Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 17.[1] Reactions of the Compounds $[Ru_3(CO)_{12}]$, $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$, and $[Os_3(CO)_{10}(cyclo\text{-}C_8H_{14})_2]$ with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$; Crystal Structures of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (Two Isomers) and $[Os_3W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)]$ *

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Reactions between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) and $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ or $[Ru_3(CO)_{12}]$, in tetrahydrofuran and toluene, respectively, afford the cluster compounds $[MW_2(\mu_3\text{-}RC_2R)(CO)_7(\eta\text{-}C_5H_5)_2]$ (M = Os or Ru). The molecular structure of the osmiumditungsten compound was established by a single-crystal *X*-ray diffraction study, which shows that the crystallographic asymmetric unit contains two distinct isomeric molecules (1a) and (1b). In both isomers a OsW_2 triangle is μ_3-(η^2-||) bridged by the $C_2(C_6H_4Me\text{-}4)_2$ ligand but in (1a) the vector joining the ligated carbon atoms of the alkyne lies essentially parallel to the W–W edge [3.159(2) Å], whereas in (1b) it lies essentially parallel to an Os–W edge [2.981(2) Å]. In both isomers the osmium and tungsten atoms carry three and two CO ligands, respectively, but in (1b) one of these groups is strongly semi-bridging [W–C–O 156(3)°]. The isomers (1a) and (1b) undergo interesting dynamic processes in solution as deduced by variable-temperature ^1H n.m.r. studies. The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Os_3(CO)_{10}(\eta^2\text{-}C_8H_{14})_2]$ react slowly in toluene at room temperature to afford the tetranuclear cluster $[Os_3W(\mu_3\text{-}CR)(CO)_{11}(\eta\text{-}C_5H_5)]$, the structure of which was established by *X*-ray diffraction. The molecule has an essentially Os_3W tetrahedral core, with an Os_2W face capped by the tolylidyne ligand. Each osmium carries three terminal CO groups and the tungsten atom is bonded to a $\eta\text{-}C_5H_5$ ligand as well as to two CO groups, one of which is semi-bridging [W–C–O 159(2)°]. The Os–Os edge [2.795(1) Å] of the capped face is marginally longer than the non-bridged Os–Os edges [2.790(1) and 2.791(1) Å]. In contrast, the Os–W edges [2.874(1) and 2.867(1) Å] of the capped face are shorter than the remaining Os–W separation [2.915(1) Å]. The μ_3-CR ligand is slightly asymmetrically bridging: μ_3-C–Os 2.142(14) and 2.048(15), μ_3-C–W 2.138(15) Å.

We have previously shown [2] that reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) and $[Fe_2(CO)_9]$ affords the dimetal complex $[FeW(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ as well as two trimetal species $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[FeW_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$. Continuing our use of the tolylidynetungsten compound as a precursor to heteronuclear transition-metal clusters containing tungsten, we wished to examine reactions of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with carbonyl compounds of osmium and ruthenium in order to compare the nature of the products with those obtained from $[Fe_2(CO)_9]$. However, whereas the latter reacts with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ at ambient temperatures, it was not anticipated that the tungsten compound would react with the trimetal compounds $[M_3(CO)_{12}]$ (M = Ru or Os) under such mild conditions. It is well known that enneacarbonyldi-iron readily reacts with alkynes, often at relatively low temperatures, whereas the dodecacarbonyls of triruthenium and triosmium require considerable thermal activation. The similar reactivity patterns toward metal carbonyl species shown by alkynes and by $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ [3] thus suggested that the latter was unlikely to react with $[Os_3(CO)_{12}]$ at temperatures below which the tungsten compound decomposes at an appreciable rate. Accordingly, reactions of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with the species $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ [4] and $[Os_3(CO)_{10}(\eta^2\text{-cyclo-}C_8H_{14})_2]$ [5] were investigated since both these compounds are more reactive than $[Os_3(CO)_{12}]$. In the cyclo-octenetriosmium complex the $Os_3(CO)_{10}$ fragment is lightly stabilised, while $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ is known to react with the donor molecule PMe_2Ph, releasing methane and forming $[Os_3(CO)_{10}(PMe_2Ph)_2]$. It thus seemed possible that $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ would react with one or other of the triosmium compounds to yield a tetranuclear Os_3W cluster. The reaction of the tungsten compound with $[Ru_3(CO)_{12}]$ was also studied, since the latter is known to react slowly with alkynes at *ca.* 50—100 °C, at which temperatures the carbyne-tungsten complex is stable. A preliminary account of some aspects of the work described herein has been reported.[6]

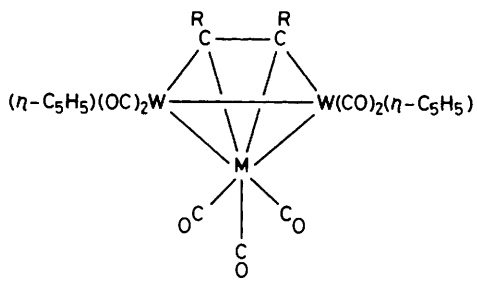
Results and Discussion

The reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ in tetrahydrofuran at 60 °C afforded a dark red crystalline compound (1) in moderate yield. Examination of the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the compound, discussed below, showed that the complex underwent dynamic behaviour in solution. In the i.r. spectrum of (1) seven CO stretching bands were observed, including one (1 835 cm^{-1}) in the semi-bridging region. It was evident that a single-crystal *X*-ray diffraction study was necessary to establish the molecular structure, and fortunately suitable crystals were available.

The *X*-ray results revealed an asymmetric unit containing

* μ_3-[1,2-Bis(*p*-tolyl)ethanetetrayl-C^1(Os,W),C^2(Os,W)]-1,1,1,2,2,3,3-heptacarbonyl-2,3-bis(η-cyclopentadienyl)-*triangulo*-osmium-ditungsten and 1,1,1,2,2,2,3,3,3,4,4-undecacarbonyl-4-η-cyclopentadienyl-1,2,4-μ_3-(*p*-tolylmethylidyne)-*tetrahedro*-triosmium-tungsten(3 *Os–Os*)(3 *Os–W*).

