Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 91.[1] Steric Implications in the Reactions of the Complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W, R = C_6H_4Me-4, C_6H_4OMe-2, or $C_6H_3Me_2$-2,6) with the Compounds $[Mo(CO)_3(NCMe)_3]$ and $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (thf = tetrahydrofuran); Crystal Structure of $[Mo_3(\mu\text{-}CC_6H_3Me_2\text{-}2,6)_2(CO)_6(\eta\text{-}C_5H_5)_2]$*

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The compounds $[Mo(CO)_3(NCMe)_3]$ and $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) in Et_2O at room temperature afford the trimetal complexes $[MoM_2(\mu\text{-}CR)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W, R = $C_6H_3Me_2$-2,6; M = Mo, R = C_6H_4OMe-2). In contrast, $[Mo(CO)_3(NCMe)_3]$ and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ yield the μ-alkyne complex $[Mo_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$. An *X*-ray diffraction study established the structure of $[Mo_3(\mu\text{-}CC_6H_3Me\text{-}2,6)_2(CO)_6(\eta\text{-}C_5H_5)_2]$. The three metal atoms form the spine of the molecule [Mo–Mo 2.802(1) Å, Mo–Mo–Mo 124.8(1)°], and the metal–metal bonds are bridged in an essentially symmetrical manner by the alkylidyne groups [μ-C–Mo 1.986(5) and 2.100(5) Å]. Each metal atom carries two carbonyl groups, but one of these ligands on each of the terminal molybdenum atoms semi-bridges a metal–metal bond [Mo–C–O 169.8(5)°]. The molecule has crystallographic C_2 symmetry. The two almost isosceles μ-CMo_2 triangles share an Mo apex, with a dihedral angle of 79° between the planes defined by the triangles. Moreover, the two carbonyl groups attached to the central Mo atom are each, respectively, coplanar with one of the μ-CMo_2 triangles. The arrangement of the ligating groups around the central Mo atom is in agreement with extended-Hückel molecular orbital calculations on the model isolobal molecule $[Mo(CO)_2(\eta\text{-}C_2H_2)_2]$. The lowest energy results for a structure in which the alkyne ligands are orthogonal to each other, and are each parallel to one of the CO groups. The reactions of the species $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) with $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (thf = tetrahydrofuran) were also investigated and shown to give the dimetal compounds $[MCu(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$.

The addition of metal–ligand fragments to the carbon–metal triple bonds of the reagents $[M(\equiv CR)(CO)_2L]$ {M = Cr, Mo, or W; R = alkyl or aryl; L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]} is now a well established procedure for synthesising compounds with heteronuclear metal–metal bonds.[2] The initial products are dimetal complexes, but these often undergo further reaction to yield cluster compounds in which the metal atoms form polyhedral, chain, or ring structures.[3] Recently it has become increasingly apparent that the steric properties of the R and L groups in the alkylidynemetal precursors are of primary importance in dictating the formulation of the products isolated. Thus treatment of the species $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ [R = C_6H_4Me-4 (**1a**) or C_6H_4OMe-2 (**1b**)] with $[Fe_2(CO)_9]$ gives, respectively, as the major products the 34-valence-electron compounds $[MoFe(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ [R = C_6H_4Me-4 (**2a**)[4a] or C_6H_4OMe-2 (**2b**)[4b]], whereas $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ (**1c**), containing the more bulky xylyl group, affords the 32-valence-electron complex $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ (**3a**). Similarly, the reagents $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ [M = W (**1d**) or Cr (**1e**)] with $[Fe_2(CO)_9]$ exclusively afford the electronically unsaturated '$Fe(CO)_3$' adducts $[MFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ [M = W (**3b**) or Cr (**3c**)].[4b] The compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ [L = $HB(pz)_3$ (**1f**) or η-C_5Me_5 (**1g**)] illustrate the importance of the nature of the L group in controlling these reactions. Treatment of (**1f**) with $[Fe_2(CO)_9]$ gives $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ (**3d**) as the only product.[4c] In contrast, (**1g**) with an equivalent of $[Fe_2(CO)_9]$ affords an approximately 1:1 equilibrium mixture of the two dimetal compounds $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(\eta\text{-}C_5Me_5)]$ [n = 6 (**2c**) or 5 (**3e**)].[4d] The delicate balance between the 32- and 34-valence-electron dimetal compounds has been demonstrated by spectroscopic studies on CO-saturated solutions of the former which reveal the existence of an equilibrium with the latter complexes.[4b–d]

The iron atoms in the compounds of type (**2**) acquire an 18-electron closed shell through the C≡M linkages formally donating two electrons. In the complexes (**3**), however, four-electron donation to the iron centres is invoked, a feature supported by spectroscopic and *X*-ray diffraction data and theoretical studies.[4b,c] The recognition that C≡M groups can function either as two- or four-electron donors has prompted us to extend some earlier studies. Treatment of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with the complexes $[M'(CO)_3(NCMe)_3]$ (M′ = Mo or W) affords the trimetal compounds $[M'W_2(\mu\text{-}$

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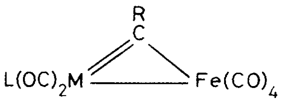
* 1,1,2,2,3,3-Hexacarbonyl-1,3-bis(η-cyclopentadienyl)-1,2;2;3-bis(μ-2′,6′-dimethylphenylmethylidyne)-trimolybdenum (2*Mo–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

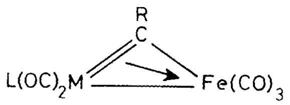
Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.

$[M(\equiv CR)(CO)_2L]$

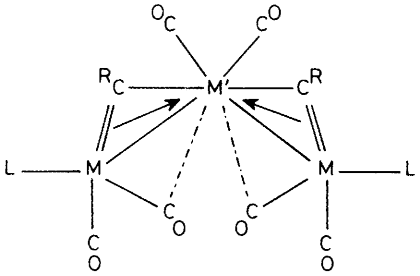
	M	R	L
(**1a**)	Mo	C_6H_4Me-4	η-C_5H_5
(**1b**)	Mo	C_6H_4OMe-2	η-C_5H_5
(**1c**)	Mo	C_6H_3Me-2,6	η-C_5H_5
(**1d**)	W	$C_6H_3Me_2$-2,6	η-C_5H_5
(**1e**)	Cr	$C_6H_3Me_2$-2,6	η-C_5H_5
(**1f**)	W	C_6H_4Me-4	$HB(pz)_3$
(**1g**)	W	C_6H_4Me-4	η-C_5Me_5
(**1h**)	W	C_6H_4Me-4	η-C_5H_5



