Reactions of Co-ordinated Ligands. Part 43.[1] Alkyne Linking Reactions at Dimetal Centres. Synthesis and Structures of $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8H_4Bu^t_4)\}(\eta\text{-}C_5H_5)_2]$, $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}CH{=}CHBu^tC_6H_2Bu^t_3)\}(\eta\text{-}C_5H_5)_2]$, and $[FeMo(CO)_2(C_4Me_2Ph_2)(\eta\text{-}C_5H_5)_2]$ *

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Addition of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ to a solution of $[Mo(NCMe)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$ in tetrahydrofuran affords the two complexes $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8H_4Bu^t_4)\}(\eta\text{-}C_5H_5)_2]$ (**1**) and $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}CH{=}CHBu^tC_6H_2Bu^t_3)\}(\eta\text{-}C_5H_5)_2]$ (**2**), structurally identified by n.m.r. spectroscopy and single-crystal *X*-ray crystallography. In (**1**) a C_8 chain bridges the Mo $\cdots$ Mo vector [Mo(1)–Mo(2) 2.639(1) Å], the chain beginning and ending with σ bonds to Mo(2). Carbons C(1), C(2), C(3) and C(6), C(7), C(8) each form an η^3-allylic interaction with Mo(1) with C(4) and C(5) bonded as an η^2-alkene to Mo(2). In contrast, complex (**2**) can be described as a 5-vinyl substituted C_6 'fly-over' complex where the C_8 ligand bonds *via* a C–Mo σ bond to Mo(2) and an η^4-diene-like interaction to Mo(1). One of the carbons, C(2), symmetrically bridges the Mo_2 unit [Mo(1)–Mo(2) 2.705(5) Å]. The mechanism of formation of these complexes is discussed. An attempt to extend these reactions to $[Mo(NCMe)(\eta^2\text{-}PhC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ resulted in the formation of the dinuclear complexes $[FeMo(CO)_2(C_4Me_2Ph_2)(\eta\text{-}C_5H_5)_2]$ (**3**) and $[FeMo(CO)_2(C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ (**4**), the former being structurally characterised by *X*-ray crystallography.

One possible reaction pathway[2] for the nickel-catalysed formation of cyclo-octatetraene from ethyne (the Reppe reaction[3]), which has attracted attention,[4–12] involves the stepwise linking of ethyne at two metal centres. However, such linking reactions are not at all that well understood and our observations[6,12,13] that one-electron reduction of the molybdenum cations of $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_nH_m)][BF_4]$ ($n = m = 5$, $n = 9$, $m = 7$) formed dimolybdenum species containing four or three linked but-2-yne molecules provided an opportunity to gain greater insight into such carbon–carbon bond forming reactions. Thus, it was especially interesting to observe that with the $\eta\text{-}C_5H_5$ substituted cation, linking of four but-2-yne molecules occurs leading to the formation of an (octamethyloctatrienediylidene)dimolybdenum 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; whereas reduction of the corresponding η^5-indenyl cation gives the 'fly-over' complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(\eta^5\text{-}C_9H_7)_2]$. In attempting to understand the inter-relationship of these reactions we have examined the reduction of the η-cyclopentadienyl substituted cations carrying unsymmetrically substituted alkynes.

Results and Discussion

There was a rapid colour change when the one-electron reducing agent $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ was added to a stirred solution of $[Mo(NCMe)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$ in tetrahydrofuran (thf) at 0 °C. Chromatographic work-up of the reaction mixture at low temperature (−40 °C) gave, on elution with hexane, the di-iron complex $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, followed by two complexes (**1**) and (**2**), which were isolated as blue-black and green crystalline materials respectively. Examination of the mass and n.m.r. spectra (see Experimental section) suggested that these complexes were isomeric dinuclear species $[Mo_2A_4(\eta\text{-}C_5H_5)_2]$ (A = alkyne) each containing four 3,3-dimethylbut-1-yne molecules. Initially it was thought that both of these isomers were complexes containing a C_8 chain beginning and ending with σ bonds to one molybdenum atom, *i.e.* (octatrienediylidene)dimolybdenum species; however, single crystal *X*-ray crystallography showed that the situation was in fact more interesting.

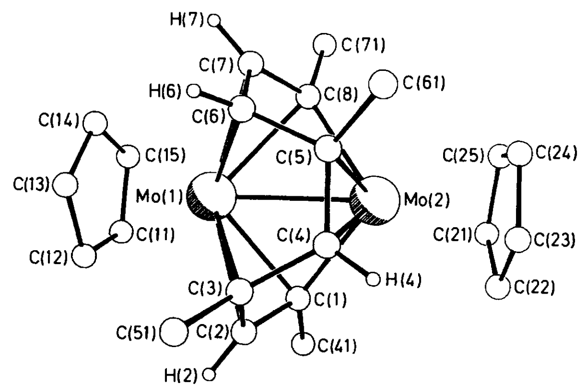


Figure 1. Molecular structure of (1). Only quaternary carbons of the t-butyl groups are shown [C(41), C(51), C(61), C(71)] for clarity. Hydrogen atoms of the cyclopentadienyl groups have been omitted

An *X*-ray crystallographic study of (**1**) established the molecular geometry shown in Figure 1; bond lengths and angles are listed in Table 1. The structure closely resembles that

* μ-[2,2,11,11-Tetramethyl-5,7-di-t-butyldodeca-4,6,8-triene-3,10-diylidene-$C^{3,6,7,10}$(Mo^1),$C^{3-5,8-10}$(Mo^2)]-bis(η-cyclopentadienylmolybdenum) (*Mo=Mo*), μ-[7,7-dimethyl-2,4-di-t-butyl-5-(t-butylvinyl)-octa-1,3,5-triene-1,6-diyl-$C^{1,5,5\alpha,5\beta,6}$(Mo^1), C^{1-6}(Mo^2)]-bis(η-cyclopentadienylmolybdenum)(*Mo=Mo*),and 2,2-dicarbonyl-1,2-bis(η-cyclopentadienyl)-μ-[1,3-dimethyl-2,4-diphenylbuta-1,3-diene-1,4-diyl-$C^{1,4}$(Mo), C^{1-4}(Fe)]ironmolybdenum (*Mo–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