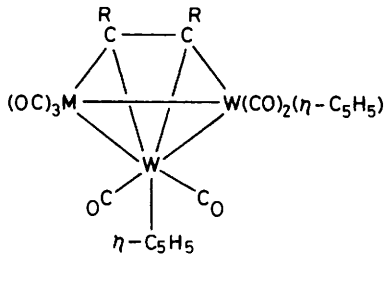
Supplementary data available (No. SUP 23522, 78 pp.): observed and calculated structure factors, H-atom co-ordinates, thermal parameters, complete bond length and angle data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



M

(1a) Os

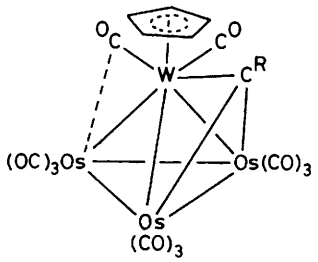
(2a) Ru



M

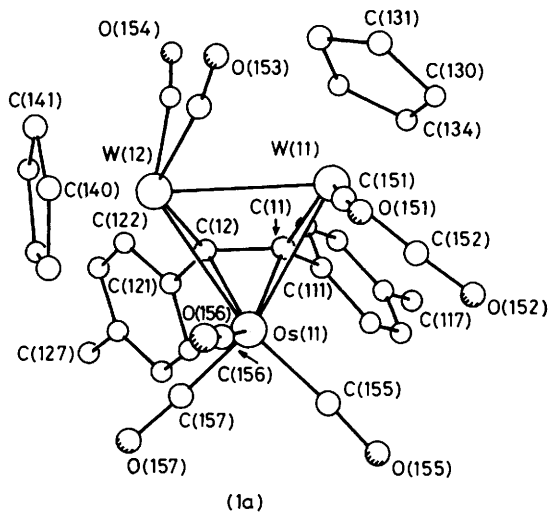
(1b) Os

(2b) Ru

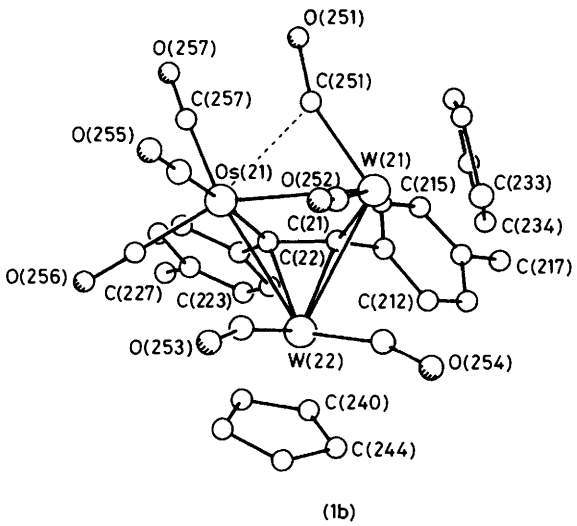


(3)

R = C_6H_4Me-4



(1a)



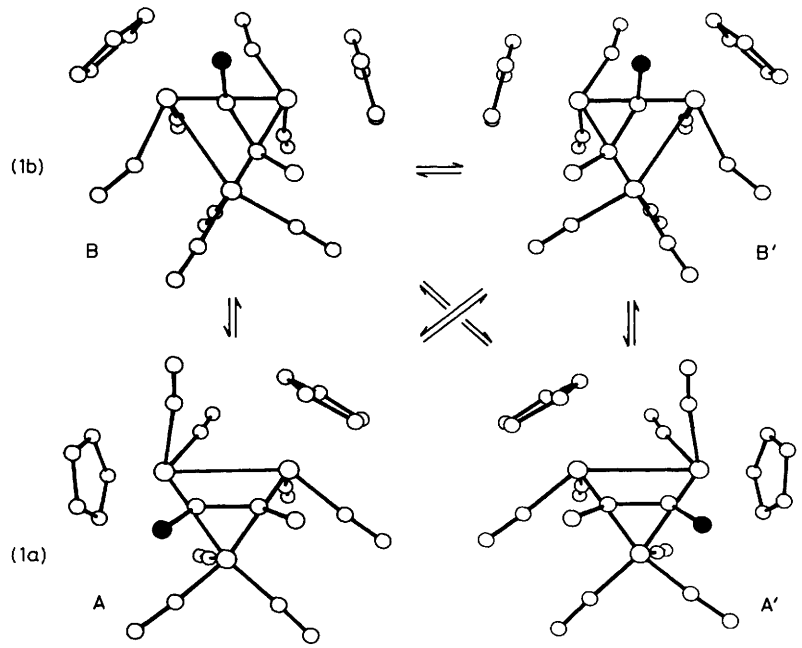
(1b)

Figure 1. Molecular structures of the two isomers (1a) and (1b) of the compound $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ showing the atom numbering scheme

two isomeric molecules, and these are shown in Figure 1. Selected bond distances and angles for the two isomers (1a) and (1b) are listed in Table 1. It is immediately apparent that in the course of the reaction two CC_6H_4Me-4 groups have coupled to form the alkyne $C_2(C_6H_4Me\text{-}4)_2$, which in both isomers is bound to an OsW_2 triangle of metal atoms. As mentioned above, one of the products of the reaction of $[Fe_2(CO)_9]$ with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ has a structure in which two molecules of the latter have combined to form C–C and W–W bonds, as has occurred with (1). However, the structure of $[FeW_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$ [2] differs from those of (1a) or (1b), as discussed below. It is interesting that the reaction between $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ affords a mono-osmium complex, rather than a Os_3W cluster species. It is possible, however, that (1) is produced as a consequence of the breakdown of a cluster of higher metal nuclearity.