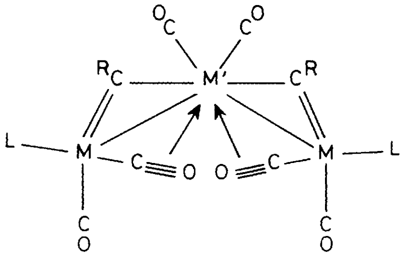
	M	R	L
(**2a**)	Mo	C_6H_4Me-4	η-C_5H_5
(**2b**)	Mo	C_6H_4OMe-2	η-C_5H_5
(**2c**)	W	C_6H_4Me-4	η-C_5Me_5



	M	R	L
(**3a**)	Mo	$C_6H_3Me_2$-2,6	η-C_5H_5
(**3b**)	W	$C_6H_3Me_2$-2,6	η-C_5H_5
(**3c**)	Cr	$C_6H_3Me_2$-2,6	η-C_5H_5
(**3d**)	W	C_6H_4Me-4	$HB(pz)_3$
(**3e**)	W	C_6H_4Me-4	η-C_5Me_5



(I)



(II)

	M	M′	R	L
(**4a**)	W	Mo	C_6H_4Me-4	η-C_5H_5
(**4b**)	W	W	C_6H_4Me-4	η-C_5H_5
(**4c**)	W	W	C_6H_4Me-4	η-C_5Me_5
(**4d**)	W	Mo	C_6H_4Me-4	η-C_5Me_5
(**4e**)	W	Mo	Me	$HB(pz)_3$
(**4f**)	W	Mo	$C_6H_3Me_2$-2,6	η-C_5H_5
(**4g**)	Mo	Mo	$C_6H_3Me_2$-2,6	η-C_5H_5
(**4h**)	Mo	Mo	C_6H_4OMe-2	η-C_5H_5

CC_6H_4Me-4)$_2$(CO)$_6$(η-C_5H_5)$_2$] [M′ = Mo (**4a**) or W (**4b**)].[5a] Subsequently, the related species [M′W_2(μ-CR)$_2$(CO)$_6L_2$] [R = C_6H_4Me-4, L = η-C_5Me_5, M′ = W (**4c**) or Mo (**4d**); R = Me, L = HB(pz)$_3$, M′ = Mo (**4e**)] were prepared.[5b]

At the time (**4a**) and (**4b**) were discovered it was anticipated that these species might adopt the structure (**I**) shown, in which the C≡W groups donate four electrons to the molybdenum or tungsten atoms of the M′(CO)$_2$ fragments, thereby enabling the central metal atom to attain a filled 18-electron shell. However, an *X*-ray diffraction study on (**4a**) revealed that one carbonyl ligand on each tungsten atom adopts a μ-σ,η^2-CO bonding mode [structure (**II**)].[5a] This feature, and the other ligands present, allow the molybdenum atom to acquire an 18-electron configuration without the necessity for the C≡W fragments having to donate four electrons. Moreover, the spectroscopic properties of (**4a**) were in accord with the structure established for the solid state. Thus in the i.r. spectrum, whether measured in CH_2Cl_2 solutions or as a suspension in Nujol, there was an absorption at *ca.* 1 690 cm^{-1} characteristic for a μ-σ,η^2-CO group.[6,7] On this basis it was assumed that (**4b**)—(**4e**) also had structures akin to (**4a**), since these trimetal species had essentially similar properties. However, not all of these species showed a well defined i.r. band near 1 700 cm^{-1}.

The work with the iron–molybdenum and –tungsten species (**2**) and (**3**) established that four-electron donation by C≡M fragments was favoured by bulky groups, *e.g.* $CC_6H_3Me_2$-2,6 or HB(pz)$_3$. Accordingly, it was of interest to investigate reactions between [Mo(CO)$_3$(NCMe)$_3$] and alkylidyne–molybdenum and –tungsten reagents not previously studied, in order to test whether evidence could be obtained for the existence of complexes of formulation [MoM_2(μ-CR)$_2$(CO)$_6L_2$] but with structures of type (**I**).

Results and Discussion

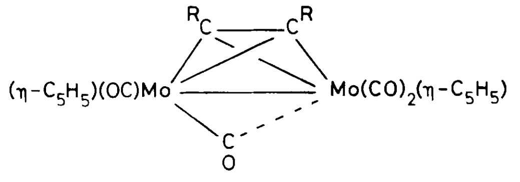
Initially an attempt was made to prepare the trimolybdenum compound [Mo$_3$(μ-CC_6H_4Me-4)$_2$(CO)$_6$(η-C_5H_5)$_2$], the molybdenum analogue of (**4b**). It was anticipated that this trimolybdenum species would have a structure of type (**II**), with two μ-σ,η^2-CO ligands. However, treatment of a suspension of [Mo(CO)$_3$(NCMe)$_3$] in Et_2O with (**1a**) afforded an unstable brown material which on standing or attempted purification by chromatography yielded [Mo(CO)$_6$], and the red μ-alkyne-dimolybdenum complex [Mo$_2${μ-C_2(C_6H_4Me-4)$_2$}(CO)$_4$(η-C_5H_5)$_2$] (**5**). It is likely that the initially formed dark brown material was the desired trimetal compound [Mo$_3$(μ-CC_6H_4-Me-4)$_2$(CO)$_6$(η-C_5H_5)$_2$], but that it is unstable giving [Mo(CO)$_6$] and (**5**). The coupling of alkylidyne groups to afford μ-alkyne di- or tri-metal complexes has been a common feature of many reactions in this area.[8] Indeed compound (**5**) was one of several products formed in the reaction between [W(≡CC_6H_4-Me-4)Br(CO)$_4$] and [Mo$_2$(CO)$_4$(η-C_5H_5)$_2$].[8b] More logically, (**5**) is also produced on treatment of [Mo$_2$(CO)$_6$(η-C_5H_5)$_2$] with the alkyne C_2(C_6H_4Me-4)$_2$,[9] but data characterising (**5**) (Tables 1 and 2) have not been previously reported.

In contrast with the failure to isolate a stable species [Mo$_3$(μ-CC_6H_4Me-4)$_2$(CO)$_6$(η-C_5H_5)$_2$], reactions between [Mo(CO)$_3$(NCMe)$_3$] and the alkylidynemetal compounds

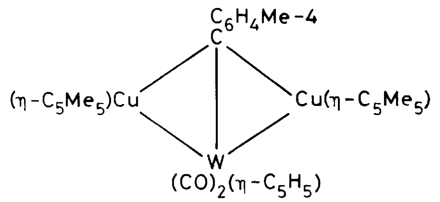
Table 1. Analytical[a] and physical data for the complexes

