Reactions of Co-ordinated Ligands. Part 36.[1] The Synthesis, Structure, and Reactivity of the Three-alkyne 'Fly-over' Complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(\eta^5\text{-}C_9H_7)_2]$; Formation and Structure of $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(CO)_2(\eta^5\text{-}C_9H_7)_2]$†

Lee Brammer, Michael Green,* A. Guy Orpen, Kathleen E. Paddick, and David R. Saunders
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

One-electron reduction of $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_9H_7)][BF_4]$ with sodium or magnesium amalgam in thf affords the three-alkyne 'fly-over' complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(\eta^5\text{-}C_9H_7)_2]$ (**1**). The structure of (**1**) has been established by *X*-ray crystallography. The dinuclear complex contains two molybdenum atoms at an interatomic distance consistent with the presence of a triple bond [Mo(1)–Mo(2) 2.305(2) Å]. Each molybdenum carries an η^5-bonded indenyl ligand, and is also bonded (σ and η^3) to a C_6Me_6 fragment in a 'fly-over' mode beginning and ending with different molybdenum atoms. The mechanism of formation of (**1**) is discussed. It is interesting that (**1**) does not react with an excess of but-2-yne. However, treatment of the 30-electron species with CO at room temperature leads to the rapid formation of the 34-electron dicarbonyl species $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(CO)_2(\eta^5\text{-}C_9H_7)_2]$ (**2**) whose structure was established by *X*-ray crystallography. The effect of the addition of two carbonyl ligands is to lengthen the Mo–Mo distance to 2.933(1) Å, a length compatible with a bond order of unity. The increase in the Mo–Mo distance spanned by the C_6Me_6 fragment is accompanied by an uncoiling of the 'fly-over' unit. An isomeric dicarbonyl species (**3**) with higher symmetry (C_2 instead of C_1) is formed in refluxing hexane, suggesting that (**2**) is the kinetically controlled product. In contrast, 2,6-xylyl isocyanide reacts at room temperature with (**1**) to form $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(CNC_6H_3Me_2\text{-}2,6)_2(\eta^5\text{-}C_9H_7)_2]$ (**4**), which is isostructrual with (**3**), *i.e.* the thermodynamically controlled product. The formation of these molecules is discussed in the context of related species obtained on the thermal reaction of alkynes with the dinuclear complex $[Mo_2(\mu\text{-alkyne})(CO)_4(\eta\text{-}C_5H_5)_2]$.

Some forty years ago, Reppe *et al.*[2] discovered that cyclo-octatetraene (C_8H_8) could be prepared catalytically by reacting ethyne with a nickel salt. Although this remarkable reaction opened the way for the successful development of cyclo-octatetraene chemistry,[3] the mechanistic details of the reaction path(s) followed in the ethyne cyclisation reaction are still not understood. Recent[4] labelling experiments have established that in the nickel-catalysed cyclo-octatetraene synthesis the initial connectivity of the ethyne carbon atoms remains intact. This is consistent with the original 'zipper' mechanism[5] or with a stepwise topological equivalent involving the linking of the ethyne molecules at two adjacent metal centres. This latter alternative has recently attracted attention with the observations that the complex $[Ni_2(C_8H_8)_2]$ is a catalyst for the cyclo-tetramerisation of ethyne,[6] the four-alkyne 'fly-over' $[Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$ reacts[7] with CO to give C_8H_8, and the sequential linking of alkynes can apparently occur at dichromium and dimolybdenum centres.[8–10] We have previously found that the one-electron reduction of the cation $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ leads to the linking of four but-2-yne molecules and the formation of a octamethylocta-trienediylidenedimolybdenum complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8Me_8)\}(\eta\text{-}C_5H_5)_2]$, where the C_8 chain begins and ends with σ bonds to one molybdenum atom.[10,11] In exploring the related reaction of the η^5-indenyl analogue $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_9H_7)][BF_4]$[12] we have observed significant differences in the chemistry leading to the formation of a three-alkyne 'fly-over' complex.

Results and Discussion

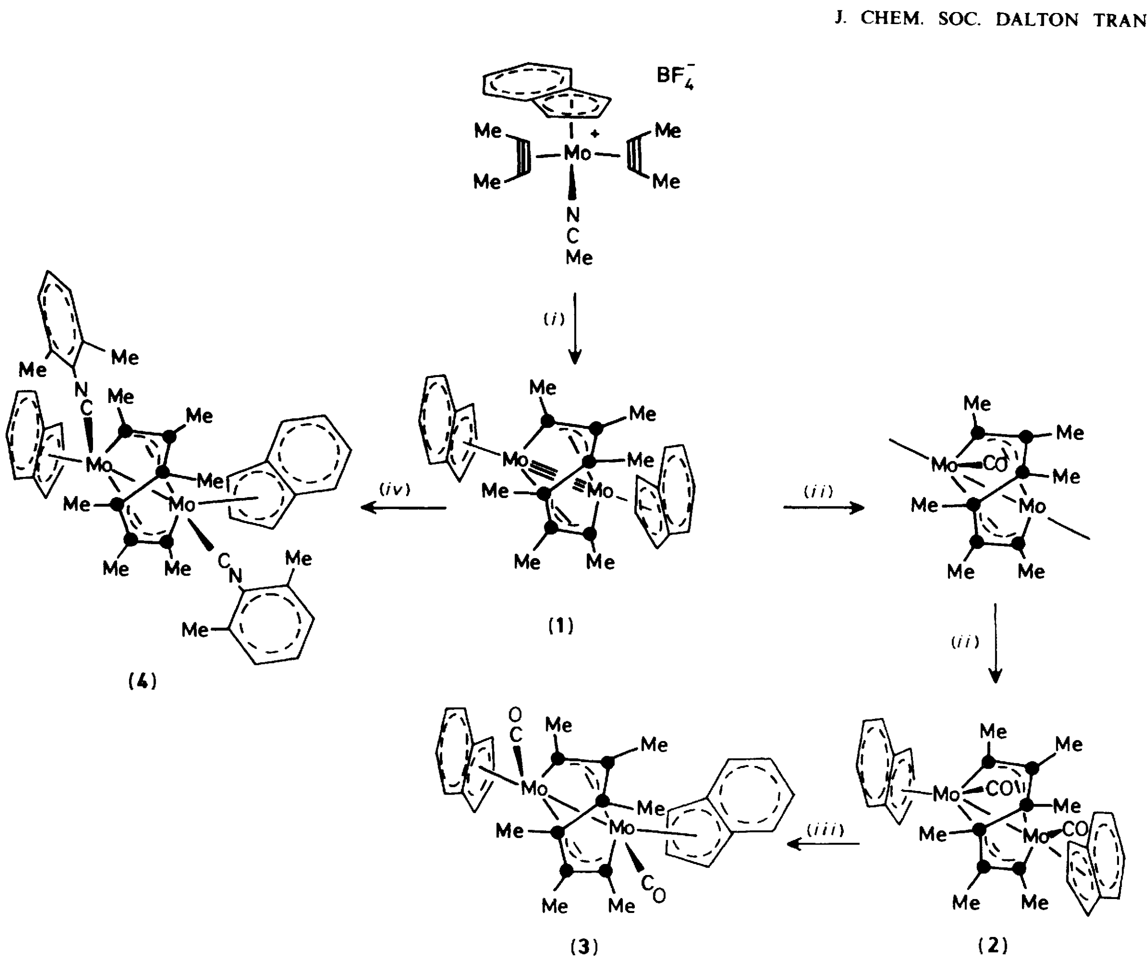
Reaction of a tetrahydrofuran (thf) solution of $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_9H_7)][BF_4]$[12] with a suspension of sodium- or magnesium-amalgam at room temperature afforded on chromatographic work-up a green crystalline air-sensitive complex (**1**) (10% yield with Na/Hg, 26% yield with Mg/Hg). Elemental analysis, a mass spectrum, and ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy suggested that the molecule was a dinuclear species with the molecular formula $[Mo_2(C_6Me_6)(\eta^5\text{-}C_9H_7)_2]$. The ^1H spectrum showed only three methyl environments implying that the molecule was possibly a three-alkyne 'fly-over' complex (Scheme 1) with C_2 symmetry. In contrast with the molecule $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8Me_8)\}(\eta\text{-}C_5H_5)_2]$,[10,11] (**1**) was reactive towards both carbon monoxide and 2,6-xylyl isocyanide. When carbon monoxide was bubbled through a hexane solution of (**1**) a carbonyl band appeared in the i.r. spectrum at 1 886 cm^{-1}. Column chromatography of the reaction mixture afforded an air-sensitive dicarbonyl species (**2**), which analysed and showed n.m.r. resonances consistent with the formula $[Mo_2(C_6Me_6)(CO)_2(\eta^5\text{-}C_9H_7)_2]$. In contrast with the parent complex, the ^1H spectrum of (**2**) showed the presence of six inequivalent methyl resonances. In refluxing hexane, however, CO reacts with (**1**) to give an isomeric dicarbonyl species (**3**), which exhibited three ^1H methyl environments. The corresponding reaction with 2,6-xylyl isocyanide

---

† μ-σ,2—4-η:σ',5—7-η'-3,4,5,6-Tetramethylocta-3,5-diene-2,7-diylidene-bis(η^5-indenylmolybdenum) and -bis[carbonyl(η^5-indenyl)-molybdenum] respectively.

Supplementary data available (No. SUP 56398, 8 pp.): H-atom co-ordinates, thermal parameters, complete bond parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.



Scheme 1. Indenyl ligand omitted for clarity in intermediate: (*i*) + 1 e; (*ii*) + CO; (*iii*) + CO refluxing hexane; (*iv*) + 2,6-xylyl isocyanide

also proceeded under mild conditions affording on chromatography orange crystals of (**4**). The i.r. spectrum showed a co-ordinated isocyanide stretch at 2 065 cm^{-1}, and analysis and n.m.r. spectroscopy suggested the molecule could be formulated as $[\mathrm{Mo_2(C_6Me_6)(CNC_6H_3Me_2\text{-}2,6)_2(\eta^5\text{-}C_9H_7)_2}]$. However, the ^{1}H spectrum showed the presence of three methyl environments implying that the bis(isocyanide) complex had the same symmetry as the dicarbonyl complex (**3**).

In order to clarify the structural problems posed by these observations the crystal structures of (**1**) and (**2**) were determined by conventional single-crystal *X*-ray diffraction techniques. Details of structure solution and refinement for each are given in the Experimental section. Tables 1 and 2 list selected derived bond lengths and interbond angles for (**1**) and (**2**) respectively. The molecular geometries of (**1**) and (**2**) are displayed in Figures 1 and 2 respectively. In the solid state both structures consist of isolated molecules, separated by normal van der Waals contact distances.

