Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 97.[1] Synthesis and Crystal Structures of the Molybdenumditungsten Compounds $[MoW_2\{\mu\text{-}\sigma,\sigma'\text{:}\eta^4\text{-}C(Ph)C(Ph)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ and $[MoW_2(\mu\text{-}C_2Ph_2)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]\cdot 0.5CH_2Cl_2$ *

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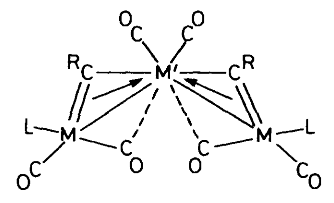
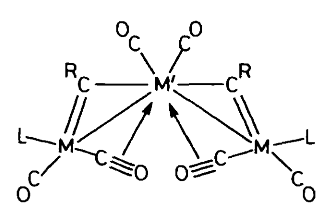
Treatment of $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with PhC≡CPh in n-hexane at reflux temperatures affords a chromatographically separable mixture of the two trimetal compounds $[MoW_2\{\mu\text{-}\sigma,\sigma'\text{:}\eta^4\text{-}C(Ph)C(Ph)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**2**) and $[MoW_2(\mu\text{-}C_2Ph_2)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (**3**), the structures of which have been established by *X*-ray diffraction. In the molecule of (**2**) there is a bent W–Mo–W [143.2(1)°] spine with one short [2.562(1) Å] and one long [2.987(1) Å] metal–metal bond. The longer of the two Mo–W linkages is bridged by a $C(Ph)C(Ph)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)$ fragment, with all four carbon atoms of the C_4 chain ligating the molybdenum atom, and with the two terminal carbon atoms σ bonded to the tungsten. Each tungsten atom carries two CO groups and a C_5H_5 ring, and the molybdenum is also co-ordinated by two CO ligands. All six CO groups deviate slightly from linearity [M(Mo or W)–C–O 171.4—173.9°] due to their weakly semi-bridging the metal–metal bonds. The structure of compound (**3**) is based on an essentially equilateral triangle of metal atoms with the W–W bond [2.752(1) Å] weakly semi-bridged by two CO groups (mean W–C–O 170°) and with the Mo–W bonds (mean 2.706 Å) bridged, respectively, by the alkynes C_2Ph_2 and $C_2(C_6H_4Me\text{-}4)_2$. Each tungsten atom is co-ordinated by a C_5H_5 ring, and the molybdenum atom is ligated by two CO groups. The molecule is an interesting example of an unsaturated trimetal cluster with 44 valence electrons. The n.m.r. data (^1H and $^{13}C\text{-}\{^1H\}$) for complexes (**2**) and (**3**) are in agreement with the structures established by *X*-ray diffraction.

We have previously reported[2] a series of trimetal compounds of formulation $[M_2M'(\mu\text{-}CR)_2(\mu\text{-}CO)_2(CO_4)L_2]$ {(**1**) M and M′ = Mo or W; R = Me or aryl; L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]}. These species were prepared by treating the complexes $[M'(CO)_3(NCMe)_3]$ with the reagents $[M(\equiv CR)(CO)_2L]$. Structural studies (*X*-ray diffraction, and i.r. and n.m.r. spectroscopy) revealed that the complexes (**1**) can exist in the solid state in one or other of two isomeric forms [(**I**) and (**II**)], or as a mixture of both isomers in solution.

In the compounds (**1**) the presence of two alkylidyne ligands bridging the metal–metal bonds makes it likely that these species would react readily with alkynes. Previously we have shown[3] that dimetal compounds containing one μ-alkylidyne group react with alkynes to afford molecules having a variety of different structures. This is because coupling of the alkylidyne fragments with alkyne molecules to form C–C bonds is often accompanied by CO and hydrogen migratory processes. In general, these reactions are less complex, forming fewer products, if the C≡C bond in the alkyne employed carries aryl substituents. It was for this reason that PhC≡CPh was used as a model substrate in the work described below.



(**I**)



(**II**)

Results and Discussion

In refluxing n-hexane, a mixture of PhC≡CPh and the species (**1a**; M = W, M′ = Mo, R = C_6H_4Me-4, L = η-C_5H_5) yielded two chromatographically separable compounds. It was not possible to deduce the molecular structures of these complexes from microanalytical and spectroscopic data, although it was

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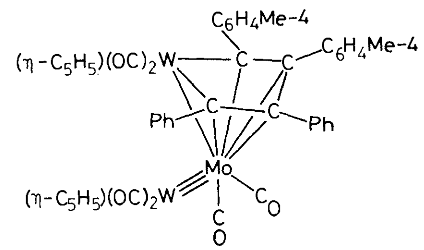
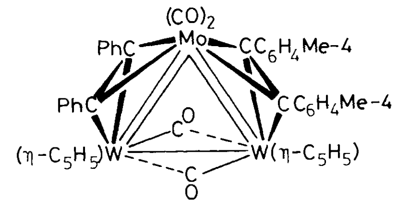
* 1,1,2,2,3,3-Hexacarbonyl-1,3-bis(η-cyclopentadienyl)-1,2-μ-[1′,2′-diphenyl-3′,4′-bis(*p*-tolyl)buta-1′,3′-diene-1′,4′-diyl-$C^{1,4}$(Mo,W′)$C^{2,3}$-(Mo)]-2-molybdenum-1,3-ditungsten(*Mo*–*W*^{1},*Mo*≡*W*^{2})-dichloromethane (1/2) and 1,1,2,3-tetracarbonyl-2,3-bis(η-cyclopentadienyl)-1,2-μ-diphenylacetylene-1,3-μ-di-*p*-tolylacetylene-*triangulo*-molybdenumditungsten(2*Mo*=*W*)-dichloromethane (2/1)

