene*.—An excess (2.0 mmol) of propa-1,2-diene was condensed (−196 °C) into a tube containing [Mo$_2$(μ-σ:η^3-CHCHCMe$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] **(1)** (0.20 g, 0.04 mmol) dissolved in CH$_2$Cl$_2$ (40 cm^3). The tube and contents were heated at 50 °C for *ca.* 2 h. The initial red solution became dark red-brown, and following removal of the volatiles *in vacuo* the reaction mixture was chromatographed on an alumina packed column. Elution with diethyl ether gave a bright yellow band, which was collected and recrystallised (−20 °C) from methylene chloride–hexane to give yellow *crystals* of **(2)** (0.11 g, 50%) (Found: C, 48.5; H, 4.2%; *M*, 542. C$_{22}$H$_{22}$Mo$_2$O$_4$ requires C, 48.7; H, 4.1%; *M*, 542); $\nu_{max.}$ at 1 947s, 1 927s, 1 867s, 1 847s cm^{-1} (CH$_2$Cl$_2$). N.m.r.: ^{1}H (CDCl$_3$), δ 5.45 (s, 5 H, C$_5$H$_5$), 5.37 (s, 5 H, C$_5$H$_5$), 4.65 [d, 1 H, H^2, *J*(H^{1}H^2) 10.3], 3.26, 3.02 [AB system, 2 H, CH$_2$, *J*(HH) 3.42], 2.86 (s, 2 H, CH$_2$), 2.06 [d, 1 H, H^1, *J*(H^{1}H^2) 10.3], 0.90 (s, 3 H, Me), 0.76 (s, 3 H, Me); ^{13}C-{^{1}H} (CDCl$_3$), δ 240.69 (CO), 238.95 (CO), 106.79 (C^2), 93.85 (C$_5$H$_5$), 90.46 (C$_5$H$_5$), 73.96 (C^6), 64.37 (C^5), 59.97 (C^4), 37.08 (CH$_2$), 31.16 (CH$_2$), 30.86 (Me), and 22.49 p.p.m. (Me).

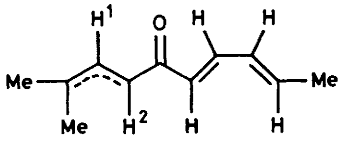


(*b*) 3-*Methylbuta*-1,2-*diene*. A similar reaction between **(1)** (0.15 g, 0.3 mmol) and 3-methylbuta-1,2-diene (3 mmol) in CH$_2$Cl$_2$ (40 cm^3) afforded on elution with diethyl ether, and recrystallisation (−20 °C) from methylene chloride–hexane yellow *crystals* of **(3)** (0.09 g, 50%) (Found: C, 49.8; H, 4.8%; *M*, 570. C$_{24}$H$_{26}$Mo$_2$O$_4$ requires C, 50.5; H, 4.6%; *M*, 570); $\nu_{max.}$ at 1 939s, 1 923s, 1 851s cm^{-1} (CH$_2$Cl$_2$). N.m.r.: ^{1}H (CDCl$_3$), δ 5.32 (s, 5 H, C$_5$H$_5$), 5.21 (s, 5 H, C$_5$H$_5$), 4.55 [d, 1 H, H^2, *J*(H^{2}H^1) 10.3], 3.01 [d, 1 H, H^1, *J*(H^{1}H^2) 10.3], 2.95 [d, 1 H, H^3, *J*(H^{3}H^4) 3.66], 2.01 (s, 3 H, Me), 1.91 (s, 3 H, Me), 1.12 (s, 3 H, Me), 1.10 (s, 3 H, Me), 1.05 [d, 1 H, H^4, *J*(H^{4}H^3) 3.66];

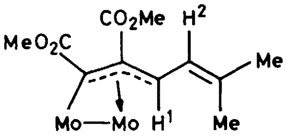


^{13}C-{^{1}H} (CDCl$_3$), δ 242.51 (CO), 240.2 (CO), 238.95 (CO), 235.30 (CO), 94.81 (C$_5$H$_5$), 93.38 (C$_5$H$_5$), 88.54 (C^2), 76.97 (C^6 or C^3), 76.09 (C^3 or C^6), 66.16 (C^5), 54.66 (C^4), 30.74 (Me), 28.94 (C^1), 27.19 (Me), 24.40 (Me), and 23.16 p.p.m. (Me).