In the crystal structure of (**1**) there are two crystallographically distinct molecules each having approximate C_2 symmetry, which are closely similar in geometry. Each molecule contains two molybdenum atoms at an interatomic distance appropriate[13] for a triple bond [Mo(1)–Mo(2) 2.305(2) Å].* Each molybdenum atom carries an η^5-bonded indenyl ligand and is ligated in an η^3 and σ manner by the $\mathrm{C_6Me_6}$ ligand formed by linear trimerisation of but-2-yne. The $\mathrm{C_6Me_6}$ fragment bonds to the dimolybdenum unit in the 'fly-over' mode, describing a puckered S-shape beginning and ending with σ bonds to different molybdenum atoms (see Figure 1). The gross molecular geometry of (**2**) is closely related to that of (**1**), with the exception that each molybdenum carries a terminal carbonyl ligand. As a consequence the valence-electron count around the dimolybdenum centre rises to 34 [from 30 in (**1**)], and the Mo(1)–Mo(2) distance is substantially increased to 2.933(1) Å, consistent with a Mo–Mo bond order of unity. Table 3 lists selected geometric parameters for (**1**) and (**2**) to facilitate comparison.

The 'fly-over' ligand in both (**1**) and (**2**) binds in a $\sigma,\eta^3{:}\eta^3,\sigma$ fashion, that is as a pair of linked μ-allylidene ligands each acting as a σ donor to one molybdenum, and as an η^3-allyl type donor to the other. The Mo–C σ interaction shows the shortest Mo–C distances, average lengths 2.149(7) Å in (**1**), 2.122(5) and 2.163(5) Å in (**2**) [*cf.* Mo–η^3-C 2.249(10)—2.298(21) Å for (**1**) and 2.224(5)—2.332(4) Å for (**2**)]. A number of complexes are now known which contain the μ-allylidene (σ,η^3) fragment, both as such and as part of a larger ligand, *e.g.* $[\mathrm{Ru_2\{\mu\text{-}C(Me)C(Me)CH_2\}(CO)_2(\eta\text{-}C_5H_5)_2}]$,[14] $[\mathrm{Mo_2(\mu\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2}]$,[15] $[\mathrm{Co(\eta\text{-}C_5H_5)W\{\mu\text{-}C(C_6H_4Me\text{-}\mathit{p})C(Me)CHMe\}(CO)_2(\eta\text{-}C_5H_5)}]$,[16] $[\mathrm{Mo_2\{\mu\text{-}(\sigma,\eta^3{:}\eta^2{:}\eta^3,\sigma\text{-}C_8Me_8)\}(\eta\text{-}C_5H_5)_2}]$,[10,11] and $[\mathrm{W_2\{\mu\text{-}[\sigma,\eta^3{:}\eta^2\text{-}C(Me)C(Me)CHCHCMe_2]\}(CO)_8}]$.[17] In general for simple allylidenes the $\mathrm{M^1\text{–}C_\alpha(\sigma)}$ interaction (Scheme 2) is the shortest, and the $\mathrm{M^2\text{–}C_\gamma}$

---

* Molecular dimensions quoted are averaged over the two independent molecules and C_2 molecular symmetry here and throughout the discussion of (**1**) except where stated to the contrary. Estimated standard deviations derived from least-squares refinement in the least significant digit are given in parentheses here and throughout this paper.

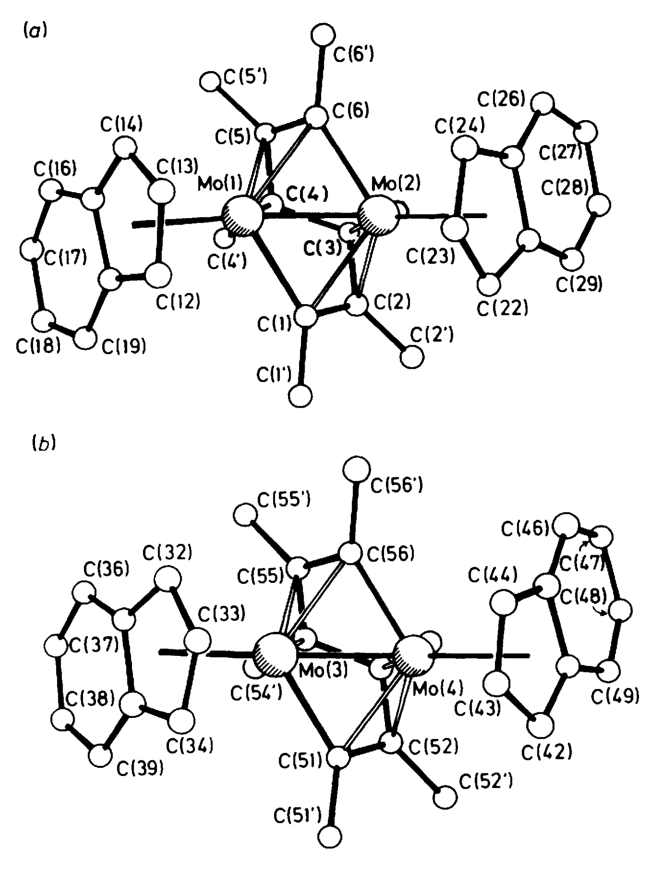
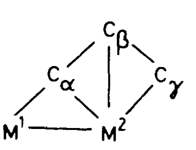


Figure 1. Molecular geometry and atomic labelling scheme for the two independent molecules, (*a*) and (*b*), of (**1**). All hydrogen atoms have been omitted for clarity



Scheme 2.

the longest of the M–C distances. In the more complex ligands where C_γ carries substituent atom(s) directly bonded to the dimetal unit the M^2–C_β and M^2–C_γ distances are much closer in length as is the case here. The effect of adding two carbonyl ligands to (**1**) to form (**2**) on the Mo–C_α, –C_β, –C_γ bond lengths is relatively small, the most marked difference being that the Mo–C_γ distance becomes the longest of the η^3 bonds in (**2**) (but by a smaller margin, *ca.* 0.05 Å, than is the case for simple μ-allylidenes where the difference is *ca.* 0.2 Å). The origin of the variation of M^2–C_β *vs.* M^2–C_γ distances might be steric, involving interactions between the substituents at C_γ and other ligands or the metal atoms, which prevent short M^2–C_γ lengths; these interactions cannot exist if the substituents at C_γ are themselves ligands. The C–C distances within the μ-allylidene fragments, C_α–C_β and C_β–C_γ, show no significant variation either within or between (**1**) and (**2**), and are similar to those in the μ-allylidene species mentioned above.

Other six-carbon chain 'fly-over' complexes, for which structural data are available, include $[\mathrm{Co_2\{\mu\text{-}CHCHC(Bu^t)C(Bu^t)CHCH\}(CO)_4}]$ (**I**), $[\mathrm{Co_2\{\mu\text{-}C_6(CF_3)_3H_3\}(CO)_4}]$ (**II**), $[\mathrm{Re_2(\mu\text{-}C_6Ph_6)(CO)_4(CNR)_2}]$ (**III**) (R = $\mathrm{CH_2SO_2C_6H_4Me}$-*p*) and $[\mathrm{Re_2(\mu\text{-}C_6Ph_6)(CO)_4(\eta^2\text{-}C_2Ph_2)}]$ (**IV**).[18] In these com-

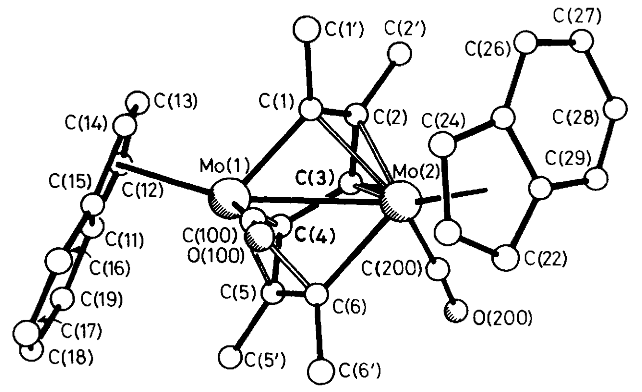
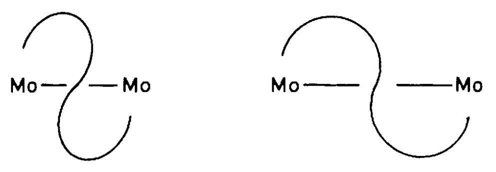


Figure 2. Molecular geometry and atomic labelling scheme for (**2**)

plexes, as in (**1**) and (**2**), the constraints of folding around the dimetal unit imply that there is a substantial dihedral angle at the central C–C bond of the six-carbon chain where the two near-planar μ-allylidene fragments link [*e.g.* the torsion angles C(2)–C(3)–C(4)–C(5) 132.4(16)° in (**1**) and −106.4(5)° in (**2**), *cf.* other angles in Table 3]. This bond [C(3)–C(4) 1.493(16) Å in (**1**) and 1.515(7) Å in (**2**)] is the longest within the six-carbon chain in both (**1**) and (**2**) [*cf.* the C–Me distances in the range 1.507—1.543 Å in (**1**) and (**2**)], as would be expected since the substantial twisting about C(3)–C(4) will reduce the π interaction between the planar allylidene subunits. Clearly the most dramatic effect of the addition of two carbonyl ligands to (**1**) to form (**2**) is on the Mo–Mo distance, and the increase in the Mo–Mo length spanned by the $\mathrm{C_6Me_6}$ ligand is accompanied by an uncoiling of the 'fly-over' unit. Thus, the dihedral angle between C(3)–C(4) and Mo(1)–Mo(2) is 20.7° for (**1**) and 32.2° for (**2**) [*cf.* 23, 28.1, and 29.2° for (**II**), (**III**), and (**IV**) respectively, where the metal–metal distances are 2.459(6), 2.786(1), and 2.849(1) Å respectively]. The changes in torsion angles about C(3)–C(4) in (**1**) and (**2**) (see Table 3) further emphasise this uncoiling effect (Scheme 3). As might be expected the intra-chain C–C–C bond angles show smaller changes, the most marked being for C(2)–C(3)–C(4), which enlarges by *ca.* 6° on going from (**1**) to (**2**). The Mo–C–Mo angle at the bridging carbon undergoes a considerable increase on going from (**1**) to (**2**) (as is required geometrically), from 63.2(5) to 83.6(2)°, whilst the Mo–C_α σ bond lengths remain virtually constant.



Scheme 3.