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



(2)



(3)

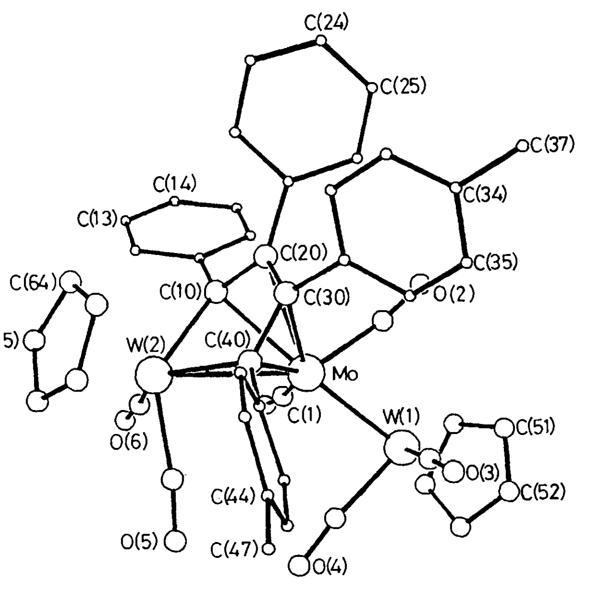


Figure 1. The molecular structure of [MoW$_2${μ-σ,σ′:η^4-C(Ph)C(Ph)C(C$_6$H$_4$Me-4)C(C$_6$H$_4$Me-4)}(CO)$_6$(η-C$_5$H$_5$)$_2$] (2) showing the crystallographic numbering scheme

apparent from their $^{13}\text{C-}\{^{1}\text{H}\}$ n.m.r. spectra that μ-CC$_6$H$_4$Me-4 groups were not present. Single-crystal *X*-ray diffraction studies were carried out on both products and from the results of this work they were identified as having the formulations [MoW$_2${μ-σ,σ′:η^4-C(Ph)C(Ph)C(C$_6$H$_4$Me-4)C(C$_6$H$_4$Me-4)}(CO)$_6$(η-C$_5$H$_5$)$_2$] (**2**) and [MoW$_2$(μ-C$_2$Ph$_2$){μ-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$] (**3**).

The molecular structure of compound (**2**) is shown in Figure 1, and selected bond distances and angles are listed in Table 1. Like its precursor (**1a**),[2a] compound (**2**) is a trimetal species having a non-linear W-Mo-W spine [143.2(1)°, compared with 148.2(2)° in (**1a**)]. However, whereas in (**1a**) the two Mo-W separations [2.938(1) Å] are the same, in complex (**2**) the distances are very different [Mo-W(1) 2.562(1), Mo-W(2) 2.987(1) Å]. The short Mo-W(1) distance strongly suggests multiple bonding. It may be compared with the Mo-W single bond distances in the molecules [MoW{μ-C(C$_6$H$_4$Me-4)C(=CH$_2$)C(H)MeC(O)}(CO)$_6$(η-C$_5$H$_5$)] [3.131(1) Å], [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] [2.971(2) Å],[4] and (**1a**) [2.938(1) Å].[2a] Indeed, it is necessary to invoke a Mo≡W linkage if W(1) is to have a filled 18-electron valence shell.

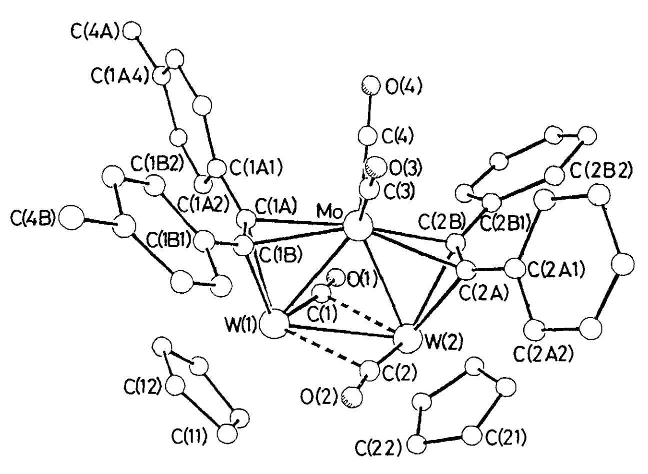


Figure 2. The molecular structure of [MoW$_2$(μ-C$_2$Ph$_2$){μ-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$] (3) showing the crystallographic numbering scheme