(*c*) trans-*Penta*-1,3-*diene*. A solution of **(1)** (0.30 g, 0.06 mmol) and *trans*-penta-1,3-diene (0.20 g, 3.0 mmol) in CH$_2$Cl$_2$ (40 cm^3) contained in a Young's tube was heated at 50 °C for 48 h. The volatile material was removed *in vacuo*, and the residue chromatographed on alumina. Elution with hexane–diethyl ether (1:1) afforded a red band containing [$Mo_2(CO)_6(\eta$-$C_5H_5)_2$] followed by a yellow band which was collected. Recrystallisation (−78 °C) from hexane–tetrahydrofuran afforded orange-yellow *crystals* of (4) (0.06 g, 25%) (Found: C, 57.0; H, 5.4%; *M*, 380. $C_{18}H_{20}MoO_3$ requires C, 56.9; H, 5.3%; *M*, 380); $\nu_{max.}$ at 1 947s, 1 859s, 1 651w, 1 623w cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 7.26 (unresolved multiplet, 1 H, CH), 6.26 [d, 1 H, CH, *J*(HH) 4.15], 6.21 [d, 1 H, CH, *J*(HH) 4.64], 5.16 (s, 5 H, C_5H_5), 5.09 [d, 1 H, H^1, $J(H^1H^2)$ 9.53], 2.49 [d, 1 H, H^2, $J(H^2H^1)$ 9.53], 1.89 (s, 3 H, Me), 1.88 [d, 3 H, Me, *J*(HH) 3.9], 1.19 (s, 3 H, Me); ^{13}C-{^1H} ($CDCl_3$), δ 242.5 (CO), 238.4 (CO), 196.1 (CO, ketonic), 141.2 (CH), 139.7 (CH), 130.6 (CH), 128.2 (CH), 94.6 (C_5H_5), 83.9 (CMe_2), 71.9 (CH), 49.9 (CH), 30.3 (Me), 23.2 (Me), and 18.8 (Me) p.p.m.



(*d*) *Dimethyl acetylenedicarboxylate*. A solution of (1) (0.3 g, 0.6 mmol) and $C_2(CO_2Me)_2$ (0.2 cm^3, 1.6 mmol) in CH_2Cl_2 (20 cm^3) contained in a Young's tube was heated at 50 °C for 3 h. The volatile material was removed *in vacuo* and the residue chromatographed on alumina. Elution with diethyl ether gave a red band, which was collected, and recrystallised from hexane–diethyl ether to give red *crystals* of (5) (0.10 g, 26%) (Found: C, 46.6; H, 3.8. $C_{25}H_{24}Mo_2O_8$ requires C, 46.6; H, 3.7%); $\nu_{max.}$ at 1 949s, 1 909s, 1 837s, 1 769m, 1 711m, 1 681m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 5.28 (s, 5 H, C_5H_5), 5.20 [d, 1 H, H^2, $J(H^1H^2)$ 12], 5.19 (s, 5 H, C_5H_5), 3.82 (s, 3 H, CO_2Me), 3.74 (s, 3 H, CO_2Me), 2.80 [d, 1 H, H^1, $J(H^1H^2)$ 12], 1.81 [d, 3 H, Me, *J*(MeH) 1], 1.77 [d, 3 H, Me, *J*(MeH) 1] (H^2 obscured by solvent resonance); ^{13}C-{^1H} (CD_2Cl_2), δ 250.0 (CO), 245.9 (CO), 241.2 (CO), 236.9 (CO), 179.0, 174.9, 170.0 (CO_2Me and CCO_2Me), 140.7 (CCO_2Me), 122.5 (CH), 105.1 (CMe_2), 97.4 (C_5H_5), 95.3 (C_5H_5), 80.9 (CH), 53.3 (CO_2Me), 53.1 (CO_2Me), 26.6 (Me), and 18.5 p.p.m. (Me).



