Triosmium Clusters with Ligands derived from αβ-Unsaturated Ketones. *X*-Ray Crystal Structures of $[Os_3H(CO)_{10}(\textit{cis}\text{-}MeC{=}CHCOMe)]$ and $[Os_3H(OH)(CO)_9(PMe_2Ph)]$ †

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The compounds $[Os_3H_2(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ both react with the enones RCH=CHCOMe (R = H, Me, or Ph) by metallation at the vinylic C–H groups to give compounds of type $[Os_3H(CO)_{10}(RC_4H_4O)]$, certain of which were also obtained from $[Os_3H_2(CO)_{10}]$ and CH≡CCOMe. Three isomers of $[Os_3H(CO)_{10}(C_4H_5O)]$ were isolated, containing $CH_2{=}CCOMe$ and *cis*- and *trans*-CH=CHCOMe respectively. The most stable isomer, $[Os_3H(CO)_{10}(\textit{cis}\text{-}CH{=}CHCOMe)]$, is decarbonylated at 130 °C to give $[Os_3H(CO)_9(\textit{cis}\text{-}CH{=}CHCOMe)]$ and contains a linear Os_3 chain and a terminal hydride replaceable by Cl from CCl_4. The substituted compounds $[Os_3H(CO)_{10}(\textit{cis}\text{-}RC{=}CHCOMe)]$ (R = Me or Ph) have a different structure; crystals of the compound with R = Me are monoclinic, space group *C*2/*c*, with a = 17.377(2), b = 14.293(2), c = 16.476(2) Å, β = 91.79(3)°, and Z = 8. The structure was solved *via* the heavy-atom method and refined to R = 0.034 using 2 906 diffractometer data with $I \geqslant 1.5\sigma(I)$. The structure is based on that of $[Os_3(CO)_{12}]$ with a chelating MeC=CHCOMe ligand occupying an axial and an equatorial site. The bridging hydride is not replaced by Cl in CCl_4 solution. Unable to obtain good crystals of $[Os_3H(CO)_{10}(\textit{cis}\text{-}CH{=}CHCOMe)]$, $[Os_3H_2(CO)_9(PMe_2Ph)]$ was treated with $CH_2{=}CHCOMe$ in an attempt to obtain a PMe_2Ph-substituted derivative but instead $[Os_3H(OH)(CO)_9(PMe_2Ph)]$, was obtained, the crystals of which are monoclinic, space group $P2_1/n$, with a = 17.535(2), b = 9.500(1), c = 14.326(2) Å, β = 101.86(1)°, and Z = 4. The structure was solved by the heavy-atom method and refined to R = 0.041 using 3 474 diffractometer data with $I \geqslant 1.5\sigma(I)$.

We have shown that $[Os_3(CO)_{12}]$ and $[Os_3H_2(CO)_{10}]$ react with aldehydes and ketones to give oxidative-addition products.[1,2] Aldehydes on reaction with $[Os_3(CO)_{12}]$ [1,2] or with $[Os_3(CO)_{10}(MeCN)_2]$ [3] give μ-acyl clusters of type $[Os_3H(\mu\text{-}RCO)(CO)_{10}]$ (R = alkyl or aryl) which can be prepared alternatively by reaction of $[Os_3(CO)_{12}]$ with LiR followed by H^+.[4] Cyclohexanone reacts with $[Os_3(CO)_{12}]$ to give a double-oxidative-addition product $[Os_3H_2(CO)_9(\mu_3\text{-}C_6H_8O)]$ in which two α-hydrogen atoms from the same carbon atom have been transferred to the metal atoms.[2] A feature of this chemistry, which we did not expect, is the strong tendency to form products in which the organic carbonyl groups are co-ordinated through oxygen. This is also found in the formation of $[Os_3H_2(CO)_9(C_6H_4O)]$ from phenol; the ligand is trapped in its dienone form with the keto-function co-ordinated through oxygen.[5,6] Normally one would expect ketones to be poor ligands when co-ordinating through oxygen atoms to metal atoms in low oxidation states. However, when involved in chelating or bridging ligands it seems that the oxygen atoms are readily co-ordinated.

As a route to other ketonic derivatives of clusters we have treated but-3-yn-2-one (CH≡CCOMe) and but-3-en-2-one ($CH_2{=}CHCOMe$) with $[Os_3H_2(CO)_{10}]$ knowing that this dihydride is quite reactive towards simple alkenes, alkynes, and other unsaturated species.[7–11] By co-ordinating these ligands through the unsaturated carbon–carbon bonds, we hoped to be able to examine the effects of the keto-function and its tendency to co-ordinate.