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

Mo(1)–Mo(2)	2.639(1)	C(5)–C(61)	1.561(4)	Mo(1)–C(1)	2.245(2)	C(6)–C(7)	1.410(4)
Mo(1)–C(2)	2.309(3)	C(7)–C(8)	1.410(3)	Mo(1)–C(3)	2.408(3)	C(8)–C(71)	1.561(5)
Mo(1)–C(6)	2.250(2)	C(41)–C(42)	1.546(5)	Mo(1)–C(7)	2.269(3)	C(41)–C(43)	1.540(3)
Mo(1)–C(8)	2.317(4)	C(41)–C(44)	1.531(5)	Mo(1)–C(11)	2.388(4)	C(51)–C(52)	1.510(6)
Mo(1)–C(12)	2.367(5)	C(51)–C(53)	1.516(5)	Mo(1)–C(13)	2.342(4)	C(51)–C(54)	1.509(4)
Mo(1)–C(14)	2.337(4)	C(61)–C(62)	1.527(4)	Mo(1)–C(15)	2.354(4)	C(61)–C(63)	1.549(4)
Mo(2)–C(1)	2.143(3)	C(61)–C(64)	1.535(5)	Mo(2)–C(4)	2.213(3)	C(71)–C(72)	1.537(4)
Mo(2)–C(5)	2.293(2)	C(71)–C(73)	1.549(6)	Mo(2)–C(8)	2.118(3)	C(71)–C(74)	1.528(4)
Mo(2)–C(21)	2.410(3)	C(11)–C(12)	1.376(7)	Mo(2)–C(22)	2.443(2)	C(11)–C(15)	1.337(6)
Mo(2)–C(23)	2.429(3)	C(12)–C(13)	1.407(6)	Mo(2)–C(24)	2.416(4)	C(13)–C(14)	1.371(9)
Mo(2)–C(25)	2.409(4)	C(14)–C(15)	1.358(6)	C(1)–C(2)	1.425(4)	C(21)–C(22)	1.414(5)
C(1)–C(41)	1.562(3)	C(21)–C(25)	1.400(5)	C(2)–C(3)	1.409(3)	C(22)–C(23)	1.383(4)
C(3)–C(4)	1.506(4)	C(23)–C(24)	1.415(5)	C(3)–C(51)	1.559(4)	C(24)–C(25)	1.401(4)
C(4)–C(5)	1.432(4)			C(5)–C(6)	1.503(3)		
Mo(2)–Mo(1)–C(1)	51.3(1)	Mo(2)–C(1)–C(41)	129.7(2)	Mo(2)–Mo(1)–C(2)	73.6(1)	C(2)–C(1)–C(41)	117.9(3)
C(1)–Mo(1)–C(2)	36.4(1)	Mo(1)–C(2)–C(1)	69.3(1)	Mo(2)–Mo(1)–C(3)	72.7(1)	Mo(1)–C(2)–C(3)	76.5(2)
C(1)–Mo(1)–C(3)	63.3(1)	C(1)–C(2)–C(3)	119.1(3)	C(2)–Mo(1)–C(3)	34.7(1)	Mo(1)–C(3)–C(2)	68.8(2)
Mo(2)–Mo(1)–C(6)	72.8(1)	Mo(1)–C(3)–C(4)	93.7(2)	C(1)–Mo(1)–C(6)	115.6(1)	C(2)–C(3)–C(4)	114.1(2)
C(2)–Mo(1)–C(6)	106.0(1)	Mo(1)–C(3)–C(51)	130.7(2)	C(3)–Mo(1)–C(6)	72.7(1)	C(2)–C(3)–C(51)	120.8(3)
Mo(2)–Mo(1)–C(7)	73.5(1)	C(4)–C(3)–C(51)	117.9(2)	C(1)–Mo(1)–C(7)	124.7(1)	Mo(2)–C(4)–C(3)	105.7(2)
C(2)–Mo(1)–C(7)	136.5(1)	Mo(2)–C(4)–C(5)	74.5(2)	C(3)–Mo(1)–C(7)	107.4(1)	C(3)–C(4)–C(5)	119.7(2)
C(6)–Mo(1)–C(7)	36.3(1)	Mo(2)–C(5)–C(4)	68.5(1)	Mo(2)–Mo(1)–C(8)	50.1(1)	Mo(2)–C(5)–C(6)	98.3(1)
C(1)–Mo(1)–C(8)	95.0(1)	C(4)–C(5)–C(6)	112.6(2)	C(2)–Mo(1)–C(8)	123.6(1)	Mo(2)–C(5)–C(61)	128.8(2)
C(3)–Mo(1)–C(8)	114.6(1)	C(4)–C(5)–C(61)	125.6(2)	C(6)–Mo(1)–C(8)	63.3(1)	C(6)–C(5)–C(61)	113.8(2)
C(7)–Mo(1)–C(8)	35.8(1)	Mo(1)–C(6)–C(5)	102.9(1)	Mo(1)–Mo(2)–C(1)	54.8(1)	Mo(1)–C(6)–C(7)	72.5(1)
Mo(1)–Mo(2)–C(4)	73.4(1)	C(5)–C(6)–C(7)	116.2(2)	C(1)–Mo(2)–C(4)	79.7(1)	Mo(1)–C(7)–C(6)	71.1(2)
Mo(1)–Mo(2)–C(5)	73.7(1)	Mo(1)–C(7)–C(8)	73.9(2)	C(1)–Mo(2)–C(5)	108.5(1)	C(6)–C(7)–C(8)	116.4(2)
C(4)–Mo(2)–C(5)	37.0(1)	Mo(1)–C(8)–Mo(2)	72.9(1)	Mo(1)–Mo(2)–C(8)	57.0(1)	Mo(1)–C(8)–C(7)	70.2(2)
C(1)–Mo(2)–C(8)	104.2(1)	Mo(2)–C(8)–C(7)	112.0(2)	C(4)–Mo(2)–C(8)	108.7(1)	Mo(1)–C(8)–C(71)	135.0(2)
C(5)–Mo(2)–C(8)	79.4(1)	Mo(2)–C(8)–C(71)	129.6(2)	Mo(1)–C(1)–C(2)	74.2(1)	C(7)–C(8)–C(71)	116.9(2)
Mo(2)–C(1)–C(2)	111.4(2)			Mo(1)–C(1)–C(41)	127.9(2)		

Table 2. Proton and ^{13}C n.m.r. data for complexes (**1**)—(**4**); chemical shifts in p.p.m. relative to $SiMe_4$, coupling constants in Hz

Compound	^{1}H (δ)[b]	^{13}C-{^{1}H} (δ)[b]
(**1**)[a]	6.88 [s, 1 H, H(2)], 6.73 {dd, 1 H, H(6), ^3J[H(6)H(7)], 3.7, ^4J[H(6)H(4)] 2.0}, 5.46 [s, 5 H, C_5H_5, (A)], 4.48 {d, 1 H, H(7), ^3J[H(6)H(7)] 3.7}, 4.38 [s, 5 H, C_5H_5, (B)], 1.55 {d, 1 H, H(4), ^4J[H(6)H(4)] 2.0}, 1.46 [s, 9 H, Bu^t, (C)], 1.34 [s, 18 H, Bu^t, (A and B)], 1.01 [s, 9 H, Bu^t, (D)]	203.42, 190.38 [C(1) and C(8)], 98.45 [C(6)], 97.17 [C(2)], 95.73 [C_5H_5, (A)], 92.55, 92.10 [C(3), C(5)], 85.32 [C_5H_5, (B)], 54.71 [C(7)], 49.69 [C(4)], 44.39, 43.91, 39.14, 38.29 (quaternary carbons in Bu^t group), 35.18 [Bu^t, (A)], 34.10 [Bu^t, (B)] 33.05 [Bu^t, (C)], 32.37 [Bu^t, (D)]
(**2**)	9.32 {dd, 1 H, H(6), ^4J[H(4)H(6)] 1.1, ^4J[H(6)H(8)] 1.8}, 5.36 (s, 5 H, C_5H_5), 5.21 {d, 1 H, H(8), ^4J[H(6)H(8)] 1.8}, 4.51 (s, 5 H, C_5H_5), 3.37 {dd, 1 H, H(4), ^4J[H(4)H(6)] 1.1, ^3J[H(4)H(5)] 10.0}, 1.65 (s, 9 H, Bu^t), 1.32 (s, 9 H, Bu^t), 1.23 (s, 9 H, Bu^t), 0.77 (s, 9 H, Bu^t), −3.31 {d, 1 H, H(5), ^3J[H(4)H(5)] 10.0}	149.8, 136.1 [C(6)], 109.4, 91.6 (C_5H_5), 90.4, 85.5 (C_5H_5), 81.1 [C(8)], 75.7 [C(4)], 74.7 [C(5)], 43.4, 38.6, 38.2, 33.5 (quaternary carbons in Bu^t group), 35.7, 33.0, 32.8, 31.9 (Bu^t)
(**3**)	7.27 (br m, 10 H, Ph), 4.21 (s, 5 H, C_5H_5), 4.05 (s, 5 H, C_5H_5), 2.62 (s, 3 H, Me), 1.71 (s, 3 H, Me)	243.2 (CO), 240.1 (CO), 162.7 (C_α), 158.8 (C_α), 155.6, 141.9, 131.5, 130.3, 129.5, 128.3, 128.0, 127.8, 127.5, 127.2, 126.6, 124.4 (Ph), 119.7 (C_β), 107.2 (C_β), 89.0 (C_5H_5), 76.0 (C_5H_5), 34.8 (Me), 20.6 (Me)
(**4**)	7.20, 7.05, 6.84 (br m, 20 H, Ph), 4.49 (s, 5 H, C_5H_5), 4.29 (s, 5 H, C_5H_5)	239.4 (CO), 163.8 (C_α), 155.5—141.5 (Ph), 116.5 (C_β), 90.4 (C_5H_5), 78.5 (C_5H_5)

[a] ^{95}Mo (C_6D_6), δ −285 ($\Delta\upsilon_{\frac{1}{2}}$ 100 Hz), +763 ($\Delta\upsilon_{\frac{1}{2}}$ 385 Hz), spectrum measured on a Varian XL 300 spectrometer operating at 19.5 MHz. Chemical shifts referenced to Na_2MoO_4 (0.2 mol dm^{-3}) at 0.0 p.p.m., positive values to high frequency. [b] In the ^{13}C and ^{1}H spectra the letters A, B, C, and D refer to a correlation between ^{1}H and ^{13}C spectra obtained by a two-dimensional experiment.