(*e*) *But-2-yne*. Reaction of (1) (0.5 g, 1 mmol) with but-2-yne (4 mmol) in CH_2Cl_2 (30 cm^3) afforded (4 h) on column chromatography and elution with hexane–methylene chloride (5:1), and recrystallisation (−78 °C) from hexane–methylene chloride red *crystals* of (6) (0.25 g, 43%) (Found: C, 49.2; H, 4.2. $C_{25}H_{24}Mo_2O_5$ requires C, 49.3; H, 4.1%); $\nu_{max.}$ at 1 940s, 1 865s, 1 605m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 5.30 (s, 5 H, C_5H_5), 5.16 [d, 1 H, H^2, *J*(HH) 9.8], 5.08 (s, 5 H, C_5H_5), 2.87 [d, 1 H, H^1, *J*(HH) 9.8], 2.84 (s, 3 H, Me), 2.04 (s, 3 H, Me), 1.92 (s, 3 H, Me), 1.18 (s, 3 H, Me); ^{13}C-{^1H} (CD_2Cl_2), δ 250.7 (*C*Me), 243.8 (CO), 239.2 (CO), 199.8 (CO, ketonic), 135.8 (*C*Me), 93.8 (C_5H_5), 93.4 (C_5H_5), 83.7 (CMe_2), 73.0 (CH), 47.0 (CH), 33.6 (Me), 30.5 (Me), 23.3 (Me), and 12.9 p.p.m. (Me). At −40 °C in $CDCl_3$, resonances are observed at 251.9, 151.0, 250.6, 243.8, and 239.2 p.p.m. (CO).

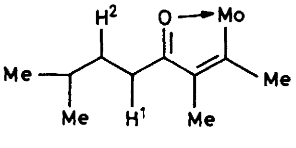
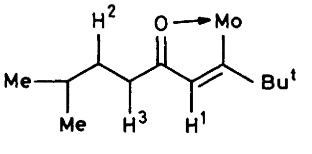


Table 4. Structure analyses *

Complex	(2)	(6)	(9)·CH_2Cl_2
Crystal colour and habit	Orange-red prism	Dark red plate	Deep green prism
Approx. crystal size/mm	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.05	0.4 × 0.3 × 0.12
2θ Range/°	3—55	3—50	3—60
No. of data collected	4 792	4 423	3 705
No. of unique data	4 204	3 928	3 322
No. of observed data (NO)	3 927	3 543	3 228
Transmission coefficient range	0.80—0.72		
Anisotropic atoms	Mo,O,C	Mo,O,C	Mo,O,C
Isotropic atoms	H	H	H
No. of parameters refined (NV)	283	300	318
Final *R*	0.026	0.033	0.031
R′	0.027	0.034	0.035
g	0.0002	0.000 51	0.000 63
S	1.30	1.23	1.26
Largest final difference electron density features (e Å^{-3})	+0.3 −0.5	+0.7 −0.9	+1.0 −0.6

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$; $S = [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{\frac{1}{2}}$.

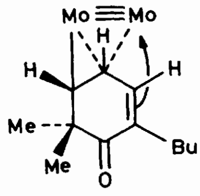
(*f*) 3,3-*Dimethylbut*-1-*yne*. An excess of 3,3-dimethylbut-1-yne (0.4 cm^3, 3.2 mmol) was added to a solution of (1) (0.3 g, 0.6 mmol) in CH_2Cl_2 (20 cm^3) contained in a Young's tube, and the tube and contents were heated at 50 °C for 5 h. Removal of the solvent *in vacuo*, chromatography on alumina and elution with hexane–diethyl ether (1:1) gave a red band, which on recrystallisation (−20 °C) from diethyl ether–hexane (1:2) gave red *crystals* of (8) (0.1 g, 40%) (Found: C, 52.0; H, 4.6. $C_{26}H_{28}Mo_2O_5$ requires C, 51.0; H, 4.6%); $\nu_{max.}$ at 1 955s, 1 935s, 1 909m, 1 861s, 1 611w cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 7.03 (s, 1 H, H^1), 5.41 (s, 5 H, C_5H_5), 5.12 (s, 5 H, C_5H_5), 4.98 [d, 1 H, H^2, $J(H^2H^3)$ 9.8], 2.82 [d, 1 H, H^3, $J(H^3H^2)$ 9.8], 1.82 (s, 3 H, Me), 1.33 (s, 9 H, Bu^t), 1.13 (s, 3 H, Me); ^{13}C-{^1H} ($CDCl_3$), δ 274.2 (CBu^t), 253.7 (CO), 201.4 (CO, ketonic), 129.6 (CH), 93.4 (C_5H_5), 93.3 (C_5H_5), 81.1 (CMe_2), 70.8 (CH_2), 48.9 (CH_3), 32.6 (CMe_3), 30.4 (Me), and 23.0 p.p.m. (Me).