The Mo-W(2) bond is bridged by a C(Ph)C(Ph)C(C$_6$H$_4$Me-4)C(C$_6$H$_4$Me-4) fragment. Four carbon atoms of the latter ligate the molybdenum atom [Mo-C(10) 2.349(7), Mo-C(20) 2.434(6), Mo-C(30) 2.394(6), Mo-C(40) 2.282(7) Å], and two are attached to the tungsten [W(2)-C(10) 2.194(7), W(2)-C(40) 2.196(7) Å]. In the reaction between compound (**1a**) and PhC≡CPh the C$_4$ group has evidently formed *via* a coupling of the two *p*-tolylmethylidyne groups in the former with a molecule of the alkyne. Moreover, in order to produce the bridge system present in (**2**), one of the μ-CC$_6$H$_4$Me-4 ligands in (**1a**) has migrated from one of the tungsten centres to the other, in order to form the C(30)-C(40) bond. Within the C$_4$ chain the C-C distances [C(10)-C(20) 1.44(1), C(20)-C(30) 1.43(1), C(30)-C(40) 1.43(1) Å] reflect electron delocalisation between this group of atoms. The W(2)-C(10) and W(2)-C(40) bond lengths (see below) are very similar to the corresponding distances (mean 2.188 Å) in the compounds [WFe{μ-C(C$_6$H$_4$Me-4)C(O)C(Me)C(Me)}(CO)$_5$(η-C$_5$Me$_5$)],[3d] in which the terminal carbon atoms of the C$_4$ chain are also σ bonded to the tungsten.

Each tungsten atom in compound (**2**) carries a cyclopentadienyl ring and two carbonyl groups, and the molybdenum atom is also co-ordinated by two carbonyl ligands. All six CO groups weakly semi-bridge the metal-metal bonds, with M(Mo or W)-C-O angles ranging from 171.4 to 173.9°.

The co-ordination of the molybdenum atom in compound (**2**) is of interest. It is attached to all five atoms of the C(10)C(20)C(30)C(40)W(2) ring. Since the groups W(CO)$_2$(η-C$_5$H$_5$) and CR (R = alkyl or aryl) are isolobal,[5] the C$_4$W ring attached to the molybdenum can be regarded as a pseudo-cyclopentadienyl ligand. This feature, together with the arrangement of the C(1)O(1), C(2)O(2), and W(1)(CO)$_2$(η-C$_5$H$_5$) groups around the molybdenum, leads to the familiar piano-stool structure, which often results when a η^5-C$_5$H$_5$ ring and three monodentate ligands are co-ordinated to a metal centre. However, this description for (**2**) should not be overemphasised since the larger size of a tungsten atom, compared with carbon, results in the C(10)C(20)C(30)C(40)W(2) ring being non-planar. This is reflected in a dihedral angle of 21° between the planes defined by the atoms C(10)W(2)C(40) and C(10)C(20)C(30)C(40).

The molecular structure of compound (**3**) is shown in Figure 2, and selected internuclear distances and angles are given in

Table 1. Selected internuclear distances (Å) and angles (°) for $[MoW_2\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C(Ph)C(Ph)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ (**2**), with estimated standard deviations (e.s.d.s) in parentheses

W(1)–Mo	2.562(1)	W(1) · · · C(1)	2.739(8)	W(1) · · · C(2)	2.525(7)
W(1)–C(4)	1.94(1)	W(2)–Mo	2.987(1)	W(2)–C(5)	2.011(8)
W(2)–C(6)	1.997(8)	W(2)–C(10)	2.194(7)	W(2)–C(40)	2.196(7)
Mo(1)–C(1)	1.956(8)	Mo–C(2)	1.956(8)	Mo–C(10)	2.349(7)
Mo–C(20)	2.434(6)	Mo–C(30)	2.394(6)	Mo–C(40)	2.282(7)
C(1)–O(1)	1.17(1)	C(2)–O(2)	1.17(1)	C(3)–O(3)	1.18(1)
C(4)–O(4)	1.16(1)	C(5)–O(5)	1.16(1)	C(6)–O(6)	1.15(1)
C(10)–C(20)	1.44(1)	C(20)–C(30)	1.43(1)	C(30)–C(40)	1.43(1)
Mo–W(1)–C(3)	82.6(3)	Mo–W(1)–C(4)	80.1(1)	C(3)–W(1)–C(4)	83.7(4)
Mo–W(2)–C(5)	82.1(2)	Mo–W(2)–C(6)	86.4(2)	C(5)–W(2)–C(6)	80.9(3)
Mo–W(2)–C(10)	51.2(2)	Mo–W(2)–C(40)	49.4(2)	C(10)–W(2)–C(40)	74.9(3)
W(1)–Mo–W(2)	143.2(1)	W(1)–Mo–C(1)	73.3(2)	W(2)–Mo–C(1)	92.3(2)
W(1)–Mo–C(2)	66.4(2)	W(2)–Mo–C(2)	147.9(2)	C(1)–Mo–C(2)	86.0(3)
W(1)–Mo–C(10)	155.9(2)	W(2)–Mo–C(10)	46.7(2)	W(1)–Mo–C(20)	148.9(2)
W(2)–Mo–C(20)	67.9(2)	W(1)–Mo–C(30)	137.3(2)	W(2)–Mo–C(30)	68.6(2)
W(1)–Mo–C(40)	133.5(2)	W(2)–Mo–C(40)	46.9(2)	Mo–C(1)–O(1)	173.9(7)
Mo–C(2)–O(2)	171.4(7)	W(1)–C(3)–O(3)	172.4(7)	W(1)–C(4)–O(4)	173.1(8)
W(2)–C(5)–O(5)	172.8(8)	W(2)–C(6)–O(6)	173.2(7)	W(2)–C(10)–Mo	82.1(2)
W(2)–C(10)–C(11)	126.8(5)	Mo–C(10)–C(11)	124.0(5)	W(2)–C(10)–C(20)	113.2(5)
Mo–C(10)–C(20)	75.7(4)	C(11)–C(10)–C(20)	117.8(6)	Mo–C(20)–C(10)	69.3(4)
Mo–C(20)–C(21)	138.5(5)	C(10)–C(20)–C(21)	123.1(6)	Mo–C(20)–C(30)	71.3(4)
C(10)–C(20)–C(30)	116.2(6)	C(21)–C(20)–C(30)	119.9(6)	Mo–C(30)–C(20)	74.3(4)
Mo–C(30)–C(31)	127.7(5)	C(20)–C(30)–C(31)	120.7(6)	Mo–C(30)–C(40)	68.0(4)
C(20)–C(30)–C(40)	124.2(6)	W(2)–C(40)–Mo	83.7(2)	W(2)–C(40)–C(30)	114.4(5)
Mo–C(40)–C(30)	76.6(4)	W(2)–C(40)–C(41)	120.7(5)	Mo–C(40)–C(41)	130.1(5)
C(30)–C(40)–C(41)	119.6(6)				