found[6,13] for [Mo_2{μ-(σ,η^3:η^2:η^3,σ-C_8Me_8)}(η-C_5H_5)$_2$] in that it contains a C_8 chain bridging the Mo··· Mo vector. The chain begins and ends with σ bonds to Mo(2) from C(1) and C(8). Carbons C(1), C(2), C(3) and C(6), C(7), C(8) each form an η^3-allylic interaction with Mo(1) while C(4) and C(5) are bonded as an η^2-alkene fragment to Mo(2). The co-ordination sphere of each molybdenum atom is completed by an η^5-bonded cyclopentadienyl ligand. The e.a.n. (effective atomic number) rule for each molybdenum is satisfied by a single covalent bond and a dative bond from Mo(1) to Mo(2). While the relevance of this formalism is debatable the bond length, 2.639(1) Å, is consistent with double bond character [see ref. 13 for discussion of this and other features of the Mo_2C_8 core of (**1**)]. Unlike in the complex [Mo_2{μ-(σ,η^3:η^2:η^3,σ-C_8Me_8)}(η-

$C_5H_5)_2]$, the C_8 ring in (**1**) is asymmetric as a result of the Bu^t and H substituents. Thus, carbons C(1), C(3), C(5), and C(8) carry Bu^t groups whilst C(2), C(4), C(6), and C(7) carry hydrogens.

Proton and $^{13}C-\{^1H\}$ n.m.r. spectral data for (**1**) are given in Table 2. The protons H(2), H(4), H(6), and H(7) have been assigned on the basis of their respective couplings while that of the carbons, C(2), C(4), C(6), and C(7) follows from off-resonance experiments. The chemical shifts of the C_8 ring protons vary by over 5 p.p.m., which probably results from magnetic anisotropy associated with the C_8 ring. The ^{13}C chemical shifts do not differ markedly from those expected on the basis of compounds with similar structure.

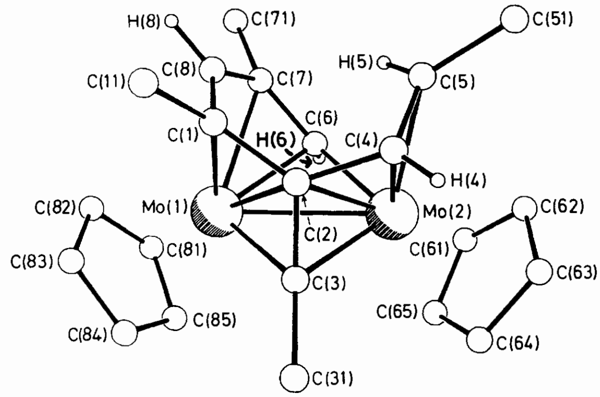


Figure 2. Molecular structure of (**2**), drawn as for (**1**)

Although elemental analysis showed that the second product of the reaction, (**2**), was isomeric with (**1**), examination of the ^1H and $^{13}C-\{^1H\}$ spectra (Table 2) indicated that the organic moiety was bonded to the $Mo_2(\eta-C_5H_5)_2$ core in a very different way to that found in (**1**). This was confirmed by single crystal *X*-ray crystallography on (**2**) as its toluene solvate. The molecular geometry of (**2**) is displayed in Figure 2 and selected bond lengths and interbond angles are listed in Table 3.

The molecular structure of (**2**) shows a dimolybdenum unit bridged by a *branched* chain $C_8H_4Bu^t_4$ ligand, each molybdenum carrying an η^5-cyclopentadienyl ligand. The C_8 ligand acts as a neutral 10 electron donor thus implying a formal Mo–Mo bond order of two, consistent with the observed Mo(1)–Mo(2) bond length of 2.705(5) Å. The C_8 ligand binds *via* a C–Mo σ-bond to Mo(2) [C(6)–Mo(2) 2.065(15) Å] and an η^4-diene-like interaction to Mo(1) [*via* C(6), C(7), C(8), and C(1)]. The carbon atom C(1) is singly bonded to C(2) which symmetrically bridges the Mo_2 unit [C(2)–Mo(1) 2.285(14), C(2)–Mo(2), 2.234(16)] and is further bonded to C(3) and C(4). The carbon skeleton at C(2) is near planar [sum of C–C(2)–C angles = 358.6°] implying that C(2) is involved in a three-centre Mo_2C interaction using a near-pure *p* orbital to bind to Mo(1) and Mo(2). The carbon atom C(3) acts as a symmetrically bridging alkylidene function [Mo(1)–C(3) 2.145(14), Mo(2)–C(3) 2.145(15) Å]. Finally, C(4) and C(5) form an exocyclic vinyl group η^2-bonded to Mo(2), hydrogens H(4) and H(5) adopting a *trans* configuration. The geometry of the C_8 ligand may be conceptually derived from that of a C_6 'fly-over' [C(6), C(7), C(8), C(1), C(2), and C(3)] beginning with a σ-bond to Mo(2) [C(6)–Mo(2)] and ending with a Mo(1)–C(3) σ bond. The distortion required to accommodate the η^2-exocyclic

