Reaction of Polynuclear Acetylide Clusters. Synthesis of Pentanuclear Heterometallic Clusters by Addition of $[M(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ to $[MOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (M = Mo or W). Crystal Structures of $[Mo_2Os_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]\cdot 2H_2O$ and $[MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$‡

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Both the cluster acetylide complexes $[MOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ [M = Mo, (**1**); or W, (**2**)] react with $[Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ to give in low yield planar pentanuclear complexes $[MMoOs_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ [M = Mo, (**3**); or W, (**4**)] which contain a C_4 hydrocarbon fragment derived from head-to-tail coupling between the two acetylide fragments. The C_4 chain of these complexes also undergoes twisting in solution, indicated by variable-temperature ^1H n.m.r. studies. Reaction of complex (**1**) with $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ does not produce the coupling product but induces C–C bond scission of $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ giving a novel carbide–alkylidyne complex $[MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)(\eta\text{-}C_5H_5)_2]$ (**5**) in low yield. The structures of complexes (**3**) and (**5**) have been determined by single-crystal *X*-ray diffraction studies. Crystal data for (**3**): space group $P2_1/n$, $a = 9.583(3)$, $b = 25.175(10)$, $c = 16.300(7)$ Å, $\beta = 91.26(3)°$, $Z = 4$, $R = 0.051$, and $R' = 0.053$. Crystal data for (**5**): space group $P\bar{1}$, $a = 10.072(6)$, $b = 13.217(3)$, $c = 14.800(3)$ Å, $\alpha = 95.41(2)$, $\beta = 93.17(4)$, $\gamma = 109.14(4)°$, $Z = 2$, $R = 0.056$, and $R' = 0.062$.

The chemistry of mixed-metal cluster complexes has been the subject of intensive research for many years.[1] The reason is that the different reactivities of different metals present in such complexes may show patterns of reactivity or structure very different from those of the homometallic analogues. In seeking to develop a systematic method to synthesize mixed-metal complexes by using the concept of isolobal analogy,[2] Stone and co-workers[3] have used $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ as a basic building block to prepare many mixed-metal clusters of different nuclearities, containing a bridging alkylidyne fragment.[3] Recently, we have applied a similar strategy of using metal acetylide complexes $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ to prepare several tri- and tetra-nuclear mixed-metal clusters containing a multisite, cluster-bound, bridging acetylide fragment.[4]

In order further to extend this idea of using acetylide complexes as a building block to prepare clusters of high nuclearities, we have treated the tetranuclear acetylide complexes $[MOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ [M = Mo, (**1**); or W, (**2**)] with $[M(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (M = Mo or W) to prepare pentanuclear cluster complexes. In this report we describe structural studies of two such novel pentanuclear cluster complexes. Interestingly, changing the transition metal of the acetylide complexes has led to the isolation of completely different cluster complexes: one is generated by the coupling of two acetylide ligands of different origin, whereas the second is derived from a C–C bond cleavage of the acetylide ligand of the incoming mononuclear metal acetylide.

Experimental

General Information and Materials.—Infrared spectra were recorded on a Perkin-Elmer 580 or a Bomen M-100 FT-IR spectrometer, ^1H and ^{13}C n.m.r. spectra on a Bruker AM-400 (400.13 MHz) or a Varian Gemini-300 (300 MHz) instrument, and mass spectra on a JEOL-HX110 instrument operating in electron-impact or fast atom bombardment (f.a.b.) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. Their progress was monitored by analytical thin-layer chromatography (t.l.c.) (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on commercially available preparative t.l.c. plates (Kieselgel 60 F_{254}, E. Merck). Elemental analyses were performed at the NSC Regional Instrument Center at National Cheng Kung University, Tainan, Taiwan.

The acetylide complexes $[M(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (M = W or Mo) were prepared by the reaction of phenylacetylene with the appropriate chloride complexes $[M(CO)_3Cl(\eta\text{-}C_5H_5)]$ in the presence of CuI as catalyst.[5] The mixed-metal acetylide complexes $[MoOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ and $[WOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ were prepared from the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with the appropriate metal acetylide complexes $[M(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$.[6]

Phenylacetylene with its α-carbon labelled approximately 30% by ^{13}C was prepared from a four-step reaction: treatment of benzaldehyde with ^{13}C-labelled Grignard reagent MgMe(I) in diethyl ether to give the ^{13}C-labelled *s*-phenylethyl alcohol; dehydration of the alcohol in the presence of a catalytic amount of $KHSO_4$ to yield styrene; bromination of the styrene in $CHCl_3$ solution at room temperature followed by treatment with excess of sodium amide in liquid ammonia to provide the required ^{13}C-labelled phenylacetylene.

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

Non-S.I. unit employed: cal = 4.184 J.