Table 2. Selected internuclear distances (Å) and angles (°) for $[MoW_2(\mu\text{-}C_2Ph_2)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]\cdot 0.5CH_2Cl_2$ (**3**) with e.s.d.s in parentheses

W(1)–W(2)	2.752(1)	W(1)–Mo	2.708(2)	W(1)–C(1)	1.96(3)
W(1) · · · C(2)	2.60(3)	W(1)–C(1A)	2.17(2)	W(1)–C(1B)	2.20(2)
W(2)–Mo	2.704(2)	W(2) · · · C(1)	2.58(3)	W(2)–C(2)	1.94(3)
W(2)–C(2A)	2.17(2)	W(2)–C(2B)	2.17(2)	Mo–C(3)	1.93(2)
Mo–C(4)	1.96(3)	Mo–C(1A)	2.35(2)	Mo–C(1B)	2.29(2)
Mo–C(2A)	2.31(2)	Mo–C(2B)	2.25(2)	C(1)–O(1)	1.17(3)
C(2)–O(2)	1.20(3)	C(3)–O(3)	1.21(3)	C(4)–O(4)	1.16(3)
C(1A)–C(1B)	1.35(3)	C(2A)–C(2B)	1.32(3)		
W(2)–W(1)–Mo	59.4(1)	W(2)–W(1)–C(1)	63.7(6)	Mo–W(1)–C(1)	77.3(5)
W(2)–W(1)–C(2)	42.4(5)	Mo–W(1)–C(2)	66.1(4)	C(1)–W(1)–C(2)	106.0(8)
Mo–W(1)–C(1A)	56.4(5)	Mo–W(1)–C(1B)	54.5(5)	C(1A)–W(1)–C(1B)	36.1(7)
W(1)–W(2)–Mo	59.5(1)	W(1)–W(2)–C(1)	43.1(5)	Mo–W(2)–C(1)	68.6(4)
W(1)–W(2)–C(2)	64.6(6)	Mo–W(2)–C(2)	75.2(5)	C(1)–W(2)–C(2)	107.7(8)
Mo–W(2)–C(2A)	55.2(4)	Mo–W(2)–C(2B)	53.5(5)	C(2A)–W(2)–C(2B)	35.5(7)
W(1)–Mo–W(2)	61.1(1)	C(3)–Mo–C(4)	88.1(9)	W(1)–Mo–C(1A)	50.1(4)
W(1)–Mo–C(1B)	51.3(4)	C(1A)–Mo–C(1B)	33.9(7)	W(2)–Mo–C(2A)	50.6(4)
W(2)–Mo–C(2B)	51.0(4)	C(2A)–Mo–C(2B)	33.8(6)	W(1)–C(1)–W(2)	73.2(6)
W(1)–C(1)–O(1)	169(2)	W(2)–C(1)–O(1)	116(2)	W(1)–C(2)–W(2)	73.0(7)
W(1)–C(2)–O(2)	114(2)	W(2)–C(2)–O(2)	171(2)	Mo–C(3)–O(3)	174(2)
Mo–C(4)–O(4)	174(2)	W(1)–C(1A)–Mo	73.5(5)	W(1)–C(1A)–C(1A1)	142(1)
Mo–C(1A)–C(1A1)	127(1)	W(1)–C(1A)–C(1B)	73.1(9)	Mo–C(1A)–C(1B)	71(1)
C(1A1)–C(1A)–C(1B)	140(2)	W(1)–C(1B)–Mo	74.2(5)	W(1)–C(1B)–C(1A)	71(1)
Mo–C(1B)–C(1A)	76(1)	W(1)–C(1B)–C(1B1)	137(1)	Mo–C(1B)–C(1B1)	131(1)
C(1A)–C(1B)–C(1B1)	141(2)	W(2)–C(2A)–Mo	74.1(5)	W(2)–C(2A)–C(2A1)	141(1)
Mo–C(2A)–C(2A1)	129(1)	W(2)–C(2A)–C(2B)	72(1)	Mo–C(2A)–C(2B)	71(1)
C(2A1)–C(2A)–C(2B)	141(2)	W(2)–C(2B)–Mo	75.5(6)	W(2)–C(2B)–C(2A)	72(1)
Mo–C(2B)–C(2A)	76(1)	W(2)–C(2B)–C(2B1)	135(1)	Mo–C(2B)–C(2B1)	132(1)
C(2A)–C(2B)–C(2B1)	140(2)				