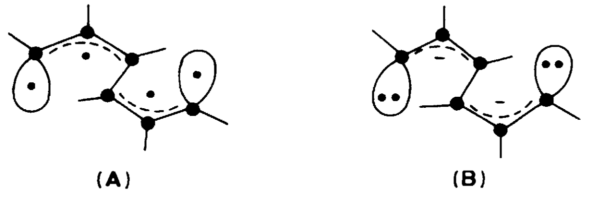
The observation that there is some flexibility in the range of the metal–metal distances which may be spanned by the 'fly-over' ligand leads us to consider the effect of this ligand on the Mo–Mo interaction and its length. Formally triply bonded Mo≡Mo species have been observed to show Mo–Mo distances between 2.15 and 2.55 Å.[13] These complexes may be divided into two categories. The first consists largely of $\mathrm{Mo_2L_6}$ complexes where the metal is in formal oxidation state +3 (L = uninegative ligand, *e.g.* $\mathrm{NR_2}$, OR, $\mathrm{CR_3}$ *etc.*) where the Mo≡Mo bond may be thought of as being of the $\sigma^2\pi^4$ type. These show short Mo–Mo distances, *e.g.* 2.214 Å in $[\mathrm{Mo_2(NEt_2)_6}]$[19] and

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

Mo(1)–Mo(2)	2.303(2)	Mo(1)–C(1)	2.137(16)	Mo(4)–C(52)	2.287(20)	Mo(4)–C(53)	2.239(17)
Mo(1)–C(4)	2.273(14)	Mo(1)–C(5)	2.329(18)	Mo(4)–C(56)	2.146(17)	Mo(4)–C(41)	2.584(21)
Mo(1)–C(6)	2.259(14)	Mo(1)–C(15)	2.566(19)	Mo(4)–C(42)	2.486(24)	Mo(4)–C(43)	2.327(27)
Mo(1)–C(14)	2.446(20)	Mo(1)–C(13)	2.362(19)	Mo(4)–C(44)	2.297(26)	Mo(4)–C(45)	2.505(23)
Mo(1)–C(12)	2.337(19)	Mo(1)–C(11)	2.510(20)	C(1)–C(1′)	1.527(24)	C(1)–C(2)	1.371(22)
Mo(2)–C(1)	2.241(15)	Mo(2)–C(2)	2.290(16)	C(2)–C(2′)	1.520(24)	C(2)–C(3)	1.454(22)
Mo(2)–C(3)	2.252(15)	Mo(2)–C(6)	2.157(17)	C(3)–C(3′)	1.533(23)	C(3)–C(4)	1.505(23)
Mo(2)–C(24)	2.365(21)	Mo(2)–C(23)	2.361(20)	C(4)–C(4′)	1.527(21)	C(4)–C(5)	1.422(23)
Mo(2)–C(22)	2.426(19)	Mo(2)–C(21)	2.563(18)	C(5)–C(5′)	1.535(26)	C(5)–C(6)	1.406(23)
Mo(2)–C(25)	2.476(17)	Mo(3)–Mo(4)	2.307(3)	C(6)–C(6′)	1.512(23)	C(51)–C(51′)	1.514(27)
Mo(3)–C(51)	2.154(19)	Mo(3)–C(54)	2.274(18)	C(51)–C(52)	1.397(28)	C(52)–C(52′)	1.528(30)
Mo(3)–C(55)	2.287(18)	Mo(3)–C(56)	2.241(17)	C(52)–C(53)	1.449(27)	C(53)–C(53′)	1.543(28)
Mo(3)–C(33)	2.367(21)	Mo(3)–C(32)	2.443(21)	C(53)–C(54)	1.481(27)	C(54)–C(54′)	1.562(25)
Mo(3)–C(31)	2.602(20)	Mo(3)–C(35)	2.513(20)	C(54)–C(55)	1.400(26)	C(55)–C(55′)	1.484(31)
Mo(3)–C(34)	2.335(20)	Mo(4)–C(51)	2.256(19)	C(55)–C(56)	1.439(26)	C(56)–C(56′)	1.557(29)

Mo(2)–Mo(1)–C(1)	60.5(4)	Mo(4)–Mo(3)–C(54)	78.8(5)	C(53)–C(54)–C(54′)	119.7(15)
C(1)–Mo(1)–C(4)	74.6(6)	Mo(4)–Mo(3)–C(55)	82.0(5)	C(53)–C(54)–C(55)	113.1(16)
C(1)–Mo(1)–C(5)	106.9(6)	C(54)–Mo(3)–C(55)	35.8(6)	Mo(3)–C(55)–C(54)	71.6(10)
Mo(2)–Mo(1)–C(6)	56.4(4)	C(51)–Mo(3)–C(56)	107.9(7)	C(54)–C(55)–C(55′)	123.0(19)
C(4)–Mo(1)–C(6)	62.0(5)	C(55)–Mo(3)–C(56)	37.1(6)	C(54)–C(55)–C(56)	112.7(17)
Mo(1)–Mo(2)–C(2)	81.2(4)	Mo(3)–Mo(4)–C(51)	56.3(5)	Mo(3)–C(56)–Mo(4)	63.4(5)
Mo(1)–Mo(2)–C(3)	78.1(4)	C(51)–Mo(4)–C(52)	35.8(7)	Mo(4)–C(56)–C(55)	113.0(12)
C(2)–Mo(2)–C(3)	37.3(6)	C(51)–Mo(4)–C(53)	62.0(6)	Mo(4)–C(56)–C(56′)	125.1(13)
C(1)–Mo(2)–C(6)	107.3(6)	Mo(3)–Mo(4)–C(56)	60.3(5)	C(3′)–C(3)–C(4)	117.6(13)
C(3)–Mo(2)–C(6)	73.1(5)	C(52)–Mo(4)–C(56)	108.2(7)	Mo(1)–C(4)–C(4′)	119.1(10)
Mo(4)–Mo(3)–C(51)	60.6(5)	Mo(1)–C(1)–C(1′)	124.5(11)	Mo(1)–C(4)–C(5)	74.2(9)
C(51)–Mo(3)–C(54)	74.2(7)	Mo(1)–C(1)–C(2)	115.1(11)	C(4′)–C(4)–C(5)	126.0(15)
C(51)–Mo(3)–C(55)	106.6(7)	C(1′)–C(1)–C(2)	120.2(15)	Mo(1)–C(5)–C(5′)	125.6(12)
Mo(4)–Mo(3)–C(56)	56.3(5)	Mo(2)–C(2)–C(2′)	125.1(12)	Mo(1)–C(5)–C(6)	69.4(9)
C(54)–Mo(3)–C(56)	63.1(6)	Mo(2)–C(2)–C(3)	69.9(9)	C(5′)–C(5)–C(6)	126.8(16)
Mo(3)–Mo(4)–C(52)	82.2(5)	C(2′)–C(2)–C(3)	122.3(14)	Mo(1)-C(6)–C(5)	74.9(9)
Mo(3)–Mo(4)–C(53)	77.6(5)	Mo(2)–C(3)–C(3′)	122.5(11)	Mo(1)–C(6)–C(6′)	128.7(11)
C(52)–Mo(4)–C(53)	37.3(7)	Mo(2)–C(3)–C(4)	99.9(9)	C(5)–C(6)–C(6′)	120.2(16)
C(51)–Mo(4)–C(56)	107.6(7)	C(2)–C(3)–C(4)	113.6(13)	Mo(3)–C(51)–C(51′)	121.8(14)
C(53)–Mo(4)–C(56)	74.1(7)	Mo(1)–C(4)–C(3)	96.7(9)	Mo(3)–C(51)–C(52)	114.8(14)
Mo(1)–C(1)–Mo(2)	63.4(4)	C(3)–C(4)–C(4′)	116.8(13)	C(51′)–C(51)–C(52)	122.8(18)
Mo(2)–C(1)–C(1′)	127.3(11)	C(3)–C(4)–C(5)	112.3(13)	Mo(4)–C(52)–C(52′)	126.0(14)
Mo(2)–C(1)–C(2)	74.9(9)	Mo(1)–C(5)–C(4)	69.9(9)	Mo(4)–C(52)–C(53)	69.5(10)
Mo(2)–C(2)–C(1)	70.4(9)	C(4)–C(5)–C(5′)	121.9(16)	C(52′)–C(52)–C(53)	127.2(19)
C(1)–C(2)–C(2′)	126.5(15)	C(4)–C(5)–C(6)	111.3(16)	Mo(4)–C(53)–C(53′)	121.9(13)
C(1)–C(2)–C(3)	111.2(14)	Mo(1)–C(6)–Mo(2)	62.8(4)	Mo(4)–C(53)–C(54)	100.8(12)
Mo(2)–C(3)–C(2)	72.7(9)	Mo(2)–C(6)–C(5)	115.2(11)	C(53′)–C(53)–C(54)	116.9(15)
C(2)–C(3)–C(3′)	121.0(14)	Mo(2)–C(6)–C(6′)	124.5(11)	Mo(3)–C(54)–C(54′)	120.0(12)
Mo(2)–Mo(1)–C(4)	79.1(4)	Mo(3)–C(51)–Mo(4)	63.0(5)	Mo(3)–C(54)–C(55)	72.6(10)
Mo(2)–Mo(1)–C(5)	81.8(5)	Mo(4)–C(51)–C(51′)	126.3(14)	C(54′)–C(54)–C(55)	122.4(16)
C(4)–Mo(1)–C(5)	36.0(6)	Mo(4)–C(51)–C(52)	73.3(11)	Mo(3)–C(55)–C(55′)	127.2(14)
C(1)–Mo(1)–C(6)	107.3(6)	Mo(4)–C(52)–C(51)	70.9(11)	Mo(3)–C(55)–C(56)	69.7(10)
C(5)–Mo(1)–C(6)	35.6(6)	C(51)–C(52)–C(52′)	123.9(19)	C(55′)–C(55)–C(56)	124.4(18)
Mo(1)–Mo(2)–C(1)	56.1(4)	C(51)–C(52)–C(53)	109.0(18)	Mo(3)–C(56)–C(55)	73.2(10)
C(1)–Mo(2)–C(2)	35.2(6)	Mo(4)–C(53)–C(52)	73.1(11)	Mo(3)–C(56)–C(56′)	128.1(13)
C(1)–Mo(2)–C(3)	62.5(5)	C(52)–C(53)–C(53′)	119.1(17)	C(55)–C(56)–C(56′)	121.7(16)
Mo(1)–Mo(2)–C(6)	60.7(4)	C(52)–C(53)–C(54)	116.3(16)		
C(2)–Mo(2)–C(6)	106.8(6)	Mo(3)–C(54)–C(53)	96.5(11)		

2.167 Å in $[Mo_2(CH_2SiMe_3)_6]$.[20] The second category involves molybdenum atoms in formal oxidation state +1, *e.g.* 2.448(1) Å in $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$[21] and 2.504(1) Å in $[Mo_2(CO)_2\{\mu\text{-}(\eta^2{:}\eta^2\text{-}C_{10}H_{10})\}(\eta\text{-}C_5H_5)_2]$.[22] For these the longer triple bond may be considered to arise from a d^5–d^5 interaction giving an electron configuration $\sigma^2\pi^4\delta^2\delta^{*2}$. The situation is less clear-cut for Mo–Mo single-bonded species although a wide range of Mo–Mo distances have also been observed, *e.g.* from 2.954 Å in $[Mo_2(\mu\text{-}Br)_2(CO)_4(\eta\text{-}C_4Ph_4)_2]$[23] to 3.235 Å in $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.[24] The Mo–Mo distances for (**1**) and (**2**) fall in the middle, and at the lower end of the Mo≡Mo and Mo–Mo ranges respectively. The formal oxidation states in (**1**) and (**2**) are not readily assignable. Viewing the C_6Me_6 ligand as a neutral, 8-electron donor (**A**) (Scheme 4) leads to Mo^I (d^5–d^5 electron count), and as a tetra-anionic, 12-electron donor (**B**) to Mo^{III} (d^3–d^3 electron count). The real situation undoubtedly lies between these formal extremes. The Mo–Mo distances observed will presumably be a consequence both of the balance between descriptions (**A**) and (**B**) and the compressibility (or



Scheme 4.