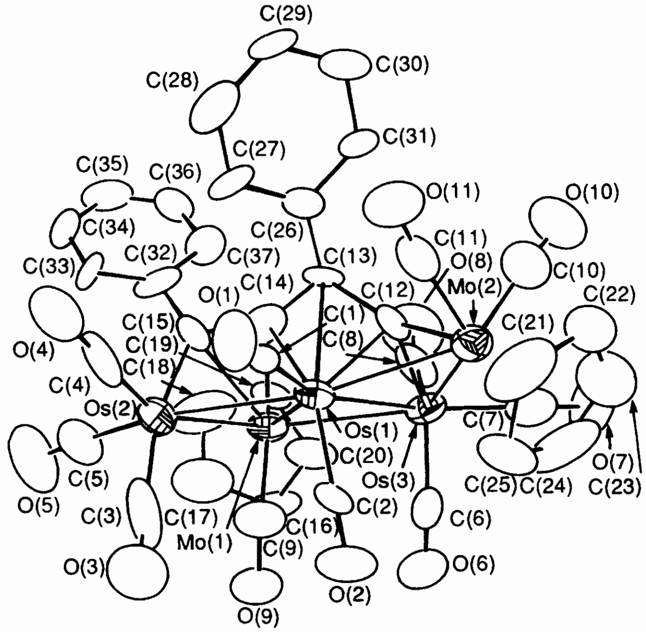


Figure 1. ORTEP diagram of complex (**3**) showing the atomic numbering scheme

Preparations.—$[Mo_2Os_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ (**3**). A toluene solution (25 cm^3) of $[MoOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (40 mg, 0.035 mmol) and $[Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (30 mg, 0.087 mmol) was heated at reflux under nitrogen. The colour of the solution turned from orange to dark brown within 30 min. After evaporation of the solvent *in vacuo*, the residue was separated by t.l.c. [silica gel, dichloromethane–hexane (2:3)] giving 6.1 mg of the coupling product $[Mo_2Os_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ as a brown material (0.0042 mmol, 12%). Crystals of complex (**3**) suitable for *X*-ray diffraction were obtained by recrystallization from a dichloromethane–methanol mixture at room temperature. Mass spectrum (f.a.b., ^{192}Os, ^{98}Mo): *m*/*z* 1 412 (M^+). I.r.(C_6H_{12}): ν(CO) 2 058s, 2 030vs, 2 006vs, 1 990s, 1 986m, 1 976w, 1 964m, 1 950vw, and 1 943(br)w cm^{-1}. ^1H N.m.r. (400 MHz, $CDCl_3$, 240 K): δ 8.05 (d), 7.61 (d), 7.52 (d), 7.38 (q), 7.18 (br), 7.14 (q), 7.05 (q), 5.41 (s, C_5H_5, 4.58 H), 5.02 (s, C_5H_5, 0.42 H), 4.79 (s, C_5H_5, 0.42 H), and 4.71 (s, C_5H_5, 4.58 H) (Found: C, 31.05; H, 1.50. Calc. for $C_{37}H_{24}Mo_2O_{13}Os_3$: C, 30.90; H, 1.7%).

$[MoWOs_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ (**4**). A toluene solution (35 cm^3) of $[WOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (147 mg, 0.12 mmol) and $[Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (63 mg, 0.182 mmol) was heated at reflux under nitrogen. The colour of the solution turned from orange to dark brown within 2.5 h. After evaporation of the solvent under vacuum, the residue was separated by t.l.c. [silica gel, dichloromethane–hexane (1:1)], giving 19 mg of the coupling product $[MoWOs_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ as a brown material (0.012 mmol, 11%). Crystalline (**4**) was obtained by recrystallization from a mixture of dichloromethane and methanol at room temperature. Mass spectrum (f.a.b., ^{98}Mo, ^{192}Os, ^{184}W): *m*/*z* 1 498 (M^+). I.r.(C_6H_{12}): ν(CO) 2 058m, 2 029s, 2 003vs, 1 987s, 1 980m, 1 968m, 1 959s, 1 946vw, and 1 937(br)w cm^{-1}. ^1H N.m.r. (400 MHz, $CDCl_3$, 236 K): δ 8.01 (d), 7.61 (br), 7.38 (m), 7.18 (br), 7.10 (d), 7.04 (m), 5.43 (s, C_5H_5, 3.97 H), 5.08 (s, C_5H_5, 1.03 H), 4.78 (s, C_5H_5, 1.03 H), and 4.69 (s, C_5H_5, 3.97 H) (Found: C, 28.95; H, 1.50. Calc. for $C_{37}H_{24}MoO_{13}Os_3W$: C, 29.10; H, 1.60%).

$[MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)(\eta\text{-}C_5H_5)_2]$ (**5**). A toluene solution (35 cm^3) of $[MoOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (103 mg, 0.09 mmol) and slight excess of $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (55 mg, 0.13 mmol) was heated at reflux under nitrogen. The colour of the solution turned from orange to dark brown over a period of 2.5 h. After evaporation of the solvent under vacuum, the residue was separated by t.l.c. [silica gel, dichloromethane–hexane (1:1)] giving 19 mg of $[MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)(\eta\text{-}C_5H_5)_2]$ as a brown material (0.013 mmol, 14%). Crystals suitable for *X*-ray diffraction were obtained by recrystallization from a layered solution of dichloromethane–methanol at room temperature. The reaction with ^{13}C-labelled $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ was performed under similar conditions. Mass spectrum (f.a.b., ^{98}Mo, ^{192}Os, ^{184}W): *m*/*z* 1 414 (M^+). I.r.(C_6H_{12}): ν(CO) 2 064vs, 2 084vw, 2 006m, 2 003vs, 1 990m, 1 974vw, 1 967w, 1 956w, and 1 949vw cm^{-1}. ^1H N.m.r. (300 MHz, $CDCl_3$, 294 K): δ 7.47—7.09 (m, 10 H), 5.98 (s, C_5H_5, 5 H), and 4.83 (s, C_5H_5, 5 H) (Found: C, 27.85; H, 1.45. Calc. for $C_{35}H_{22}Cl_2MoO_8Os_3W$: C, 28.20; H, 1.50%).