	Compound	Colour	Yield (%)	$\nu_{max.}$(CO)[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
(**4f**)	[$MoW_2(\mu$-$CC_6H_3Me_2$-2,6)$_2(CO)_6(\eta$-$C_5H_5)_2$]	Black	35	2 002w, 1 965vs, 1 932m, 1 857m	40.4 (41.0)	2.6 (2.8)
(**4g**)	[$Mo_3(\mu$-$CC_6H_3Me_2$-2,6)$_2(CO)_6(\eta$-$C_5H_5)_2$]	Black	42	1 998w, 1 970vs, 1 935m, 1 864m	49.0 (49.6)	3.3 (3.4)
(**4h**)	[$Mo_3(\mu$-CC_6H_4OMe-2)$_2(\mu$-CO)$_2(CO)_4(\eta$-$C_5H_5)_2$]	Black	44	1 962w(sh), 1 943vs, 1 891vs, 1 860w(sh), 1 813w, 1 586w, 1 568w	46.4 (46.0)	3.6 (3.9)
(**5**)	[$Mo_2\{\mu$-$C_2(C_6H_4Me$-4)$_2\}(CO)_4(\eta$-$C_5H_5)_2$]	Red	29	1 986vw, 1 958w, 1 922vs, 1 838m(br)	55.9 (56.3)	3.5 (3.8)
(**7b**)	[$MoCu(\mu$-$CC_6H_3Me_2$-2,6)(CO)$_2(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$]	Red	64	1 966vs, 1 874m(br)	58.4 (58.6)	5.6 (5.5)
(**7c**)	[$WCu(\mu$-$CC_6H_3Me_2$-2,6)(CO)$_2(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$]	Red	83	1 955vs, 1 866m(br)	50.4 (50.3)	4.8 (4.7)

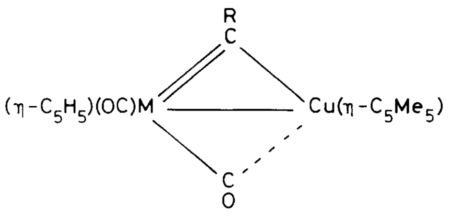
[a] Calculated values are given in parentheses. [b] In CH_2Cl_2.



(**5**) R = C_6H_4Me-4



(**6**)



	M	R
(**7a**)	W	C_6H_4Me-4
(**7b**)	Mo	$C_6H_3Me_2$-2,6
(**7c**)	W	$C_6H_3Me_2$-2,6

(**1b**)—(**1d**) gave the expected trimetal complexes [$MoM_2(\mu$-$CR)_2(CO)_6(\eta$-$C_5H_5)_2$] [M = W, R = $C_6H_3Me_2$-2,6 (**4f**); M = Mo, R = $C_6H_3Me_2$-2,6 (**4g**), or C_6H_4OMe-2 (**4h**)], data for which are summarised in Tables 1 and 2. Compounds (**4f**)—(**4h**) all gave fast atom bombardment (f.a.b.) mass spectra with molecular ion isotope patterns in accord with the formulations. The i.r. spectra of the complexes in the CO region are of interest. The spectrum of (**4h**) is the most complicated, displaying seven absorptions. This number of bands probably arises because of the presence of more than one diastereoisomer, due to different orientations of the $Mo(CO)_2(\eta$-$C_5H_5)$ groups, a feature observed previously in the spectra of trimetal compounds.[4a,10] The observation of bands at 1 586 and 1 568 cm^{-1} perhaps suggests the presence of molecules with structures having μ-σ,η^2-CO groups, but the low intensity of these absorptions makes the assignment tentative. In the carbonyl region, the i.r. spectra of compounds (**4f**) and (**4g**) show four bands, and there is no absorption in the range 1 686—1 728 cm^{-1} as found in the spectra of (**4a**), (**4b**), (**4d**), and (**4e**).[5] Interestingly, the i.r. spectrum of (**4c**) also shows no band below 1 830 cm^{-1}. However, the absence in the spectra of (**4c**), (**4f**), and (**4g**) of bands assignable to a μ-σ,η^2-CO group does not unequivocally rule out a structure of type (**II**) since the absorptions are of low intensity and might not have been observed for this reason.

The ^{13}C-$\{^1H\}$ n.m.r. data for compounds (**4f**)—(**4h**) are informative since characteristic peaks for the μ-C nuclei occur at δ 373.3, 395.0, and 372.3 p.p.m., respectively. These values may be compared with those for (**4a**) (δ 360.1), (**4d**) (356.4), and (**4e**) (336.7 p.p.m.) wherein the central metal atom is also molybdenum. The ^{13}C-$\{^1H\}$ n.m.r. spectra of (**4f**)—(**4h**) each show three peaks for CO environments. This pattern was also observed in the spectra of (**4a**)—(**4e**).[5a,b] In the case of (**4g**) coalescence of these signals occurs at room temperature and under these conditions the μ-C and $C^1(C_6H_3)$ peaks are broad. When the spectrum is measured at −40 °C all the expected signals are observed. The carbon nuclei of the aromatic rings in (**4f**)—(**4h**) give rise to six resonances, indicating that the two rings in each species are chemically equivalent but that each half of the rings are not.

The n.m.r. data for (**4f**)—(**4h**) thus did not resolve whether these molecules have structures of type (**I**) or (**II**), although for (**4f**) and (**4g**) the absence of a CO band in the i.r. spectra below 1 700 cm^{-1} provided tentative evidence for (**I**). A single-crystal *X*-ray diffraction study was therefore carried out on (**4g**). The results are summarised in Table 3, and the structure of the molecule is shown in Figures 1 and 2.

The molecular structure has crystallographic C_2 symmetry and may be described as comprising two almost isosceles CMo_2 triangles which share an apex [Mo(2)] and subtend a dihedral angle of 79°. The Mo(1)–Mo(2)–Mo(1a) angle is 124.8(1)°, to be compared with a W–Mo–W angle of 148.2(2)° in (**4a**).[5a] Of interest is the disposition of the CO ligands attached to the molybdenum atoms Mo(1) and Mo(1a) in (**4g**). The groups C(2)O(2) and C(2a)O(2a) are terminally bound, with essentially linear attachments to their metal atoms: Mo(1)–C(2)–O(2) or Mo(1a)–C(2a)–O(2a) 173.3(5)°. The ligands C(3)O(3) and C(3a)O(3a), however, weakly semibridge the Mo–Mo bonds [*viz.* Mo(1)–C(3)–O(3) 169.8(5)°, Mo(1)–C(3) 1.970(5), Mo(2)···C(3) 2.71 Å]. However, the Mo(2)···O(3) or Mo(2a)···O(3a) separations (3.41 Å) are non-bonding. The corresponding distance in compound (**4a**), which has a structure of type (**II**), is 2.53(1) Å.[5a] Hence the