Further elution with diethyl ether gave a green band, which on recrystallisation (−20 °C) from hexane–methylene chloride afforded dark green *crystals* of (9) (0.05 g, 20%) (Found: C, 46.7; H, 4.7%; *M*, 556. $C_{24}H_{28}Mo_2O_3$ requires C, 46.7; H, 4.7%; *M*, 556); $\nu_{max.}$ at 1 803m, 1 705m, 1 595m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 5.33 (s, 5 H, C_5H_5), 5.20 (m, 1 H, CH), 5.04 (s, 5 H, C_5H_5), 4.33 (m, 1 H, CH), 4.13 (m, 1 H, CH), 1.47 (s, 3 H, Me), 1.06 (s, 9 H, Bu^t), 0.83 (s, 3 H, Me); the resonances at 4.13, 4.33, and 5.20 p.p.m. form an ABX spin system with ^4J(AX) −0.75, ^3J(AB) 7.25, and ^3J(BX) 6.31 Hz (NUMARIT); ^{13}C-{^1H}

Table 5. Atomic co-ordinates ($\times 10^4$) for (**2**)

Atom	*x*	*y*	*z*
Mo(1)	263(1)	1 695(1)	1 878(1)
Mo(2)	5 061(1)	3 443(1)	2 548(1)
O(1)	633(4)	1 363(2)	−101(2)
O(2)	−735(3)	3 481(2)	695(2)
O(3)	5 170(2)	1 658(1)	1 442(2)
O(4)	6 499(3)	4 131(2)	1 180(2)
C(1)	524(4)	1 470(2)	645(3)
C(2)	−377(3)	2 833(2)	1 146(2)
C(3)	2 504(3)	1 387(2)	2 488(2)
C(4)	2 377(3)	2 348(2)	2 469(2)
C(5)	1 641(3)	2 704(2)	3 011(2)
C(6)	2 860(3)	2 903(2)	1 810(2)
C(7)	2 929(3)	3 873(2)	1 841(2)
C(8)	3 504(3)	4 358(2)	1 259(2)
C(9)	3 640(3)	5 384(2)	1 389(2)
C(10)	3 295(3)	4 048(2)	277(2)
C(11)	−1 807(4)	1 052(3)	1 561(3)
C(12)	−1 501(4)	1 557(3)	2 429(3)
C(13)	−431(4)	1 138(3)	3 146(3)
C(14)	−45(4)	390(3)	2 755(3)
C(15)	−889(5)	329(3)	1 755(3)
C(16)	4 947(4)	3 709(4)	4 108(2)
C(17)	5 703(5)	4 415(2)	3 932(2)
C(18)	6 828(5)	4 023(4)	3 875(3)
C(19)	6 768(5)	3 111(4)	4 011(3)
C(20)	5 640(5)	2 916(3)	4 154(2)
C(21)	5 137(3)	2 325(2)	1 866(2)
C(22)	5 939(3)	3 883(2)	1 677(2)
H(3a)	2 897(27)	1 104(19)	2 066(19)
H(3b)	2 569(30)	1 084(21)	3 074(23)
H(5a)	1 733(27)	2 430(18)	3 622(19)
H(5b)	1 457(35)	3 344(21)	3 016(24)
H(6)	2 815(23)	2 577(16)	1 228(17)
H(7)	2 704(22)	4 180(15)	2 294(16)



(CD$_2$Cl$_2$), δ 262.7 (CO), 253.6 (CO), 204.6 (CO, ketonic), 94.6 (C$_5$H$_5$), 92.7 (C$_5$H$_5$), 85.9 (*C*CMe$_3$), 62.3 (CH), 56.4 (CH), 55.9 (CH), 42.9 (*C*Me$_2$ or *C*Me$_3$), 35.4 (Me), 31.4 (C*Me*$_3$), and 26.7 p.p.m. (Me).