Table 2. The core of the molecule is a metal triangle, the Mo–W edges of which are transversely bridged by the alkyne ligands C_2Ph_2 and $C_2(C_6H_4Me\text{-}4)_2$, respectively, while the W–W bond is semi-bridged by two CO groups [W(1)–C(1)–O(1) 169(2), W(2)–C(2)–O(2) 171(2)°]. The molybdenum atom carries two terminal carbonyl ligands, and each tungsten atom is co-ordinated by a cyclopentadienyl ring. Overall the molecule has 44 cluster valence electrons (c.v.e.s) rather than the 48 required to give each of the three metal atoms in the cluster 18-electron shells. Although 44 c.v.e. trimetal compounds are common among some of the later transition elements, such structures are uncommon with the metals Mo or W which adhere more closely to the 18-electron formalism. In agreement with the electronic unsaturation, the metal–metal connectivities in (**3**) are some-

what shorter than those observed in electronically saturated polynuclear metal species, but comparable with the metal–metal bond distances in other unsaturated cluster compounds. Thus the W–W distance [2.752(1) Å] in (**3**) is significantly shorter than those in the electronically saturated molecules $[W_2\{\mu\text{-}C(Me)B(H)Et\}(CO)_4(\eta\text{-}C_5H_5)_2]$ [2.978(2) Å][6] and $[W_2Os\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ [two isomers, 3.159(2) and 3.017(2) Å],[7] but is very similar to that found in the 46 c.v.e. species $[W_2Fe\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ [2.747(1) Å].[8] Similarly, the Mo–W distances in (**3**) [mean 2.706 Å] are appreciably shorter than those in $[MoW\{\mu\text{-}C(C_6H_4OMe\text{-}2)C(Me)O\}(CO)_4(\eta\text{-}C_5H_5)_2]$ [2.935(1) Å][9] or (**1a**) [2.938(1) Å],[2a] but are comparable with that [2.660(2) Å] found in $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (C_9H_7 = indenyl), a 32 c.v.e. complex.[10] It is probable that the metal–metal bonding within the triangle in (**3**) is delocalised. However, to accord with the 18-electron formalism we have chosen to indicate Mo=W and W–W bonds in the formula displayed.

Compound (**3**) results from addition of PhC≡CPh to (**1a**), accompanied by a coupling of the two μ-*p*-tolylmethylidyne groups in the latter to form the $\mu\text{-}C_2(C_6H_4Me\text{-}4)_2$ alkyne. We obtained no evidence that (**3**) is an intermediate in the formation of (**2**), and the pathways by which (**2**) and (**3**) are formed from (**1a**) are presently obscure.

The spectroscopic (i.r. and n.m.r.) properties of compounds (**2**) and (**3**) (see Experimental section) are in accord with the structures established by *X*-ray crystallography. The ^1H n.m.r. spectrum of complex (**2**) shows resonances for two non-equivalent Me-4 groups and two non-equivalent C_5H_5 rings. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum broad peaks at δ 232.2 and 225.3 p.p.m. are ascribed to the $Mo(CO)_2$ and $W(1)(CO)_2$ groups (Figure 1), respectively, on the basis of their chemical shifts, the broadness of these signals being due to site exchange. Two sharp resonances at δ 220.9 and 220.7 p.p.m. are attributed to the $W(2)(CO)_2$ group since they both show $^{183}W\text{–}^{13}C$ coupling (*ca.* 130 Hz). Complex (**3**) has a more symmetrical structure, and if the very minor difference between the substituents on the alkyne carbon atoms is ignored there is a mirror plane through the $Mo(CO)_2$ group and the midpoint of the W(1)–W(2) bond. A mirror plane is also defined by the metal atoms and the midpoints of the ligated $\mu\text{-}C_2$ groups. Consequently, in the ^1H n.m.r. spectrum of (**3**) there is only one C_5H_5 and one Me-4 resonance, a feature also found in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum. The $Mo(CO)_2$ group gives rise to a signal at δ 232.3 p.p.m., and the two semi-bridging CO ligands resonate at δ 231.7 p.p.m. [*J*(WC) 98 Hz]. Peaks at δ 114.9 and 113.1 p.p.m. are tentatively ascribed to the $\mu\text{-}C_2$ groups.

The results described herein shows that the compounds (**1**) are likely to be interesting reagents for use in further syntheses. Indeed preliminary work indicates that low-valent metal fragments combine with the complexes (**1**) to afford cluster species.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C, and all solvents were freshly distilled over appropriate drying agents prior to use. Chromatography was carried out on alumina (Brockman, activity II), and the compounds were handled using Schlenk-tube techniques under dry oxygen-free nitrogen. The compound (**1a**) was prepared by the method previously reported.[2a] The instrumentation used for the spectroscopic measurements has been described in previous parts of this series.[2,3] The n.m.r. chemical shifts are listed in p.p.m., and values are positive to high frequency of $(SiMe_4)$ with coupling constants in Hz. Measurements were at room temperature.