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	$^{1}H(\delta)$[b]	$^{13}C(\delta)$[c]
(4f)	1.69, 2.21 (s × 2, 6 H, Me_2-2,6), 5.50 (s, 5 H, C_5H_5), 6.8–7.2 (m, 3 H, C_6H_3)	[d] 373.3 (μ-C), 236.3, 230.1, 213.6 (CO), 164.5 [$C^1(C_6H_3)$], 126.9, 126.7, 126.4, 126.3, 124.6 (C_6H_3), 93.6 (C_5H_5), 21.1 (Me_2-2,6)
(4g)	1.69, 2.16 (s × 2, 6 H, Me_2-2,6), 5.40 (s, 5 H, C_5H_5), 6.99—7.15 (m, 3 H, C_6H_3)	[e] 395.0 (μ-C), 238.5, 237.1, 224.1 (CO), 164.0 [$C^1(C_6H_3)$], 127.7, 127.5, 127.4, 125.7, 123.0 (C_6H_3), 95.8 (C_5H_5), 22.2, 22.0 (Me_2-2,6)
(4h)	[f] 3.25 (s, 3 H, OMe), 5.45 (s, 5 H, C_5H_5), 7.27—7.35 (m, 4 H, C_6H_4)	372.3 (μ-C), 251.2, 231.0, 223.4 (CO), 159.7 [$C^1(C_6H_4)$], 139.6, 133.4, 130.9, 122.4, 110.6 (C_6H_4), 92.0 (C_5H_5), 56.5 (OMe)
(5)	2.31 (s, 3 H, Me-4), 5.15 (s, 5 H, C_5H_5), 6.94, 7.01 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8]	[g] 231.6, 228.8 (CO), 141.6 [$C^1(C_6H_4)$], 134.2, 128.2, 127.8 (C_6H_4), 80.8 (μ-C_2), 20.1 (Me-4)
(7b)	[h] 1.64 (s, 15 H, C_5Me_5), 1.99 (s, 6 H, Me_2-2,6), 5.38 (s, 5 H, C_5H_5), 7.02 (br, 3 H, C_6H_3)	[d] 318.2 (μ-C), 228.0 (CO), 153.2 [$C^1(C_6H_3)$], 131.1, 126.6, 125.6 (C_6H_3), 105.8 (*C*$_5$Me$_5$), 92.1 (C_5H_5), 20.4 (Me_2-2,6), 8.0 (C_5*Me*$_5$)
(7c)	[h] 1.60 (s, 15 H, C_5Me_5), 1.94 (s, 6 H, Me_2-2,6), 5.41 (s, 5 H, C_5H_5), 6.99 (br, 3 H, C_6H_3)	293.6 [μ-C, J(WC) 155], 216.6 [CO, J(WC) 177], 156.4 [$C^1(C_6H_3)$], 138.6, 127.1, 125.7 (C_6H_3), 107.2 (*C*$_5$Me$_5$), 90.2 (C_5H_5), 22.3 (Me_2-2,6), 9.6 (C_5*Me*$_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] Measured in $CDCl_3$, unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 p.p.m.). [d] Measured at −20 °C. [e] Measured at −40 °C in $CDCl_3$. [f] Measured in $C_6D_5CD_3$. [g] Measured at −70 °C. [h] Measured in CD_2Cl_2.

Table 3. Selected bond distances (Å) and angles (°) for the complex [$Mo_3(\mu\text{-}CC_6H_3Me_2\text{-}2,6)_2(CO)_6(\eta\text{-}C_5H_5)_2$] **(4g)**

Mo(1)–Mo(2)	2.802(1)	Mo(1)–C(1)	1.986(5)	Mo(1)–C(2)	1.989(6)	Mo(1)–C(3)	1.970(5)
Mo(2)–C(1)	2.100(5)	Mo(2)–C(4)	1.957(5)	C(1)–C(11)	1.465(7)	C(2)–O(2)	1.151(7)
C(3)–O(3)	1.152(6)	C(4)–O(4)	1.154(5)	Mo(2) · · · C(2)	3.22	Mo(2) · · · O(2)	4.00
Mo(2) · · · C(3)	2.71	Mo(2) · · · O(3)	3.41	Mo(1)–C(cp) range 2.317(6)—2.365(5)			

C(1)–Mo(1)–Mo(2)	48.4(1)	C(2)–Mo(1)–Mo(2)	82.5(2)	C(2)–Mo(1)–C(1)	101.5(2)
C(3)–Mo(1)–Mo(2)	66.4(2)	C(3)–Mo(1)–C(1)	110.6(2)	C(3)–Mo(1)–C(2)	90.0(2)
C(1)–Mo(2)–Mo(1)	45.0(1)	C(4)–Mo(2)–Mo(1)	117.3(1)	C(4)–Mo(2)–C(1)	72.4(2)
C(11)–C(1)–Mo(2)	143.1(4)	Mo(2)–C(1)–Mo(1)	86.5(2)	C(11)–C(1)–Mo(1)	130.2(3)
O(4)–C(4)–Mo(2)	178.2(5)	O(2)–C(2)–Mo(1)	173.3(5)	O(3)–C(3)–Mo(1)	169.8(5)
C(4)–Mo(2)–C(4a)	87.7(3)	Mo(1)–Mo(2)–Mo(1a)	124.8(1)	C(1)–Mo(2)–C(1a)	167.4(3)
C(1)–Mo(2)–C(4a)	98.3(2)	C(1)–Mo(2)–Mo(1a)	143.9(1)		

Torsion angles

C(1)–Mo(1)–Mo(2)–C(4)	−4.0(3)	C(1)–Mo(1)–Mo(2)–Mo(1a)	−134.2(2)	C(1)–Mo(1)–Mo(2)–C(1a)	166.3(3)
C(1)–Mo(1)–Mo(2)–C(4a)	89.7				

Angles between planes

(*i*) Mo(1), Mo(2), C(1); (*ii*) Mo(2), Mo(1a), C(1a); (*iii*) C(4), Mo(2), C(4a); (*iv*) C(11), C(12), C(13), C(14), C(15), C(16); maximum deviation 0.02 Å
(*i*)–(*ii*) 79.0; (*i*)–(*iii*) 100.6; (*i*)–(*iv*) 81.7

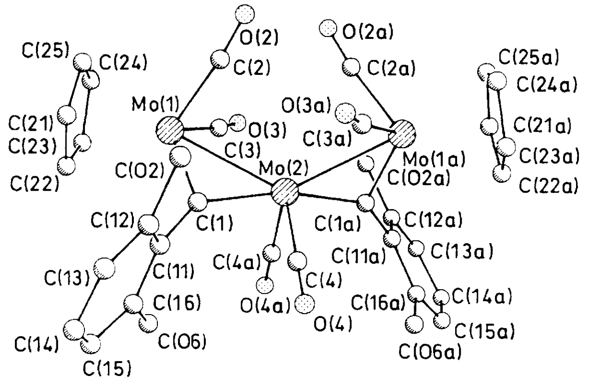


Figure 1. The molecular structure of [$Mo_3(\mu\text{-}CC_6H_3Me_2\text{-}2,6)_2(CO)_6(\eta\text{-}C_5H_5)_2$] **(4g)** showing the crystallographic numbering system