X-Ray Crystallography.—Diffraction measurements were carried out on a Nonius CAD-4 fully automated four-circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections, with 2θ in the range 2.5—50°, obtained by using the CAD-4 automatic search, centre, index, and least-squares routines. All data reduction and structural refinement were performed using the NRCC-SDP-VAX packages. The structures were solved by the Patterson method and refined by least-squares recycle; all non-hydrogen atoms were refined with anisotropic thermal parameters. The data collection and refinement parameters for complexes (**3**) and (**5**) are given in Table 1. Atomic positional parameters for complex (**3**) are in Table 2, selected bond angles and lengths in Table 3. The corresponding parameters for complex (**5**) are given in Tables 4 and 5, respectively.

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

Results and Discussion

Synthesis and Characterization of $[MMoOs_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ [M = Mo, (**3**); *or* W, (**4**)].—The pentanuclear clusters $[MMoOs_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ [M = Mo, (**3**); or W, (**4**)] have been obtained in low yield by treatment of cluster complexes (**1**) and (**2**) with metal acetylide $[Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ in a 1:2 molar ratio in refluxing toluene solution. The reaction for the WOs_3 acetylide complex is quite slow (about 2.5 h) relative to that for its $MoOs_3$ analogue which is completed within 30 min. This observation is consistent with the fact that the complexes of third-row transition-metal elements are more stable and less reactive than their congeners of the second-row elements. The products have easily been separated from other products by t.l.c. on silica gel followed by recrystallization, yielding dark brown crystals.

The formulation of complex (**3**) was initially determined from its f.a.b. mass spectrum which indicates a parent ion at *m*/*z* 1 412, corresponding to a composition $C_{37}H_{20}Mo_2O_{11}Os_3$. This suggests that the formation of complex (**3**) involves a condensation of the acetylide cluster $[MOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ with 1 equivalent of $[Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$. The i.r. spectrum of complex (**3**) shows absorptions attributed to the terminal CO ligands, as expected from the solid-state structure. Complex (**4**) is assigned a similar structure on the basis of its f.a.b. mass spectrum and i.r. spectrum in the region of CO absorptions.

Crystal Structure of Complex (**3**).—In the crystal there are two water molecules, probably due to the use of methanol to

Table 1. Experimental data for the *X*-ray diffraction studies*

Compound	(3)	(5)
Formula	$C_{37}H_{20}Mo_2O_{11}Os_3{\cdot}2H_2O$	$C_{34}H_{20}MoO_8Os_3W{\cdot}CH_2Cl_2$
M	1 439.06	1 491.84
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	9.583(3)	10.072(6)
b/Å	25.175(10)	13.217(3)
c/Å	16.300(7)	14.800(3)
α/°		95.41(2)
β/°	91.26(3)	93.17(4)
γ/°		109.14(4)
U/Å^3	3 931(1)	1 845(1)
Z	4	2
D_c/g cm^{-3}	2.431	2.685
$F(000)$	2 646.91	1 347.46
2θ (max.)	44.9°	49.8°
Scan parameter	0.7 + 0.35 tan θ	0.80 + 0.35 tan θ
Scan speed (variable, °/min)	16.48/2 to 16.48/10	16.48/2 to 16.48/9
h, *k*, *l* ranges	−10 to 10, 0—27, 0—17	−11 to 11, 0—15, −17 to 17
Crystal size/mm	0.10 × 0.10 × 0.40	0.10 × 0.50 × 0.50
μ(Mo-K_α)/mm^{-1}	10.34	13.99
Transmission factors (maximum, minimum)	0.997, 0.263	1.000, 0.088
Standard reflections (3 every 7 200 s)	15% Decomposition	No decomposition (±2%)
No. of unique data	5 126	6 471
Data with $I > 2\sigma(I)$	2 779	4 847
No. of atoms and parameters refined	79, 487	72, 452
Maximum Δ/σ ratio	0.143	0.438
R, *R'*	0.051, 0.053	0.056, 0.062
Goodness of fit	2.03	2.87
Residual electron density/e Å^{-3} (maximum, minimum)	2.30, −1.35	5.21, 3.15

* Features common to all determinations: 297 K; λ(Mo-K_α) = 0.709 30 Å; Nonius CAD-4 diffractometer; scan mode θ—2θ; absorption correction, ψ scan; $w = 1/\sigma^2(F_o)$; goodness of fit $= [\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{\frac{1}{2}}$ (N_o = number of observations, N_v = number of variables).

grow suitable crystals under humid conditions. The molecular geometry and atomic labelling is shown in Figure 1 and the interatomic distances and angles are collected in Table 3.

The Mo_2Os_3 system defines a planar edge-bridged rhomboidal or a very flat double-butterfly geometry and is associated with 76 outer valence electrons. Atoms Os(1), Os(3), and Mo(1) constitute the metal triangle in the centre and these atoms are associated with two CO, three CO, and one CO and a C_5H_5 ligand, respectively. There are two further transition-metal atoms which are located on the edges of this metal triangle. Atom Os(2) lies on the edge of the Os(1)–Mo(1) bond and is associated with three CO ligands, whereas atom Mo(2) occupies the edge of the Os(1)–Os(3) bond and is co-ordinated to two CO ligands and capped by a C_5H_5 group. All the metal–metal bonds lie in a fairly narrow range, 2.833(3)—2.895(3) Å, except for Os(1)–Os(3) 2.745(2) Å and Os(3)–Mo(1) 3.004(4) Å.