Table 3. Selected bond lengths (Å) and bond angles (°) for (**2**)·C_7H_8

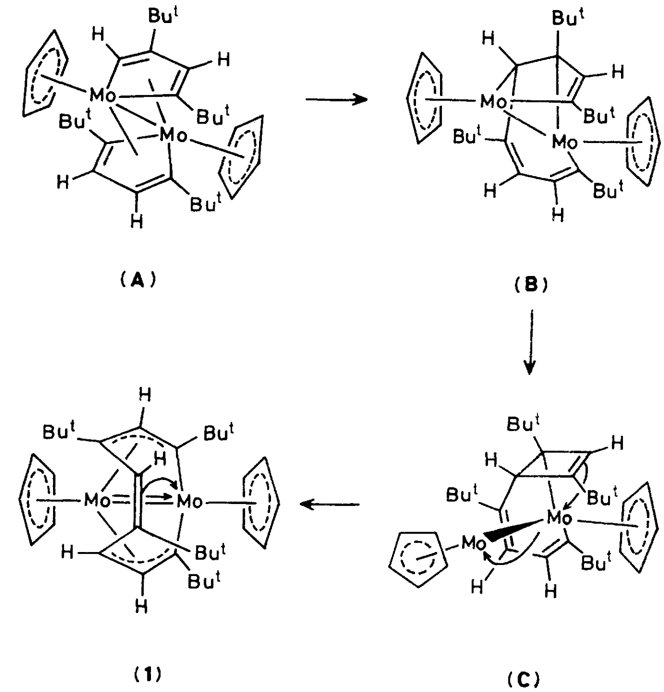
Mo(1)–Mo(2)	2.705(5)	C(4)–C(5)	1.413(22)	Mo(1)–C(1)	2.142(16)	C(5)–C(51)	1.558(20)
Mo(1)–C(2)	2.285(14)	C(6)–C(7)	1.372(23)	Mo(1)–C(3)	2.145(14)	C(7)–C(8)	1.421(22)
Mo(1)–C(6)	2.141(16)	C(7)–C(71)	1.613(22)	Mo(1)–C(7)	2.309(15)	C(11)–C(12)	1.488(26)
Mo(1)–C(8)	2.227(14)	C(11)–C(13)	1.536(28)	Mo(1)–C(81)	2.282(16)	C(11)–C(14)	1.494(25)
Mo(1)–C(82)	2.322(18)	C(31)–C(32)	1.533(23)	Mo(1)–C(83)	2.362(16)	C(31)–C(33)	1.537(25)
Mo(1)–C(84)	2.371(16)	C(31)–C(34)	1.581(22)	Mo(1)–C(85)	2.284(15)	C(51)–C(52)	1.527(24)
Mo(2)–C(2)	2.234(16)	C(51)–C(53)	1.490(24)	Mo(2)–C(3)	2.145(15)	C(51)–C(54)	1.535(24)
Mo(2)–C(4)	2.100(15)	C(71)–C(72)	1.456(35)	Mo(2)–C(5)	2.347(14)	C(71)–C(73)	1.435(34)
Mo(2)–C(6)	2.065(15)	C(71)–C(74)	1.467(36)	Mo(2)–C(61)	2.312(18)	C(81)–C(82)	1.367(32)
Mo(2)–C(62)	2.347(18)	C(81)–C(85)	1.359(25)	Mo(2)–C(63)	2.394(22)	C(82)–C(83)	1.428(24)
Mo(2)–C(64)	2.395(17)	C(83)–C(84)	1.384(26)	Mo(2)–C(65)	2.356(20)	C(84)–C(85)	1.394(27)
C(1)–C(2)	1.478(23)	C(61)–C(62)	1.367(24)	C(1)–C(8)	1.443(22)	C(61)–C(65)	1.350(27)
C(1)–C(11)	1.579(23)	C(62)–C(63)	1.466(27)	C(2)–C(3)	1.476(20)	C(63)–C(64)	1.424(26)
C(2)–C(4)	1.452(21)	C(64)–C(65)	1.441(26)	C(3)–C(31)	1.536(22)	C(07)–C(06)	1.351(58)
Mo(2)–Mo(1)–C(1)	85.0(5)	C(2)–C(1)–C(11)	121.4(13)	Mo(2)–Mo(1)–C(2)	52.4(4)	C(8)–C(1)–C(11)	115.0(13)
C(1)–Mo(1)–C(2)	38.8(6)	Mo(1)–C(2)–Mo(2)	73.5(4)	Mo(2)–Mo(1)–C(3)	50.9(4)	Mo(1)–C(2)–C(1)	65.4(8)
C(1)–Mo(1)–C(3)	73.8(6)	Mo(2)–C(2)–C(1)	124.3(11)	C(2)–Mo(1)–C(3)	38.8(5)	Mo(1)–C(2)–C(3)	65.5(7)
Mo(2)–Mo(1)–C(6)	48.8(4)	Mo(2)–C(2)–C(3)	67.1(8)	C(1)–Mo(1)–C(6)	93.1(6)	C(1)–C(2)–C(3)	121.2(12)
C(2)–Mo(1)–C(6)	84.9(5)	Mo(1)–C(2)–C(4)	135.2(11)	C(3)–Mo(1)–C(6)	99.3(6)	Mo(2)–C(2)–C(4)	65.5(8)
Mo(2)–Mo(1)–C(7)	76.0(4)	C(1)–C(2)–C(4)	126.2(13)	C(1)–Mo(1)–C(7)	71.4(6)	C(3)–C(2)–C(4)	111.2(13)
C(2)–Mo(1)–C(7)	85.5(5)	Mo(1)–C(3)–Mo(2)	78.2(5)	C(3)–Mo(1)–C(7)	117.7(5)	Mo(1)–C(3)–C(2)	75.8(9)
C(6)–Mo(1)–C(7)	35.7(6)	Mo(2)–C(3)–C(2)	73.6(8)	Mo(2)–Mo(1)–C(8)	90.3(4)	Mo(1)–C(3)–C(31)	137.7(10)
C(1)–Mo(1)–C(8)	38.5(6)	Mo(2)–C(3)–C(31)	132.4(11)	C(2)–Mo(1)–C(8)	67.8(5)	C(2)–C(3)–C(31)	133.9(13)
C(3)–Mo(1)–C(8)	106.6(5)	Mo(2)–C(4)–C(2)	75.5(8)	C(6)–Mo(1)–C(8)	68.4(6)	Mo(2)–C(4)–C(5)	81.3(9)
C(7)–Mo(1)–C(8)	36.5(6)	C(2)–C(4)–C(5)	116.9(13)	Mo(1)–Mo(2)–C(2)	54.1(4)	Mo(2)–C(5)–C(4)	62.2(8)
Mo(1)–Mo(2)–C(3)	50.9(4)	Mo(2)–C(5)–C(51)	132.6(12)	C(2)–Mo(2)–C(3)	39.3(5)	C(4)–C(5)–C(51)	123.3(13)
Mo(1)–Mo(2)–C(4)	91.6(4)	Mo(1)–C(6)–Mo(2)	80.0(5)	C(2)–Mo(2)–C(4)	39.0(6)	Mo(1)–C(6)–C(7)	78.9(10)
C(3)–Mo(2)–C(4)	69.3(5)	Mo(2)–C(6)–C(7)	127.8(11)	Mo(1)–Mo(2)–C(5)	100.7(4)	Mo(1)–C(7)–C(6)	65.5(8)
C(2)–Mo(2)–C(5)	64.3(5)	Mo(1)–C(7)–C(8)	68.6(8)	C(3)–Mo(2)–C(5)	102.2(6)	C(6)–C(7)–C(8)	123.1(14)
C(4)–Mo(2)–C(5)	36.5(6)	Mo(1)–C(7)–C(71)	138.6(10)	Mo(1)–Mo(2)–C(6)	51.2(4)	C(6)–C(7)–C(71)	120.6(14)
C(2)–Mo(2)–C(6)	88.0(6)	C(8)–C(7)–C(71)	115.8(14)	C(3)–Mo(2)–C(6)	101.8(6)	Mo(1)–C(8)–C(1)	67.6(8)
C(4)–Mo(2)–C(6)	106.7(6)	Mo(1)–C(8)–C(7)	74.9(8)	C(5)–Mo(2)–C(6)	85.0(5)	C(1)–C(8)–C(7)	130.6(14)
Mo(1)–C(1)–C(2)	75.8(9)			Mo(1)–C(1)–C(8)	73.9(8)		
C(2)–C(1)–C(8)	119.1(15)			Mo(1)–C(1)–C(11)	142.1(11)		

vinyl group at C(2) leads to C(1) being bonded to Mo(1), and to the bridging site for C(2), rather than both these carbons being bonded only to Mo(2) as they would be in a true C_6 'fly-over'.[12]

The ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra for **(2)** have been interpreted in a similar manner to those of **(1)**. The assignment of the ^1H spectrum is based primarily on coupling constants, but a much wider range of chemical shifts is observed for the four hydrogens, *viz.* δ 9.32 to −3.31 p.p.m. The origin of the high field signal at −3.31 p.p.m., is unclear, but may arise either from a close proximity to Mo(2) or an unusually large magnetic anisotropy effect associated with part of the molecule.

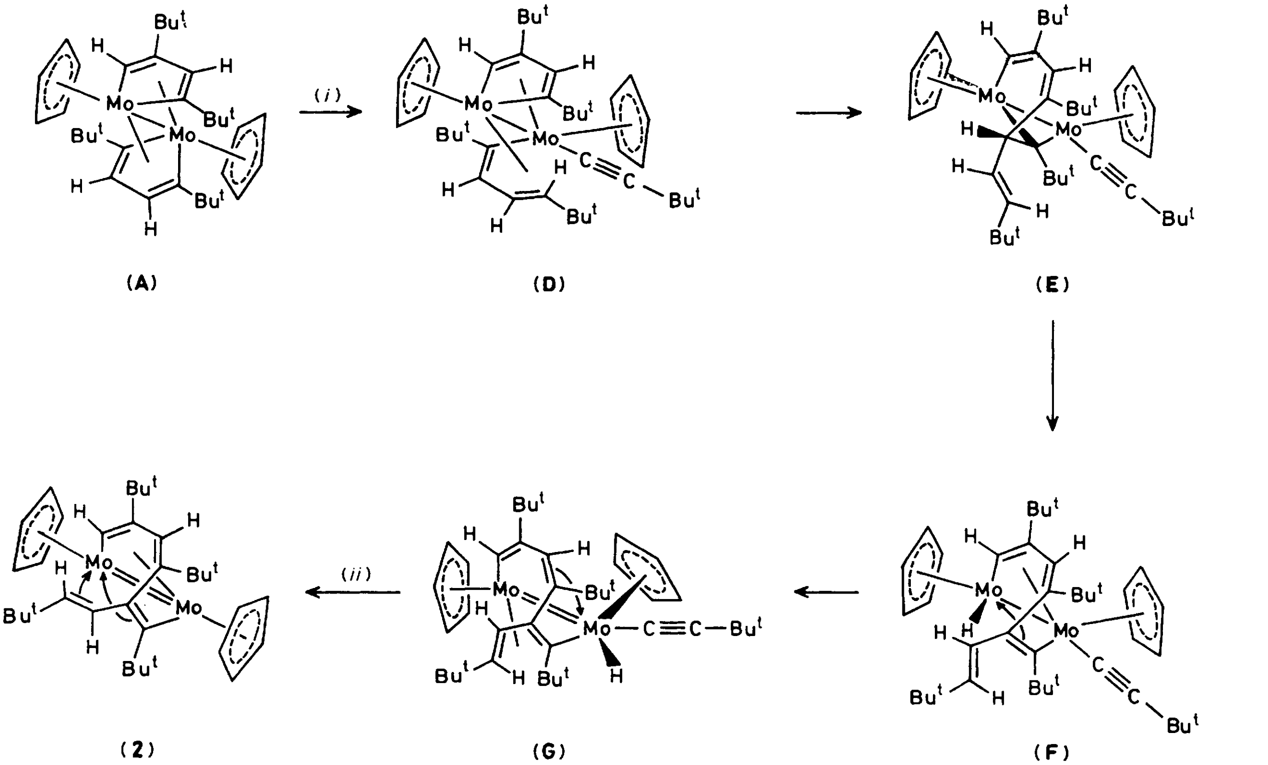
In the *X*-ray study these four hydrogens atoms were not directly located but were placed in calculated positions about their respective carbon atoms assuming sp^2 hybridisation. Figure 2 shows a twist along the C(4)–C(5) axis giving a C(2)–C(4)–C(5)–C(51) torsion angle of 166.1(1.5)° consistent with some 'bending back' of substituents at C(4) and C(5), caused by some rehybridisation at C(4) and C(5). Thus, it is probable that H(5) is twisted toward Mo(2) less severely than illustrated in Figure 2, due to this $sp^2 \rightarrow sp^3$ rehybridisation. Values obtained from the calculated position of H(5) indicate that it is closer to Mo(2) than is C(5) [Mo(2)–H(5) 2.32 Å, Mo(2)–C(5) 2.34 Å] although, for the reasons given above, this represents a lower value on the likely Mo ··· H distance. This proximity to Mo(2) might result in the large upfield shift observed in the ^1H spectrum. However, H(5) also lies over the plane defined by C(6), C(7), C(8), and C(1), and an alternative possibility is that H(5) is in an area of high magnetic shielding resulting from magnetic anisotropy associated with this part of the molecule. Since it is more likely that H(5) is in an unusual environment, rather than H(4), the coupling of 1.1 Hz between either H(4) or H(5) and H(6) is assigned to ^4J[H(4)H(6)]. The ^{13}C n.m.r. spectrum has been partially assigned on the basis of off-resonance experiments. For C(1), C(2), C(3), and C(7) only three signals are observed, the position of the fourth being unclear. Since a definite assignment has not been made, it is not possible to assign a chemical shift to the unusual C(2) carbon.