The Reaction between PhC≡CPh *and* $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1a**).—A mixture of complex (**1a**) (0.17 g, 0.17 mmol) and PhC≡CPh (0.13 g, 0.70 mmol) in n-hexane (30 cm^3) was heated at reflux for 45 min. After cooling to room temperature, solvent was decanted and the residue was washed with light petroleum (2 × 10 cm^3), dissolved in Et_2O (10 cm^3), and chromatographed. Elution with the same solvent removed a yellow eluate which after removal of solvent *in vacuo* gave yellow *microcrystals*. These were recrystallised from n-hexane–CH_2Cl_2 (4:1) to afford $[MoW_2\{\mu\text{-}\sigma,\sigma'\text{:}\eta^4\text{-}C(Ph)C(Ph)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ (**2**) (0.04 g, 20%) (Found: C, 44.2; H, 3.0. $C_{46}H_{34}MoO_6W_2\cdot 2CH_2Cl_2$ requires C, 43.8; H, 2.9%), $\nu_{max.}$(CO) at 1 995s, 1 938s, 1 857m(br), and 1 814w(br) cm^{-1} (in CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 2.16, 2.22 (s × 2, 6 H, Me-4), 4.99, 5.48 (s × 2, 10 H, C_5H_5), and 6.60—7.60 (m, 18 H, Ph and C_6H_4); $^{13}C\text{-}\{^1H\}$ $(CD_2Cl_2\text{–}CH_2Cl_2)$, δ 232.2 (br, MoCO), 225.3 (br, WCO), 220.9 [WCO, *J*(WC) 129], 220.7 [WCO, *J*(WC) 130], 167.6—124.8 (μ-CPh and $\mu\text{-}CC_6H_4$), 93.2, 89.9 (C_5H_5), 21.2 and 20.9 (Me-4). Mass spectrum (fast atom bombardment): M^+, 1 148 (calc. 1 148).

Further elution of the chromatography column with $CH_2Cl_2\text{–}Et_2O$ (1:1) removed a purple fraction which was concentrated to a volume of *ca.* 2 cm^3. Addition of light petroleum (*ca.* 8 cm^3) and cooling to *ca.* −10 °C gave black-violet *crystals* of $[MoW_2(\mu\text{-}C_2Ph_2)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]\cdot 0.5CH_2Cl_2$ (**3**) (0.038 g, 20%) (Found: C, 47.4; H, 3.1. $C_{44}H_{34}MoO_4W_2\cdot 0.5CH_2Cl_2$ requires C, 47.1; H, 3.1%), $\nu_{max.}$(CO) at 1 922vs(br) and 1 858s(br) cm^{-1} (in CH_2Cl_2). N.m.r.: ^1H (CD_2Cl_2), δ 2.32 (s, 6 H, Me-4), 5.59 (s, 10 H, C_5H_5), and 7.06—7.71 (m, 18 H, Ph and C_6H_4); $^{13}C\text{-}\{^1H\}$ $(CD_2Cl_2\text{–}CH_2Cl_2)$, δ 232.3 (MoCO), 231.7 [WCO, *J*(WC) 98], 145.8—127.0 (Ph and C_6H_4), 114.9, 113.1 (μ-*C*Ph and μ-*C*C_6H_4Me-4), 95.3 (C_5H_5), and 21.5 (Me-4).

Crystal Structure Determinations.—(*a*) $[MoW_2\{\mu\text{-}\sigma,\sigma'\text{:}\eta^4\text{-}C(Ph)C(Ph)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)_2]\cdot 2CH_2Cl_2$ (**2**). Crystals of complex (**2**) were grown from CH_2Cl_2–light petroleum mixtures as yellow prisms. Diffracted intensities were collected on a Nicolet $P2_1$ diffractometer at 293 K, from a crystal of dimensions *ca.* 0.70 × 0.25 × 0.20 mm. Of the 8 723 data collected (Wyckoff ω scans, 2θ ⩽ 50°), 6 342 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarisation and *X*-ray absorption effects, the latter by an empirical method based upon azimuthal scan data.[11]

Crystal data. $C_{46}H_{34}MoO_6W_2\cdot 2CH_2Cl_2$, $M = 1\,316.3$, monoclinic, space group $P2_1/c$, $a = 17.280(7)$, $b = 13.592(5)$, $c = 19.678(7)$ Å, $\beta = 81.87(3)°$, $U = 4\,575(3)$ Å^3, $Z = 4$, $D_c = 1.91$ g cm^{-3}, $F(000) = 2\,528$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 85.1$ cm^{-1}.

The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters *ca.* $1.2U_{equiv.}$ of the parent carbon atoms (aryl and η-C_5H_5), or a common refined isotropic thermal parameter (Me). Refinement by blocked-cascade least squares led to $R = 0.038$ ($R' = 0.040$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,5|F|^2]$ giving a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 1.7 or < −1.1 e Å^{-3}.

(*b*) $[MoW_2(\mu\text{-}C_2Ph_2)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]\cdot 0.5CH_2Cl_2$ (**3**). Crystals of complex (**3**) were grown from CH_2Cl_2–light petroleum mixtures as black prisms. Diffracted intensities were collected at 293 K, from a crystal with well