Furthermore, all the CO ligands on the three osmium atoms and the two CO ligands on the atom Mo(2) are approximately linear with angles ranging from 168(3) to 179(3)°, whereas ligand C(9)O(9) on atom Mo(1) is bent slightly with an angle 163(3)°, characteristic of a semi-bridging CO interaction.[7] The C_4 hydrocarbyl fragment lies on top of the Mo_2Os_3 double-butterfly skeleton and is co-ordinated in multisite fashion with its skeletal C(12) carbon bound to three metal atoms, Os(1), Os(3), and Mo(2); C(13) to Os(1); C(14) to Os(1) and Mo(1); and C(15) to Os(2) and Mo(1), respectively. This bonding fashion is rather unusual, in that the C_4 hydrocarbyl fragment interacts *via* two $2\sigma + 1\pi$ bonding interactions supplying a total of eight electrons to the cluster orbitals.[8] Furthermore, we attribute this multisite interaction to be the main driving force to support the observed, unique planar arrangement of the M_5 cluster core structure. The dihedral angles between the planes Os(1)–Os(2)–Mo(1) and Os(1)–Os(3)–Mo(1) and between the Os(1)–Os(3)–Mo(1) and Os(1)–Os(3)–Mo(2) are 177.88(7) and 167.2(1)°, respectively. Formal electron counts at the individual metals (neutral ligands and metal assumed) are 17e at Os(2), 18e at Os(3), Mo(1), and Mo(2), and 20e at Os(1).

The observed position of the two $Mo(C_5H_5)$ fragments of this molecule suggests that atoms Os(1), Os(2), Mo(1), and Os(3), which exhibit a rhomboidal geometry, are derived from the cluster $[MoOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ and that Mo(2) is derived from the incoming metal acetylide $[Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$, respectively. Thus, the formation of the C_4 fragment is considered to be a head-to-tail coupling between the cluster-bonded acetylide and the incoming metal acetylide ligands. The results obtained here represent the first example of coupling between two acetylide ligands; however, coupling between the cluster-bonded acetylide with analogous alkyne ligands has been observed in the related trinuclear complexes $[WOs_2(CO)_8(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$[9] and $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$.[10]

Solution Fluxionality of Complexes (3) *and* (4).—The ^1H n.m.r. spectrum of complex (3) at 294 K shows one very broad C_5H_5 signal at δ 5.38 and one relatively sharp C_5H_5 signal at δ 4.74, in addition to several broad aromatic proton signals. This strongly suggests the existence of at least two isomers undergoing rapid interconversion in solution. When the temperature was decreased to 240 K the spectrum exhibited four C_5H_5 signals at δ 5.41, 5.02, 4.79, and 4.71 with relative intensity 1:0.09:0.09:1, suggesting the presence of two isomers in the

Table 2. Atomic co-ordinates for complex (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.878 91(12)	0.098 30(5)	0.202 69(8)	C(24)	0.961(4)	0.118 1(20)	−0.058(3)
Os(2)	0.874 87(13)	0.052 75(6)	0.363 61(9)	C(25)	1.073(4)	0.115 1(15)	−0.002(3)
Os(3)	0.669 51(13)	0.087 30(6)	0.086 30(9)	C(26)	0.760(3)	0.216 8(13)	0.269 3(20)
Mo(1)	0.643 2(3)	0.039 93(12)	0.254 44(19)	C(27)	0.827(3)	0.222 4(14)	0.345 1(19)
Mo(2)	0.889 8(3)	0.163 31(13)	0.057 67(19)	C(28)	0.854(3)	0.270 3(18)	0.377 1(22)
C(1)	1.043(3)	0.130 3(13)	0.255 3(18)	C(29)	0.805(3)	0.317 9(14)	0.336 7(22)
C(2)	0.990(3)	0.045 4(12)	0.152 6(19)	C(30)	0.733(3)	0.314 4(14)	0.263 6(23)
C(3)	1.026(3)	0.003 6(19)	0.339 6(23)	C(31)	0.707(3)	0.263 4(13)	0.230 3(19)
C(4)	0.972(3)	0.093 2(16)	0.426 4(23)	C(32)	0.602(3)	0.120 9(13)	0.423 1(20)
C(5)	0.808(3)	0.010 7(15)	0.447 4(22)	C(33)	0.627(3)	0.117 1(13)	0.502 4(17)
C(6)	0.682(3)	0.016 2(15)	0.055 3(20)	C(34)	0.531(4)	0.135 2(16)	0.553 0(19)
C(7)	0.636(4)	0.106 6(16)	−0.027 6(25)	C(35)	0.410(3)	0.159 3(14)	0.526 1(23)
C(8)	0.477(4)	0.098 7(15)	0.110 1(23)	C(36)	0.384(3)	0.164 4(15)	0.444 4(22)
C(9)	0.788(4)	−0.011 0(15)	0.231(3)	C(37)	0.475(3)	0.147 4(15)	0.388 0(21)
C(10)	0.747(4)	0.213 7(16)	0.024 1(23)	O(1)	1.145 6(20)	0.148 6(11)	0.281 2(14)
C(11)	0.969(3)	0.215 8(14)	0.133 7(19)	O(2)	1.056(3)	0.013 4(10)	0.122 2(17)
C(12)	0.739(3)	0.149 6(13)	0.145 6(18)	O(3)	1.114 5(21)	−0.024 1(12)	0.325 4(17)
C(13)	0.726 2(23)	0.167 0(11)	0.232 1(18)	O(4)	1.034 2(24)	0.122 0(11)	0.474 4(17)
C(14)	0.699(3)	0.121 1(14)	0.281 8(19)	O(5)	0.766 2(24)	−0.016 7(12)	0.498 4(16)
C(15)	0.703(3)	0.100 2(14)	0.359 0(20)	O(6)	0.684 0(24)	−0.028 9(11)	0.040 0(16)
C(16)	0.502(4)	−0.038 1(14)	0.233(3)	O(7)	0.606(3)	0.115 4(13)	−0.093 2(15)
C(17)	0.540(3)	−0.028 1(16)	0.321(3)	O(8)	0.369 4(21)	0.113 8(14)	0.125 9(19)
C(18)	0.470(3)	0.016 2(17)	0.344(3)	O(9)	0.851 2(23)	−0.051 1(9)	0.212 8(15)
C(19)	0.398(4)	0.036 2(14)	0.271 8(24)	O(10)	0.651 9(23)	0.242 0(11)	−0.000 2(17)
C(20)	0.423(3)	0.002 3(15)	0.205(3)	O(11)	1.025 1(20)	0.248 7(10)	0.169 4(15)
C(21)	1.108(4)	0.174 1(19)	0.008(3)	O(12)	0.365(3)	0.247 1(14)	0.150 1(20)
C(22)	1.017(4)	0.203 3(17)	−0.047 6(24)	O(13)	0.339(4)	0.340 9(17)	0.191 7(23)
C(23)	0.935(4)	0.167 4(19)	−0.082(3)				