The isomers of (1) conform to the two possible rotamers of $\mu_3\text{-}(\eta^2\text{-}\|)$ alkyne bonding [7,8] to a M_2M' triangle of metal atoms. This is in contrast with the structure of $[FeW_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$ which, with 46 cluster valence electrons, is 'unsaturated', has essentially a $\mu_3\text{-}(\eta^2\text{-}\perp)$ mode of alkyne bonding, and has a tungsten–tungsten separation corresponding to a W=W bond.[2]

In the more symmetric isomer (1a), the ligated carbon atoms of the alkyne lie parallel to the W(11)—W(12) bond to which



Scheme. Proposed dynamic behaviour for the isomers of (1). For clarity, only C(1) atoms of C_6H_4Me-4 groups are shown. Coalescence temperatures are approximately −75 (B ⇌ B'), −45 (A ⇌ B and A' ⇌ B'), and 0 °C (A ⇌ B' and A' ⇌ B)

Table 1. Selected internuclear distances (Å) and angles (°) for the central core atoms of the two isomers of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ [a]

(1a)		(1b)	
(*a*) Distances			
Os(11)–W(11)	2.863(2)	Os(21)–W(21)	2.981(2)
Os(11)–W(12)	2.839(2)	Os(21)–W(22)	2.876(2)
W(11)–W(12)	3.159(2)	W(21)–W(22)	3.017(2)
W(11)–C(11)	2.12(2)	W(21)–C(21)	2.19(2)
W(12)–C(12)	2.11(3)	Os(21)–C(22)	2.05(2)
C(11)–C(12)	1.47(3)	C(21)–C(22)	1.43(3)
Os(11)–C(11)	2.32(2)	W(22)–C(21)	2.21(3)
Os(11)–C(12)	2.31(3)	W(22)–C(22)	2.30(2)
		Os(21)···C(251)	2.51(3)
W–C(O) mean	2.01(3)	W–C(O) mean	2.00(3)
Os–C(O)	1.84(3)	Os–C(O)	1.93(3)
W–(η-C_5H_5) in the range 2.23—2.49(2)			
(*b*) Angles			
W(11)–C(11)–C(12)	112(1)	W(21)–C(21)–C(22)	116(1)
W(12)–C(12)–C(11)	115(1)	C(21)–C(22)–Os(21)	107(1)
W(12)–W(11)–C(11)	67.0(5)	W(22)–Os(21)–C(22)	52.6(5)
C(12)–W(12)–W(11)	65.9(6)	Os(21)–W(21)–C(21)	64.0(6)
C(11)–C(12)–C(121)	117(2)	C(21)–C(22)–C(221)	124(2)
C(12)–C(11)–C(111)	122(2)	C(22)–C(21)–C(211)	121(2)
W–C–O (mean)	173(2)	W–C–O (mean)	168 [b]
Os–C–O (mean)	175(2)	Os–C–O (mean)	177(2)

[a] Estimated standard deviations are in parentheses in Tables 1—4. [b] Excluding W–C(251)–O(251), 156(3)°.

they are σ bonded, with η^2 co-ordination to Os(11). In contrast, in the less symmetric (1b), C(22)–C(21) lies on the OsW_2 face parallel to Os(21)–W(21). Thus the alkyne is σ bonded to Os(21) and W(21), and η^2 co-ordinated to W(22). The less symmetrical isomer (1b) has a strongly semi-bridging CO ligand [W(21)–C(251)–O(251) 156(3)°], the presence of which was indicated by the i.r. spectrum. Two other CO groups [W(22)–C(253)–O(253) and W(22)–C(254)–O(254)] are semi-bridging to a lesser degree [165(2)°]. In isomer (1a), one CO ligand shows a tendency to semi-bridge [W(12)–C(153)–O(153) 169(2)°]. Both structures may be regarded as dimetallacyclobutadienes [9] bonded to $Os(CO)_3$ and $W(CO)_2(\eta\text{-}C_5H_5)$ fragments, respectively.

The difference between (1a) and (1b) is most clearly seen in the Scheme, which depicts simplified projections of the molecules viewed normal to the metal triangles. Both isomers are chiral and belong to the point group C_1. The inclusion of their enantiomers in the Scheme emphasizes the chirality, and facilitates the discussion of the fluxional behaviour (below) observed in solution.

The relative energies of (1a) and (1b) are evidently delicately balanced to allow for both isomers to exist in the crystal. In other clusters based on a M_2M' framework with a μ_3-(η^2-||) RC_2R ligand, in the solid state the alkyne either lies parallel to the M–M edge, *e.g.* in $[Ni_2M'(\mu_3\text{-}PhC_2Ph)(CO)_3(\eta\text{-}C_5H_5)_2]$ (M' = Fe or Ru),[10] or lies parallel to a M–M' edge, *e.g.* in $[Fe_2Ni(\mu_3\text{-}PhC_2Ph)(CO)_6(\eta\text{-}C_5H_5)]^-$.[11]

Since our original communication,[6] compound (1) has been independently prepared, and (1a) and (1b) also identified by an *X*-ray diffraction study.[12] Consequently, the *X*-ray diffraction results are not discussed in detail herein, and attention is directed at the interesting fluxional behaviour of (1) in solution.

The dynamic behaviour of (1) became apparent from variable-temperature ^1H n.m.r. studies which showed that (1a) and (1b) were both present in solution in a 1 : 1 ratio. Although the *X*-ray diffraction results showed the existence of non-equivalent cyclopentadienyl and tolyl groups, the ^1H spectrum at room temperature had only one resonance for each of these moieties. However, at −90 °C the limiting spectrum consistent with the presence of the two isomers (1a) and (1b) was reached. Both isomers are chiral (Scheme : enantiomeric pairs A and A', and B and B'), hence the −90 °C spec-

trum shows for each isomer two resonances for the η-C_5H_5 groups and two resonances for the Me-4 groups. For (1a) the signals are at δ 4.98 and 5.35 (η-C_5H_5) and 2.23 and 2.25 (Me-4), while for (1b) they are at δ 4.98 and 5.11 (η-C_5H_5) and 2.27 and 2.32 p.p.m. (Me-4). The signal at δ 4.98 is double the intensity of the resonances at δ 5.11 and 5.35 and therefore corresponds to two coincident signals.