Table 3. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**2**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	3 045(1)	5 161(1)	5 247(1)	C(32)	522(5)	7 264(6)	7 622(5)
W(2)	3 620(1)	7 476(1)	7 262(1)	C(33)	−262(5)	7 342(6)	7 570(5)
Mo	2 895(1)	5 993(1)	6 426(1)	C(34)	−538(5)	7 256(7)	6 960(6)
C(1)	3 802(4)	5 122(5)	6 379(4)	C(35)	14(5)	7 083(7)	6 372(5)
O(1)	4 333(4)	4 604(5)	6 415(3)	C(36)	805(4)	6 978(6)	6 428(4)
C(2)	2 276(5)	4 791(6)	6 407(4)	C(37)	−1 396(6)	7 312(9)	6 906(8)
O(2)	1 900(4)	4 072(5)	6 486(3)	C(40)	2 534(4)	7 536(5)	6 803(4)
C(3)	2 352(5)	6 212(7)	5 049(4)	C(41)	2 340(4)	8 419(5)	6 412(4)
O(3)	1 943(4)	6 812(5)	4 853(3)	C(42)	1 847(5)	9 150(6)	6 737(5)
C(4)	3 845(6)	6 167(7)	5 071(5)	C(43)	1 684(6)	10 012(6)	6 395(6)
O(4)	4 337(5)	6 732(6)	4 899(4)	C(44)	2 014(6)	10 182(6)	5 736(6)
C(5)	4 123(4)	7 924(6)	6 329(4)	C(45)	2 505(5)	9 454(7)	5 402(5)
O(5)	4 460(4)	8 246(6)	5 829(3)	C(46)	2 652(5)	8 586(6)	5 727(4)
C(6)	4 559(4)	6 602(6)	7 153(4)	C(47)	1 862(8)	11 144(8)	5 393(8)
O(6)	5 133(3)	6 168(5)	7 128(3)	C(51)	2 510(6)	3 779(7)	4 778(5)
C(10)	2 988(4)	6 123(5)	7 602(4)	C(52)	2 776(7)	4 348(7)	4 238(5)
C(11)	3 273(4)	5 303(6)	8 024(4)	C(53)	3 565(7)	4 425(7)	4 196(5)
C(12)	3 781(4)	5 466(6)	8 495(4)	C(54)	3 806(6)	3 875(7)	4 735(6)
C(13)	4 018(5)	4 690(7)	8 873(5)	C(55)	3 115(7)	3 483(7)	5 091(5)
C(14)	3 780(5)	3 759(7)	8 790(5)	C(61)	4 239(5)	8 794(6)	7 688(5)
C(15)	3 279(5)	3 571(6)	8 317(4)	C(62)	3 480(6)	9 077(6)	7 592(5)
C(16)	3 034(5)	4 328(6)	7 945(4)	C(63)	2 943(5)	8 557(6)	8 060(5)
C(20)	2 162(4)	6 181(5)	7 569(3)	C(64)	3 355(5)	7 939(7)	8 440(4)
C(21)	1 561(4)	5 622(6)	8 046(4)	C(65)	4 157(5)	8 099(7)	8 213(4)
C(22)	1 550(5)	5 794(9)	8 744(4)	C(7)	3 908(9)	4 050(11)	1 263(7)
C(23)	942(6)	5 438(10)	9 232(5)	Cl(1)	4 495(2)	3 531(3)	614(2)
C(24)	366(6)	4 887(10)	8 986(6)	Cl(2)	3 371(3)	3 132(4)	1 787(2)
C(25)	379(5)	4 695(7)	8 329(5)	C(8)	83(13)	560(13)	1 057(14)
C(26)	973(4)	5 054(5)	7 843(4)	Cl(3)	−861(3)	368(4)	1 309(4)
C(30)	1 921(4)	6 929(5)	7 134(4)	Cl(4)	263(4)	1 626(6)	546(3)
C(31)	1 065(4)	7 050(5)	7 054(4)				