(*g*) 3-*Methylbut*-1-*yne*. Similarly, reaction of (**1**) (0.3 g, 0.6 mmol) with 3-methylbut-1-yne (3.5 mmol) afforded red *crystals* of (**10**) (0.11 g, 42%) (Found: C, 49.5; H, 4.5%; *M*, 598. C$_{25}$H$_{26}$Mo$_2$O$_5$ requires C, 50.1; H, 4.4%; *M*, 598); $\nu_{max.}$ at 1 935s, 1 863s, 1 610w cm^{-1} (CH$_2$Cl$_2$). N.m.r.: ^{1}H (CDCl$_3$), δ 6.97 (s, 1 H, H^1), 5.35 (s, 5 H, C$_5$H$_5$), 5.12 (s, 5 H, C$_5$H$_5$), 4.98 [d, 1 H, H^2, *J*(H^{2}H^3) 9.8], 3.77 [septet, 1 H, C*H*Me$_2$, *J*(HH) 6.7], 2.82 [d, 1 H, H^3, *J*(H^{3}H^2) 9.8], 1.86 (s, 3 H, Me), 1.25 [d, 3 H, Me, *J*(HH) 6.7], 1.18 [d, 3 H, Me, *J*(HH) 6.7], 1.13 (s, 3 H, Me); ^{13}C-{^{1}H} (CDCl$_3$), 276.1 (*C*Pr^i), 250.8 (CO), 249.9 (CO), 242.3 (CO), 238.2 (CO), 200.9 (CO, ketonic), 126.0 (CH), 93.3 (C$_5$H$_5$), 92.9 (C$_5$H$_5$), 80.8 (*C*Me$_2$), 71.3 (CH$_2$), 49.16 (*C*HMe$_2$ or CH$_3$), 46.5 (CH$_3$ or *C*HMe$_2$), 30.48 (Me), 23.2 (Me), 23.13 (Me), and 23.03 p.p.m. (Me).

Further elution with diethyl ether gave green *crystals* of (**11**) (0.4 g, 18%) (Found: C, 50.6; H, 5.0. C$_{23}$H$_{26}$Mo$_2$O$_2$ requires C, 50.9; H, 4.8%); $\nu_{max.}$ at 1 895m, 1 783m, 1 639m cm^{-1} (CH$_2$Cl$_2$). N.m.r.: ^{1}H (CD$_2$Cl$_2$) δ 5.26 (s, 5 H, C$_5$H$_5$), 5.12 (s, 5 H, C$_5$H$_5$), 4.98 (complex multiplet, 1 H, CH), 4.42 (cm, 1 H, CH), 3.95 (cm, 1 H, CH), 3.31 (cm, 1 H, C*H*Me$_2$), 1.42 (s, 3 H, Me), 1.27—1.16 (cm, 6 H, CH*Me*$_2$), 0.82 (s, 3 H, Me); the resonances at 3.95, 4.42, and 4.98 form an ABX spin system with ^{3}*J*(AB) 5.9, ^{4}*J*(AX) 1.0, ^{3}*J*(BX) 7.3 Hz (NUMARIT); ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 266.8 (CO), 260.2 (CO), 206.4 (CO, ketonic), 95.7 (C$_5$H$_5$), 93.4 (C$_5$H$_5$), 64.5 (CH), 59.3 (CH), 56.16 (CH), 42.11 (*C*Me$_2$), 37.55 (*C*HMe$_2$), 35.6 (Me), 26.6 (Me), 25.1 (Me), and 24.3 p.p.m. (Me).

Table 6. Atomic co-ordinates ($\times 10^4$) for (**6**)