Results and Discussion

Synthesis and Characterisation of Reaction Products.—The alkyne CH≡CCOMe and alkene $CH_2{=}CHCOMe$ react with $[Os_3H_2(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ to give compounds (1)—(4) (Scheme 1). The reaction of but-3-yn-2-one with the bis(acetonitrile) compound gives quite a low yield of a known type of alkyne complex, $[Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}CH{\equiv}CCOMe)]$, based on its orange colour and its i.r. spectrum in the ν(CO) region which is quite characteristic of μ_3-alkyne complexes of this type.[7,12] The ^1H n.m.r. spectrum shows the expected low-field singlet (δ 10.40) characteristic of μ_3-terminal alkynes while ν(CO) absorptions at 1 863 and 1 673 cm^{-1} may be assigned to metal-bridging CO and a non-co-ordinated conjugated ketone respectively. From the other reactions we obtained three isomers, (1)—(3), of general formula $[Os_3H(CO)_{10}(C_4H_5O)]$, each with very different ^1H n.m.r. spectra and ν(CO) i.r. absorptions indicating that they have quite different structures. Scheme 1 summarises how these are related synthetically and we have shown that they have the structures illustrated. The two isomers (1) and (2) were obtained in 52 and 19% yields from the reaction of the alkyne with $[Os_3H_2(CO)_{10}]$ and were readily characterised as compounds resulting from the two orientations of addition of Os–H across the triple bond. Addition of osmium at the β position predominates over its addition at the α position. These products do not interconvert under the conditions of the preparation and may be readily separated by chromatography. Compound (1) contains the *trans*-CH=CHCOMe ligand bound only through carbon [ν(CO) 1 706 cm^{-1} for the free ketone] and the proton–proton coupling constant for the *trans*-hydrogen atoms (12.8 Hz) may be compared with the corresponding value for $[Os_3H(CO)_9(\mu\text{-}CH{=}CH_2)]$ of 14.9 Hz.[7] Given that compound (1) has the same co-ordination geometry as the $CH{=}CH_2$ compound (they do have very similar i.r. carbonyl absorptions), the keto-function is well removed from osmium and cannot co-ordinate. In the other

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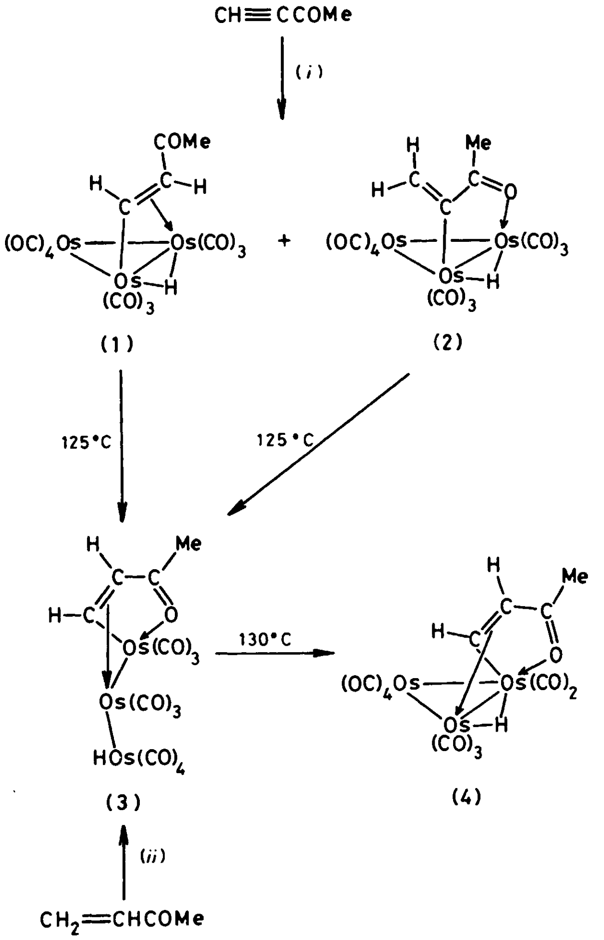
† 1,1,2,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-hydrido-1-(1′-methyl-3′-oxobut-1′-en-1′-yl-*C*$^{1'}$*O*)-*triangulo*-triosmium and 1,1,2,2,2,3,3,3,3-nonacarbonyl-1-dimethylphenylphosphine-1,2-μ-hydrido-1,2-μ-hydroxo-*triangulo*-triosmium.

Supplementary data available (No. SUP 23968, 59 pp.): structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme 1. (*i*) $[Os_3H_2(CO)_{10}]$, 25 °C; (*ii*) $[Os_3(CO)_{10}(MeCN)_2]$ or $[Os_3H_2(CO)_{10}]$, 50 °C