Table 3. Selected interatomic distances (Å) and angles (°) of complex (**3**) with estimated standard deviations (e.s.d.s) in parentheses

Os(1)–Os(2)	2.864(2)	Os(1)–Os(3)	2.745(2)
Os(1)–Mo(1)	2.839(3)	Os(1)–Mo(2)	2.879(4)
Os(2)–Mo(1)	2.833(3)	Os(3)–Mo(1)	3.004(4)
Os(3)–Mo(2)	2.895(3)		
Os(2)–Os(1)–Mo(1)	59.58(8)	Os(2)–Os(1)–Os(3)	124.62(6)
Os(3)–Os(1)–Mo(1)	65.08(8)	Os(2)–Os(1)–Mo(2)	168.87(9)
Mo(1)–Os(1)–Mo(2)	125.6(1)	Os(3)–Os(1)–Mo(2)	61.90(8)
Os(1)–Os(2)–Mo(1)	59.77(7)	Os(1)–Mo(2)–Os(3)	56.78(7)
Os(1)–Os(3)–Mo(2)	61.32(8)	Os(1)–Os(3)–Mo(1)	58.96(7)
Os(1)–Mo(1)–Os(2)	60.65(7)	Mo(1)–Os(3)–Mo(2)	119.1(1)
		Os(1)–Mo(1)–Os(3)	55.96(7)
C_4 Hydrocarbon fragment			
Os(1)–C(12)	2.07(3)	Os(3)–C(12)	1.95(3)
Mo(2)–C(12)	2.09(3)	Os(1)–C(13)	2.32(2)
Os(1)–C(14)	2.25(3)	Mo(1)–C(14)	2.15(4)
Os(2)–C(15)	2.03(3)	Mo(1)–C(15)	2.34(4)
C(12)–C(13)	1.48(4)	C(13)–C(14)	1.44(5)
C(14)–C(15)	1.36(5)		
Os(1)–C(12)–Os(3)	86(1)	Os(2)–C(15)–Mo(1)	80(1)
Mo(2)–C(12)–C(13)	133(2)	Os(1)–C(14)–Mo(1)	80(1)
C(2)–C(14)–C(15)	145(3)	C(1)–C(13)–C(14)	108(3)
		Os(2)–C(15)–C(14)	106(2)
Carbonyl ligands			
Mo(1)–C(9)	1.93(4)	Os(2) · · · C(9)	2.80(4)
Os(1) · · · C(9)	2.92(4)		
Os(2) · · · C(9)–O(9)	121(3)	Mo(1)–C(9)–O(9)	163(3)
Mo(2)–C(10)–O(10)	174(3)	Os(1) · · · C(9)–O(9)	126(3)
		Mo(2)–C(11)–O(11)	170(3)

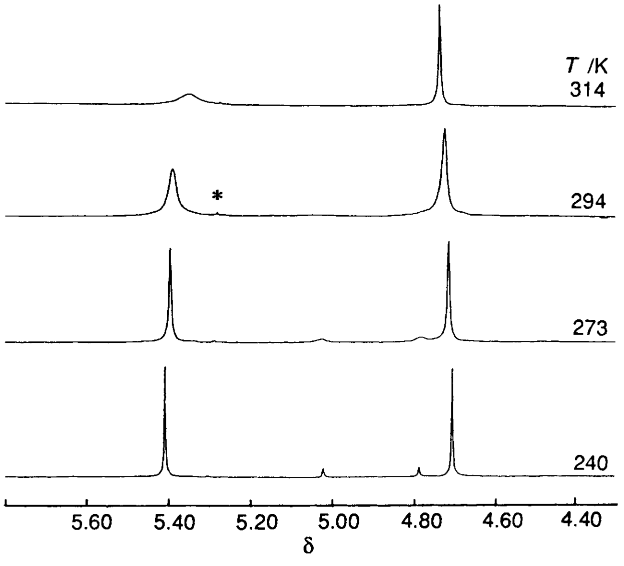


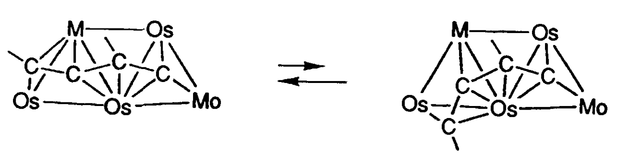
Figure 2. Variable-temperature ^1H n.m.r. spectra of complex (**3**) in $CDCl_3$, showing the region of the C_5H_5 signals. The signal marked with an asterisk is due to a trace amount of CH_2Cl_2 solvent

ratio of 1:0.09 (Figure 2). The ^1H n.m.r. spectrum ($CDCl_3$, 236 K) of the analogous complex (**4**) also shows four sharp C_5H_5 signals at δ 5.43, 5.08, 4.78, and 4.69 in the ratio of 1:0.26:0.26:1, as the low-temperature-limiting spectrum. When the temperature of the solution was gradually increased, coalescence of the signals at δ 4.78 and 4.69 and at 5.43 and 5.08 was observed at 294 and 319 K, respectively. The activation parameter $\Delta G^\ddagger$ has been calculated from variable-temperature ^1H n.m.r. studies as 14.8 kcal mol^{-1} (T_c = 314 K) for complex (**3**) and 15.1 kcal mol^{-1} (T_c = 319 K) for complex (**4**), respectively.