Atom	*x*	*y*	*z*
Mo(1)	3 049(1)	1 014(1)	1 202(1)
Mo(2)	−280(1)	−3 258(1)	3 376(1)
O(5)	1 228(3)	−172(3)	1 841(2)
O(6)	2 850(4)	−2 274(4)	422(2)
O(7)	6 667(4)	724(4)	1 494(2)
O(8)	−2 891(4)	−4 669(4)	4 446(2)
O(9)	1 050(5)	−1 917(4)	5 225(2)
C(1)	5 280(6)	2 631(5)	2 944(3)
C(2)	3 793(5)	1 537(4)	2 561(3)
C(3)	2 758(5)	910(4)	3 099(2)
C(4)	3 039(6)	1 159(6)	4 078(3)
C(5)	1 338(5)	24(4)	2 660(2)
C(6)	−40(5)	−649(4)	3 071(2)
C(7)	−1 403(4)	−1 491(4)	2 570(2)
C(8)	−2 757(5)	−2 189(4)	2 909(3)
C(9)	−4 051(5)	−3 201(5)	2 309(3)
C(10)	−3 369(5)	−1 416(5)	3 606(3)
C(11)	1 150(6)	2 648(6)	642(3)
C(12)	2 556(6)	3 558(5)	1 048(3)
C(13)	3 810(6)	3 355(5)	604(3)
C(14)	3 181(6)	2 289(5)	−71(3)
C(15)	1 510(5)	1 842(5)	−51(3)
C(16)	2 896(5)	−1 085(5)	712(3)
C(17)	5 325(5)	790(5)	1 405(3)
C(18)	−1 949(5)	−4 153(5)	4 038(3)
C(19)	561(5)	−2 387(5)	4 526(3)
C(20)	−338(7)	−5 376(7)	2 504(5)
C(21)	708(9)	−5 521(7)	3 307(4)
C(22)	1 988(7)	−4 421(8)	3 333(4)
C(23)	1 787(7)	−3 592(7)	2 609(4)
C(24)	393(8)	−4 124(7)	3 089(4)
H(6)	−53(41)	−268(37)	3 485(22)
H(7)	−1 370(43)	−1 656(40)	2 012(23)

Protonation of (**6**) *with Tetrafluoroboric Acid*.—HBF$_4$·Et$_2$O (0.4 mmol) was added dropwise to a solution (−78 °C) of (**6**) (0.2 g, 0.4 mmol) in tetrahydrofuran–methylene chloride (1 : 1) (10 cm^3). The resultant orange precipitate was collected, washed with diethyl ether (3 × 10 cm^3), and recrystallised (−20 °C) from diethyl ether–methylene chloride to afford orange *crystals* of (**7**) (0.18 g, 78%) (Found: C, 43.5; H, 4.2. C$_{25}$H$_{25}$BF$_4$MoO$_5$ requires C, 42.9; H, 3.7%); $\nu_{max.}$ at 2 043m, 1 993m, 1 955s, 1 877m, 1 601w cm^{-1} (CH$_2$Cl$_2$). N.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 5.89 (s, 5 H, C$_5$H$_5$), 5.24 (s, 5 H, C$_5$H$_5$), 5.04 [d, 1 H, H^2, *J*(HH) 9.4], 3.94 [q, 1 H, H^1, *J*(HH) 6.20], 2.66 [d, 1 H, H^3, *J*(HH) 9.4], 2.49 (s, 3 H, Me), 2.08 [d, 3 H, Me, *J*(HH) 6.20], 1.90 (s, 3 H, Me); ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 241.9 (CO), 239.2 (CO), 230.8 (CO), 221.0 (CO), 181.5 (CO, ketonic), 97.2 (C$_5$H$_5$), 95.6 (C$_5$H$_5$), 88.5 (*C*Me$_2$), 74.2 (CH), 72.1 (CH), 59.8 (*C*Me), 37.1 (CH), 30.3 (Me), 23.3 (Me), 18.1 (Me), and 14.9 p.p.m. (Me).