Table 2. Selected bond lengths (Å) and angles (°) for (**2**)

Mo(2)–Mo(1)	2.933(1)	Mo(2)–C(200)	1.955(5)	C(3)–C(4)	1.515(7)	C(4)–C(4′)	1.528(7)
Mo(2)–C(1)	2.268(5)	Mo(2)–C(2)	2.269(5)	C(4)–C(5)	1.440(7)	C(5)–C(5′)	1.518(7)
Mo(2)–C(3)	2.332(4)	Mo(2)–C(6)	2.163(5)	C(5)–C(6)	1.422(7)	C(6)–C(6′)	1.520(7)
Mo(2)–C(21)	2.426(5)	Mo(2)–C(22)	2.305(5)	C(11)–C(12)	1.436(8)	C(11)–C(15)	1.433(7)
Mo(2)–C(23)	2.334(5)	Mo(2)–C(24)	2.365(5)	C(11)–C(19)	1.424(8)	C(12)–C(13)	1.402(8)
Mo(2)–C(25)	2.473(5)	Mo(1)–C(100)	1.981(5)	C(13)–C(14)	1.411(8)	C(14)–C(15)	1.434(8)
Mo(1)–C(1)	2.122(5)	Mo(1)–C(4)	2.294(5)	C(15)–C(16)	1.432(8)	C(16)–C(17)	1.353(10)
Mo(1)–C(5)	2.255(5)	Mo(1)–C(6)	2.224(5)	C(17)–C(18)	1.405(10)	C(18)–C(19)	1.346(9)
Mo(1)–C(11)	2.463(5)	Mo(1)–C(12)	2.362(6)	C(21)–C(22)	1.439(7)	C(21)–C(25)	1.440(7)
Mo(1)–C(13)	2.343(6)	Mo(1)–C(14)	2.311(5)	C(21)–C(29)	1.412(7)	C(22)–C(23)	1.407(7)
Mo(1)–C(15)	2.441(5)	O(200)–C(200)	1.164(6)	C(23)–C(24)	1.408(8)	C(24)–C(25)	1.426(7)
O(100)–C(100)	1.158(6)	C(1)–C(1′)	1.529(7)	C(25)–C(26)	1.404(8)	C(26)–C(27)	1.351(9)
C(1)–C(2)	1.406(7)	C(2)–C(2′)	1.507(8)	C(27)–C(28)	1.409(11)	C(28)–C(29)	1.355(9)
C(2)–C(3)	1.448(7)	C(3)–C(3′)	1.528(7)				

Mo(2)–Mo(1)–C(1)	50.2(1)	C(1)–Mo(1)–C(5)	106.1(2)	C(3)–C(4)–C(5)	121.0(4)
Mo(2)–Mo(1)–C(4)	69.1(1)	Mo(2)–Mo(1)–C(6)	47.1(1)	Mo(1)–C(5)–C(4)	73.0(3)
C(1)–Mo(1)–C(4)	78.9(2)	C(1)–Mo(1)–C(6)	96.4(2)	C(4)–C(5)–C(5′)	124.1(4)
C(100)–Mo(1)–C(5)	110.3(2)	C(5)–Mo(1)–C(6)	36.9(2)	C(4)–C(5)–C(6)	113.3(4)
C(4)–Mo(1)–C(5)	36.9(2)	Mo(1)–Mo(2)–C(1)	46.0(1)	Mo(2)–C(6)–Mo(1)	83.5(2)
C(100)–Mo(1)–C(6)	76.1(2)	Mo(1)–Mo(2)–C(2)	70.3(1)	Mo(1)–C(6)–C(5)	72.1(3)
C(4)–Mo(1)–C(6)	63.6(2)	C(1)–Mo(2)–C(2)	36.1(2)	Mo(1)–C(6)–C(6′)	128.8(3)
Mo(1)–Mo(2)–C(200)	112.7(2)	C(200)–Mo(2)–C(3)	65.4(2)	Mo(2)–C(2)–C(2′)	126.7(4)
C(200)–Mo(2)–C(1)	127.8(2)	C(2)–Mo(2)–C(3)	36.6(2)	Mo(2)–C(2)–C(3)	74.0(3)
C(200)–Mo(2)–C(2)	96.7(2)	C(200)–Mo(2)–C(6)	75.6(2)	C(2′)–C(2)–C(3)	121.4(4)
Mo(1)–Mo(2)–C(3)	69.1(1)	C(2)–Mo(2)–C(6)	105.8(2)	Mo(2)–C(3)–C(3′)	128.7(3)
C(1)–Mo(2)–C(3)	62.4(2)	Mo(1)–C(100)–O(100)	173.2(4)	Mo(2)–C(3)–C(4)	100.8(3)
Mo(1)–Mo(2)–C(6)	49.4(1)	Mo(2)–C(1)–C(1′)	124.9(3)	C(3′)–C(3)–C(4)	115.0(4)
C(1)–Mo(2)–C(6)	94.4(2)	Mo(2)–C(1)–C(2)	72.0(3)	Mo(1)–C(4)–C(4′)	124.0(3)
C(3)–Mo(2)–C(6)	79.8(2)	C(1′)–C(1)–C(2)	119.2(4)	Mo(1)–C(4)–C(5)	70.1(3)
Mo(2)–C(200)–O(200)	173.3(5)	Mo(2)–C(2)–C(1)	71.9(3)	C(4′)–C(4)–C(5)	119.9(4)
Mo(2)–C(1)–Mo(1)	83.7(2)	C(1)–C(2)–C(2′)	125.1(5)	Mo(1)–C(5)–C(5′)	127.1(3)
Mo(1)–C(1)–C(1′)	121.8(3)	C(1)–C(2)–C(3)	113.3(4)	Mo(1)–C(5)–C(6)	71.0(3)
Mo(1)–C(1)–C(2)	117.7(3)	Mo(2)–C(3)–C(2)	69.3(3)	C(5′)–C(5)–C(6)	122.5(5)
Mo(2)–Mo(1)–C(100)	75.4(1)	C(2)–C(3)–C(3′)	116.9(4)	Mo(2)–C(6)–C(5)	115.5(3)
C(100)–Mo(1)–C(1)	95.3(2)	C(2)–C(3)–C(4)	118.5(4)	Mo(2)–C(6)–C(6′)	123.0(3)
C(100)–Mo(1)–C(4)	138.1(2)	Mo(1)–C(4)–C(3)	103.3(3)	C(5)–C(6)–C(6′)	118.7(4)
Mo(2)–Mo(1)–C(5)	70.9(1)	C(3)–C(4)–C(4′)	111.7(4)		

expansibility) of the 'fly-over' ligand. The evidence to hand does not allow distinction between these factors.

The indenyl ligands show some distortion from regular η^5-co-ordination to molybdenum in both (**1**) and (**2**). As has been noted in a number of structures the metal–C_5 ring distances show a pronounced slip towards η^3-bonding of the allyl-like carbons of the indenyl ligand. Thus, the Mo–C(12),C(13),C(14) lengths are shorter than Mo–C(11),C(15) in both (**1**) and (**2**) (by *ca.* 0.1 Å). The degree of slippage has been quantified[25] by a parameter Δ, which is the distance between the C_5 ring centroid and the point where the normal to the C_5 plane through the metal passes through the C_5 plane; Δ has values 0.24 for (**1**) and 0.140 and 0.154 Å for (**2**), *cf.* $[Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8)(\eta^5\text{-}C_9H_7)_2]$[25] shows Δ = 0.226 and 0.121 Å. The $\eta^5 \rightarrow \eta^3$ slippage is accompanied by some distortion away from planarity involving the C_5 ring. Thus, the dihedral angles between C_3 and C_8 segments about the line joining C(12) and C(14) are 4.8° for (**1**) and 6.3 and 5.0° for (**2**). A smaller distortion is observed at the junction between C_5 and C_6 rings [dihedral angles about C(11)–C(15) are 2.0° for (**1**) and 3.8 and 1.9° for (**2**)]. These distortions move the C_6 ring carbon atoms away from the metal atoms (*cf.* similar distortions in η^3-allyl ligands for the substituents in the *anti*-sites on the terminal carbons).

The carbonyl ligands in (**2**) occupy rather different sites. That bound to Mo(1) lies above the Mo(1)–Mo(2) vector [Mo(2)–Mo(1)–C(100) 75.4(1)°] in the crevice between the ends of the C_6Me_6 chain, and therefore is *cisoid* to both C_α carbons [C(6)–Mo(1)–C(100) 76.1(2), C(1)–Mo(1)–C(100) 95.3(2)°]. The other carbon monoxide ligand [C(200)–O(200)] lies *cisoid* to one C_α [C(6)] and one C_γ [C(3)] [C(6)–Mo(2)–C(200) 75.6(2), C(3)–Mo(2)–C(200) 65.4(2)°], and is therefore splayed further away from the Mo–Mo vector [Mo(1)–Mo(2)–C(200) 112.7(2)°]. The Mo(1)–C(100) distance [1.981(5) Å] is somewhat longer than Mo(2)–C(200) [1.955(5) Å] perhaps because of an incipient semi-bridging interaction with Mo(2) [C(100) ••• Mo(2) 3.097(5) Å].