There are two possible explanations of the observed solution fluxionality. The first involves a twisting of the C_4 hydrocarbon

Table 4. Atomic co-ordinates for complex (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.217 59(7)	0.324 38(5)	0.102 73(6)	C(21)	0.369 1(18)	0.251 5(12)	0.054 2(14)
Os(2)	0.169 10(7)	0.278 62(6)	0.283 21(6)	C(22)	0.395 7(20)	0.213 6(14)	−0.035 8(15)
Os(3)	0.065 07(8)	0.428 71(6)	0.210 86(6)	C(23)	0.532 3(21)	0.245 6(14)	−0.064 0(16)
W	0.441 40(7)	0.406 04(5)	0.244 34(6)	C(24)	0.557 6(23)	0.208 6(16)	−0.146 8(18)
Mo	0.324 32(16)	0.174 95(11)	0.182 67(13)	C(25)	0.450(3)	0.142 3(17)	−0.208 3(17)
C(1)	0.250 6(23)	0.428 1(17)	0.019 1(14)	C(26)	0.314(3)	0.109 4(17)	−0.186 0(17)
C(2)	0.045 3(22)	0.246 2(16)	0.033 2(18)	C(27)	0.289 2(23)	0.144 5(16)	−0.096 6(17)
C(3)	−0.017 1(25)	0.191 7(18)	0.295 8(21)	C(28)	0.382 8(21)	0.275 5(14)	0.315 0(17)
C(4)	0.175 2(21)	0.328 8(17)	0.401 3(17)	C(29)	0.432 6(22)	0.238 8(14)	0.395 3(15)
C(5)	0.036(3)	0.497 9(21)	0.314 9(20)	C(30)	0.345(3)	0.180 5(21)	0.454 7(19)
C(6)	−0.124 2(24)	0.347 2(19)	0.176 7(20)	C(31)	0.398(4)	0.142 3(24)	0.527 7(21)
C(7)	0.060 3(22)	0.535 0(18)	0.135 3(18)	C(32)	0.538(3)	0.164(3)	0.541 9(21)
C(8)	0.113 7(24)	0.122 9(18)	0.163 9(23)	C(33)	0.635(3)	0.224 0(22)	0.489 7(20)
C(9)	0.260 4(19)	0.428 2(13)	0.229 8(18)	C(34)	0.577(3)	0.258 4(18)	0.412 8(20)
C(10)	0.523 5(22)	0.575 1(17)	0.341 0(22)	C(35)	0.924(4)	0.786(3)	0.345(3)
C(11)	0.586(3)	0.511 8(21)	0.375 6(19)	O(1)	0.276 1(18)	0.495 4(12)	−0.026 3(12)
C(12)	0.672 3(23)	0.491 3(18)	0.317 4(21)	O(2)	−0.059 0(16)	0.198 7(12)	−0.009 0(14)
C(13)	0.663 3(22)	0.535 0(16)	0.241 0(17)	O(3)	−0.138 1(16)	0.147 4(14)	0.301 3(16)
C(14)	0.566(3)	0.589 9(14)	0.245 3(18)	O(4)	0.176 1(17)	0.364 3(13)	0.478 8(13)
C(15)	0.270 0(23)	−0.009 7(14)	0.179 4(16)	O(5)	0.024 9(22)	0.545 3(16)	0.384 9(16)
C(16)	0.366 1(23)	0.036 6(15)	0.250 5(16)	O(6)	−0.238 7(17)	0.289 4(14)	0.148 1(16)
C(17)	0.494 3(22)	0.096 6(16)	0.221 5(16)	O(7)	0.078 8(19)	0.605 5(13)	0.092 1(14)
C(18)	0.474 5(21)	0.084 7(15)	0.128 0(18)	O(8)	0.003 2(15)	0.059 8(10)	0.137 5(12)
C(19)	0.332 5(25)	0.018 5(14)	0.097 9(16)	Cl(1)	0.992 7(14)	0.758 6(8)	0.250 1(10)
C(20)	0.435 9(17)	0.326 9(12)	0.127 9(14)	Cl(2)	1.017 6(17)	0.900 4(11)	0.408 8(13)



(**3a**) M = Mo, 92%
(**4a**) M = W, 80%

(**3b**) 8%
(**4b**) 20%

Scheme.