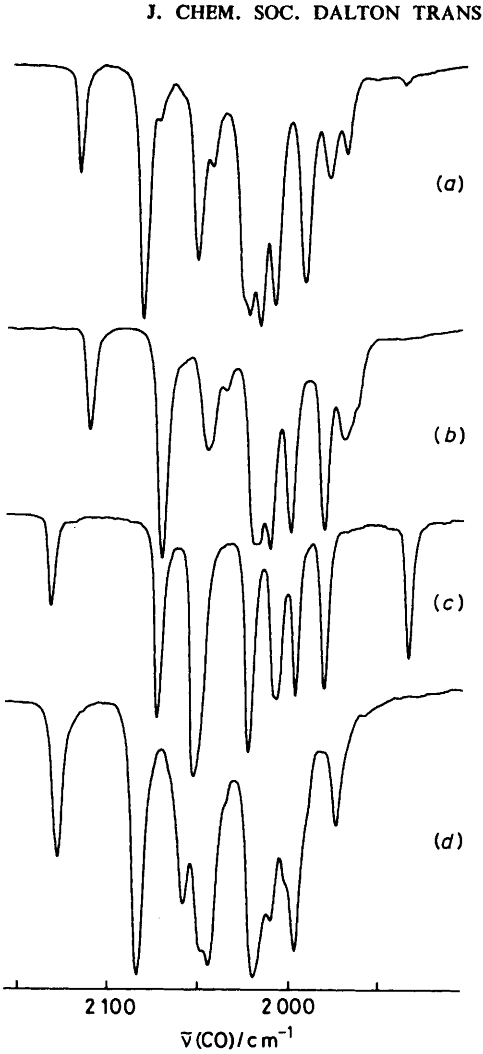


Figure 1. Infrared spectra of cyclohexane solutions of (*a*) $[Os_3H(CO)_{10}$(*cis*-CH=CHCOMe)], (3); (*b*) $[Os_3H(CO)_{10}$(*cis*-CH=CH-C_5H_4N)], (*c*) $[Os_3H(CO)_{10}$(*cis*-MeC=CHCOMe)], (6), and (*d*) $[Os_3Cl(CO)_{10}$(*cis*-CH=CHCOMe)], (5), showing the similarities between (*a*) and (*b*) and differences from the other spectra

regio isomer, compound (2), the CH_2=CCOMe ligand could bridge the metal atoms as in (1) with the C=C bond co-ordinated and the ketone free. However, spectra point to ketone co-ordination [ν(CO) 1 564 cm^{-1}] and a free alkene function. Compound (2) is related closely in structure to the oxidative-addition product of cyclohex-2-enone $[Os_3H(CO)_{10}(C_6H_4O)]$ which we have already reported.[2]

Isomer (3) is the most interesting and the most stable thermodynamically since the other two isomers both readily give isomer (3) at elevated temperatures. Structural characterisation of this isomer was difficult spectroscopically. The C=C and ketone groups both appear to be co-ordinated (data in Table 1). The *cis* geometry at the double bond then requires the ligand to chelate. The ^1H n.m.r. shift for the hydride is rather low (δ −9.70) possibly indicating terminal bonding. Electron counting requires only two Os–Os bonds. Unable to obtain crystals suitable for a single-crystal *X*-ray study, we were initially unable to establish a structure. However, Figure 1 shows a close similarity of the ν(CO) absorptions, and hence structure, with that of the compound $[Os_3H(CO)_{10}$(*cis*-CH=CHC$_5H_4N$)] formed by metallation of 2-vinylpyridine; the *X*-ray structure of this compound has been determined.[13] The hydride ligand in the vinylpyridine derivative is terminal; the ^1H n.m.r. shift is also rather low. The structure corresponds directly with that we have illustrated in Scheme 1 for compound (3) with the COMe group replaced by the 2-pyridyl group.

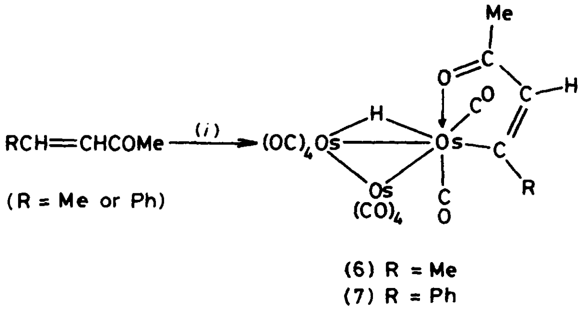
Thermal decarbonylation of compound (3) gives $[Os_3H(CO)_9$(*cis*-CH=CHCOMe)], compound (4). While we cannot define its structure with certainty, the C=C and COMe groups are both co-ordinated and it would seem that loss of CO has required the three osmium atoms to reform an equilateral triangle with three Os–Os bonds. The structure shown for compound (4) in Scheme 1 is consistent with the spectra and is directly comparable to that established for $[Ru_2H(CO)_6$(PhC=CHCOMe)].[14] Consistent with there being a terminal hydride ligand in compound (3) is its reaction with carbon tetrachloride at room temperature over 48 h. The hydride is replaced by chloride to give $[Os_3Cl(CO)_{10}$(*cis*-CH=CHCOMe)], compound (5), which is not the structural analogue of compound (3) since the COMe group is no longer co-ordinated [ν(CO) 1 723 cm^{-1}]. The C=C bond remains co-ordinated. Spectrum (*d*) in Figure 1 is clearly very different from spectrum (*a*), consistent with a significant structural change. Bridging of the chloride and displacement of the acyl group would still only necessitate two Os–Os bonds. Isomers (1) and (2) do not react with CCl_4 under these conditions.