Examination of the ^1H and ^{13}C n.m.r. data (see Experimental section) for (**1**) and (**2**) shows that the solid-state structure is adopted in solution. Comparison with the ^{13}C data[14–17] for other μ-allylidene complexes suggests that in (**1**) the resonances at 204.6, 116.9, and 99.2 p.p.m. may be assigned to C_α, C_β, and C_γ respectively. Both the ^1H and ^{13}C data for the dicarbonyl species (**2**) reflect the relative asymmetry [C_1 instead of C_2 in (**1**)] of the complex as shown by the presence of resonances due to inequivalent η^5-indenyl, terminal carbonyl ligands and six CMe groups. When (**1**) was reacted with carbon monoxide in refluxing hexane, a low yield of a forest-green complex (**3**) was obtained. Examination of the mass, i.r., and ^1H n.m.r. spectra suggested that (**3**) was an isomer of (**2**). The mass spectrum showed a parent ion and peaks corresponding to the consecutive loss of two carbon monoxide ligands. The i.r. spectrum showed a single terminal carbonyl band at 1 909 cm^{-1}, and in contrast with (**2**) the ^1H spectrum exhibited one indenyl and three CMe environments. The bis(2,6-xylyl isocyanide) adduct (**4**) clearly adopts the same geometry (Scheme 1) as in (**3**), *i.e.* C_2 symmetry, as is evident from both the ^1H and ^{13}C-

Table 3. A comparison of selected geometric parameters for (**1**) and (**2**)

	(**1**)[a]	(**2**)
Bond lengths (Å)		
Mo(1)–Mo(2)	2.305(2)	2.933(1)
Mo(1)–C(1)	2.149(7)	2.122(5)
Mo(2)–C(6)		2.163(5)
Mo(2)–C(1)	2.298(21)	2.268(5)
Mo(1)–C(6)		2.224(5)
Mo(2)–C(2)	2.289(21)	2.269(5)
Mo(1)–C(5)		2.255(5)
Mo(2)–C(3)	2.260(17)	2.332(4)
Mo(1)–C(4)		2.294(5)
Mo(1)–C(11)	2.501(18)	2.463(5)
Mo(2)–C(21)		2.426(5)
Mo(1)–C(12)	2.339(30)	2.362(6)
Mo(2)–C(22)		2.305(5)
Mo(1)–C(13)	2.354(18)	2.343(6)
Mo(2)–C(23)		2.334(5)
Mo(1)–C(14)	2.450(26)	2.311(5)
Mo(2)–C(24)		2.365(5)
Mo(1)–C(15)	2.579(22)	2.441(5)
Mo(2)–C(25)		2.473(5)
C(1)–C(2)	1.403(27)	1.406(7)
C(6)–C(5)		1.422(7)
C(2)–C(3)	1.431(24)	1.448(7)
C(5)–C(4)		1.440(7)
C(3)–C(4)	1.493(16)	1.515(7)
C(1)–C(1′)	1.528(20)	1.529(7)
C(6)–C(6′)		1.520(7)
C(2)–C(2′)	1.517(25)	1.507(8)
C(5)–C(5′)		1.518(7)
C(3)–C(3′)	1.541(15)	1.528(7)
C(4)–C(4′)		1.528(7)

	(**1**)[a]	(**2**)
Bond angles (°)		
Mo(1)–C(1)–C(1′)	124.0(14)	121.8(3)
Mo(2)–C(6)–C(6′)		123.0(3)
Mo(1)–C(1)–C(2)	114.6(11)	117.7(3)
Mo(2)–C(6)–C(5)		115.5(3)
C(1)–C(2)–C(3)	111.1(13)	113.3(4)
C(6)–C(5)–C(4)		113.3(4)
C(2)–C(3)–C(4)	113.9(16)	118.5(4)
C(5)–C(4)–C(3)		121.0(4)
Torsion angles (°)		
Mo(1)–C(1)–C(2)–C(2′)	164.9(32)	164.8(4)
Mo(2)–C(6)–C(5)–C(5′)		164.1(4)
Mo(1)–C(1)–C(2)–C(3)	−6.8(45)	−9.6(6)
Mo(2)–C(6)–C(5)–C(4)		−12.4(5)
C(1′)–C(1)–C(2)–C(2′)	−4.6(77)	−2.2(7)
C(6′)–C(6)–C(5)–C(5′)		2.5(7)
C(1′)–C(1)–C(2)–C(3)	178.8(24)	−176.6(4)
C(6′)–C(6)–C(5)–C(4)		−174.0(4)
C(1)–C(2)–C(3)–C(3′)	176.0(42)	174.5(4)
C(6)–C(5)–C(4)–C(4′)		−179.4(4)
C(1)–C(2)–C(3)–C(4)	36.0(35)	29.7(6)
C(6)–C(5)–C(4)–C(3)		34.0(6)
C(2′)–C(2)–C(3)–C(3′)	−0.8(24)	−0.2(7)
C(5′)–C(5)–C(4)–C(4′)		5.1(7)
C(2′)–C(2)–C(3)–C(4)	148.5(38)	−145.0(5)
C(5′)–C(5)–C(4)–C(3)		−142.4(5)
C(2)–C(3)–C(4)–C(4′)	−78.3(33)	103.7(5)
C(5)–C(4)–C(3)–C(3′)		108.2(5)
C(2)–C(3)–C(4)–C(5)	132.4(16)	−106.4(5)
C(3′)–C(3)–C(4)–C(4′)	71.2(25)	−41.7(6)

Deviation (Å) from plane of six-membered ring in indenyl group

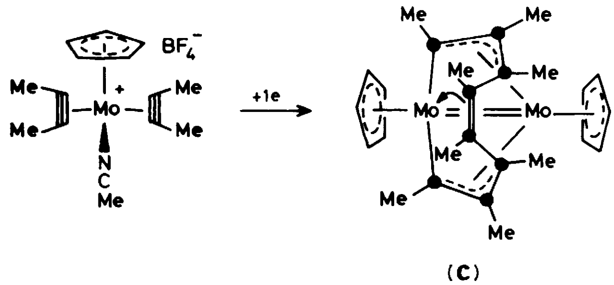
	(**1**)[a]	(**2**)[b]
R.m.s. deviation of 6 'in-plane' carbons	0.0155	0.0095
C(12)	−0.022	−0.057
C(13)	−0.098	−0.125
C(14)	−0.031	−0.015
Mo(1)	+2.100	+1.997

[a] All parameters of compound (**1**) used in this Table are averaged over the two independent molecules and the C_2 symmetry of each molecule. [b] Mean value for two indenyl groups used.

$\{^1H\}$ data where resonances corresponding to one η^5-indenyl environment, three CMe groups, and one isocyanide ligand are observed. Interestingly, the 2,6-xylyl isocyanide ligands do not freely rotate since two xylyl methyl signals are observed in the ^1H spectrum. This is possibly due to the presence of parallel indenyl and benzene rings. These results suggest that in the reaction of (**1**) with carbon monoxide, which presumably involved a stepwise process (Scheme 1), kinetic control affords the complex (**2**) with C_1 symmetry. Under more forcing conditions the thermodynamically controlled product (**3**) with C_2 symmetry is obtained. In the reaction with 2,6-xylyl isocyanide the kinetic product is not observed, rapid rearrangement occurring to give the isolated complex (**4**) with C_2 symmetry.

It is interesting to compare these observations with those of Knox, Stone, and co-workers[8,9] where the thermal reaction of the complexes $[Mo_2(\mu\text{-alkyne})(CO)_4(\eta\text{-}C_5H_5)_2]$ with alkynes under forcing conditions was studied. Diphenylacetylene in refluxing octane was reported[8] to react with $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ to give $[Mo_2(HC_2H)(PhC_2Ph)_2(\eta\text{-}C_5H_5)_2]$. Similarly, $MeO_2CC{\equiv}CCO_2Me$ reacted with $[Mo_2(\mu\text{-}Me_3SiC_2SiMe_3)(CO)_4(\eta\text{-}C_5H_5)_2]$ to give $[Mo_2(Me_3SiC_2SiMe_3)\{C_4(CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$.[9] Both of these compounds were assigned 'fly-over' structures analogous to (**1**) on the basis of ^1H and ^{13}C n.m.r. data; however, neither of these complexes was structurally characterised by *X*-ray crystallography. In the latter reaction a low yield of a dicarbonyl species was also obtained, which was formulated as $[Mo_2\{\mu\text{-}C(SiMe_3)C(SiMe_3)C_4(CO_2Me)_4\}(CO)_2(\eta\text{-}C_5H_5)_2]$, and related dicarbonyl species again in low yield were obtained from the reaction of $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(\mu\text{-}MeO_2CC_2CO_2Me)(CO)_4(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC{\equiv}CCO_2Me$.[8,9] These dicarbonyl complexes are possibly structurally related to (**2**) and (**3**). In view of the forcing conditions used in their preparation it is likely that these molecules are the thermodynamically controlled products analogous to (**3**), *i.e.* with C_2 symmetry, and it is not surprising that no evidence was obtained for the existence of dicarbonyl species with lower symmetry as in (**2**). In their study Knox, Stone, and co-workers did not establish or consider a relationship between the 'fly-over' complexes $[Mo_2\{\mu\text{-}(\sigma,\eta^3\text{:}\eta^3,\sigma\text{-}C_6R_6)\}(\eta\text{-}C_5H_5)_2]$ and the dicarbonyl adducts, it being suggested that $[Mo_2\{\mu\text{-}C_2(CO_2Me)_2C_2H_2C_2(CO_2Me)_2\}(CO)_2(\eta\text{-}C_5H_5)_2]$ was only formed *via* a transient di- or tri-carbonyl mono-ethyne complex, whereas $[Mo_2(\mu\text{-}C_2H_2C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ had its orgin in a bis-alkylidene complex $[Mo_2(\mu\text{-}C_4Ph_4)(CO)(\eta\text{-}C_5H_5)_2]$.