As the temperature is raised, the η-C_5H_5 resonances for (1b) broaden (T_c *ca.* −75 °C) and become a single sharp peak at *ca.* −65 to −70 °C with δ 5.05. Over the temperature range −90 to −65 °C the two Me-4 signals for (1b), and all the resonances for (1a), remain unchanged. These observations can be explained by the interconversion B ⇌ B′ (Scheme) where a ' windscreen-wiper ' movement of the bridging alkyne group renders the η-C_5H_5 ligands of the enantiomers of (1b) apparently equivalent. The movement of the alkyne over the $Os(CO)_3$ vertex does not render the Me-4 groups equivalent and hence the resonances at δ 2.27 and 2.32 are unchanged.

Increasing the temperature further causes the η-C_5H_5 resonance for (1b), and the two η-C_5H_5 signals for (1a) at 4.98 and 5.35 to coalesce at *ca.* −45 to −50 °C. The limiting spectrum for this second process is attained above −40 °C with the appearance of a single sharp η-C_5H_5 resonance (δ 5.07). Concomitantly, the four peaks due to Me-4 groups change to two resonances of equal intensity at δ 2.24 and 2.27. These observations are consistent with a dynamic process A ⇌ B and A′ ⇌ B′ resulting from a further ' windscreen-wiper ' motion of the alkyne over one $W(CO)_2$(η-C_5H_5) vertex of the metal triangle. However, a combination of the two processes [(*i*) B ⇌ B′, and (*ii*) A ⇌ B, A′ ⇌ B′] at *ca.* −40 °C does not lead to Me-4 group site exchange, and hence two Me-4 resonances are still observed. This interesting result may be appreciated by following the filled carbon atom (●) of the alkyne ligand in the Scheme through the steps A ⇌ B ⇌ B′ ⇌ A′.

As the temperature is raised further the two Me-4 resonances coalesce at *ca.* 0 °C, and at ambient temperatures a sharp singlet is observed (δ 2.24). Site exchange of the Me-4 groups can be achieved by a third ' windscreen-wiper ' motion of the alkyne across the remaining $W(CO)_2$(η-C_5H_5) vertex (A ⇌ B′ and A′ ⇌ B). This corresponds at ambient temperatures to a free rotation of the $C_2(C_6H_4Me\text{-}4)_2$ ligand on the OsW_2 triangular face. Because the vertices of the triangle have metal atoms with different or differently oriented substituents each vertex presents a different energy barrier to alkyne rotation, and it is these barriers which determine the fluxional behaviour in solution.

Interpretation of the n.m.r. data for (1) was assisted by similar studies on the rutheniumditungsten compound (2), which also exists as a mixture of two isomers, but from the relative intensities of the ^1H n.m.r. resonances at −90 °C it can be deduced that an isomer ratio (2a) : (2b) of 1 : 9 prevails. The different proportions of the two isomers present allowed the resonances due to each isomer to be readily assigned. Compound (2) was prepared in low yield (10%) by heating [W(≡CR)$(CO)_2$(η-C_5H_5)] with [$Ru_3(CO)_{12}$] in toluene. The i.r. spectrum of (2) was very similar to that of (1), including a band (1 830 cm^{-1}) due to a semi-bridging CO group. The structures of (1) and (2) differ only by the replacement of an $Os(CO)_3$ group by the isolobal fragment $Ru(CO)_3$.

Reaction between [W(≡CR)$(CO)_2$(η-C_5H_5)] and [$Os_3(CO)_{10}$(η²-C_8H_{14})$_2$] occurred slowly at room temperature to afford a red-brown crystalline compound [$Os_3W(\mu_3\text{-}CR)(CO)_{11}$(η-$C_5H_5$)] (3). Microanalysis and a field-desorption (f.d.) mass spectrum established that (3) was a tetranuclear metal cluster. The ^1H and ^{13}C-{^1H} n.m.r. spectra were also in accord with the formulation proposed. Moreover, in the ^{13}C-{^1H} spectrum a characteristic [1-3] resonance for a μ_3-C group was observed at δ 264.7 p.p.m. In order to fully establish the molecular structure of (3), a single-crystal *X*-ray diffraction study was carried out. The molecule is shown in Figure 2, and Table 2 lists internuclear distances and angles.

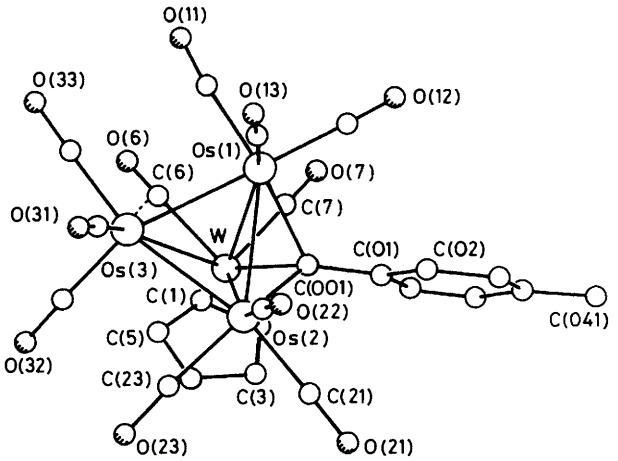


Figure 2. Molecular structure of the complex [$Os_3W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}$(η-$C_5H_5$)] (3) showing the atom numbering scheme

Compound (3) has an Os_3W core which is essentially tetrahedral, with an Os_2W face capped by a triply bridging CC_6H_4-Me-4 ligand. The three osmium atoms are each bonded to three CO groups, while the tungsten atom also carries two CO ligands. One of the latter, however, is semi-bridging [W–C(6)–O(6) 159(2)°]. The tungsten atom is also bonded to a η-C_5H_5 group. The structure can be viewed as one in which a metalla-alkyne, ' (η-C_5H_5)$(OC)_2W{\equiv}CR$ ', is μ_3-(η²-⊥) bound to an $Os_3(CO)_9$ fragment. In this respect (3) has a structure related to that of [$Fe_3(\mu_3\text{-}PhC_2Ph)(CO)_9$].[13] Compound (3) has 60 cluster valence electrons and is, therefore, saturated. However, simple electron counting for the individual metal atoms leads to 19 for the tungsten atom and 17 for Os(3), and this probably accounts for the strongly semi-bridging C(6)O(6) ligand.