Two substituted derivatives of compound (3) have been prepared by the reaction of $[Os_3H_2(CO)_{10}]$ or $[Os_3(CO)_{10}(MeCN)_2]$ with RCH=CHCOMe (R = Me or Ph) (Scheme 2). These compounds $[Os_3H(CO)_{10}$(RC=CHCOMe)], (6; R =

Table 1. Infrared and ^{1}H n.m.r. data

Compound	ν(CO)^a/cm^{-1}	ν(CO)(ketone) ^{b}/cm^{-1}	^{1}H N.m.r.	
			δ	J/Hz
(1) [$Os_3H^x(CO)_{10}$(*trans*-$CH^y{=}CH^zCOMe$)]	2 110m, 2 069vs, 2 058s, 2 027vs, 2 023 (sh), 2 014m, 2 002m, 1 989w, 1 983m	1 706	2.28(s, Me), 4.12(d, H^z), 8.19(dd, H^y), −19.36(dd, H^x)	J_{yz} 12.8, J_{xy} 1.9, J_{xz} 0.7 ^{c}
(2) [$Os_3H^x(CO)_{10}(CH_2{}^{y,z}{=}CCOMe)$]	2 106m, 2 066vs, 2 052s, 2 023vs, 2 009m, 2 003vs, 1 995m, 1 985m, 1 977m	1 564	2.35(s, Me), 6.93(d, H^y), 7.45(dd, H^z), −12.70(s, H^x)	J_{yz} 1.5, J_{xz} 0.5 ^{d}
(3) [$Os_3H^x(CO)_{10}$(*cis*-$CH^y{=}CH^zCOMe$)]	2 115m, 2 080vs, 2 051s, 2 025 (sh), 2 023s, 2 017vs, 2 010s, 1 994s, 1 980m, 1 971w	1 489	1.91(s, Me), 4.68(d, H^z), 9.01(d, H^y), −9.70(s, H^x)	J_{yz} 5.8
(4) [$Os_3H^x(CO)_9$(*cis*-$CH^y{=}CH^zCOMe$)]	2 099m, 2 061vs, 2 020s, 2 009s, 1 993s, 1 978m	1 480	1.96(s, Me), 4.07(dd, H^z), 7.18(dd, H^y), −11.97(dd, H^x)	J_{yz} 4.6, J_{xz} 1.8, J_{xy} 0.8
(5) [$Os_3Cl(CO)_{10}$(*cis*-$CH^x{=}CH^yCOMe$)]	2 130m, 2 086vs, 2 061s, 2 052 (sh), 2 047vs, 2 022s, 2 012s, 2 004 (sh), 1 999vs, 1 977m	1 723	1 98(s, Me), 4.93(d, H^y), 9.16(d, H^x)	J_{xy} 6.0
(6) [$Os_3H^w(CO)_{10}(Me^xC{=}CH^yCOMe^z)$]	2 129m, 2 071s, 2 051vs, 2 022s, 2 008m, 1 998m, 1 982m, 1 938m	1 537	2.36(s, Me^z), 3 02(s, Me^x), 6.61(s, H^y), −15.36(s, H^w)	
(7) [$Os_3H^x(CO)_{10}(PhC{=}CH^yCOMe^z)$]	2 128w, 2 073m, 2 052vs, 2 023vs, 2 009m, 1 998m, 1 986m, 1 942w		2.47(s, Me^z), 6.76(s, H^y), −15.52(s, H^x)	
(8) [$Os_3H^w(OH^x)(CO)_9(PMe_2{}^{y,z}Ph)$]	2 092m, 2 050vs, 2 013vs, 2 005vs, 1 982w, 1 974m, 1 967m, 1 946m		2.21(d, Me^y), 2.10(d, Me^z), −1.60(d, H^x), −12.65(d, H^w)	J_{Py} 9.6, J_{Pz} 9.6, J_{Px} 3.9, J_{Pw} 8.7

[a] In cyclohexane. [b] KBr disc. [c] J_{xz} only resolved for H^x signal. [d] J_{xz} only resolved for H^z signal.



Scheme 2. (*i*) [$Os_3H_2(CO)_{10}$] or [$Os_3(CO)_{10}(MeCN)_2$]

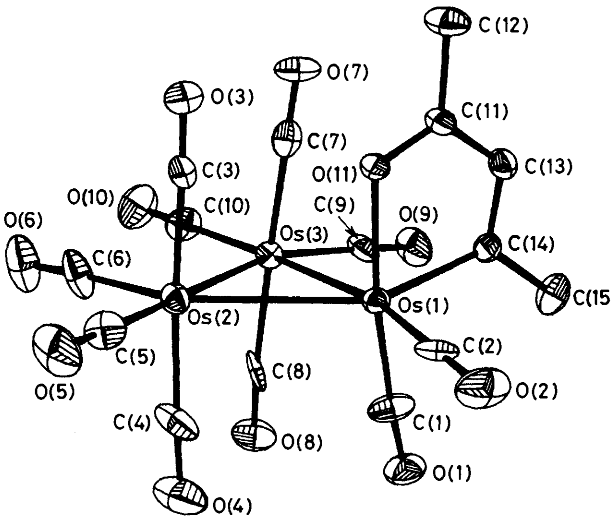


Figure 2. Molecular structure of [$Os_3H(CO)_{10}(MeC{=}CHCOMe)$], compound (6)