The formation of **(1)** and the related octamethyl-substituted dimolybdenum complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8Me_8)\}(\eta\text{-}C_5H_5)_2]$ is especially interesting in that four alkyne molecules link together to form a C_8 chain bonded to only one molybdenum centre. Structurally related molecules $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8(CO_2Me)_6H_2\}(\eta\text{-}C_5H_5)_2]$ and $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8(CO_2Me)_8\}(\eta\text{-}C_5H_5)_2]$ have also been isolated from the reaction of $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC{\equiv}CCO_2Me$ under forcing conditions and it was suggested [5,7] that in these reactions the C_8 chain is built up sequentially *via* the intermediates $[Mo_2\{\mu\text{-}(\sigma,\eta^2:\eta^2,\sigma\text{-}C_4R_4)\}(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ and $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6R_6)\}(\eta\text{-}C_5H_5)_2]$. The basis for the assertion that a C_6 'fly-over' complex reacts with a further alkyne molecule to form a $Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8)\}$ system rested on the observation [7] that the molecule $[Mo_2(\mu\text{-}C_2H_2C_4Ph_4)(\eta\text{-}C_5H_5)_2]$, which was thought to be a $\mu\text{-}\sigma,\eta^3:\eta^3,\sigma\text{-}C_6$ 'fly-over' complex, reacts with an excess of $MeO_2CC{\equiv}CCO_2Me$ in refluxing octane over a period of 4 d to give two isomeric adducts $[Mo_2(HC_2H)(PhC_2Ph)_2(MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$, which were tentatively assigned $\mu\text{-}\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8$ structures. This has not, however, been confirmed by *X*-ray crystallography, and therefore there is also the possibility that these complexes are $\mu\text{-}\sigma,\eta^4:\eta^4,\sigma\text{-}C_8$ species, *i.e.* four-alkyne 'fly-over' complexes. Relating to this, we have observed [12] that the *X*-ray crystallographically identified three-alkyne 'fly-over' complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Me_6)\}(\eta^5\text{-}C_9H_7)_2]$ does *not* react with an excess of but-2-yne, which led to the suggestion [12] that $\mu\text{-}\sigma,\eta^3:\eta^3,\sigma\text{-}C_6$ and $\mu\text{-}\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8$ systems are formed *via* competitive reaction pathways, and that the C_6 'fly-over' complexes are *not* precursors of C_8 (octatrienediylidene)dimolybdenum complexes. Thus, there remains the question as to how **(1)** and $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8Me_8)\}(\eta\text{-}C_5H_5)_2]$ are formed on one-electron reduction of the cations $[Mo(NCMe)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$, and of course, there is also the problem as to the origin of **(2)**, which in a sense may be viewed as a vinyl-substituted C_6 'fly-over' complex.



Scheme 1.

In seeking to explain how the dinuclear complex $[Ni_2(C_8H_8)_2]$ functions as a catalyst for the cyclotetramerisation of ethyne, it was suggested by Wilke [4] that one cyclo-octatetraene ligand is first displaced by four ethyne molecules so that two adjacent nickel–cyclopentadiene systems can be formed. These couple together to form a four-ethyne 'fly-over' complex which then collapses to C_8H_8. This idea can be extended to provide a possible explanation for the initial stages of the formation of the dimolybdenum complexes $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^2:\eta^3,\sigma\text{-}C_8R_8)\}(\eta\text{-}C_5H_5)_2]$. As was previously [12] discussed, irreversible one-electron reduction of $[Mo(NCMe)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$ probably affords a molybdenum-centred odd-electron species which can dimerise to form a dimolybdenum complex containing the four 3,3-dimethylbut-1-yne ligands needed to assemble the C_8 chain present in **(1)**. Coupling of these four alkyne ligands can then lead to the formation of two adjacent molybdacyclopentadiene rings, which for steric reasons would be expected to be placed on opposite faces of the Mo–Mo system. Because of the unsymmetrical nature of the alkynes a number of isomeric metallacyclopentadienes can in principle be formed. However, if it is assumed that this is indeed the first step then it is likely that only the head to head and head to tail arrangement shown in Scheme 1 can lead to the formation of **(1)**. Thus, if the intermediate **(A)** undergoes a migratory insertion reaction between a co-ordinated alkene system of the head to tail bonded metallacyclopentadiene ring and the σ-bonded $MoC(Bu^t){=}CH$ system of the head to head bonded metallacyclopentadiene the intermediate **(B)** is formed. Reductive elimination then provides a pathway to the bicyclic species **(C)**, in which all four alkynes are now bonded to one of the molybdenum centres. Because the cyclobutene moiety can bond to one of the metal centres *via* its π system, it is possible



Scheme 2. (*i*) + Bu^tC_2H; (*ii*) − Bu^tC_2H

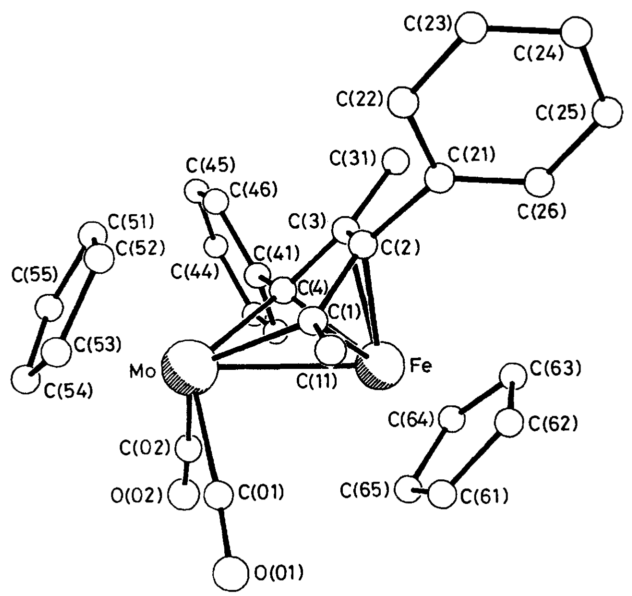


Figure 3. Molecular structure of (3); all phenyl, methyl, and cyclopentadienyl group hydrogens have been omitted for clarity

that a disrotatory ring-opening reaction can occur transforming (C) into (1) with the ring substituents in the correct position.