The Os(1)–Os(2) edge [2.795(1) Å], which is part of the face capped by the tolylidyne ligand, is marginally longer than the Os(1)–Os(3) [2.790(1) Å] and Os(2)–Os(3) [2.791(1) Å] edges. The mean Os–Os separation [2.792 Å] is *ca.* 0.09 Å shorter than that in [$Os_3(CO)_{12}$] [2.877(3) Å],[14] and is close to the non-hydrido-bridged Os–Os edges in the complexes [$Os_3W(\mu\text{-}H)_3(CO)_{11}$(η-$C_5H_5$)] [2.825(2) and 2.827(2) Å] and [$Os_3W(\mu\text{-}H)(CO)_{12}$(η-$C_5H_5$)] [2.784(2) and 2.799(2) Å].[15] This supports the proposal [15] that M–M distances in tetranuclear clusters are generally 0.05—0.10 Å shorter than those in triangular clusters.

The Os(1)–W [2.874(1) Å] and Os(2)–W [2.867(1) Å] edges of the capped face are *ca.* 0.04—0.05 Å shorter than that found for Os(3)–W [2.915(1) Å]. Notwithstanding the influence of the μ_3-CR group, these Os–W distances are close to those found for the non-hydrido-bridged Os–W separations in the compounds [$Os_3W(\mu\text{-}H)_3(CO)_{11}$(η-$C_5H_5$)] [2.880(3) Å] and [$Os_3W(\mu\text{-}H)(CO)_{12}$(η-$C_5H_5$)] [2.909(2), 2.915(2), and 2.934(2) Å] mentioned above. The chemically equivalent μ_3-C–Os(1) [2.142(14) Å] and μ_3-C–Os(2) [2.048(15) Å] bonds are significantly different, but the mean value [2.095 Å] is close to the μ_3-C–W distance [2.138(15) Å].

It is interesting that it was possible to isolate a triosmium cluster from the reaction between [W(≡CR)$(CO)_2$(η-C_5H_5)] and [$Os_3(CO)_{10}$(η²-C_8H_{14})$_2$], whereas reaction of the tungsten compound with [$Os_3(\mu\text{-}H)_2(CO)_{10}$] leads to breakdown of the

Table 2. Selected internuclear distances (Å) and angles (°) for the central core atoms in $[Os_3W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)]$ (3)

(*a*) Distances

Os(1)–Os(2)	2.795(1)	Os(2)–W	2.867(1)
Os(1)–Os(3)	2.790(1)	Os(3)–W	2.915(1)
Os(1)–W	2.874(1)	Os(2)–Os(3)	2.791(1)
Os(1)–C(001)	2.142(14)	W–C(001)	2.138(15)
Os(2)–C(001)	2.048(15)	C(001)–C(01)	1.50(2)
W–C(6)	2.04(2)	W–C(7)	1.982(15)
C(6)–O(6)	1.13(3)	C(7)–O(7)	1.16(2)
Os(3)–C(6)	2.54(2)		

(*b*) Angles

Os(3)–Os(1)–C(001)	93.8(4)	C(001)–Os(1)–C(11)	146.8(7)
Os(1)–Os(2)–C(001)	49.6(4)	C(001)–Os(1)–C(13)	122.0(6)
W–Os(2)–C(001)	48.1(4)	C(001)–Os(1)–C(12)	85.7(6)
Os(3)–Os(2)–C(001)	95.9(5)	C(001)–Os(2)–C(21)	83.4(6)
W–Os(1)–C(001)	47.8(4)	C(001)–Os(2)–C(22)	118.5(7)
Os(2)–Os(3)–C(6)	102.8(4)	C(001)–Os(2)–C(23)	146.0(9)
Os(1)–Os(3)–C(6)	73.6(4)	C(001)–W–Os(1)	47.9(4)
C(6)–Os(3)–C(31)	88.1(6)	C(001)–W–Os(2)	45.5(4)
C(6)–Os(3)–C(32)	94.3(8)	C(001)–W–Os(3)	90.5(4)
C(6)–Os(3)–C(33)	75.1(7)	Os(3)–C(6)–O(6)	122.0(15)
Os(1)–C(001)–W	84.4(5)	W–C(6)–O(6)	159(2)
Os(1)–C(001)–C(01)	124.1(10)	W–C(7)–O(7)	175(1)
W–C(001)–C(01)	135.7(12)	Os(1)–C(001)–Os(2)	83.7(5)
		Os(2)–C(001)–W	86.4(5)
		Os(2)–C(001)–C(01)	126.0(10)
Os–C–O (mean)	176(2)		

Os_3 triangle in the latter species. However, formation of (1) occurred in a reaction employing relatively vigorous conditions and hence isolation of (1) may be thermodynamically controlled.

Experimental

All experiments were carried out under oxygen-free nitrogen, using Schlenk-tube techniques. Light petroleum is that fraction of b.p. 40—60 °C, and all solvents were dried and distilled under nitrogen prior to use. The n.m.r. measurements were made with JEOL FX 90Q and FX 200 instruments with, unless otherwise stated, $[^2H_2]$dichloromethane as solvent for ^1H spectra, and $[^2H_2]$dichloromethane–CH_2Cl_2 for $^{13}C\text{-}\{^1H\}$ spectra. Infrared bands were measured in methylcyclohexane, using a Nicolet MX-1 FT spectrophotometer. The compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$,[16] $[Os_3(CO)_{10}(cyclo\text{-}C_8H_{14})_2]$,[5] and $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$[4] were made by methods previously described.