μ-σ,η^2-CO bonding mode present in **(4a)** is absent in **(4g)** a feature best seen in Figure 2. As expected, Mo(2) carries two terminally bound carbonyl groups C(4)O(4) and C(4a)O(4a) [Mo(2)–C(4)–O(4) 178.2(5)°]. Thus the central molybdenum atom shows an unusual mode of co-ordination in that it is formally a 14-electron centre if the two C≡Mo fragments are considered to act as two-electron donors. However, if the C≡Mo moieties act as four-electron donors, as in the representation **(I)** the Mo(2) atom would acquire an 18-electron shell. In support of this concept, the presence of the semi-bridging C(3)O(3) and C(3a)O(3a) ligands indicates that Mo(2) is electronically saturated, leading to a compensatory transfer of negative charge

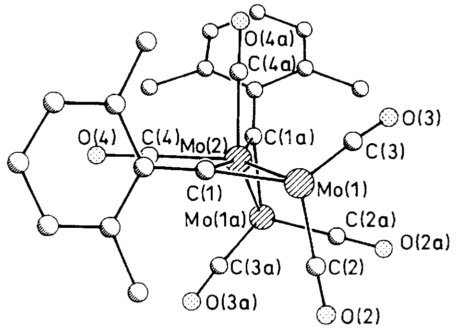


Figure 2. The structure of compound **(4g)** emphasising the disposition of the CO groups but with the C_5H_5 rings omitted for clarity

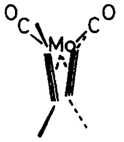
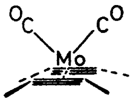
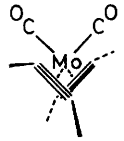
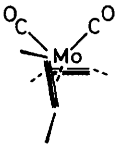
Conformation (θ_1,θ_2)		$E(d^6)$/eV	$E(d^0)$/eV	
(A)	(0,0)	+0.67	+0.03	
(B)	(90,90)	+0.80	+0.14	
(C)	(45,45)	0.00	0.00	
		by definition		
(D)	(0,90)	+0.25	+0.26	

Figure 3. Calculated energies for selected conformations of $[Mo(CO)_2(\eta-C_2H_2)_2]$ (d^6) and $[Mo(CO)_2(\eta-C_5H_5)_2]^{6+}$ (d^0). Energies are given relative to conformation (**C**)

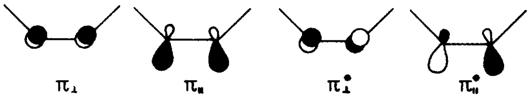


Figure 4. Frontier orbitals of the *cis*-bent alkyne ligand

via these carbonyl ligands to Mo(1) and Mo(1a).[11] It seems likely that the presence of the methyl substituents in the $C_6H_3Me_2$-2,6 groups of (**4g**) impedes formation of a structure of type (**II**) as found in the solid state for (**4a**), a molecule which contains the less sterically demanding C_6H_4Me-4 moieties.

Thus in the crystalline state, the electronic relationship between the structures of compounds (**4a**) and (**4g**) is akin to that between (**2a**) and (**3a**), with the C≡M groups functioning as two-electron donors in (**2a**) and (**4a**), and as four-electron donors in (**3a**) and (**4g**). It is likely that (**4f**) has a structure similar to (**4g**) since the i.r. spectra of the two species are very similar (Table 1). Whether (**4h**) adopts a structure of type (**I**) or (**II**) is unresolved. It is possible that in solution each of the compounds (**4**) exists as a rapidly equilibrating mixture of the two isomers. Indeed, structures (**I**) and (**II**) are so similar that little energy would be required for their interconversion. In those complexes in which there is a band in the i.r. spectrum which might be due to a μ-σ,η^2-CO group this absorption, as mentioned earlier, is very weak. Hence in an isomeric mixture in solution the proportion of molecules with structure (**II**) seems likely to be small.

The Mo–Mo distances in (**4g**) [2.802(1) Å] are somewhat shorter than those generally found (*ca.* 2.95—3.10 Å) in complexes in which molybdenum–molybdenum single bonds are spanned by organic groups.[12] The metal–metal separation in (**4g**) is perhaps best compared with that in $[Mo_2Fe\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_6(\eta-C_5H_5)_2$ [2.764(1) Å],[4a] which is also electronically unsaturated, and for which a degree of metal–metal multiple bonding has been invoked. A theoretical interpretation of the structural data for the heteronuclear dimetal compounds (**2a**) and (**3a**)[4b] led to the conclusion that the unsaturation in the latter is delocalised throughout the μ-CMoFe ring system in a manner reminiscent of the isolobally related cyclopropenium cation $C_3H_3^+$. A similar conclusion may be drawn from the data for the μ-CMo_2 rings in the homonuclear trimetal compound (**4g**), since the C(1)–Mo(1) and C(1)–Mo(2) distances differ by only *ca.* 5%. Moreover, the value for C(1)–Mo(1) [1.986(5) Å] is virtually the same as that [1.976(2) Å] for the μ-C–Mo distance in (**3a**), indicating that the net effect upon co-ordination of $Mo(CO)_2$ and $Fe(CO)_3$ fragments to (**1c**) is virtually identical.

A noteworthy feature of the structure of compound (**4g**) is the orientation of the two μ-CMo_2 planes with respect to the carbonyl ligands bound to Mo(2). Thus the C(4)O(4) group is essentially coplanar with Mo(1), Mo(2), and C(1), and because of the C_2 symmetry this is also true of the C(4a)O(4a) ligand with respect to Mo(1a), Mo(2), and C(1a). The C(4) atom is displaced from the Mo(1)Mo(2)C(1) plane by 0.14 Å, and the torsional angle C(1)–Mo(1)–Mo(2)–C(4) is −4.0(3)°. This structural feature is best seen in Figure 2. Furthermore, the Mo(1)–Mo(2)–Mo(1a) angle [124.8(1)°] results in a substantial gap in the co-ordination sphere of Mo(2), which is only partially filled by the semi-bridging C(3)O(3) and C(3a)O(3a) groups. In (**4a**) the metal atom spine is less bent (148.2°) than in (**4g**) but the presence of the two μ-σ,η^2-CO ligands results in the co-ordination sites around the central molybdenum atom being filled.

We have performed a series of extended-Hückel molecular orbital (e.H.m.o.) calculations to determine whether electronic effects might be responsible for the observed conformation of (**4g**). These calculations have been based on the model compound $[Mo(CO)_2(\eta-C_2H_2)_2]$ which is mapped with (**4g**) by the isolobal relationship: $Mo(CO)_2(\eta-C_5H_5) \xleftrightarrow[\circ]{} CH \xleftrightarrow[\circ]{} C-C_6H_3Me_2$-2,6. The conformational preference for the disposition of the ligands in $[Mo(CO)_2(\eta-C_2H_2)_2]$ should reflect the influence of electronic factors in the compounds (**4**), without being so sensitive to steric (non-bonded) interactions. Previous studies[13,14] have demonstrated the importance of electronic factors in determining the conformations in a variety of alkynemetal complexes.