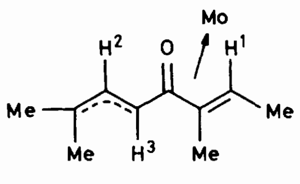


Table 7. Atomic co-ordinates (× 10^4) for (**9**)·CH_2Cl_2

Atom	x	y	z
Mo(1)	2 508(1)	0	1 673(1)
Mo(2)	1 314(1)	−86(1)	3 437(1)
Cl(1)	9 177(3)	1 691(2)	−2 603(2)
Cl(2)	6 967(4)	605(3)	−1 783(2)
O(1)	5 210(4)	−328(3)	4 487(4)
O(2)	−1 388(8)	−921(5)	978(6)
O(3)	5 304(4)	1 826(3)	4 222(3)
C	7 616(10)	873(6)	−3 052(7)
C(1)	4 016(5)	−192(3)	3 519(4)
C(2)	−304(9)	−565(5)	1 814(6)
C(3)	6 357(7)	1 586(6)	1 949(7)
C(4)	4 759(7)	3 035(4)	1 717(6)
C(5)	3 904(7)	1 947(4)	−145(5)
C(6)	4 605(6)	2 003(4)	1 378(5)
C(7)	3 440(4)	1 561(3)	1 991(4)
C(8)	1 701(4)	1 448(3)	1 191(4)
C(9)	585(4)	1 252(3)	1 827(4)
C(10)	953(5)	1 430(4)	3 193(4)
C(11)	2 464(6)	2 044(3)	3 864(4)
C(12)	3 079(8)	2 032(5)	5 379(5)
C(13)	1 951(9)	3 033(4)	3 374(6)
C(14)	3 884(5)	1 764(3)	3 435(4)
C(15)	2 623(17)	−1 471(5)	951(10)
C(16)	1 464(14)	−974(9)	−144(10)
C(17)	2 315(15)	−319(6)	−545(7)
C(18)	3 932(13)	−428(5)	278(8)
C(19)	4 105(13)	−1 098(5)	1 199(8)
C(20)	722(10)	175(6)	5 372(7)
C(21)	−547(8)	−356(6)	4 473(7)
C(22)	133(9)	−1 213(5)	4 269(7)
C(23)	1 844(10)	−1 184(5)	5 063(6)
C(24)	2 186(9)	−342(5)	5 754(5)
H(8)	1 273(42)	1 551(26)	197(34)
H(9)	−486(62)	1 102(37)	1 249(51)
H(10)	43(81)	1 672(51)	3 386(61)

X-*Ray Diffraction Studies.—Crystal Data for* (**2**). $C_{22}H_{22}Mo_2O_4$, $M = 542.1$, monoclinic, $a = 10.731(1)$, $b = 14.652(3)$, $c = 14.655(1)$ Å, $\beta = 110.972(8)°$, $U = 2\,151.5(5)$ Å^3, space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 1.67$ g cm^{-3}, $F(000) = 1\,080$, μ(Mo-K_α) 11.61 cm^{-1}.

For (**6**). $C_{24}H_{25}Mo_2O_5$, $M = 584.1$, triclinic, $a = 8.591(2)$, $b = 8.906(3)$, $c = 15.701(4)$ Å, $\alpha = 89.10(2)$, $\beta = 99.65(2)$, $\gamma = 99.06(2)°$, $U = 1\,169.5(6)$ Å^3, $Z = 2$, $D_c = 1.66$ g cm^{-3}, $F(000) = 584$, μ(Mo-K_α) = 10.77 cm^{-1}, space group $P\bar{1}$ (no. 2).

For (**9**). $C_{24}H_{28}Mo_2O_3{\cdot}CH_2Cl_2$, $M = 641.1$, monoclinic, $a = 8.745(5)$, $b = 14.571(7)$, $c = 10.909(4)$ Å, $\beta = 112.87(3)°$, $U = 1\,281(1)$ Å^3, space group $P2_1$ (no. 4), $Z = 2$, $D_c = 1.66$ g cm^{-3}, $F(000) = 444$, μ(Mo-K_α) = 11.64 cm^{-1}.

Diffraction measurements were made on small single crystals of (**2**), (**6**), and (**9**) sealed under N_2 in thin-walled glass capillaries. Intensity data were collected for unique volumes of reciprocal space using graphite-monochromated Mo-K_α *X*-radiation ($\lambda = 0.710\,69$ Å) on a Nicolet *P*3*m* diffractometer. In each case integrated intensities were obtained by Wyckoff ω scans with scan speed varied between 2.0 and 29.3° min^{-1} based on a 2-s prescan. An absorption correction was applied to the data for (**2**), based on a six parameter fit to 400 azimuthal scan data. Duplicate and symmetry related measurements were averaged and those intensities with $I > 2\sigma(I)$ were retained for use in structure determination. The structures were solved by conventional heavy-atom (Patterson and difference Fourier) methods and refined by blocked-cascade full-matrix least squares. Methyl and cyclopentadienyl group hydrogens were constrained to idealised geometries with C–H = 0.96 Å, H–C–H = 109.5° and were assigned fixed isotropic vibrational parameters of magnitude *ca.* 1.2 times the effective $U_{iso.}$ of their attached carbon. Other hydrogen atoms were directly located and refined without constraints. Intensity data were assigned weights $w = [\sigma_c^2(F_o) + g(F_o)^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in (F_o) based on counting statistics and g was chosen to minimise the variation in $\Sigma w[|F_o| - |F_c|]^2$ with $|F_o|$. Details of data collections and structure refinements are given in Table 4. The structures were refined to convergence (shift/e.s.d. < 0.1 for all parameters) at the residuals listed in Table 4. Final electron-density syntheses were essentially featureless. Complex neutral-atom scattering factors were taken from ref. 36. All calculations were performed with programs of the SHELXTL package on a Data General Eclipse (R) minicomputer. Final refined atomic positional parameters are given in Tables 5—7 for (**2**), (**6**), and (**9**) respectively.