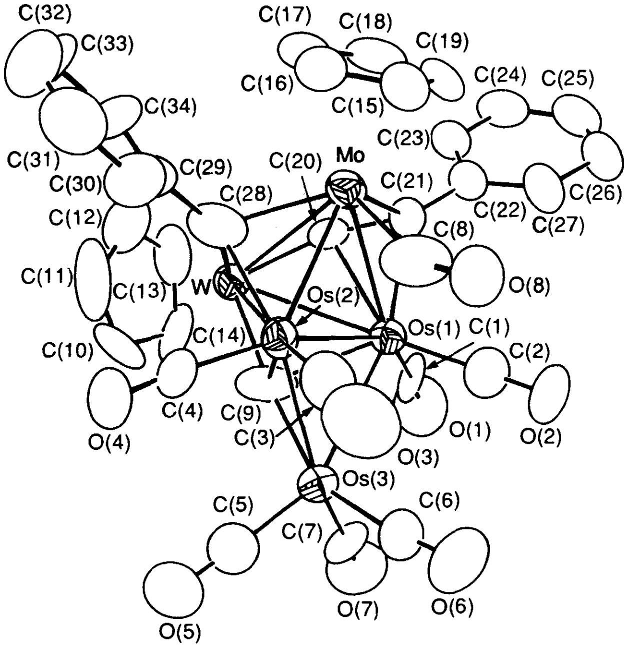


Figure 3. ORTEP diagram of complex (**5**) showing the atomic numbering scheme

fragment on the planar M_5 cluster surface; the second involves a rotation of the terminal $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment. We prefer the first and propose that the exchange is due to migration of the terminal CPh group of the C_4 hydrocarbon from one Os–Mo edge to the adjacent Os–Os edge, as indicated in the Scheme. Increase of the proportion of isomer (**b**) on substitution of the molybdenum by tungsten is considered to support the proposed mechanism, since we have observed that tungsten tends to bond less effectively to the β-carbon of the co-ordinated C_2 acetylide ligand with respect to the corresponding second-row element (such as molybdenum);[11] therefore, a decrease in the ratio (**4a**):(**4b**) is expected. Furthermore, our proposal agrees with recent reports of the rotational motion of the C_2 acetylide[12] and alkyne[13] ligands on the triangular face of several trinuclear clusters.

The second possibility of the rotation of the remote $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment[14] can be eliminated due to a similar argument. No variation of the ratio (**4a**):(**4b**) is expected if the exchange is due to the latter process.

Synthesis and Characterization of $[MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)(\eta\text{-}C_5H_5)_2]$ (**5**).—Treatment of $[MoOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ with the tungsten acetylide complex $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ in refluxing toluene produced a pentanuclear cluster complex (**5**) in low yield. The ^1H n.m.r. spectrum shows several multiplets in the region δ 7.47—7.09 due to two phenyl rings and two singlets at δ 5.98 and 4.83 due to C_5H_5. The exact formula of (**5**) was determined from the f.a.b. mass spectrum which exhibits a parent ion at *m*/*z* 1 414, corresponding to a composition $C_{34}H_{20}MoO_8Os_3W$. Based on these spectroscopic data, we conclude that complex (**5**) consists of a M_5 cluster core, two phenylacetylide moieties, and eight CO ligands, three CO ligands less than in the corresponding complexes (**3**) and (**4**). In order to determine the structure unambiguously, an *X*-ray diffraction study was carried out.

Crystal Structure of Complex (**5**).—The cluster complex crystallizes with one dichloromethane solvent molecule. There are no uncommon intermolecular contacts between individual

Table 5. Selected interatomic distances (Å) and angles (°) of complex (**5**) with e.s.d.s in parentheses

Os(1)–Os(2)	2.828(1)	Os(1)–Os(3)	2.840(2)
Os(1)–W	2.845(2)	Os(1)–Mo	2.855(2)
Os(2)–Os(3)	2.796(1)	Os(2)–W	2.832(2)
Os(2)–Mo	2.795(2)	W–Mo	2.924(2)
Os(2)–Os(1)–Os(3)	59.12(4)	Os(2)–Os(1)–W	59.89(4)
Os(2)–Os(1)–Mo	58.94(5)	Os(3)–Os(1)–W	86.83(5)
Os(3)–Os(1)–Mo	118.05(5)	W–Os(1)–Mo	61.72(5)
Os(2)–Mo–W	59.30(5)	Os(1)–Os(2)–Os(3)	60.67(4)
Os(1)–Os(2)–W	60.36(5)	Os(1)–Os(2)–Mo	61.01(5)
Os(3)–Os(2)–W	87.93(5)	Os(3)–Os(2)–Mo	121.67(5)
W–Os(2)–Mo	62.60(5)	Os(1)–Os(3)–Os(2)	60.21(3)
Os(1)–W–Os(2)	59.75(4)	Os(1)–W–Mo	59.30(5)
Os(2)–W–Mo	58.09(5)	Os(1)–Mo–Os(2)	60.05(4)
Os(1)–Mo–W	58.98(5)		
Carbide atom			
Os(1)–C(9)	2.16(2)	Os(2)–C(9)	2.14(2)
Os(3)–C(9)	1.97(2)	W–C(9)	1.94(2)
Os(3)–C(9)–W	172(1)	Os(1)–C(9)–Os(2)	82.4(6)
Acetylide fragment			
Os(1)–C(20)	2.20(2)	W–C(20)	1.92(2)
Mo–C(20)	2.21(2)	Os(1)–C(21)	2.17(2)
Mo–C(21)	2.24(2)	C(20)–C(21)	1.38(3)
W–C(20)–C(21)	154(2)	C(20)–C(21)–C(22)	140(2)
Os(1)–C(20)–Mo	80.7(5)	Os(1)–C(21)–Mo	80.7(7)
Alkylidyne fragment			
Os(2)–C(28)	2.19(2)	W–C(28)	2.04(2)
Mo–C(28)	2.20(2)		
Os(2)–C(28)–Mo	79.1(8)	Os(2)–C(28)–W	83.9(7)
		W–C(28)–Mo	87.2(7)
Carbonyl ligands			
Mo–C(8)	2.00(2)	Mo–C(8)–O(8)	154(2)
Os(1) ··· C(8)	2.78(2)	Os(1) ··· C(8)–O(8)	123(2)
Os(2) ··· C(8)	2.47(3)	Os(2) ··· C(8)–O(8)	128(2)

molecules in the crystal. The geometry and atomic labelling scheme is shown in Figure 3 and selected interatomic distances and angles are collected in Table 5.