Clearly further work is needed to substantiate these ideas. However, it is interesting that a possible pathway* to the second product of the reduction reaction, *i.e.* the dinuclear complex (2), also has its origin in the intermediate (A) in Scheme 1. In a series of careful control experiments it was found that the relative proportions of the products (1) and (2) were related to the concentration of free 3,3-dimethylbut-1-yne present in the reaction mixture. For example, in a typical experiment and in the absence of free Bu^tC_2H, 0.400 g of purple (1) and 0.030 g of dark green (2) were obtained, whereas, addition of five molar equivalents of Bu^tC_2H gave 0.350 g of (1) and 0.125 g of (2). These observations can be explained if it is assumed that protolysis with retention[14] of stereochemistry of one of the σ-bonds of the head to head coupled molybdacyclopentadiene by an acidic hydrogen of Bu^tC_2H occurs, leading to ring-opening, and formation of (D), a σ-butadienyl acetylide complex (Scheme 2). Then migratory insertion of the weaker σ-vinyl group carrying the Bu^t substituent on the α-position into the co-ordinated alkene of the σ-butadienyl ligand provides access to the intermediate (E), a vinyl substituted C_6 'fly-over', which with the exception of the hydrogen atom on C(5), carries the substituents in the correct positions to form (2). The reaction sequence is then completed *via* β-hydrogen elimination [(E) $\rightleftharpoons$ (F)], hydrogen transfer from one molybdenum centre to another [(F) $\rightleftharpoons$ (G)], followed by reductive elimination of Bu^tC_2H [(G)→(2)].

The subtle nature of these alkyne coupling reactions was further underlined when an attempt was made to study the related reactions of PhC_2Me substituted cations. Thus, treatment of $[Mo(NCMe)(\eta^2\text{-}PhC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$[15] with $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ in thf affords, after purification, a dark green material (3). Proton and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra for (3) showed two cyclopentadienyl groups together with two sets of methyl and phenyl resonances. This information together with the observation of two terminal carbonyl absorptions in the i.r. spectrum indicated a complex of molecular formula $[FeMo(CO)_2(PhC_2Me)_2(\eta\text{-}C_5H_5)_2]$. This was confirmed and

* At first sight the most obvious pathway to (2) would involve the reaction of a C_6 'fly-over' complex $[Mo_2\{\mu\text{-}(\sigma,\eta^3:\eta^3,\sigma\text{-}CHCBu^tCHCBu^tCHCBu^t)\}(\eta\text{-}C_5H_5)_2]$ with a further molecule of 3,3-dimethylbut-1-yne. However, it is difficult to see how an 'insertion' reaction could occur into the CH bond located in the 5-position of the C_6 'fly-over'.

Table 4. Selected bond lengths (Å) and bond angles (°) for (**3**)

Mo–Fe	2.743(1)	C(21)–C(22)	1.371(7)	Mo–C(1)	2.192(5)	C(21)–C(26)	1.370(7)
Mo–C(4)	2.188(5)	C(22)–C(23)	1.395(8)	Mo–C(51)	2.344(5)	C(23)–C(24)	1.365(10)
Mo–C(52)	2.360(6)	C(24)–C(25)	1.369(9)	Mo–C(53)	2.330(6)	C(25)–C(26)	1.385(9)
Mo–C(54)	2.301(5)	C(41)–C(42)	1.390(7)	Mo–C(55)	2.307(5)	C(41)–C(46)	1.394(7)
Mo–C(01)	1.981(5)	C(42)–C(43)	1.389(7)	Mo–C(02)	2.014(5)	C(43)–C(44)	1.370(8)
Fe–C(1)	2.015(5)	C(44)–C(45)	1.364(8)	Fe–C(2)	2.055(5)	C(45)–C(46)	1.391(7)
Fe–C(3)	2.080(5)	C(51)–C(52)	1.395(8)	Fe–C(4)	1.995(5)	C(51)–C(55)	1.395(8)
Fe–C(61)	2.060(6)	C(52)–C(53)	1.414(9)	Fe–C(62)	2.062(5)	C(53)–C(54)	1.403(8)
Fe–C(63)	2.078(5)	C(54)–C(55)	1.415(8)	Fe–C(64)	2.084(6)	C(61)–C(62)	1.384(8)
Fe–C(65)	2.067(6)	C(61)–C(65)	1.401(9)	C(1)–C(2)	1.402(7)	C(62)–C(63)	1.420(8)
C(1)–C(11)	1.512(7)	C(63)–C(64)	1.404(8)	C(2)–C(3)	1.408(6)	C(64)–C(65)	1.405(9)
C(2)–C(21)	1.561(7)	C(01)–O(01)	1.157(7)	C(3)–C(4)	1.396(6)	C(02)–O(02)	1.138(6)
C(3)–C(31)	1.524(7)			C(4)–C(41)	1.554(6)		

Fe–Mo–C(1)	46.6(1)	Fe–C(2)–C(1)	68.3(3)	Fe–Mo–C(4)	46.0(1)	Fe–C(2)–C(3)	71.1(3)
C(1)–Mo–C(4)	72.3(2)	C(1)–C(2)–C(3)	117.5(4)	Fe–Mo–C(01)	82.1(2)	Fe–C(2)–C(21)	131.1(3)
C(1)–Mo–C(01)	81.9(2)	C(1)–C(2)–C(21)	122.9(4)	C(4)–Mo–C(01)	126.2(2)	C(3)–C(2)–C(21)	119.6(4)
Fe–Mo–C(02)	85.6(1)	Fe–C(3)–C(2)	69.1(3)	C(1)–Mo–C(02)	130.7(2)	Fe–C(3)–C(4)	66.7(3)
C(4)–Mo–C(02)	82.7(2)	C(2)–C(3)–C(4)	112.3(4)	C(01)–Mo–C(02)	79.6(2)	Fe–C(3)–C(31)	129.3(3)
Mo–Fe–C(1)	52.2(1)	C(2)–C(3)–C(31)	123.1(4)	Mo–Fe–C(2)	77.6(1)	C(4)–C(3)–C(31)	124.5(4)
C(1)–Fe–C(2)	40.3(2)	Mo–C(4)–Fe	81.8(2)	Mo–Fe–C(3)	78.5(1)	Mo–C(4)–C(3)	117.8(3)
C(1)–Fe–C(3)	71.8(2)	Fe–C(4)–C(3)	73.3(3)	C(2)–Fe–C(3)	39.8(2)	Mo–C(4)–C(41)	120.7(3)
Mo–Fe–C(4)	52.1(1)	Fe–C(4)–C(41)	134.1(3)	C(1)–Fe–C(4)	80.3(2)	C(3)–C(4)–C(41)	117.4(4)
C(2)–Fe–C(4)	70.2(2)	C(2)–C(21)–C(22)	117.0(4)	C(3)–Fe–C(4)	40.0(2)	C(2)–C(21)–C(26)	123.9(4)
Mo–C(1)–Fe	81.3(2)	C(22)–C(21)–C(26)	119.0(5)	Mo–C(1)–C(2)	114.7(3)	C(4)–C(41)–C(42)	122.8(4)
Fe–C(1)–C(2)	71.4(3)	C(4)–C(41)–C(46)	118.7(4)	Mo–C(1)–C(11)	123.0(3)	C(42)–C(41)–C(46)	118.5(4)
Fe–C(1)–C(11)	128.8(4)	Mo–C(01)–O(01)	176.0(5)	C(2)–C(1)–C(11)	120.5(4)	Mo–C(02)–O(02)	175.1(4)

the molecular structure determined by an *X*-ray diffraction study, the results of which are shown in Figure 3, selected bond lengths being listed in Table 4. The molecule consists of a molybdenum and an iron atom singly bonded to each other [2.743(1) Å] and bridged by a μ-C_4 group derived from the head to tail linkage of two PhC_2Me ligands. The C_4 fragment is σ-bonded to the molybdenum atom through C(1) and C(4), 2.192(5) and 2.188(5) Å respectively, forming a molybdacyclopentadienyl unit η^5-bonded to iron. The carbons C(1) and C(3) carry methyl groups while C(2) and C(4) carry phenyl substituents. Carbons C(1) and C(4), the α-carbons, form a quasi tetrahedral C_2M_2 core with the two metal atoms and are significantly closer to the iron than the β carbons C(2) and C(3). The C–C bond lengths in the C_4 ligand are almost equal and these four atoms are coplanar implying some delocalisation in the ring. The molybdenum lies 0.59 Å out of this plane on the opposite side to the iron atom. This is similar to the situation found[7] in $[Cr_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$, but in contrast to the ferrole structures where the ferracyclopentadienyl ring is coplanar to within 0.05 Å. Both metals are η^5-bonded to a cyclopentadienyl ring and the molybdenum carries two terminally bonded carbonyl ligands.