Me) and (7; R = Ph), are isostructural, but with a different structure from that of compound (3). This is clearly apparent from n.m.r. and i.r. data (Table 1); in particular the hydride ligands now appear from their higher-field n.m.r. shifts to be bridging. Doubting if a structure could be established in any other way, we carried out an *X*-ray structure determination for compound (6). The molecular structure is shown in Figure 2. Table 2 contains fractional atomic co-ordinates while Tables 3 and 4 contain bond lengths and interbond angles respectively. Since the compounds (3) and (6) are simply related by the replacement of a hydrogen atom by a methyl group, the gross change in structure is remarkable. Compound (6) is structurally related to [$Os_3(CO)_{12}$] with the MeC=CHCOMe chelate replacing two CO ligands and with the acetyl group co-ordinated axially. Unlike compound (3), (6) contains a non-co-ordinated C=C unit, three Os–Os bonds, and a bridging hydride ligand. Although the latter was not detected, the long Os(1)–Os(2) distance [3.030(1) Å] and the large Os–Os–CO (equatorial) angles associated with this Os–Os contact [121.2(3) and 112.8(3)°] indicate that the hydride bridges these osmium atoms. The hydride therefore lies *trans* to the Os–C σ bond of the chelate and presumably close to the Os_3 plane. The CO ligands are axially or equatorially disposed as in [$Os_3(CO)_{12}$], while the axial CO *trans* to the ketonic oxygen atom experiences greater π donation from osmium and is associated with a shorter Os–C bond [1.88(1) Å] than the other axial CO ligands [1.96(1), 1.93(1), 1.97(1), and 1.98(1) Å]. The structural differences between clusters (3) and (6) are hardly predictable but introduction of the extra

Table 2. Positional parameters and their estimated standard deviations for compound (6)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.313 32(3)	0.464 85(4)	0.161 63(3)	C(2)	0.349 3(9)	0.432(1)	0.265 7(9)
Os(2)	0.159 88(3)	0.565 60(4)	0.161 54(4)	C(3)	0.217 7(8)	0.683(1)	0.156(1)
Os(3)	0.230 59(3)	0.506 29(4)	0.011 86(3)	C(4)	0.110(1)	0.446(1)	0.172(1)
O(1)	0.263 3(8)	0.264 8(8)	0.142 5(9)	C(5)	0.115(1)	0.606(1)	0.263(1)
O(2)	0.373 4(9)	0.404(1)	0.328 0(8)	C(6)	0.082(1)	0.612(2)	0.088(1)
O(3)	0.248 7(7)	0.752 7(9)	0.154 6(9)	C(7)	0.295 3(9)	0.619(1)	0.012 1(9)
O(4)	0.082 4(9)	0.374(1)	0.185(1)	C(8)	0.167 9(8)	0.391(1)	0.019(1)
O(5)	0.084 8(8)	0.630(1)	0.317 3(8)	C(9)	0.304 8(9)	0.439(1)	−0.051(1)
O(6)	0.034 3(8)	0.636(1)	0.044(1)	C(10)	0.161(1)	0.555(1)	−0.072(1)
O(7)	0.332 6(8)	0.683 1(8)	0.006 3(8)	C(11)	0.432 5(8)	0.603(1)	0.139(1)
O(8)	0.137 1(8)	0.323 2(9)	0.021 3(8)	C(12)	0.475(1)	0.697(1)	0.141(1)
O(9)	0.346 2(7)	0.398(1)	−0.087 3(8)	C(13)	0.463 3(8)	0.519(1)	0.107 8(9)
O(10)	0.122 3(9)	0.583(1)	−0.121 0(9)	C(14)	0.418 5(8)	0.442(1)	0.112(1)
O(11)	0.366 1(5)	0.600 5(7)	0.165 9(6)	C(15)	0.452(1)	0.349(1)	0.089(1)
C(1)	0.279(1)	0.341(1)	0.149(1)	H(13)	0.519(7)	0.516(9)	0.091(7)

Table 3. Bond lengths (Å) for compound (6)

Os(1)–Os(2)	3.030(1)	Os(2)–C(4)	1.934(12)	O(2)–C(2)	1.170(11)	O(10)–C(10)	1.106(12)
Os(1)–Os(3)	2.878(0)	Os(2)–C(5)	1.952(11)	O(3)–C(3)	1.129(11)	O(11)–C(11)	1.250(10)
Os(1)–O(11)	2.144(6)	Os(2)–C(6)	1.902(11)	O(4)–C(4)	1.153(14)	C(11)–C(12)	1.535(13)
Os(1)–C(1)	1.878(10)	Os(3)–C(7)	1.967(11)	O(5)–C(5)	1.108(12)	C(11)–C(13)	1.419(13)
Os(1)–C(2)	1.865(10)	Os(3)–C(8)	1.977(12)	O(6)–C(6)	1.136(13)	C(13)–C(14)	1.350(12)
Os(1)–C(14)	2.048(9)	Os(3)–C(9)	1.932(10)	O(7)–C(7)	1.125(12)	C(13)–H(13)	1.02(7)
Os(2)–Os(3)	2.916(0)	Os(3)–C(10)	1.939(10)	O(8)–C(8)	1.112(13)	C(14)–C(15)	1.508(12)
Os(2)–C(3)	1.964(10)	O(1)–C(1)	1.125(11)	O(9)–C(9)	1.116(11)		