Acknowledgements

We thank the S.E.R.C. for support.

References

1 Part 37, W. E. Carroll, M. Green, A. G. Orpen, C. J. Schaverien, I. D. Williams, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1986, 1021.
2 W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117.
3 G. W. Parshall, D. L. Thorn, and T. H. Tulip, *Chem. Technol.*, 1982, 571.
4 G. K. Barker, W. E. Carroll, M. Green, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1071.
5 M. Green, A. G. Orpen, C. J. Schaverien, and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 181.
6 D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2079.
7 F. A. Cotton and M. D. La Pride, *J. Am. Chem. Soc.*, 1968, **90**, 5418.
8 M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 1067.
9 J. W. Faller, D. F. Chodosh, and D. Katahiva, *J. Organomet. Chem.*, 1980, **187**, 227.
10 D. S. Gill, P. K. Baker, M. Green, K. E. Paddick, M. Murray, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 986.
11 J. W. Faller, D. L. White, and K. H. Chao, *Organometallics*, 1983, **2**, 400.
12 S. R. Allen, P. K. Baker, S. G. Barnes, M. Bottrill, M. Green, A. G. Orpen, I. D. Williams, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1983, 927.
13 S. R. Allen, M. Green, N. C. Norman, K. E. Paddick, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1983, 1625.
14 J. W. Faller, R. H. Crabtree, and A. Hebib, *Organometallics*, 1985, **4**, 929.
15 M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1687.
16 R. Ben-Shosan and R. Pettit, *Chem. Commun.*, 1968, 247.
17 A. Nakamura, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 543.
18 A. Kuhn, C. L. Burschka, and H. Werner, *Organometallics*, 1982, **1**, 496.
19 A. F. Dyke, S. A. R. Knox, and P. J. Naish, *J. Organomet. Chem.*, 1980, **199**, C47.
20 T. C. Flood, in 'Topics in Stereochemistry,' Wiley, New York, 1981, vol. 12.
21 M. Green and M. Bottrill, *J. Chem. Soc., Dalton Trans.*, 1979, 820.
22 M. Green and R. I. Hancock, *J. Chem. Soc. A*, 1966, 194.
23 C. E. Summer, jun., J. A. Collier, and R. Pettit, *Organometallics*, 1982, **1**, 1350.
24 A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 803.
25 J. Levisalles, F. Rose-Munch, H. Rudler, J. Davan, and Y. Dromzee, *J. Chem. Soc., Chem. Commun.*, 1981, 152.
26 J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 3002.
27 T. C. Clarke, C. S. Yannoni, and T. J. Katz, *J. Am. Chem. Soc.*, 1983, **105**, 7787.
28 A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 861.
29 L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1982, **104**, 889.
30 W. A. Herrmann and C. Baver, *Organometallics*, 1982, **1**, 1101.

31 W. J. Laws and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1020.
32 F. A. Cotton and R. A. Walton, in 'Multiple Bonds between Metal Atoms,' John Wiley, New York, 1982, p. 183.
33 Y. N. Al-Obaidi, M. Green, N. D. White, J-M. Bassett, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 494.
34 J. R. Norton, *Acc. Chem. Res.*, 1979, **12**, 139.
35 See B. K. Carpenter, in 'Determination of Organic Reaction Mechanisms,' Wiley-Interscience, New York, 1984, p. 3.
36 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 18*th November* 1985; *Paper* 5/2036