Both ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra are consistent with this structure being maintained in solution and show inequivalent methyl and phenyl resonances. In addition the ^{13}C spectrum shows signals at 162.7, 158.8, 119.7, and 107.2 p.p.m. The former two are assigned to the α C_4 ring carbons and the latter pair to the β carbons.

Complex (**4**) is obtained in a like manner from the cation of $[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$.[15] Proton and ^{13}C-$\{^1H\}$ n.m.r. spectra are consistent with a structure similar to (**3**), but with a mirror plane bisecting the C_4 ring and parallel to the Mo–Fe vector.

These latter observations suggest that reaction of the cations of $[Mo(NCMe)(\eta^2\text{-}RC_2R')_2(\eta\text{-}C_5H_5)][BF_4]$ with $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ can lead to a simple one-electron transfer, but there is also a competitive nucleophilic substitution reaction, which in the case of the phenyl-substituted alkyne systems become dominant. It will be particularly interesting to study the reactivity of these latter cations towards other reducing agents.

Experimental

The ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra were recorded on JEOL FX 90 Q, FX 200, and Varian XL 300 spectrometers as appropriate. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Reduction of $[Mo(NCMe)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$.—To a stirred suspension of $[Mo(NCMe)(\eta^2\text{-}Bu^tC_2H)_2(\eta\text{-}C_5H_5)][BF_4]$ (2.0 g, 4.37 mmol) in tetrahydrofuran (thf) (20 cm^3) a solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$, derived from $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.8 g, 2.26 mmol), in thf was added at 0 °C, and the mixture stirred for 4 h. The solvent was removed *in vacuo*, and the resulting dark oil redissolved in hexane–diethyl ether (20:1). Filtration through an alumina plug (1 cm) gave a dark solution from which the solvent was removed. The residue was redissolved in hexane and chromatographed on an alumina-packed column, which was cooled to −40 °C. Elution with hexane initially gave $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ followed by a dark blue-black band. This was collected and recrystallised (−78 °C) from pentane to afford blue-black *crystals* of $[Mo_2\{\mu\text{-}(\sigma,\eta^3\text{:}\eta^2\text{:}\eta^3,\sigma\text{-}C_8H_4Bu^t{}_4)\}(\eta\text{-}C_5H_5)_2]$ (**1**) (0.32 g, 22%) (Found: 63.0; H, 7.5%; *M*, 650. $C_{34}H_{50}Mo_2$ requires C, 62.8; H, 7.7%; *M*, 650), ^1H and ^{13}C-$\{^1H\}$ n.m.r. data are presented in Table 2. Further elution with hexane gave a green band. This was collected and recrystallised (−78 °C) from pentane to give green *crystals* of $[Mo_2\{\mu\text{-}(\sigma,\eta^3\text{:}\eta^3,\sigma\text{-}CH{=}CHBu^tC_6H_2Bu^t{}_3)\}(\eta\text{-}C_5H_5)_2]$ (**2**) (0.12 g, 9%) (Found: C, 63.0; H, 8.0%; *M*, 650. $C_{34}H_{50}Mo_2$ requires C, 62.8; H, 7.7%; *M*, 650), ^1H and ^{13}C-$\{^1H\}$ n.m.r. data are presented in Table 2.

Reaction of $[Mo(NCMe)(\eta^2\text{-}MeC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ *with* $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$.—A similar reaction between $[Mo(NCMe)(\eta^2\text{-}MeC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ (1.5 g, 2.9 mmol)

Table 5. Crystal data and refinement details for complexes (**1**)—(**3**)

	(1)	(2)	(3)
Formula	$C_{34}H_{50}Mo_2$	$C_{34}H_{50}Mo_2{\cdot}C_7H_8$	$C_{30}H_{26}FeMoO_2$
M	650.65	742.74	570.32
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ [non-standard setting of $P2_1/c$ (no. 14)]
a/Å	10.316(4)	11.33(2)	11.124(3)
b/Å	15.292(8)	27.37(3)	20.002(5)
c/Å	11.316(7)	11.77(2)	11.167(2)
α/°	70.71(5)		
β/°	61.87(4)	96.3(1)	92.21(2)
γ/°	84.68(4)		
U/Å^3	1 481(1)	3 628(9)	2 482(1)
Z	2	4	4
Crystal dimensions/mm	0.5 × 0.3 × 0.3	0.7 × 0.2 × 0.2	0.3 × 0.3 × 0.3
Scan rate/° min^{-1}	3.0—29.3	2.0—29.3	2.0—29.3
2θ Limits/°	3.0—60.0	3.0—50.0	3.0—50.0
No. of unique data collected	6 660	5 901	3 067
No. of data observed	5 729	3 439	2 317
Data omission factor	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
ρ(calc.)/g cm^{-3}	1.46	1.36	1.53
λ(Mo-K_α)/Å	0.710 69	0.710 69	0.710 69
μ(Mo-K_α)/cm^{-1}	8.46	6.91	11.01
F(000)	676	1 351	1 160
Temperature/K	298	298	298
Weighting scheme (g)*	0.0002	0.0003	0.0005
R	0.0239	0.1094	0.0306
R'	0.0242	0.1013	0.0310

* Of the form $[\sigma^2(F_o) + gF_o^2]^{-1}$.

and Na[Fe(CO)$_2$(η-C_5H_5)] (3.4 mmol) in thf (20 cm^3) afforded, on column chromatography (alumina, elution with CH_2Cl_2–Et_2O, 1:1), a dark green band. Collection and recrystallisation (−78 °C) from hexane gave dark green *crystals* of [FeMo(CO)$_2$($C_4Me_2Ph_2$)(η-C_5H_5)$_2$] (**3**) (0.7 g, 43%), ν_{co}(pentane) 1 965s, 1 911s cm^{-1}.

A similar reaction between [Mo(NCMe)(η^2-PhC$_2$Ph)(η-C_5H_5)][BF$_4$] (1.5 g, 2.7 mmol) and Na[Fe(CO)$_2$(η-C_5H_5)] (3.4 mmol) afforded green *crystals* of [FeMo(CO)$_2$(C_4Ph_4)(η-C_5H_5)$_2$] (**4**) (0.6 g, 37%) (Found: 69.4; H, 4.3. $C_{40}H_{30}FeMoO_2$ requires C, 69.2; H, 4.3%), ν_{co}(pentane) 1 979s, 1 921s cm^{-1}.

Crystal Structure Analyses.—Single-crystal *X*-ray diffraction studies of (**1**), (**2**)·C_7H_8, and (**3**) were carried out on Nicolet P3m diffractometers at room temperature using graphite monochromated Mo-K_α *X*-radiation (λ = 0.710 69 Å). Crystals of (**1**) and (**3**) were mounted under N_2 in thin-walled glass capillaries. That of (**2**)·C_7H_8, was coated in a cyanoacrylate glue to minimise solvent loss (which was otherwise rapid, and caused loss of crystallinity) and mounted on a glass fibre. Details of crystal data, data collection and structure analyses are given in Table 5. The crystal of (**2**)·C_7H_8 used for data collection was of moderate quality and showed a *ca.* 10% drop in diffracted intensity of check reflections during the course of the experiment, for which a correction was applied. No such effects were observed for either (**1**) or (**3**). Intensity data were collected for unique volumes of reciprocal space for each crystal with variable scan speeds, scan types, and 2θ ranges as in Table 5. For (**1**) an absorption correction based on azimuthal scan data was applied to the measured intensities. Averaging of equivalent measurements and deletion of systematic absences, and suppression of those reflections with $I < 2\sigma(I)$ left those observations used in structure solution and refinement. Structures were solved by conventional heavy-atom methods (Patterson and difference Fourier) and refinement was by

Table 6. Atomic co-ordinates (× 10^4) for (**1**)