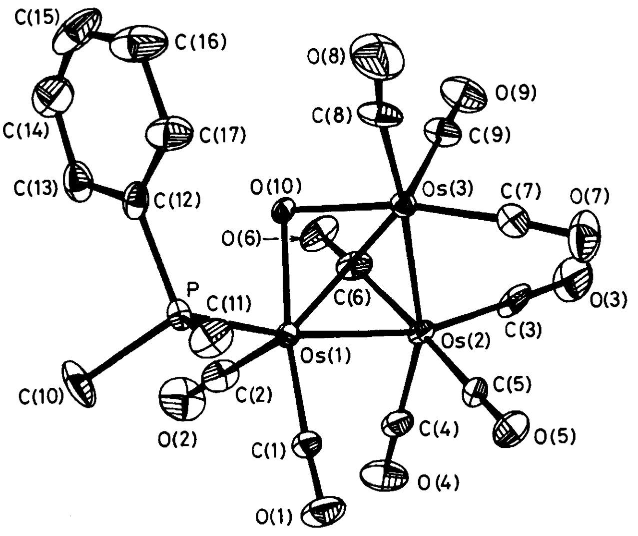


Figure 3. Molecular structure of $[Os_3H(OH)(CO)_9(PMe_2Ph)]$, compound (8)

methyl group would create unfavourable crowding in a compound with a structure like (3) and would weaken the η^2-alkene bond.

Attempting to obtain suitable crystals of a compound structurally related to cluster (3) we treated $[Os_3H_2(CO)_9(PMe_2Ph)]$ with $CH_2{=}CHCOMe$ but this reaction did not form a compound containing a C_4 ligand. Instead we obtained $[Os_3H(OH)(CO)_9(PMe_2Ph)]$, compound (8), by displacement of butanone by reactions with water. A noticeable feature of compound (8) is the high-field ^1H n.m.r. doublet at δ −1.60 (J = 3.9 Hz) for the OH group. Since we thought that there might be unusual structural features associated with this hydroxy-group, a single-crystal *X*-ray structure determination was carried out. The molecular structure of compound (8) is shown in Figure 3. Fractional atomic co-ordinates are given in Table 5 and bond lengths and interbond angles in Tables 6 and 7 respectively. The structure is as expected with the PMe_2Ph ligand positioned in the Os_3 plane *trans* to the Os(1)–Os(2) bond. This ligand produces very little distortion from molecular frameworks as found for molecules of type $[Os_3H(\mu\text{-}X)(CO)_{10}]$ (X = OMe,[15] Br,[16] $NHN{=}CMe_2$,[17] *etc.*). The two Os–OH distances are clearly similar [2.135(5) and 2.118(5) Å] as are the Os(1)–Os(2) (2.830 Å) and Os(2)–Os(3) (2.821 Å) distances. Although the hydroxy-hydrogen atom was not located it seems unlikely that its high-field n.m.r. signal is due to any structural abnormality. Rather, the high-field shift is due to a time-averaged close approach to the face of the phenyl ring; Figure 3 indicates the plausibility of this explanation.

The hydride was not located but probably bridges Os(1) and Os(3) close to the intersection of the Os(3)–C(9) and Os(1)–C(2) directions. The observed coupling to ^{31}P (8.7 Hz) is consistent with this.

In conclusion it is clear that co-ordination through oxygen atoms of a ketone is important in most of these compounds and competes effectively with co-ordination through a C=C group. In compounds (2), (6), and (7), for example, there is co-ordination of an oxygen atom but not a C=C bond. The structures obtained, however, may be sensitive to substitution as in the cases of $[Os_3H(CO)_{10}(cis\text{-}RC{=}CHCOMe)]$ (R = H, Me, or Ph) where the C=C group may be co-ordinated, with cleavage of an Os–Os bond, or it may not, depending on R.

Experimental

Syntheses.—Reaction of $[Os_3H_2(CO)_{10}]$ *with but-3-yn-2-one.* A solution of the dihydrido-complex (0.250 g) and but-3-yn-2-one (0.05 cm³) in cyclohexane (20 cm³) was allowed to stand at room temperature for 90 min, by which time the purple solution had become yellow. The solvent was removed *in*

Table 4. Bond angles (°) for compound (6)