Reaction of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ *with* $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$.—The compound $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ was prepared *in situ* by treating $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (0.43 g, 0.51 mmol) in dichloromethane (20 cm^3) with excess CH_2N_2 for 15 min. The product was filtered, solvent was removed *in vacuo*, and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.21 g, 0.51 mmol) in tetrahydrofuran (10 cm^3) added. The mixture was heated at 60 °C for 24 h, cooled to room temperature, and solvent was removed *in vacuo*. The residue was chromatographed on an alumina column (30 × 2 cm), elution with dichloromethane producing a red solution. Evaporation of solvent (vacuum) and crystallisation of the residue from dichloromethane–light petroleum (1 : 1) afforded dark red *crystals* of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (1) (60 mg, 22%) (Found: C, 35.6; H, 2.1. $C_{33}H_{24}O_7OsW_2$ requires C, 36.4; H, 2.2%); $\nu_{max.}$(CO) at 2 062w, 2 048vs, 2 010w, 1 990vs, 1 977vs, 1 916s, and 1 835w cm^{-1}. N.m.r.: ^1H (25 °C), δ 2.24 (s, 6 H, Me-4), 5.07 (s, 10 H, $\eta\text{-}C_5H_5$), and 6.7—6.9 (m, 8 H, C_6H_4). ^1H {−90 °C, signals from two isomers were of equal relative intensity}: isomer (1a), δ 2.23 (s, 3 H, Me-4), 2.25 (s, 3 H, Me-4), 4.98 (s, 5 H, $\eta\text{-}C_5H_5$), 5.35 (s, 5 H, $\eta\text{-}C_5H_5$) and 6.7—6.9 (m, 8 H, C_6H_4); isomer (1b), δ 2.27 (s, 3 H, Me-4), 2.32 (s, 3 H, Me-4), 4.98 (s, 5 H, $\eta\text{-}C_5H_5$), 5.11 (s, 5 H, $\eta\text{-}C_5H_5$), and 6.7—6.9 (m, 8 H, C_6H_4). $^{13}C\text{-}\{^1H\}$ (25 °C), δ 218.6 (WCO), 217.3 (WCO), 181.1 (OsCO), 135.1 (C^1, C_6H_4Me-4), 132.1 (C^4, C_6H_4Me-4), 129.5, 128.3 (C_6H_4), 92.3 ($\eta\text{-}C_5H_5$), and 20.9 p.p.m. (Me-4).

Reaction of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ *with* $[Ru_3(CO)_{12}]$.—A mixture of $[Ru_3(CO)_{12}]$ (0.32 g, 0.5 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1 mmol) in toluene (25 cm^3) was heated (80 °C) for 3 d. Solvent was removed *in vacuo* and the residue chromatographed on alumina. Elution with dichloromethane–light petroleum (1 : 1) afforded, in sequence, unreacted $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ru_3(CO)_{12}]$, followed by $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (60 mg), identified spectroscopically,[17] and a red product. Crystallisation of the latter from dichloromethane–light petroleum afforded red *crystals* of $[RuW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (2) (0.10 g, 10%) (Found: C, 39.3; H, 2.3. $C_{33}H_{24}O_7RuW_2$ requires C, 39.6; H, 2.4%); $\nu_{max.}$(CO) at 2 066m, 2 046s, 2 010m, 1 990vs, 1 982vs, 1 914s, and 1 830w cm^{-1}. N.m.r.: ^1H (25 °C), δ 2.25 (s, 6 H, Me-4), 5.07 (s, 10 H, $\eta\text{-}C_5H_5$), and 6.6—6.9 (m, 8 H, C_6H_4). ^1H {−90 °C, relative intensity of signals for isomers (2a): (2b), 1 : 9; resonances for former partially obscured by latter marked (*)}: isomer (2a), δ 2.26* (s, 3 H, Me-4), 2.3* (s, 3 H, Me-4), 4.96 (s, 5 H, $\eta\text{-}C_5H_5$), 5.34 (s, 5 H, $\eta\text{-}C_5H_5$), 6.5—6.9* (m, 8 H, C_6H_4); isomer (2b), δ 2.29 (s, 3 H, Me-4), 2.31 (s, 3 H, Me-4), 5.10 (s, 5 H, $\eta\text{-}C_5H_5$), 5.15 (s, 5 H, $\eta\text{-}C_5H_5$), 6.5—6.9 (m, 8 H, C_6H_4). $^{13}C\text{-}\{^1H\}$ (25 °C), δ 221.1 (WCO), 220.2 (WCO), 195.9 (RuCO), 153.1—128.0 (CC_6H_4), 92.8 ($\eta\text{-}C_5H_5$), and 20.5 p.p.m. (Me-4).

Reaction of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ *with* $[Os_3(CO)_{10}(\eta^2\text{-}C_8H_{14})_2]$.—A mixture of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.12 g, 0.30 mmol) and $[Os_3(CO)_{10}(\eta^2\text{-}C_8H_{14})_2]$ (0.27 g, 0.25 mmol) in toluene (10 cm^3) was stirred at room temperature for 5 d. Removal of solvent *in vacuo*, followed by chromatography of the residue on an alumina column (20 × 3 cm), eluting with dichloromethane–light petroleum (1 : 1), gave a residue which on crystallisation from dichloromethane–light petroleum afforded red-brown *crystals* of $[Os_3W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)]$ (3) (49 mg, 16%) (Found: C, 23.8; H, 1.0%; *M* (f.d. mass spectrum), 1 230. $C_{24}H_{12}O_{11}Os_3W$ requires C, 23.7; H, 1.0%; *M*, 1 230); m.p. 225 °C, $\nu_{max.}$ (CO) at 2 078s, 2 040vs, 2 033vs, 2 009s, 1 999w, 1 980w, 1 974w, and 1 836w br cm^{-1}. N.m.r.: ^1H (25 °C, $[^2H_1]$chloroform), δ 2.23 (s, 3 H, Me-4), 5.48 (s, 5 H, $\eta\text{-}C_5H_5$), 7.08—7.40 (m, 4 H, C_6H_4). $^{13}C\text{-}\{^1H\}$ (25 °C), δ 264.7 (μ_3-C), 181.9 (CO), 180.6 (CO), 167.5 (C^1 of C_6H_4Me-4), 138.3 (C^4 of C_6H_4), 132.2, 129.7 (C_6H_4), 90.2 ($\eta\text{-}C_5H_5$), and 21.7 p.p.m. (Me-4).

Crystal Structure Determinations.—(*a*) $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (1). Crystals of (1) grow as red prisms. Diffracted intensities were collected at 298 K from a crystal with a maximum dimension of *ca.* 0.17 mm in the range $2.9 \leqslant 2\theta \leqslant 55°$. Of the 6 387 intensities measured on a Nicolet *P3m* diffractometer, 4 967 had $I \geqslant 2\sigma(I)$, and these were used for the solution and refinement of the structure. The data were corrected for Lorentz and polarisation effects, and an empirical absorption correction was applied.