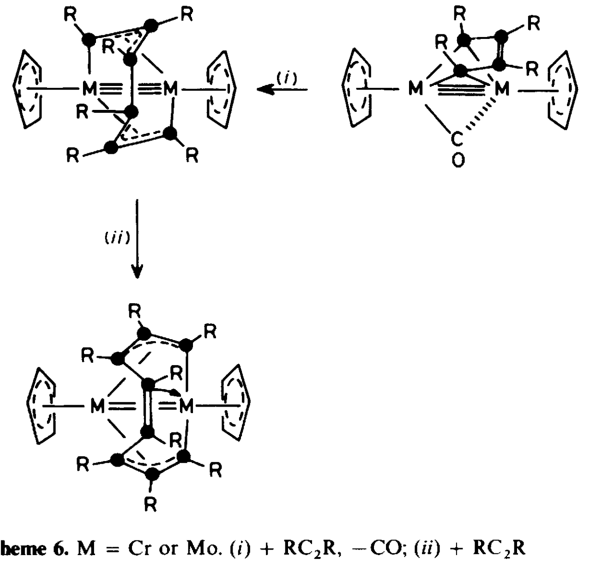
Of special interest was the observation[8] that the major



Scheme 5.

product isolated in the reaction of [Mo$_2$(μ-HC$_2$H)(CO)$_4$(η-C$_5$H$_5$)$_2$] with MeO$_2$CC≡CCO$_2$Me was the octatrienediylidenedimolybdenum complex [Mo$_2${μ-C$_8$(CO$_2$Me)$_6$H$_2$}(η-C$_5$H$_5$)$_2$] where it was shown[26] by *X*-ray crystallography that the C$_8$ chain begins and ends with σ bonds to the same molybdenum atom. As was mentioned earlier we had obtained a related complex,[10,11] which was also structurally identified by *X*-ray crystallography, by the one-electron reduction of the cationic complex [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] in thf (Scheme 5). Of additional interest was the finding[8] that although in the reaction (refluxing octane) of [Mo$_2${μ-C$_2$-(CO$_2$Me)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$] with MeO$_2$CC≡CCO$_2$Me the major product was a (octacarbomethoxyoctatrienediylidene)-dimolybdenum complex, a minor product (2%) was also formed and this was identified by *X*-ray crystallography[26] as a four-alkyne 'fly-over' complex [Mo$_2${μ-σ,η^4:η^4,σ-C$_8$(CO$_2$Me)$_8$}(η-C$_5$H$_5$)$_2$]. Thus, these observations together with our findings that the one-electron reduction of the cations [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η^5-C$_m$H$_n$)][BF$_4$] (C$_m$H$_n$ = C$_5$H$_5$ or C$_9$H$_7$) results either in the formation of a C$_6$ three-alkyne 'fly-over' or a C$_8$ octatrienediylidenedimolybdenum complex raises the question as to the possible relationship between C$_6$ 'fly-over', C$_8$ octatrienediylidene, and four-alkyne C$_8$ 'fly-over' dimolybdenum complexes. What is the role of these species in the stepwise build-up of a C$_8$ chain from alkyne molecules at a dimetal centre?

In the case of the thermal reaction of carbonyl-containing dimolybdenum species with alkynes, this problem was addressed[8] by reacting the presumed three-alkyne 'fly-over' complex [Mo$_2$(μ-C$_2$H$_2$C$_4$Ph$_4$)(η-C$_5$H$_5$)$_2$] with an excess of MeO$_2$CC≡CCO$_2$Me in refluxing octane for 4 d, resulting in the isolation of two isomeric adducts, [Mo$_2$(HC$_2$H)(PhC$_2$Ph)$_2$(MeO$_2$CC$_2$-CO$_2$Me)(η-C$_5$H$_5$)$_2$], in yields of 18 and 23%. From analytical and ^{1}H n.m.r. data only these were formulated as octatrienediylidenedimolybdenum complexes (Scheme 6). This led to the widely quoted[27–29] proposal[8] that three-alkyne C$_6$ 'fly-over' complexes are the immediate precursors of C$_8$ octatrienediylidene dimolybdenum species [Mo$_2${μ-(σ,η^3:η^2,η^3-σ-, C$_8$R$_8$)}(η-C$_5$H$_5$)$_2$]. However, although it is evident that this reaction affords dinuclear species containing four alkynes their connectivity was not established by the limited data (^{1}H n.m.r.) presented, and since no *X*-ray cryatallographic studies were reported on these isomeric species, the reaction pathway shown in Scheme 6 remains to be confirmed or disproved.



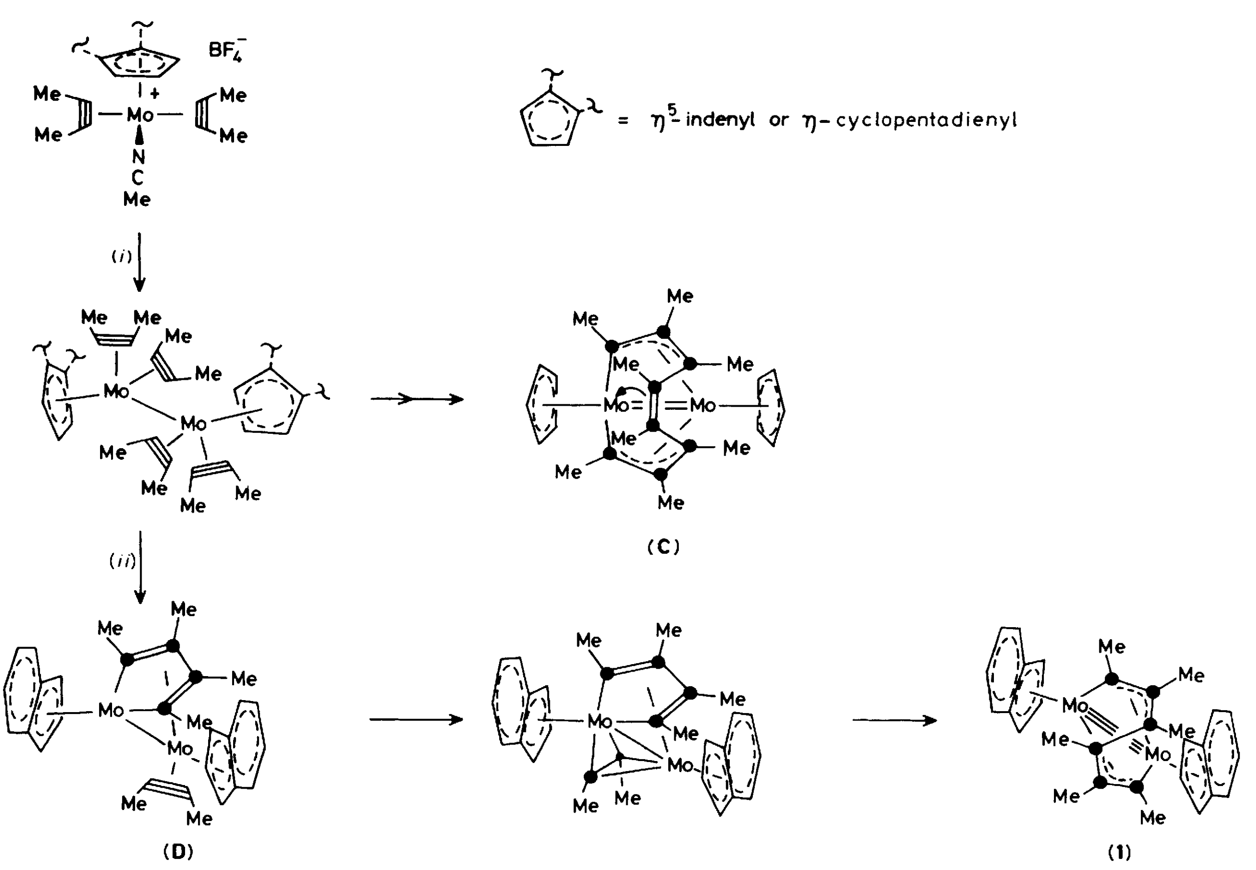
Scheme 6. M = Cr or Mo. (*i*) + RC$_2$R, −CO; (*ii*) + RC$_2$R

It was therefore important to examine the reactivity of the structurally characterised three-alkyne 'fly-over' complex (**1**) towards but-2-yne. Since the (octamethyloctatrienediylidene)-dimolybdenum complex [Mo{μ-(σ,η^3:η^2:η^3-σ-C$_8$Me$_8$)}(η-C$_5$H$_5$)$_2$] [(**C**) in Scheme 5] is formed rapidly at room temperature then it might be expected that if the cyclopentadienyl analogue of the C$_6$ 'fly-over' complex (**1**) was indeed a precursor of [Mo$_2${μ-(σ,η^3:η^2:η^3-σ-C$_8$Me$_8$)}(η-C$_5$H$_5$)$_2$] then the η^5-indenyl complex (**1**) should rapidly react with but-2-yne, particularly in view of the possible assistance which could be derived from a slippage (η^5→η^3) of the indenyl ligand. In the event, no reaction occurred when (**1**) was dissolved in *neat* but-2-yne for 600 h at room temperature. This suggests that in the case of the methyl-substituted systems, three-alkyne 'fly-over' complexes and octatrienediylidenedimolybdenum species are *not* formed sequentially, but instead arise from competitive reaction pathways which are available to some earlier intermediate in the reaction sequence.

Since cyclic voltammetric studies[30,31] show that the cations [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η^5-C$_m$H$_n$)][BF$_4$] undergo an irreversible one-electron reduction in thf, it is likely that the molybdenum-centred odd-electron species, which is probably generated, dimerises to form a molybdenum–molybdenum bond. As is shown in Scheme 7 the resultant dinuclear species now contains the four but-2-yne molecules needed to assemble a C$_8$ chain. In the case of the indenyl system competitive loss of one but-2-yne ligand could lead to the formation of an intermediate [Mo$_2$(μ-C$_4$Me$_4$)(η^2-MeC$_2$Me)(η^5-C$_9$H$_7$)$_2$] (**D**) (Scheme 7), related to the recently[32] isolated and structurally characterised molecule [W$_2$(OPr^i)$_6$(μ-C$_4$Me$_4$)(η^2-MeC$_2$Me)], which on thermal decomposition yields hexamethylbenzene. Rearrangement of the η^2-bonded but-2-yne molecule present in (**D**) to a bridging mode then clearly sets things up for a reductive-elimination reaction with concomitant C–C bond formation affording the C$_6$ 'fly-over' complex (**1**). It is interesting to note that a change in which an Mo–C bond is broken in this last step can lead to a three-alkyne system, *i.e.* a molybdenacycloheptatriene, where the C$_6$ chain begins and ends at one molybdenum centre. Such a species could be involved in the competitive formation of the octatrienediylidenedimolybdenum complexes, which might also directly arise[10] from the intermediate [Mo$_2$(η^2-MeC$_2$Me)$_4$(η-C$_5$H$_5$)$_2$]. These reaction pathways will be discussed in detail in a subsequent paper concerned with the reactions of related systems carrying unsymmetrical alkynes.