Details of the calculations, the extended-Hückel parameters, and the geometries used are given in the Appendix. We were particularly interested in investigating the effect of varying the orientation of the two alkyne ligands, and this was effected by rotating each one about vectors through the metal and midpoints of the C≡C bonds. Each conformation is then described by two parameters θ_1 and θ_2, as shown in Figure 3. The energy varies as a function of the two angles (θ_1, θ_2), and the energies of some conformations, relative to that observed in (**4g**), *i.e.* (**C**), are given in Figure 3. The calculations support the idea that there should be a substantial electronic contribution to the orientational preference in $[Mo(CO)_2(\eta-C_2H_2)_2]$. The lowest energy occurs when the alkyne ligands are orthogonal to each other, and parallel to the carbonyl ligands [conformation (**C**)]. Since (**4g**) has a precisely analogous structure it seems likely that the relative orientation of the Mo(1)–C(1) and Mo(1a)–C(1a) bonds in the latter species is also set by electronic factors. It is instructive to attempt to explain the origin of such preferences by considering how the interactions between the orbitals of the alkyne ligands and the metal centre in $[Mo(CO)_2(\eta-C_2H_2)_2]$ vary with orientation.

Previous theoretical work[14] on the co-ordination chemistry of alkynes has shown that of the four alkyne frontier orbitals (illustrated in Figure 4), only three ($\pi_\parallel$, $\pi_\parallel^*$, and $\pi_\perp$) overlap sufficiently with orbitals of the metal centre to be important in bonding. Conformational preferences arise because the $\pi_\parallel^*$ (acceptor) and $\pi_\perp$ (donor) orbitals have π symmetry with respect to the metal atom, and their overlap with the metal orbitals is strongly orientation dependent. 'Four-electron donor' behaviour involves the interaction of both $\pi_\perp$ and $\pi_\parallel^*$, and it was of interest to determine whether the energy differences noted in Figure 3 arise from the need to optimise π-donor ($\pi_\perp$) or π-acceptor ($\pi_\parallel^*$) interactions, or from a combination of these two factors.

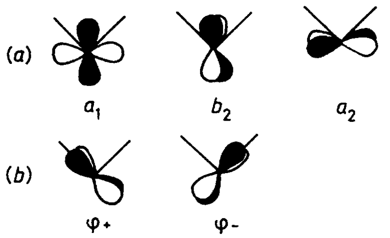


Figure 5. 't_{2g}'-type orbitals of the $Mo(CO)_2$ group

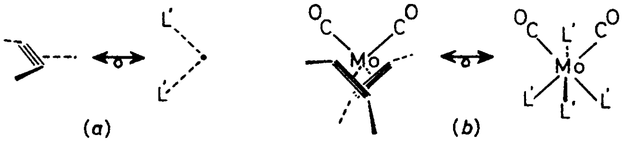


Figure 6. The isolobal replacement of four-electron donor alkynes by pairs of two-electron donor ligands (L')

To distinguish between these possibilities we have calculated the total energies for the hypothetical d^0 species $[Mo(CO)_2(\eta\text{-}C_2H_2)_2]^{6+}$. The orientational preferences here should be sensitive to any effects which arise from interaction of filled alkyne orbitals ($\pi_{\parallel}$ and $\pi_{\perp}$) with vacant metal orbitals. However, as there are no *d* electrons, contributions to the energies from metal-to-ligand back donation, as well as those from $4e^-$ (destabilising) interactions between metal *d* orbitals and the filled alkyne orbitals, are removed. Examination of the resulting energies (Figure 3) reveals that the energy differences are much smaller. In particular, the large energy difference between conformations in which the two alkyne C–C bonds are coplanar [(**A**) and (**B**)] and those in which they are perpendicular [(**C**) and (**D**)] is removed. This strongly suggests that the alkynes adopt perpendicular orientations to optimise back bonding from the filled metal orbitals. It appears that the much smaller differences between the pairs of conformations with similar *relative* alkyne orientations [(**A**) *versus* (**B**), and (**C**) *versus* (**D**)] remain when the *d* electrons are removed, suggesting that they result from differences in overlap between the four alkyne-donor orbitals and vacant metal orbitals.

To appreciate the form of the filled metal orbitals of a d^6 ML_2 moiety it is useful to consider the ML_2 group as a fragment (albeit a small one) of an octahedral complex. The three filled *d* orbitals are similar to the t_{2g} orbitals of the latter, and these are illustrated in Figure 5(*a*). Addition of the two alkyne ligands results in a stabilisation of some of these orbitals, but does not perturb the pseudo-octahedral nature of the bonding. This is especially true in the (45,45) geometry, as can be demonstrated by the conceptual replacement of the pair of alkynes by four two-electron donor ligands (L'). When an alkyne ligand behaves as a four-electron donor this replacement involves the use of the isolobal analogy shown in Figure 6(*a*).[15] So that the symmetry properties of the donor orbitals of L'_2 match those of the $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals of the alkyne, the two ligands must lie above and below the plane defined by the alkyne ligand.

Such replacement for the (45,45) conformation (**C**) [Figure 6(*b*)] leads to a complex $[M(CO)_2L'_4]$ with a distorted octahedral structure. Although the symmetry of the model complex $[Mo(CO)_2(\eta\text{-}C_2H_2)_2]$ is much lower, we might still expect to see a pseudo-octahedral splitting of the *d* orbitals. This turns out to be the case, although the distinction between metal orbitals involved in the metal–ligand σ *versus* π bonding is lost (see below). Such an approach is also less useful for the other conformations, which map onto less favourable $[M(CO)_2L'_4]$ structures, as reflected by the fact the d^0 energies for the conformations (**A**), (**B**), and (**D**) are slightly higher than that for (**C**).

The two filled metal orbitals which have π symmetry with respect to the co-ordinated alkyne ligands are a_2 and b_2 [Figure 5(*a*)]. However, if the alkyne ligands are coplanar, back donation can only occur from one of these orbitals; b_2 in the geometry (0,0) and a_2 in the geometry (90,90). When the alkyne ligands are orthogonal both orbitals are involved. The total stabilisation of the two *d* orbitals is greater because competition for π-back donation is reduced. For conformation (**C**) this is more clearly seen if linear combinations of a_2 and b_2 are taken [Φ_+ and Φ_-, Figure 5(*b*)].