Crystal data for (1). $C_{33}H_{24}O_7OsW_2$, $M = 1\,090$, Monoclinic, space group $P2_1$, $a = 10.248(11)$, $b = 18.168(25)$, $c = 16.637(16)$ Å, $\beta = 101.40(8)°$, $U = 3\,036(6)$ Å^3, $Z = 4$, $D_c =$

Table 3. Atomic positional parameters (fractional co-ordinates) for the two isomers of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (1a) and (1b)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
W(11)	0.485 47(7)	0.735 90(1)	0.184 17(5)	C(132)	0.484 3(15)	0.863 0(11)	0.127 4(9)
W(12)	0.173 96(7)	0.731 14(6)	0.120 79(4)	C(133)	0.540 4(15)	0.812 0(11)	0.079 1(9)
Os(21)	1.009 55(8)	0.353 34(5)	0.320 31(5)	C(134)	0.655 5(15)	0.781 0(11)	0.129 2(9)
W(22)	0.891 48(8)	0.338 31(5)	0.462 55(5)	C(21)	0.867(2)	0.240 8(13)	0.381 7(11)
W(21)	1.079 99(8)	0.221 06(6)	0.425 96(5)	C(211)	0.764 9(14)	0.177 2(7)	0.385 3(8)
Os(11)	0.324 91(8)	0.608 09(6)	0.191 68(5)	C(212)	0.724 8(14)	0.159 2(7)	0.458 3(8)
C(11)	0.426(2)	0.657 0(12)	0.090 5(11)	C(213)	0.640 2(14)	0.099 4(7)	0.460 7(8)
C(111)	0.519 0(14)	0.621 5(9)	0.043 5(8)	C(214)	0.595 7(14)	0.057 7(7)	0.390 2(8)
C(112)	0.608 3(14)	0.566 1(9)	0.076 0(8)	C(215)	0.635 7(14)	0.075 7(7)	0.317 3(8)
C(113)	0.695 6(14)	0.537 3(9)	0.029 6(8)	C(216)	0.720 3(14)	0.135 5(7)	0.314 8(8)
C(114)	0.693 7(14)	0.563 8(9)	−0.049 3(8)	C(217)	0.501(4)	−0.006(3)	0.396(3)
C(115)	0.604 4(14)	0.619 2(9)	−0.081 8(8)	C(22)	0.834(2)	0.302 1(11)	0.327 4(11)
C(116)	0.517 1(14)	0.648 0(9)	−0.035 4(8)	C(221)	0.695 8(11)	0.312 9(8)	0.270 6(7)
C(117)	0.787(4)	0.534(3)	−0.099(3)	C(222)	0.579 8(11)	0.283 6(8)	0.289 6(7)
C(12)	0.281(3)	0.656 5(13)	0.061 0(13)	C(223)	0.457 8(11)	0.294 5(8)	0.236 5(7)
C(121)	0.226 4(14)	0.608 4(8)	−0.013 5(7)	C(224)	0.451 8(11)	0.334 7(8)	0.164 4(7)
C(122)	0.145 4(14)	0.641 5(8)	−0.081 1(7)	C(225)	0.567 8(11)	0.364 0(8)	0.145 4(7)
C(123)	0.099 6(14)	0.600 7(8)	−0.152 1(7)	C(226)	0.689 9(11)	0.353 1(8)	0.198 5(7)
C(124)	0.134 9(14)	0.526 8(8)	−0.155 6(7)	C(227)	0.318(3)	0.346(3)	0.104(2)
C(125)	0.215 9(14)	0.493 7(8)	−0.088 1(7)	C(253)	1.036(3)	0.414 2(14)	0.472(2)
C(126)	0.261 7(14)	0.534 4(8)	−0.017 0(7)	O(253)	1.116(2)	0.461 9(11)	0.494 9(13)
C(127)	0.080(4)	0.484(2)	−0.233(2)	C(254)	0.999(3)	0.291 7(14)	0.555(2)
C(151)	0.460(3)	0.744(2)	0.299 9(14)	O(254)	1.059(3)	0.276 2(15)	0.623 5(10)
O(151)	0.459(2)	0.746 2(13)	0.367 2(10)	C(255)	1.180(3)	0.404 1(15)	0.336(2)
C(155)	0.453(3)	0.544 6(14)	0.242 1(11)	O(255)	1.286(2)	0.435 6(14)	0.344 2(14)
O(155)	0.532(3)	0.501 8(12)	0.274 9(13)	C(256)	0.931(3)	0.450 4(15)	0.296(2)
C(153)	0.243(3)	0.817 0(15)	0.198 6(14)	O(256)	0.891(3)	0.509 2(12)	0.281(2)
O(153)	0.263(2)	0.864 3(11)	0.245 3(11)	C(257)	1.002(3)	0.334 1(15)	0.207(2)
C(154)	0.225(3)	0.804(2)	0.033 9(15)	O(257)	1.002(2)	0.320 7(12)	0.143 8(10)
O(154)	0.240(2)	0.841 3(12)	−0.014 6(9)	C(251)	1.129(3)	0.233(2)	0.316(2)
C(156)	0.251(3)	0.633(2)	0.289(2)	O(251)	1.169(2)	0.213 7(12)	0.256 3(12)
O(156)	0.209(3)	0.649 5(15)	0.343 4(11)	C(252)	1.232(3)	0.294 9(13)	0.470(2)
C(157)	0.206(4)	0.542(2)	0.153 9(14)	O(252)	1.323(3)	0.329 9(14)	0.495(2)
O(157)	0.111(3)	0.500 2(14)	0.136 1(15)	C(240)	0.669(2)	0.341 4(8)	0.480 5(10)
C(152)	0.624(3)	0.672 3(15)	0.233 0(15)	C(241)	0.685(2)	0.403 1(8)	0.430 8(10)
O(152)	0.718(2)	0.635 1(11)	0.263 9(12)	C(242)	0.779(2)	0.451 3(8)	0.477 9(10)
C(140)	−0.011 8(15)	0.754 2(11)	0.183 3(8)	C(243)	0.821(2)	0.419 5(8)	0.556 7(10)
C(141)	−0.025 6(15)	0.797 1(11)	0.110 8(8)	C(244)	0.753(2)	0.351 6(8)	0.558 3(10)
C(142)	−0.039 1(15)	0.748 2(11)	0.043 0(8)	C(230)	1.028 9(14)	0.099 2(9)	0.436 2(13)
C(143)	−0.033 6(15)	0.675 1(11)	0.073 7(8)	C(231)	1.146 7(14)	0.103 3(9)	0.403 6(13)
C(144)	−0.016 8(15)	0.678 8(11)	0.160 4(8)	C(232)	1.246 3(14)	0.138 5(9)	0.462 6(13)
C(130)	0.670 5(15)	0.812 7(11)	0.208 5(9)	C(233)	1.190 0(14)	0.156 1(9)	0.531 6(13)
C(131)	0.564 7(15)	0.863 4(11)	0.207 4(9)	C(234)	1.055 6(14)	0.131 9(9)	0.515 3(13)