The MoOs$_3$W cluster core adopts an edge-bridged tetrahedral geometry or a wing-bridged butterfly geometry[15] as expected for a M$_5$ cluster species characterized by 74 valence electrons.[16] Atoms Os(1), Os(2), W, and Mo define the tetrahedral skeleton and each osmium atom is associated with two CO ligands, the W atom is capped by a C$_5$H$_5$ ligand, and the Mo atom is co-ordinated to a CO and a C$_5$H$_5$ ligand, respectively. The third osmium atom Os(3) lies on the edge of the Os(1)–Os(2) bond of the tetrahedral skeleton and is associated with three CO ligands. The metal–metal bonds are normal and lie in the range 2.795(2)—2.924(2) Å. The dihedral angles between the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(2)–W and between Os(1)–Os(2)–Os(3) and Os(1)–Os(2)–Mo are 105.79(4) and 178.93(5)°, respectively. Formal electron counts at the individual metal atoms are 17e at Os(3) and W, 18e at Os(2), and 19e at Os(1) and Mo.

The acetylide fragment, C(20)–C(21), occupies the Os(1)–W–Mo face with its α-carbon bound to all three metal atoms, and the β-carbon to two atoms Os(1) and Mo. The acetylide is considered to adopt a 1σ + 2π bonding interaction supplying a total of five electrons to the cluster.[8] The local geometry (perpendicular to one M–M bond) and the M–C distances associated with this acetylide ligand [Os(1)–C(20) 2.20(2), W–C(20) 1.92(2), Mo–C(20) 2.21(2), Os(1)–C(21) 2.17(2), and Mo–C(21) 2.24(2) Å] agree well with those observed for trinuclear acetylide complexes, such as [WOs$_2$(CO)$_8$(C≡CPh)(η-C$_5$H$_5$)],[12] [Os$_3$H(CO)$_9$(C≡CR)],[17] [Ru$_3$H(CO)$_9$(C≡CBu^t)],[18] and [CoFe$_2$(CO)$_9$(C≡CSiMe$_3$)].[19]

The most striking feature is the presence of an alkylidyne (μ$_3$-CPh) and a carbide (μ$_4$-C) fragment which are separated with a non-bonding distance C(9) ··· C(28) 3.02(3) Å. The triply bridging alkylidyne is associated with the Os(2)–W–Mo triangular face with distances Os(2)–C(28) 2.19(2), W–C(28) 2.04(2), and Mo–C(28) 2.20(2) Å, whereas the quadruply bridging carbide atom C(9) is encapsulated in the cavity of the Os$_3$W butterfly skeleton with distances Os(1)–C(9) 2.16(2), Os(2)–C(9) 2.14(2) Å, Os(3)–C(9) 1.97(2), and W–C(9) 1.94(2) Å and angles Os(3)–C(9)–W 172(1) and Os(1)–C(9)–Os(2) 82.4(6)°. The local arrangement of the carbide atom is consistent with typical long M(hinge)–C(carbide) distances, short M(wing-tip)–C(carbide) distances, and near-linear M(wing-tip)–C(carbide)–M(wing-tip) arrangements as observed in tetranuclear carbido clusters.[20]

Acetylide Carbon–Carbon Bond Cleavage.—The observed carbide and alkylidyne moieties in complex (**5**) are derived from C–C bond scission of the acetylide ligand of [W(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)]. Basically, the acetylide ligand may originate from either the tetranuclear derivative (**1**) or mononuclear complex [W(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)]. We are unable to differentiate these two possibilities from the disposition of the hydrocarbon ligands, as all the hydrocarbon ligands are co-ordinated to the tungsten atom and the cluster core has undergone reorganization during the formation of complex (**5**). In order to solve this problem we have carried out the reaction of complex (**1**) with ^{13}C-labelled acetylide complex [W(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)]. The ^{13}C n.m.r. spectrum of the labelled sample shows an enhanced signal at δ 339.3, which we assign to the carbide carbon, not an acetylide α-carbon. This assignment is consistent with the literature reports that carbide carbons give a downfield chemical shift in the range δ 267—486,[21] whereas the resonances of the α-carbon of the μ$_3$-η^2-acetylide appear in the range δ 220—115.[22]

Conclusion

Both the cluster acetylide complexes (**1**) and (**2**) react with [Mo(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)] to give planar pentametallic complexes which contain a C$_4$ hydrocarbon fragment derived from head-to-tail coupling of two acetylide fragments. The C$_4$ chain of these complexes also undergoes twisting in solution as indicated by variable-temperature ^{1}H n.m.r. studies. Furthermore, the reaction of (**1**) with [W(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)] was carried out in the hope of generating a similar coupling product. Instead, the reaction with [W(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)] produces no coupling product but induces C–C bond scission of the tungsten acetylide [W(CO)$_3$(C≡CPh)(η-C$_5$H$_5$)] producing a novel carbide–alkylidyne derivative. Although C–C bond scission of the ruthenium acetylide complex [Ru(CO)$_2$(C≡CMe)(η-C$_5$H$_5$)] has been reported,[23] our example represents the first case of a polynuclear cluster in which the resulting carbide and alkylidyne moieties are bound to the adjacent metal atoms *via* multisite interactions.

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