Atom	x	y	z
Mo(1)	3 166(1)	1 634(1)	2 815(1)
Mo(2)	2 510(1)	2 949(1)	1 023(1)
C(1)	4 556(3)	2 910(2)	1 090(2)
C(2)	4 357(3)	2 998(2)	2 380(2)
C(3)	2 917(3)	3 022(2)	3 441(2)
C(4)	1 838(3)	3 400(2)	2 886(2)
C(5)	623(2)	2 806(2)	3 244(2)
C(6)	739(3)	1 805(2)	3 969(2)
C(7)	914(3)	1 186(2)	3 227(3)
C(8)	1 776(3)	1 533(2)	1 741(3)
C(41)	6 168(3)	2 972(2)	−116(3)
C(42)	7 321(3)	2 821(2)	427(3)
C(43)	6 624(3)	3 947(2)	−1 236(3)
C(44)	6 349(3)	2 270(2)	−875(3)
C(51)	2 651(3)	3 156(2)	4 844(3)
C(52)	3 941(4)	2 948(4)	5 153(4)
C(53)	2 374(7)	4 165(3)	4 725(4)
C(54)	1 299(4)	2 594(3)	6 124(3)
C(61)	−996(3)	3 080(2)	3 683(3)
C(62)	−1 162(3)	4 112(2)	3 076(3)
C(63)	−1 834(3)	2 852(3)	5 313(3)
C(64)	−1 801(3)	2 503(2)	3 312(3)
C(71)	1 760(3)	919(2)	885(3)
C(72)	1 653(5)	−133(2)	1 641(4)
C(73)	357(4)	1 112(2)	696(4)
C(74)	3 139(4)	1 123(2)	−554(3)
C(11)	5 166(4)	689(2)	2 727(4)
C(12)	4 685(4)	984(2)	3 882(4)
C(13)	3 235(5)	587(3)	4 829(4)
C(14)	2 900(4)	76(2)	4 204(5)
C(15)	4 080(5)	156(2)	2 922(5)
C(21)	3 468(3)	3 759(2)	−1 481(5)
C(22)	3 339(3)	4 451(2)	−864(3)
C(23)	1 858(3)	4 480(2)	17(3)
C(24)	1 039(3)	3 821(2)	−48(3)
C(25)	2 049(4)	3 382(2)	−987(3)

Table 7. Atomic co-ordinates ($\times 10^4$) for (2)·C_7H_8

Atom	x	y	z
Mo(1)	2 476(1)	874(1)	1 119(1)
Mo(2)	1 080(1)	1 116(1)	2 756(1)
C(1)	3 910(16)	939(6)	2 456(13)
C(2)	3 010(13)	1 288(6)	2 783(11)
C(3)	2 260(14)	1 569(5)	1 912(11)
C(4)	2 559(14)	1 317(5)	3 890(12)
C(5)	2 286(15)	871(6)	4 406(11)
C(6)	1 440(14)	432(5)	2 137(11)
C(7)	2 501(15)	186(5)	2 259(12)
C(8)	3 620(13)	426(5)	2 378(12)
C(11)	5 280(14)	1 058(5)	2 672(12)
C(12)	5 459(19)	1 586(8)	2 453(18)
C(13)	5 975(19)	754(8)	1 872(18)
C(14)	5 710(18)	951(7)	3 892(18)
C(31)	2 207(16)	2 110(6)	1 559(12)
C(32)	1 144(17)	2 205(6)	665(13)
C(33)	3 334(15)	2 315(6)	1 117(14)
C(34)	2 031(19)	2 423(6)	2 657(13)
C(51)	2 056(17)	827(6)	5 683(12)
C(52)	3 290(16)	804(7)	6 346(13)
C(53)	1 396(18)	1 245(6)	6 123(13)
C(54)	1 442(18)	338(5)	5 868(14)
C(71)	2 539(16)	−400(6)	2 120(13)
C(72)	2 239(40)	−589(8)	3 209(24)
C(73)	1 718(26)	−581(8)	1 202(30)
C(74)	3 678(26)	−592(7)	1 834(35)
C(81)	1 868(21)	523(7)	−604(35)
C(82)	3 077(20)	481(6)	−469(14)
C(83)	3 517(16)	969(6)	−500(11)
C(84)	2 560(18)	1 286(6)	−643(12)
C(85)	1 538(17)	1 000(5)	−675(12)
C(61)	−892(16)	883(7)	2 575(15)
C(62)	−630(15)	1 020(7)	3 691(15)
C(63)	−393(19)	1 546(7)	3 672(16)
C(64)	−540(15)	1 681(6)	2 497(15)
C(65)	−837(18)	1 251(7)	1 819(17)
C(01)	8 017(33)	2 036(7)	8 670(21)
C(02)	8 794	2 010	7 831
C(03)	8 349	1 980	6 680
C(04)	7 125	1 976	6 368
C(05)	6 348	2 002	7 207
C(06)	6 793	2 033	8 358
C(07)	5 904(39)	2 040(11)	9 035(37)

blocked-cascade least squares,[16] with all atoms assigned complex neutral atom scattering factors taken from ref. 17; observations were given weights $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. In each case all non-hydrogen atoms were refined with anisotropic displacement parameters. In (1), hydrogen atoms H(2), H(4), H(6), H(7), and H(21—25) were refined isotropically and without constraints; other hydrogens were constrained to ideal geometries (C–H 0.96 Å) with methyl group hydrogens having a common isotropic displacement parameter (i.d.p.) and H(11—15) fixed i.d.p.s set at *ca.* 1.2 times those of their carbon atoms. For (2)·C_7H_8, the toluene hydrogen atoms were omitted and the ring constrained to D_{6h} geometry with C–C = 1.395 Å; all hydrogen atoms were assigned fixed i.d.p.s, set at *ca.* 1.2 times those of their carbon atoms, and constrained to idealised geometries with C–H = 0.96 Å. For (3), all hydrogen atoms were constrained to idealised geometries (C–H 0.96 Å) and methyl, cyclopentadienyl, and phenyl group hydrogens assigned separate common i.d.p.s. Refinements converged to the final residuals given in Table 5; final electron density difference syntheses showed no features of chemical significance. Final atomic positional parameters are given in Tables 6—8 for (1), (2)·C_7H_8, and (3) respectively. Additional material available

Table 8. Atomic co-ordinates ($\times 10^4$) for (3)

Atom	x	y	z
Mo	3 277(1)	7 012(1)	2 664(1)
Fe	2 680(1)	5 695(1)	2 993(1)
C(1)	1 894(4)	6 357(2)	1 848(4)
C(2)	1 031(4)	6 131(2)	2 638(4)
C(3)	1 315(4)	6 180(2)	3 874(4)
C(4)	2 449(4)	6 459(2)	4 110(4)
C(11)	1 678(5)	6 291(3)	509(4)
C(31)	499(5)	5 912(3)	4 831(4)
C(21)	−199(4)	5 824(2)	2 201(4)
C(22)	−1 064(5)	6 260(3)	1 774(5)
C(23)	−2 207(5)	6 027(4)	1 426(6)
C(24)	−2 487(6)	5 365(4)	1 526(6)
C(25)	−1 617(6)	4 933(3)	1 952(5)
C(26)	−476(5)	5 159(3)	2 287(5)
C(41)	2 829(4)	6 595(2)	5 441(4)
C(42)	3 798(4)	6 277(2)	6 019(4)
C(43)	4 087(5)	6 412(3)	7 215(4)
C(44)	3 433(5)	6 862(3)	7 847(4)
C(45)	2 481(5)	7 176(3)	7 284(5)
C(46)	2 162(5)	7 050(3)	6 089(4)
C(51)	2 111(5)	7 925(2)	3 239(5)
C(52)	1 916(6)	7 852(3)	2 004(5)
C(53)	3 024(6)	7 952(3)	1 451(5)
C(54)	3 894(5)	8 094(3)	2 358(5)
C(55)	3 323(5)	8 074(3)	3 469(5)
C(61)	3 716(5)	5 079(3)	1 974(5)
C(62)	2 617(5)	4 778(3)	2 149(5)
C(63)	2 485(5)	4 688(2)	3 399(5)
C(64)	3 536(5)	4 936(3)	3 978(5)
C(65)	4 291(5)	5 180(3)	3 098(6)
C(01)	4 248(4)	6 624(3)	1 385(5)
O(01)	4 862(3)	6 428(2)	650(3)
C(02)	4 805(4)	6 792(3)	3 609(4)
O(02)	5 710(3)	6 696(2)	4 086(3)

from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

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