Table 4. Atomic positional parameters (fractional co-ordinates) for compound (**3**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.157 56(6)	0.229 34(4)	−0.009 26(4)	C(1A)	−0.004 4(15)	0.203 8(10)	−0.095 4(11)
W(2)	0.343 33(6)	0.226 26(4)	−0.080 15(4)	C(1A1)	−0.093 8(15)	0.150 1(9)	−0.115 7(10)
Mo	0.124 60(13)	0.236 53(8)	−0.174 86(9)	C(1A2)	−0.077(2)	0.090 5(10)	−0.070 4(12)
C(11)	0.219 9(13)	0.285 9(7)	0.120 0(10)	C(1A3)	−0.160(2)	0.040 6(11)	−0.087 6(13)
C(12)	0.096 9(13)	0.288 8(7)	0.097 7(10)	C(1A4)	−0.265(2)	0.048 8(11)	−0.148 5(14)
C(13)	0.054 2(13)	0.221 9(7)	0.095 4(10)	C(4A)	−0.362(3)	−0.005 3(12)	−0.164 3(15)
C(14)	0.150 8(13)	0.177 7(7)	0.116 3(10)	C(1A5)	−0.278(2)	0.106 9(10)	−0.193 3(13)
C(15)	0.253 2(13)	0.217 3(7)	0.131 4(10)	C(1A6)	−0.194(2)	0.157 1(10)	−0.178 0(12)
C(11A)	0.135(4)	0.306 (2)	0.094(3)	C(1B)	0.004 3(14)	0.271 8(11)	−0.095 3(10)
C(12A)	0.047(4)	0.256(2)	0.086(3)	C(1B1)	−0.066(2)	0.332 5(10)	−0.100 1(11)
C(13A)	0.101(4)	0.193(2)	0.109(3)	C(1B2)	−0.185(3)	0.326 8(13)	−0.120 1(14)
C(14A)	0.223(4)	0.204(2)	0.131(3)	C(1B3)	−0.251(3)	0.386 9(13)	−0.128 4(15)
C(15A)	0.244(4)	0.274(2)	0.122(3)	C(1B4)	−0.199(2)	0.449 2(12)	−0.116 1(14)
C(21)	0.528(3)	0.269 7(9)	−0.021(2)	C(4B)	−0.270(3)	0.514 0(12)	−0.125(2)
C(22)	0.495(3)	0.227 2(9)	0.038(2)	C(1B5)	−0.083(2)	0.451 9(12)	−0.095 1(14)
C(23)	0.486(3)	0.160 5(9)	0.006(2)	C(1B6)	−0.019(3)	0.393 2(11)	−0.086 6(13)
C(24)	0.514(3)	0.161 8(9)	−0.072(2)	C(2A)	0.297 9(14)	0.264 0(10)	−0.205 8(10)
C(25)	0.540(3)	0.229 3(9)	−0.088(2)	C(2A2)	0.399 2(11)	0.372 2(7)	−0.218 6(7)
C(21A)	0.544(4)	0.256(2)	−0.052(3)	C(2A3)	0.423 3(11)	0.425 7(7)	−0.265 6(6)
C(22A)	0.516(4)	0.244(2)	0.024(3)	C(2A4)	0.372 2(11)	0.428 3(7)	−0.349 9(6)
C(23A)	0.484(4)	0.175(2)	0.026(3)	C(2A5)	0.296 9(11)	0.377 3(7)	−0.387 2(6)
C(24A)	0.492(4)	0.145(2)	−0.049(3)	C(2A6)	0.272 7(11)	0.323 8(7)	−0.340 2(6)
C(25A)	0.529(4)	0.195(2)	−0.098(3)	C(2A1)	0.323 9(11)	0.321 2(7)	−0.255 9(6)
C(1)	0.207(2)	0.140 0(11)	−0.037 2(11)	C(2B)	0.284 2(15)	0.197 8(9)	−0.208 8(11)
O(1)	0.230 7(13)	0.083 3(7)	−0.042 8(9)	C(2B2)	0.333 0(14)	0.151 0(7)	−0.333 0(10)
C(2)	0.292(2)	0.315 3(11)	−0.057 2(12)	C(2B3)	0.349 0(14)	0.096 7(7)	−0.381 9(10)
O(2)	0.276 8(12)	0.372 4(8)	−0.040 3(9)	C(2B4)	0.334 8(14)	0.031 1(7)	−0.356 5(10)
C(3)	0.062(2)	0.311 2(11)	−0.245 6(12)	C(2B5)	0.304 6(14)	0.019 7(7)	−0.282 3(10)
O(3)	0.025 1(12)	0.361 8(7)	−0.283 2(9)	C(2B6)	0.288 6(14)	0.074 0(7)	−0.233 4(10)
C(4)	0.038(2)	0.176 0(12)	−0.260 3(13)	C(2B1)	0.302 8(14)	0.139 6(7)	−0.258 8(10)
O(4)	−0.010 0(14)	0.136 0(9)	−0.306 7(10)	Cl	0.052(3)	0.044 8(15)	0.521(2)

developed faces of the types (0, 1, 0), (0, $\bar{1}$, 0), ($\bar{1}$, 0, 1), (1, 0, $\bar{1}$), (1, 0, 1), and ($\bar{1}$, 0, $\bar{1}$). Of the 5 848 data collected (θ—2θ scans, $2\theta \leqslant 50°$), 3 127 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarisation and *X*-ray absorption effects, the latter by an analytical method based upon crystal faces.[11]

Crystal data. $C_{44}H_{34}MoO_4W_2 \cdot 0.5CH_2Cl_2$, $M = 1\,132.9$, monoclinic, space group $P2_1/n$, $a = 11.894(5)$, $b = 19.876(5)$, $c = 16.747(4)$ Å, $\beta = 104.11(2)°$, $U = 3\,840(2)$ Å^3, $Z = 4$, $D_c = 1.96$ g cm^{-3}, $F(000) = 2\,164$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 65.3 cm^{-1}.

The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. The metal atoms, the ligated carbon atoms of the alkynes, and the carbonyl ligands [with the exception of C(2)O(2)] were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters *ca.* $1.2U_{\text{equiv.}}$ of the parent carbon atoms (aryl and η-C_5H_5), or a common refined isotropic thermal parameter (Me). A stable refinement could not be achieved for the methyl hydrogens of C(4A) and they were therefore not included in the final refinement. The aryl and cyclopentadienyl ring systems were refined as rigid groups [C–C(cyclopentadienyl) 1.420, C–C(aryl) 1.395 Å]. The two cyclopentadienyl rings were disordered and each was modelled by two staggered rings with site occupations in the ratios of 80:20 [W(1)] and 64:36 [W(2)], respectively. Only the cyclopentadienyl sites of major occupancy [C(11)—C(15) and C(21)—C(25)] are shown in Figure 2. The unit cell also contains *ca.* half a molecule of CH_2Cl_2 per molecule of the complex. These solvent molecules are disordered about inversion centres and only the chlorine atom was located and refined. Refinement by blocked-cascade least squares led to $R = 0.049$ ($R' = 0.049$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,65|F|^2]$ giving a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >2.4 or <-1.3 e Å^{-3}.

For both structures refinement was performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[11] Scattering factors with corrections for anomalous dispersion were taken from ref. 12. Atom co-ordinates are given in Tables 3 and 4.

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

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