Os(2)–Os(1)–Os(3)	59.1(0)	Os(1)–Os(2)–C(4)	88.7(4)	Os(1)–Os(3)–C(9)	92.0(3)	Os(2)–C(4)–O(4)	174.6(12)
Os(2)–Os(1)–O(11)	86.9(2)	Os(1)–Os(2)–C(5)	121.2(3)	Os(1)–Os(3)–C(10)	166.0(3)	Os(2)–C(5)–O(5)	175.5(11)
Os(2)–Os(1)–C(1)	100.2(4)	Os(1)–Os(2)–C(6)	140.6(4)	Os(2)–Os(3)–C(7)	90.9(3)	Os(2)–C(6)–O(6)	177.3(14)
Os(2)–Os(1)–C(2)	112.8(3)	Os(3)–Os(2)–C(3)	88.7(3)	Os(2)–Os(3)–C(8)	86.8(3)	Os(3)–C(7)–O(7)	175.0(8)
Os(2)–Os(1)–C(14)	150.6(3)	Os(3)–Os(2)–C(4)	91.3(3)	Os(2)–Os(3)–C(9)	154.6(3)	Os(3)–C(8)–O(8)	175.1(9)
Os(3)–Os(1)–O(11)	92.5(2)	Os(3)–Os(2)–C(5)	178.7(3)	Os(2)–Os(3)–C(10)	103.4(3)	Os(3)–C(9)–O(9)	177.8(9)
Os(3)–Os(1)–C(1)	87.5(3)	Os(3)–Os(2)–C(6)	82.7(4)	C(7)–Os(3)–C(8)	176.3(4)	Os(3)–C(10)–O(10)	178.8(11)
Os(3)–Os(1)–C(2)	169.5(3)	C(3)–Os(2)–C(4)	175.5(5)	C(7)–Os(3)–C(9)	90.9(4)	O(11)–C(11)–C(12)	118.0(9)
Os(3)–Os(1)–C(14)	97.0(3)	C(3)–Os(2)–C(5)	90.4(4)	C(7)–Os(3)–C(10)	93.0(4)	O(11)–C(11)–C(13)	117.7(8)
O(11)–Os(1)–C(1)	171.7(4)	C(3)–Os(2)–C(6)	91.5(5)	C(8)–Os(3)–C(9)	89.9(4)	C(12)–C(11)–C(13)	124.3(8)
O(11)–Os(1)–C(2)	93.6(3)	C(4)–Os(2)–C(5)	89.6(5)	C(8)–Os(3)–C(10)	90.3(4)	C(11)–C(13)–C(14)	116.4(8)
O(11)–Os(1)–C(14)	76.8(3)	C(4)–Os(2)–C(6)	92.9(6)	C(9)–Os(3)–C(10)	101.8(5)	C(11)–C(13)–H(13)	121(4)
C(1)–Os(1)–C(2)	87.6(4)	C(5)–Os(2)–C(6)	98.2(5)	Os(1)–O(11)–C(11)	111.5(6)	C(14)–C(13)–H(13)	122(4)
C(1)–Os(1)–C(14)	95.0(5)	Os(1)–Os(3)–Os(2)	63.1(0)	Os(1)–C(1)–O(1)	176.2(12)	Os(1)–C(14)–C(13)	114.6(6)
C(2)–Os(1)–C(14)	92.7(4)	Os(1)–Os(3)–C(7)	84.1(2)	Os(1)–C(2)–O(2)	173.8(9)	Os(1)–C(14)–C(15)	126.5(7)
Os(1)–Os(2)–Os(3)	57.9(0)	Os(1)–Os(3)–C(8)	92.3(3)	Os(2)–C(3)–O(3)	176.9(9)	C(13)–C(14)–C(15)	118.7(9)
Os(1)–Os(2)–C(3)	87.5(3)						

Table 5. Positional parameters and their estimated standard deviations for compound (8)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.602 08(3)	0.247 36(7)	0.829 22(4)	C(3)	0.735(1)	0.232(3)	1.147(1)
Os(2)	0.677 84(4)	0.278 62(7)	1.022 51(5)	C(4)	0.667(1)	0.479(2)	1.033(1)
Os(3)	0.662 96(4)	0.010 81(7)	0.935 63(5)	C(5)	0.768(1)	0.295(2)	0.966(1)
P	0.550 2(3)	0.175 6(5)	0.673 7(3)	C(6)	0.573(1)	0.235(2)	1.051(1)
O(1)	0.706 3(9)	0.449(2)	0.753(1)	C(7)	0.770(1)	−0.018(2)	0.970(1)
O(2)	0.481(1)	0.472(2)	0.836(1)	C(8)	0.649(1)	−0.161(2)	0.865(1)
O(3)	0.776(1)	0.190(3)	1.215(1)	C(9)	0.648(1)	−0.070(2)	1.054(1)
O(4)	0.661(1)	0.597(2)	1.038(2)	C(10)	0.485(2)	0.311(2)	0.597(2)
O(5)	0.823 5(8)	0.302(2)	0.932(1)	C(11)	0.625(1)	0.126(2)	0.605(1)
O(6)	0.516 2(7)	0.216(2)	1.068(1)	C(12)	0.488(1)	0.018(2)	0.666(1)
O(7)	0.837 1(9)	−0.028(2)	0.990(1)	C(13)	0.410(1)	0.038(3)	0.673(1)
O(8)	0.650(1)	−0.267(2)	0.828(2)	C(14)	0.365(2)	−0.081(3)	0.676(2)
O(9)	0.639(1)	−0.114(2)	1.122(1)	C(15)	0.392(2)	−0.207(3)	0.669(2)
O(10)	0.546 6(6)	0.082(1)	0.890 9(8)	C(16)	0.471(2)	−0.231(3)	0.664(2)
C(1)	0.665(1)	0.377(2)	0.781(1)	C(17)	0.520(1)	−0.115(2)	0.662(2)
C(2)	0.526(1)	0.388(2)	0.835(2)				

Table 6. Bond lengths (Å) for compound (8)