Experimental

The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra were recorded on JEOL FX 90 Q or FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference; SiMe$_4$ for ^{1}H and ^{13}C. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and mass



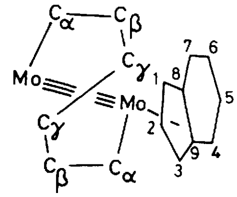
Scheme 7. (*i*) + 1 e; (*ii*) $-MeC_2Me$

spectra on a MS 902 spectrometer operating at 70 eV. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Preparation of $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(\eta^5\text{-}C_9H_7)_2]$ (**1**).—Magnesium turnings (1.0 g, 41 mmol) were added gradually to mercury (15 cm^3) with stirring. The amalgam was stirred for a further 1.5 h after the addition was complete. A solution of $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_9H_7)][BF_4]$[12] (2.4 g, 4.7 mmol) in thf (50 cm^3) was then added to the amalgam and stirred at room temperature for 2 h. The supernatant solution was collected, and the amalgam washed with thf (2 × 5 cm^3). The extracts were combined and the solvent removed *in vacuo*. The residue was dissolved in toluene and chromatographed on an alumina packed column. Elution with toluene gave a green band, which was collected and rechromatographed on alumina using diethyl ether as eluant. The resultant green band was collected, the volume of solvent reduced to *ca.* 5 cm^3 *in vacuo*. Cooling the solution to 195 K for 120 h afforded green *crystals* of (**1**) (0.472 g, 26%) (Found: C, 61.5; H, 5.5%; *M*, 584. $C_{30}H_{32}Mo_2$ requires C, 61.7; H, 5.5%; *M*, 584). N.m.r.: ^1H (C_6D_6), δ 6.80 (m), 6.68 (m), 6.33 (m), 4.73 (m) (indenyl protons, 14 H), 2.97 (s, 6 H, Me), 1.60 (s, 6 H, Me), 1.51 (s, 6 H, Me); $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 204.6 (C_α), 122.8 (C^5), 122.5 (C^7), 122.2 (C^6), 118.3 (C^4), 116.9 (C_β), 115.4 (C^8), 113.4 (C^9), 100.2 (C^2), 99.2 (C_γ), 88.4 (C^1), 86.3 (C^3), 32.1 (Me), 20.7 (Me), and 15.5 p.p.m. (Me).

Reduction with Na/Hg or $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ in thf under identical conditions gave (**1**) (10% yield).

Reactions of (**1**).—(*a*) *With carbon monoxide.* An excess of carbon monoxide was bubbled through a solution of (**1**) (0.06 g, 0.1 mmol) in hexane (5 cm^3) held at 273 K. After 1 h the solvent was removed, *in vacuo*, and the residue dissolved in diethyl ether and chromatographed on an alumina packed column. Elution with diethyl ether gave one green band, which was collected, the volume of the solvent reduced *in vacuo* to 3 cm^3 and cooled to 273 K affording (48 h) small green *crystals* of $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)(CO)_2(\eta^5\text{-}C_9H_7)_2]$ (**2**) (0.02 g, 30%) (Found: C, 59.7; H, 5.3. $C_{32}H_{32}Mo_2O_2$ requires C, 60.0; H, 5.0%); ν_{CO} (diethyl ether) 1 886s cm^{-1}. N.m.r.: ^1H (C_6D_6), δ 6.84 (m, 8 H, indenyl H^{4-7}, $H^{4'-7'}$), 5.35 [t, 1 H, H^1, $J(H^1H^2)$ 3.2, $J(H^1H^3)$ 3.2], 5.12 [d, 1 H, H^3, $J(H^3H^1)$ 3.2], 5.10 [t, 1 H, $H^{1'}$, $J(H^{1'}H^{2'})$ 1.95, $J(H^{1'}H^{3'})$ 1.95], 5.02 [d, 1 H, $H^{3'}$, $J(H^{3'}H^{2'})$ 1.95], 4.40 (m, 1 H, H^2), 4.02 (m, 1 H, $H^{2'}$), 2.87 (s, 3 H, Me), 2.71 (s, 3 H, Me), 1.33 (s, 3 H, Me), 1.30 (s, 3 H, Me), 1.18 (s, 3 H, Me), 0.96 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 243.5 (CO), 237.9 (CO), 197.3(C_α or $C_{\alpha'}$), 158.6 (C_α or $C_{\alpha'}$), 129.6, 125.3, 124.6, 124.5, 123.4, 122.6, 121.9, 119.5, 115.9, 115.4, 110.0, 108.9 (indenyl), 107.8 (C_β or $C_{\beta'}$), 106.9 (indenyl), 103.7 (C_β or $C_{\beta'}$), 99.6, 90.4, 89.5 (indenyl), 89.1 (C_γ or $C_{\gamma'}$), 85.3 (C_γ or $C_{\gamma'}$), 78.8 (indenyl), 73.8 (indenyl), 35.1 (Me), 28.0 (Me), 26.2 (Me), 24.0 (Me), 16.3 (Me), 14.4 p.p.m. (Me).



(*b*) *With carbon monoxide in refluxing hexane.* Carbon monoxide was bubbled through a refluxing solution of (**1**) (0.06

Table 4. Atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	3 480(1)	388(2)	0	C(29)	4 974(13)	2 115(24)	1 368(6)
Mo(2)	3 993(1)	1 551(2)	509(1)	C(28)	5 744(14)	2 806(23)	1 342(6)
Mo(3)	3 621(1)	6 644(2)	2 409(1)	C(27)	5 913(15)	3 897(27)	1 090(6)
Mo(4)	4 119(1)	6 037(2)	2 971(1)	C(26)	5 302(13)	4 430(25)	842(6)
C(1)	3 542(9)	−905(17)	485(4)	C(25)	4 462(11)	3 809(19)	865(5)
C(1′)	2 769(12)	−1 603(23)	674(5)	C(15)	2 877(11)	−518(21)	−601(5)
C(2)	4 332(10)	−960(19)	642(5)	C(14)	2 788(12)	1 055(22)	−564(5)
C(2′)	4 538(12)	−1 568(22)	1 012(5)	C(13)	2 243(12)	1 358(22)	−283(5)
C(3)	4 979(10)	−294(17)	410(4)	C(12)	2 030(12)	−18(20)	−112(6)
C(3′)	5 907(11)	−136(22)	535(5)	C(11)	2 401(13)	−1 253(23)	−319(6)
C(4)	4 825(8)	−592(16)	20(5)	C(19)	2 416(13)	−2 897(23)	−297(6)
C(4′)	4 982(11)	−2 236(18)	−113(4)	C(18)	2 809(13)	−3 742(25)	−545(6)
C(5)	4 880(12)	780(21)	−188(5)	C(17)	3 291(13)	−3 056(24)	−806(6)
C(5′)	5 189(12)	756(24)	−577(5)	C(16)	3 324(14)	−1 503(25)	−843(6)
C(6)	4 582(9)	2 070(16)	3(5)	C(41)	4 699(13)	5 588(23)	3 608(6)
C(6′)	4 631(10)	3 667(20)	−160(5)	C(42)	4 810(15)	7 120(28)	3 513(6)
C(51)	3 093(12)	7 809(22)	2 866(5)	C(43)	5 362(17)	7 164(33)	3 189(7)
C(51′)	3 174(16)	9 541(22)	2 915(7)	C(44)	5 529(17)	5 724(29)	3 120(8)
C(52)	2 782(13)	6 832(23)	3 132(6)	C(45)	5 162(15)	4 596(27)	3 353(6)
C(52′)	2 513(14)	7 385(33)	3 503(5)	C(46)	5 119(17)	3 071(31)	3 393(7)
C(53)	2 757(11)	5 264(20)	2 997(5)	C(47)	4 622(16)	2 361(33)	3 655(7)
C(53′)	2 466(14)	3 947(25)	3 247(6)	C(48)	4 209(16)	3 376(29)	3 904(7)
C(54)	2 558(11)	5 088(20)	2 613(5)	C(49)	4 239(14)	4 859(26)	3 889(6)
C(54′)	1 624(11)	5 329(25)	2 479(5)	C(33)	4 576(14)	7 794(23)	1 998(5)
C(55)	3 143(12)	4 148(20)	2 432(5)	C(32)	4 243(13)	6 512(23)	1 812(5)
C(55′)	2 900(19)	3 148(25)	2 126(6)	C(31)	3 365(12)	6 872(21)	1 725(5)
C(56)	3 991(11)	4 250(19)	2 577(5)	C(35)	3 171(13)	8 299(22)	1 891(5)
C(56′)	4 735(15)	3 234(27)	2 433(6)	C(34)	3 936(12)	8 872(23)	2 073(6)
C(24)	3 693(13)	4 136(25)	672(6)	C(36)	2 732(12)	6 053(24)	1 532(5)
C(23)	3 070(13)	3 209(22)	827(5)	C(37)	1 956(16)	6 762(26)	1 511(7)
C(22)	3 401(11)	2 245(22)	1 085(5)	C(38)	1 773(15)	8 104(27)	1 660(6)
C(21)	4 278(11)	2 641(20)	1 134(5)	C(39)	2 324(14)	8 942(26)	1 863(6)

g, 0.1 mmol) in hexane (10 cm^3). After 5 h the reaction mixture was filtered through Celite and the solvent removed *in vacuo*. The residue was chromatographed on an alumina packed column. Elution with hexane–diethyl ether (10:1) afforded progressively pink and purple bands which contained only traces of material which were not identified. Further elution gave a forest-green band which was collected and crystallised from hexane (273 K) to give green *crystals* of (**3**) (0.008 g, 8%); ν_{CO} (hexane) 1 909 cm^{-1}. The mass spectrum showed peaks at *m/e* 640 (*P*), 612 (*P* − CO), and 584 (*P* − 2CO). N.m.r.: ^1H (C_6D_6), δ 7.46—6.60 (m, 8 H, indenyl), 4.92 (m, 2 H, indenyl), 4.37 (m, 2 H, indenyl), 3.91 (m, 2 H, indenyl), 3.19 (s, 6 H, Me), 1.15 (s, 6 H, Me), and 0.85 p.p.m. (s, 6 H, Me).

(*c*) *With* 2,6-*xylyl isocyanide*. A solution of (**1**) (0.06 g, 0.1 mmol) and 2,6-xylyl isocyanide (0.027 g, 0.2 mmol) in diethyl ether (15 cm^3) was stirred at room temperature for 4 h. The volume of the solvent was reduced *in vacuo*, and chromatographed on alumina. Elution with diethyl ether gave a single orange-brown band, which was collected, and recrystallised (195 K, 150 h) from diethyl ether (5 cm^3) to afford orange-brown *crystals* of $[Mo_2\{\mu\text{-}\sigma,\eta^3\text{:}\eta^3,\sigma\text{-}C_6Me_6\}(CNC_6H_3Me_2\text{-}2,6)_2(\eta^5\text{-}C_9H_7)_2]$ (**4**) (0.037 g, 43%) (Found: C, 67.8; H, 5.8; N, 3.0. $C_{48}H_{50}Mo_2N_2$ requires C, 68.1; H, 6.0; N, 3.3%); ν_{NC} (CH_2Cl_2) 2 065 cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), δ 7.20 (m, 4 H, indenyl), 7.15 (br s, 4 H, H^3 and H^5, isocyanide), 7.12 (br s, 2 H, H^4, isocyanide), 6.96 (m, 4 H, indenyl), 6.87 (m, 4 H, indenyl), 5.30 (br m, 2 H, indenyl), 3.40 (s, 6 H, Me), 2.43 (s, 6 H, Me, isocyanide), 2.40 (s, 6 H, Me, isocyanide), 1.42 (s, 6 H, Me), 1.08 (s, 6 H, Me); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 186.4 (C_α), 159.6 ($\mathit{C}NC_6H_3Me_2$), 134.7 ($CN\mathit{C}_6H_3Me_2$), 132.5 ($CN\mathit{C}_6H_3Me_2$), 129.1 (indenyl), 129.0 (indenyl), 128.5 ($CN\mathit{C}_6H_3Me_2$), 128.1 (indenyl), 127.7 ($CN\mathit{C}_6H_3Me_2$), 127.5 (indenyl), 126.1 ($CN\mathit{C}_6H_3Me_2$), 115.1 (indenyl), 113.9 (indenyl), 108.3 (C_β), 91.7 (indenyl), 87.4 (C_γ), 86.1 (indenyl), 30.1 (Me), 26.0 (Me), 19.4 ($CNC_6H_3\mathit{Me}_2$), 19.0 ($CNC_6H_3\mathit{Me}_2$), and 16.9 p.p.m. (Me).