Table 4. Atomic positional parameters (fractional co-ordinates) for $[Os_3W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)]$ (3)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	−0.023 24(4)	0.200 47(4)	0.114 86(4)	O(6)	−0.202 1(10)	0.407 0(11)	0.176 5(13)
Os(2)	0.104 16(4)	0.201 46(4)	0.299 58(4)	C(7)	−0.189 8(11)	0.157 8(13)	0.214 3(11)
Os(3)	0.026 56(5)	0.375 17(4)	0.215 62(5)	O(7)	−0.252 2(9)	0.113 4(11)	0.170 0(10)
W	−0.090 66(5)	0.237 23(4)	0.298 79(4)	C(12)	−0.077 8(13)	0.083 7(13)	0.045 7(12)
C(001)	−0.013 5(11)	0.119 1(10)	0.252 2(11)	O(12)	−0.113 7(10)	0.018 9(10)	0.006 9(10)
C(01)	−0.018 9(10)	0.010 5(9)	0.256 3(11)	C(11)	−0.098 1(14)	0.287 7(12)	0.018 2(13)
C(02)	0.046 7(12)	−0.044 8(12)	0.216 7(13)	O(11)	−0.145 9(10)	0.333 7(11)	−0.038 8(10)
C(04)	−0.022 1(14)	−0.195 6(12)	0.257 5(14)	C(21)	0.135 9(11)	0.101 0(12)	0.395 8(12)
C(05)	−0.087 6(13)	−0.140 4(11)	0.300 9(13)	O(21)	0.151 7(10)	0.040 7(10)	0.457 8(10)
C(06)	−0.087 0(11)	−0.040 5(11)	0.296 8(12)	C(22)	0.212 3(13)	0.177(2)	0.242 5(14)
C(03)	0.044 4(12)	−0.147 4(12)	0.219 2(13)	O(22)	0.275 9(11)	0.155(2)	0.208 4(14)
C(041)	−0.028(2)	−0.304 8(12)	0.256(2)	C(23)	0.163(2)	0.293(2)	0.394(2)
C(13)	0.077 7(13)	0.206 4(13)	0.043 0(12)	O(23)	0.203 2(14)	0.345 4(12)	0.456 3(12)
O(13)	0.137 3(10)	0.213 3(12)	−0.000 4(11)	C(31)	0.142 5(15)	0.401 7(14)	0.177(2)
C(1)	−0.198 9(9)	0.275 9(10)	0.399 1(10)	O(31)	0.214 8(11)	0.414 3(14)	0.156 2(15)
C(2)	−0.171 9(9)	0.178 3(10)	0.422 2(10)	C(32)	0.044 2(15)	0.459 7(13)	0.327 1(15)
C(3)	−0.075 2(9)	0.177 6(10)	0.468 3(10)	O(32)	0.052(2)	0.509 0(10)	0.400 4(11)
C(4)	−0.042 4(9)	0.274 8(10)	0.473 6(10)	C(33)	−0.033 1(14)	0.468 1(13)	0.123 4(13)
C(5)	−0.118 8(9)	0.335 6(10)	0.430 9(10)	O(33)	−0.069 9(11)	0.526 4(10)	0.066 2(10)
C(6)	−0.147 8(14)	0.351 8(13)	0.212 2(14)				

2.38 g cm^{-3}, $F(000) = 2\,008$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 119.5 cm^{-1}.

The structure was solved by conventional heavy-atom and difference electron-density methods, and was refined by blocked-cascade least squares with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions and chemically equivalent hydrogen atoms were given common refined isotropic thermal parameters. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\,8|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $>$ *ca.* 2 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 18. Refinement converged at R 0.045 (R' 0.045). All calculations were carried out on an 'Eclipse' S230 Data General Minicomputer with the SHELXTL system of programs.[19] Atom co-ordinates for (1) are in Table 3.

(*b*) $[Os_3W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)]$ (3). Crystals grow as red-brown rhombs. Intensities were collected at 220 K from a crystal with a maximum dimension of *ca.* 0.19 mm, in the range $2.9 \leqslant 2\theta \leqslant 55°$. Of the 6 687 intensities measured on a Nicolet $P3m$ diffractometer, 5 024 had $I \geqslant 2\sigma(I)$ and these were used for the solution and refinement of the structure. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied.

Crystal data for (3). $C_{24}H_{12}O_{11}Os_3W$, $M = 1\,230$, Monoclinic, $a = 14.508(6)$, $b = 13.793(4)$, $c = 13.440(6)$ Å, $\beta = 101.11(14)°$, $U = 2\,639(2)$ Å^3, $Z = 4$, $D_c = 3.1$ g cm^{-3}, $F(000) = 2\,184$, space group $P2_1/n$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 189.2 cm^{-1}.

The structure was solved and refined as for compound (1). A weighting scheme of the form $w = [\sigma^2(F_o) + 0.006|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >2 e Å^{-3} except in the immediate vicinity of the metal atoms where peaks of *ca.* 5 e Å^{-3} were observed. Scattering factors and corrections for anomalous dispersion were from ref. 18. Refinement converged at R 0.063 (R' 0.063). The atom co-ordinates for (3) are in Table 4.

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