So far we have not considered the effect of the destabilising interactions between the filled metal orbitals and the alkyne donor orbitals ($\pi_{\parallel}$ and $\pi_{\perp}$). These are likely to be important because, like $\pi_{\parallel}{}^*$, the orbital $\pi_{\perp}$ has the correct symmetry (π) to interact with the metal orbitals a_2 and b_2. Although our approach cannot separate the effects of these interactions from those which arise from competitive back donation, we would expect the two effects to reinforce each other. When the alkynes are orthogonal, (**C**) and (**D**), the *d* orbital which interacts with $\pi_{\parallel}{}^*$ on one alkyne interacts with the $\pi_{\perp}$ donor orbital on the other. Rehybridisation of the metal orbitals, to maximise the former interaction, which is stabilising, and to minimise the latter, is then possible. This is not the case when the alkyne ligands are coplanar, since both $\pi_{\perp}$ orbitals interact with the same metal orbital. The resulting conformational preference is thus closely related to the tendency of π-donor and π-acceptor ligands to adopt mutually *trans* positions in co-ordination complexes.

The perpendicular configuration (**C**) of two co-ordinated alkyne ligands, or alkylidynemetal fragments as seen in (**4g**), is also seen in other systems. One closely related system is the *p*-tolylmethylidynetungsten analogue of (**4g**), the compound (**4a**). Although the alkylidynetungsten groups formally act as two-electron donors in the latter complex, they still adopt approximately orthogonal orientations. This provides further support for the idea that the conformation is set largely by the interaction of the filled orbitals on Mo(2) with acceptor orbitals of the Mo(1)≡C(1) triple bond, rather than interactions between the π-donor ($\pi_{\perp}$) orbitals and acceptor orbitals on Mo(2). Similarly, the bis(alkyne)platinum complex $[Pt(\eta\text{-}C_2Ph_2)_2]$,[16] the isolobal trimetal species $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[17a,b] and the internal platinum atoms in the derived series of chain and ring oligomers[17c] all have co-ordination environments at platinum characterised by two essentially perpendicular planes of atoms.

We have previously employed the solvent-stabilised complex $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (thf = tetrahydrofuran) as a source of the carbene isolobal fragment $Cu(\eta\text{-}C_5Me_5)$ in the synthesis of trimetallic complexes derived from addition to carbon–tungsten triple bonds. Treatment of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in thf with $[Cu(thf)(\eta\text{-}C_5Me_5)]$ affords the trimetal complex $[WCu_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (**6**).[18] There was no evidence in this synthesis for the formation of the dimetal compound $[WCu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (**7a**), although this species is a likely intermediate. Bearing in mind the pronounced effect of the $C_6H_3Me_2\text{-}2,6$ group on reducing the metal nuclearity of the products obtained when (**1c**) or (**1d**) is treated with $[Fe_2(CO)_9]$ in excess, compared with when the reagent (**1a**) or (**1h**) is used,[4a,b,19] the reactions between (**1c**) and (**1d**) with $[Cu(thf)(\eta\text{-}C_5Me_5)]$ were studied.

Treatment of (**1c**) and (**1d**), respectively, with a thf solution of an excess of $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (2—3 equivalents) afforded the binuclear metal compounds $[MCu(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ [M = Mo (**7b**) or W (**7c**)] in good yield. Data for these products are given in Tables 1 and 2. In their i.r. spectra in the carbonyl region there are the expected two bands. However, that at *ca.* 1 870 cm^{-1} indicates that one of these ligands semi-bridges the metal–metal bond. In the trimetal compound (**6**) the CO absorptions are at 1 934 and 1 855 cm^{-1}, and evidently a semi-bridging carbonyl group is present in this complex also.[18] In the $^{13}C-\{^1H\}$ n.m.r. spectra of (**7b**) and (**7c**) only one CO resonance is observed (Table 2), and this indicates dynamic behaviour involving site exchange of the carbonyl groups. The usual diagnostic peaks for the μ-C nuclei in (**7b**) and (**7c**) occur at δ 318.2 and 293.6 p.p.m., respectively. The corresponding signal in the spectrum of (**6**) (275.5 p.p.m.) is less deshielded since the alkylidyne-carbon nucleus triply bridges rather than edge bridges metal sites.[20] The isolation of the dimetal species (**7b**) and (**7c**), coupled with the evident instability of (**7a**) with respect to its ready transformation into the trimetal compound (**6**), provides a further example of how the $C_6H_3Me_2$-2,6 group reduces the metal nuclearity of the products in reactions of the reagents (**1**).[4b]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. Alumina (Brockman Activity II) was used in the chromatography columns. The reagents (**1a**)—(**1d**),[4b] and the complexes $[Mo(CO)_3(NCMe)_3]$[21] and $[Cu(thf)(\eta-C_5Me_5)]$,[18] were prepared as described previously. Analytical and other data for the new compounds are given in Tables 1 and 2. The instrumentation used to record the spectroscopic data has been listed in earlier papers in this series.[4,17]

Reactions of the Complexes $[M(\equiv CR)(CO)_2(\eta-C_5H_5)]$ *with* $[Mo(CO)_3(NCMe)_3]$.—(*i*) A suspension of $[Mo(CO)_3(NCMe)_3]$ (0.36 g, 1.2 mmol) and compound (**1c**) (0.92 g, 2.75 mmol) in Et_2O (50 cm^3) was stirred for 14 h. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (30 cm^3, 1:5), and the solution was chromatographed on a water-cooled column (2.5 × 15 cm). Elution with the same solvent mixture removed $[Mo(CO)_6]$ and unreacted (**1c**). Further elution with CH_2Cl_2–light petroleum (4:1) afforded a black eluate which was concentrated to *ca.* 5 cm^3 under reduced pressure, and then cooled to −78 °C (18 h) to give black *microcrystals* of $[Mo_3(\mu-CC_6H_3Me_2-2,6)_2(CO)_6(\eta-C_5H_5)_2]$ (**4g**) (0.48 g).

(*ii*) The compounds $[Mo(CO)_3(NCMe)_3]$ (0.36 g, 1.2 mmol) and (**1d**) (0.84 g, 2.0 mmol) were stirred in Et_2O (100 cm^3) for 17 h, and the resulting dark mixture was cooled to −78 °C for 2 h. Solvent was decanted from the precipitate, and the latter was washed with light petroleum (3 × 20 cm^3). The black residue was extracted with CH_2Cl_2 (30 cm^3), and the extract was filtered through an alumina plug (2.5 × 4 cm). Solvent was removed *in vacuo* to give black *microcrystals* of $[MoW_2(\mu-CC_6H_3Me_2-2,6)_2(CO)_6(\eta-C_5H_5)_2]$ (**4f**) (0.35 g). The compound can be recrystallised from CH_2Cl_2–n-hexane (1:20) at −78 °C.

(*iii*) A suspension of $[Mo(CO)_3(NCMe)_3]$ (0.24 g, 0.79 mmol) and (**1b**) (0.70 g, 2.1 mmol) in Et_2O (50 cm^3) was stirred for 4 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (15 cm^3, 1:4), and the solution chromatographed on a water-cooled column (2.5 × 15 cm). Elution with the same solvent mixture removed unreacted (**1b**). Further elution with CH_2Cl_2–light petroleum (4:1) removed a dark brown fraction, which was collected and freed of solvent under reduced pressure. The residue was crystallised from CH_2Cl_2–n-hexane (12 cm^3, 1:5) at −78 °C to yield green-black *microcrystals* of $[Mo_3(\mu-CC_6H_4OMe-2)_2(CO)_6(\eta-C_5H_5)_2]$ (**4h**) (0.39 g).