(*d*) *With but*-2-*yne*. The complex (**1**) (0.08 g, 0.1 mmol) was placed in a Young's tube and an excess of but-2-yne (5 cm^3) condensed (77 K) into the vessel. After 600 h at room temperature the volatile material was removed *in vacuo*. Examination of the residue by ^1H n.m.r. showed the material to be pure (**1**).

X-Ray Diffraction Studies.—*Crystal data for* (**1**). $C_{30}H_{32}Mo_2$, *M* = 584.5, orthorhombic, *a* = 15.673(10), *b* = 8.649(6), *c* = 37.49(2) Å, *U* = 5 082(6) Å^3, space group *Pna*2_1 (no. 33), *Z* = 8, D_c = 1.53 g cm^{-3}, *F*(000) = 2 367, graphite-monochromated Mo-K_α *X*-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 9.78 cm^{-1}.

Crystal data for (**2**). $C_{32}H_{32}Mo_2O_2$, *M* = 640.5, monoclinic, *a* = 13.164(2), *b* = 14.619(3), *c* = 13.718(3) Å, β = 95.59(2)°, *U* = 2 628(1) Å^3, space group *P*2_1/*c* (no. 14), *Z* = 4, D_c = 1.70 g cm^{-3}, *F*(000) = 1 296, graphite-monochromated Mo-K_α *X*-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 9.58 cm^{-1}.

Crystals of (**1**) and (**2**) are slightly air-sensitive and were therefore sealed under N_2 in thin-walled glass capillaries for *X*-ray diffraction study. Intensity data were collected at room temperature on a Nicolet *P*3*m* diffractometer using graphite-monochromated Mo-K_α *X*-radiation. In each case data were collected by θ/2θ scans [of width 2.0 + $\Delta\alpha_1\alpha_2$ and 2.4 + $\Delta\alpha_1\alpha_2$° for (**1**) and (**2**) respectively] for unique volumes of reciprocal space in the range 4 < 2θ < 50°. Absorption corrections were applied by Gaussian quadrature based on indexed crystal faces and dimensions; transmission coefficients were in the range 0.928—0.711 for (**1**) and 0.940—0.686 for (**2**). For (**1**), 4 223 intensities were measured, giving 3 431 unique data after

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	1 955(1)	1 259(1)	1 954(1)	C(11)	1 674(4)	2 829(4)	2 522(4)
Mo(2)	2 809(1)	−452(1)	1 271(1)	C(12)	1 549(4)	2 173(4)	3 282(4)
O(200)	5 173(3)	−526(3)	1 702(3)	C(13)	705(4)	1 616(4)	2 999(4)
O(100)	1 106(3)	1 220(3)	−259(3)	C(14)	343(4)	1 864(4)	2 034(4)
C(200)	4 286(4)	−536(4)	1 588(4)	C(15)	909(4)	2 636(4)	1 734(4)
C(100)	1 425(4)	1 175(3)	556(4)	C(16)	813(5)	3 210(4)	885(4)
C(1)	1 608(4)	−115(3)	2 296(4)	C(17)	1 460(6)	3 928(4)	863(5)
C(1′)	513(4)	−477(4)	2 189(4)	C(18)	2 232(6)	4 102(4)	1 620(6)
C(2)	2 376(4)	−634(3)	2 821(3)	C(19)	2 346(5)	3 528(4)	2 433(4)
C(2′)	2 210(5)	−1 527(4)	3 331(4)	C(21)	2 986(4)	−1 856(4)	360(4)
C(3)	3 362(4)	−187(3)	2 912(3)	C(22)	3 179(4)	−1 058(4)	−206(4)
C(3′)	4 221(4)	−659(4)	3 552(4)	C(23)	2 259(4)	−571(4)	−393(4)
C(4)	3 396(4)	849(3)	2 930(4)	C(24)	1 510(4)	−1 006(4)	109(4)
C(4′)	3 672(4)	1 216(4)	3 965(4)	C(25)	1 930(4)	−1 823(4)	550(4)
C(5)	3 673(3)	1 360(3)	2 098(4)	C(26)	1 521(4)	−2 532(4)	1 083(5)
C(5′)	4 309(4)	2 227(4)	2 171(4)	C(27)	2 140(6)	−3 228(4)	1 402(5)
C(6)	3 341(3)	943(3)	1 186(3)	C(28)	3 181(5)	−3 268(4)	1 241(5)
C(6′)	3 672(4)	1 360(4)	252(4)	C(29)	3 601(4)	−2 589(4)	740(4)

averaging duplicate and symmetry-equivalent observations; of these 2 872 with $I > 1.5\sigma(I)$ were used in structure solution and refinement. For (**2**), of 4 252 of data collected, 3 538 were unique and of these 3 217 with $I > 1.5\sigma(I)$ were used in structure solution and refinement. The structures were solved by conventional heavy-atom methods (Patterson and Fourier) and refined by blocked-cascade full-matrix least squares. For (**1**), hydrogen atoms were incorporated in idealised geometries with C–H 0.96 Å and fixed U_{iso} of *ca.* 1.2 times that of their attached carbon atom; non-hydrogen atoms were refined without positional constraints [except for Mo(1) whose *z* co-ordinate was fixed] and molybdenum and methyl-group carbon atoms were assigned anisotropic vibrational parameters, with others isotropic. For (**2**), all non-hydrogen atoms were refined without constraints each being assigned anisotropic vibrational parameters; hydrogen atoms were located on difference Fourier maps and refined without constraint, with isotropic vibrational parameters. Intensity data were assigned weights $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$ with *g* chosen to minimise the variation of $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$ [$g = 0.0007$ for (**1**), 0.0005 for (**2**)]. Refinement converged to final residuals* $R = 0.059$, $R' = 0.058$ for (**1**) and 0.035 and 0.035 for (**2**). Final difference electron-density syntheses showed no features of magnitude >0.85 e Å^{-3} for (**1**) and >0.73 e Å^{-3} for (**2**). Complex neutral-atom scattering factors were taken from ref. 33. All calculations were carried out with programs of the SHELXTL package[34] on a Data General Eclipse ® minicomputer. Final atomic positional parameters are given in Tables 4 and 5 for (**1**) and (**2**) respectively.

Acknowledgements

We thank the S.E.R.C. and the donors of the Petroleum Research Fund administered by the American Chemical Society for support.

References

1 Part 35, M. Green, A. G. Orpen, C. J. Schaverien, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 2483.
2 W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Liebigs Ann. Chem.*, 1948, **560**, 1.
3 G. I. Fray and R. G. Saxton, 'The Chemistry of Cyclo-octatetraene and its Derivatives,' Cambridge University Press, 1978.
4 R. E. Colburn and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1981, **103**, 6259.
5 G. N. Schrauzer and S. Eichler, *Chem. Ber.*, 1962, **95**, 550; G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem.*, 1964, **76**, 28; E-A. Reinsch, *Theor. Chim. Acta*, 1970, **17**, 309.
6 G. Wilke, *Pure Appl. Chem.*, 1978, **50**, 677.
7 W. Geilbel, G. Wilke, R. Goddard, C. Krüger, and R. Mynott, *J. Organomet. Chem.*, 1978, **160**, 139.
8 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 221; *J. Chem. Soc., Dalton Trans.*, 1982, 173.
9 J. A. Beck, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 195.
10 M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, 1981, **103**, 1269.
11 M. Green, N. C. Norman, A. G. Orpen, and C. J. Schaverien, *J. Chem. Soc., Dalton Trans.*, 1984, 2455.
12 S. R. Allen, P. K. Baker, S. F. Barnes, M. Green, L. Trollope, L. M. Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1981, 873.
13 F. A. Cotton and R. A. Walton, in 'Multiple Bonds between Metal Atoms,' John Wiley, New York, 1982, p. 183.
14 A. F. Dyke, J. E. Guerchais, S. A. R. Knox, J. Roué, R. L. Short, G. E. Taylor, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 537.
15 G. K. Barker, W. E. Carroll, M. Green, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1071.
16 J. C. Jeffrey, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1981, 1255.
17 J. Leuisalles, F. Rose-Munch, H. Rudler, J-C. Davau, Y. Dromzee, and Y. Jeaun, *J. Chem. Soc., Chem. Commun.*, 1981, 152.
18 O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 1964, 187; R. S. Dickson, P. J. Fraser, and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.*, 1972, 2278; M. J. Mays, D. W. Prest, and P. R. Raithby, *ibid.*, 1981, 771; D. B. Pourveau, R. R. Whittle, and G. L. Geoffroy, *J. Organomet. Chem.*, 1984, **273**, 333.
19 M. H. Chisholm, F. A. Cotton, B. A. Frenz, and L. Shine, *J. Chem. Soc., Chem. Commun.*, 1974, 480.
20 F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1971, 1079.
21 R. J. Klinger, W. M. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, 1978, **100**, 5034.
22 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1979, 934.
23 M. Mathew and G. J. Palenik, *J. Organomet. Chem.*, 1973, **61**, 301.
24 R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086.
25 Y. N. Al-Obaidi, M. Green, N. D. White, J-M. Bassett, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 494.

---

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

26 A. M. Boileau, A. G. Orpen, R. F. D. Stansfield, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 187.
27 M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 4389.
28 Ref. 13, p. 252.
29 F. A. Cotton and G. Wilkinson, in 'Advanced Inorganic Chemistry,' 4th edn., John Wiley, New York, 1980, p. 1159.
30 S. R. Allen, N. G. Connelly, and M. Green, unpublished work.
31 W. E. Geiger, jun., and D. Pufahl, unpublished work; personal communication to M. G.
32 M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 6806.
33 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
34 G. M. Sheldrick, 'SHELXTL, an Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data,' revision no. 4, Nicolet Instruments Ltd., Warwick, January 1983.

Received 15*th May* 1985; *Paper* 5/814