(*iv*) In a similar procedure, (**1a**) and $[Mo(CO)_3(NCMe)_3]$ gave a brown product which on standing or attempted purification by chromatography gave red *microcrystals* of $[Mo_2\{\mu-C_2(C_6H_4Me-4)_2\}(CO)_4(\eta-C_5H_5)_2]$ (**5**) (0.20 g).

Synthesis of the Complexes $[MCu(\mu-CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)]$ (M = Mo *or* W).—(*i*) A thf suspension of $Li(C_5Me_5)$ was prepared by treating pentamethylcyclopentadiene (0.14 g, 1.0 mmol) in thf (100 cm^3) at −10 °C with n-butyllithium (1 mmol, 0.60 cm^3 of a 1.6 mol dm^{-3} solution). The mixture was cooled to −78 °C and treated with CuCl (0.11 g, 1.0 mmol) and the contents of the Schlenk tube were stirred for 2 h at this temperature. The resultant dark yellow solution was then warmed to −10 °C and (**1c**) (0.24 g, 1.0 mmol) was added. Stirring was continued for 2 h at −10 °C, and for 3 h at room temperature. Solvent was removed *in vacuo*, and the residue was extracted with light petroleum (2 × 30 cm^3). The combined extracts were filtered through Celite (3 × 3 cm), reduced in volume to *ca.* 3 cm^3, and cooled to −78 °C to give red *microcrystals* of $[MoCu(\mu-CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**7b**) (0.34 g).

(*ii*) In a similar procedure to that described above for the synthesis of (**7b**), the compounds (**1d**) (1.23 g, 2.91 mmol) and $[Cu(thf)(\eta-C_5Me_5)]$ (2.91 mmol) yielded red *crystals* of $[WCu(\mu-CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**7c**) (1.50 g).

Crystal Structure Determination and Refinement.—Crystals of compound (**4g**) were grown as black prisms by diffusion of a CH_2Cl_2 solution into n-octane. Diffracted intensities were recorded at 196 K from a crystal of dimensions *ca.* 0.20 × 0.20 × 0.50 mm. Of the 2 703 reflections ($2\theta \leqslant 50°$), measured on a Nicolet R3m/V four-circle diffractometer (θ—2θ scans), 2 247 had $F \leqslant 3\sigma(F)$, and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarisation and *X*-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[22]

Crystal data. $C_{34}H_{28}Mo_3O_6$, $M = 820.4$, orthorhombic, $a = 13.002(6)$, $b = 23.694(6)$, $c = 10.035(2)$ Å, $U = 3\,092(1)$ Å^3 (at 196 K), $D_c = 1.61$ g cm^{-3}, $Z = 4$, $F(000) = 1\,623$, space group *Pnna* (no. 52), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,73$ Å, $\mu(Mo-K_\alpha) = 11.88$ cm^{-1}.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were included in calculated positions with common refined isotropic thermal parameters for groups of related H atoms. All remaining atoms were given anisotropic thermal parameters. Refinement by full-matrix least squares, with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001\,2|F|^2]$, converged at $R = 0.044$ ($R' = 0.046$). The final electron-density difference synthesis showed no peaks $\geqslant 0.8$ e Å^{-3}. Scattering factors with corrections for anomalous dispersion were from ref. 23. All calculations were carried out on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[22] Atomic co-ordinates for (**4g**) are listed in Table 4.

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

Appendix

All molecular orbital calculations were of the extended-Hückel[24] type, and employed the weighted H_{ij} formalism.[25] They were performed on a Vax 11/750 computer, using the program ICON 8.[26] The basis set parameters for C, H, and O were the standard ones,[24] those for Mo[27] are given below (ζ = Slater type orbital exponent): 5*s*, $H_{ii} = -8.34$ eV, $\zeta = 1.96$; 5*p*, $H_{ii} = -5.24$ eV, $\zeta = 1.90$; 4*d*, $H_{ii} = -10.5$ eV, $\zeta_1 = 4.54$,

Table 4. Atomic positional parameters (fractional co-ordinates, × 10^4), with estimated standard deviations in parentheses, for compound (**4g**)

Atom	*x*	*y*	*z*
Mo(1)	1 430(1)	868(1)	1 872(1)
Mo(2)	2 500	0	3 166(1)
C(1)	2 405(4)	880(2)	3 396(5)
C(2)	2 356(5)	661(2)	372(5)
C(3)	750(4)	127(2)	1 739(5)
C(4)	3 464(4)	218(2)	4 572(5)
O(2)	2 873(4)	592(2)	−544(4)
O(3)	233(3)	−262(2)	1 577(4)
O(4)	4 044(3)	356(2)	5 379(4)
C(11)	2 745(4)	1 350(2)	4 234(5)
C(12)	3 556(4)	1 698(2)	3 791(5)
C(13)	3 839(4)	2 155(2)	4 569(5)
C(14)	3 353(5)	2 278(2)	5 763(6)
C(15)	2 581(5)	1 929(2)	6 192(5)
C(16)	2 277(4)	1 453(2)	5 483(5)
C(02)	4 093(4)	1 586(2)	2 491(6)
C(06)	1 473(5)	1 069(3)	6 033(6)
C(21)	1 298(5)	1 858(2)	1 632(7)
C(22)	650(5)	1 690(3)	2 683(6)
C(23)	−123(5)	1 334(3)	2 142(7)
C(24)	57(5)	1 304(2)	752(6)
C(25)	924(6)	1 618(2)	464(7)

C_1 = 0.6097, ζ_2 = 1.90, C_2 = 0.6097 (a double-ζ expansion was used for Mo 4*d*; C_1 and C_2 are the expansion coefficients). Calculations on the d^0 complex $[Mo(CO)_2(\eta\text{-}C_2H_2)_2]^{6+}$ used the same geometry and parameters. As a one-electron method was used the energy levels are the same as those of $[Mo(CO)_2(\eta\text{-}C_2H_2)_2]$; only the orbital occupancies are affected.

The model complex $[Mo(CO)_2(\eta\text{-}C_2H_2)_2]$ was assigned the following geometry: OC–Mo–CO 90°, Mo–CO 1.98, C–O 1.20, Mo–CH 2.10, HC–CH 1.29, and C–H 1.09 Å; C–C–H 135°. The acetylene ligands were rotated about the midpoints (X^1 and X^2) of the C–C bonds, with X^1–Mo–X^2 117° and the planes Mo, X^1, X^2 and Mo, C(O), C(O) orthogonal.

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