Os(1)–Os(2)	2.830(0)	Os(2)–C(5)	1.935(9)	P–C(12)	1.844(10)	O(8)–C(8)	1.141(12)
Os(1)–Os(3)	2.801(0)	Os(2)–C(6)	2.006(10)	O(1)–C(1)	1.136(10)	O(9)–C(9)	1.095(11)
Os(1)–P	2.329(2)	Os(3)–O(10)	2.118(5)	O(2)–C(2)	1.115(11)	C(12)–C(13)	1.395(12)
Os(1)–O(10)	2.135(5)	Os(3)–C(7)	1.857(10)	O(3)–C(3)	1.155(12)	C(12)–C(17)	1.390(14)
Os(1)–C(1)	1.869(8)	Os(3)–C(8)	1.912(9)	O(4)–C(4)	1.130(12)	C(13)–C(14)	1.393(16)
Os(1)–C(2)	1.903(9)	Os(3)–C(9)	1.932(9)	O(5)–C(5)	1.164(10)	C(14)–C(15)	1.297(21)
Os(2)–Os(3)	2.821(0)	P–C(10)	1.904(9)	O(6)–C(6)	1.086(11)	C(15)–C(16)	1.410(22)
Os(2)–C(3)	1.910(9)	P–C(11)	1.856(9)	O(7)–C(7)	1.160(11)	C(16)–C(17)	1.402(16)
Os(2)–C(4)	1.923(11)						

vacuo and the residue separated by t.l.c. (SiO_2) with pentane–chloroform (1 : 1 v/v) as eluant to give two yellow bands. The slower-moving band gave [$Os_3H(CO)_{10}$(*trans*-CH=CHCO-Me)], compound (1), as yellow crystals (0.140 g, 52%) (Found: C, 18.35; H, 0.6. $C_{14}H_6O_{11}Os_3$ requires C, 18.25; H, 0.65%). The faster-moving band gave [$Os_3H(CO)_{10}(CH_2=CCOMe)$], compound (2), as yellow crystals (0.052 g, 19%) (Found: C, 18.2; H, 0.6%).

Reaction of [$Os_3H_2(CO)_{10}$] *with but*-3-*en*-2-*one*. A solution of the dihydrido-complex (0.30 g) and but-3-en-2-one (0.1 cm^3) in heptane (30 cm^3) was warmed to 40—50 °C for 3 min to give a yellow solution. Removal of the solvent *in vacuo* and t.l.c. (SiO_2) of the residue, with dichloromethane–pentane (7 : 3 v/v) as eluant, gave several yellow and red bands. Most of these contained very little material or were mixtures but one main yellow band eluted furthest and gave [$Os_3H(CO)_{10}$-(*cis*-CH=CHCOMe)], compound (3), as a yellow solid (0.109 g, 34%) (Found: C, 18.7; H, 0.7. $C_{14}H_6O_{11}Os_3$ requires C, 18.25; H, 0.65%).

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with but*-3-*en*-2-*one*. A solution of the bis(acetonitrile) complex (0.33 g) and an excess of the ketone (0.5 cm^3) in benzene (50 cm^3) showed no reaction over 2 h at room temperature. The solution was refluxed for 10 min, the solvent removed, and the residue separated by t.l.c. on SiO_2 (pentane–diethyl ether, 19 : 1 v/v, as eluant). The fastest band gave [$Os_3H(CO)_9$(CH=CHCOMe)], compound (4), as a pale yellow solid (0.004 g) while the next (main) band gave [$Os_3H(CO)_{10}$(CH=CHCOMe)], compound (3), as a yellow solid (0.182 g, 56%) which had the same spectra as that formed in the preceding reaction. A further minor band gave

Table 7. Bond angles (°) for compound (8)

Os(2)–Os(1)–Os(3)	60.1(0)	Os(1)–Os(2)–C(5)	81.8(3)	Os(2)–Os(3)–O(10)	80.9(1)	Os(1)–C(1)–O(1)	175.8(8)
Os(2)–Os(1)–P	168.4(1)	Os(1)–Os(2)–C(6)	85.1(3)	Os(2)–Os(3)–C(7)	91.2(3)	Os(1)–C(2)–O(2)	178.4(11)
Os(2)–Os(1)–O(10)	80.5(1)	Os(3)–Os(2)–C(3)	100.6(4)	Os(2)–Os(3)–C(8)	174.0(3)	Os(2)–C(3)–O(3)	170.0(12)
Os(2)–Os(1)–C(1)	95.6(3)	Os(3)–Os(2)–C(4)	157.9(3)	Os(2)–Os(3)–C(9)	89.4(3)	Os(2)–C(4)–O(4)	178.5(10)
Os(2)–Os(1)–C(2)	94.3(3)	Os(3)–Os(2)–C(5)	84.0(3)	O(10)–Os(3)–C(7)	169.6(3)	Os(2)–C(5)–O(5)	178.4(8)
Os(3)–Os(1)–P	108.4(1)	Os(3)–Os(2)–C(6)	84.2(3)	O(10)–Os(3)–C(8)	95.6(4)	Os(2)–C(6)–O(6)	177.5(9)
Os(3)–Os(1)–O(10)	48.6(1)	C(3)–Os(2)–C(4)	101.5(5)	O(10)–Os(3)–C(9)	95.4(4)	Os(3)–C(7)–O(7)	176.0(10)
Os(3)–Os(1)–C(1)	122.7(3)	C(3)–Os(2)–C(5)	95.2(4)	C(7)–Os(3)–C(8)	91.6(5)	Os(3)–C(8)–O(8)	170.8(11)
Os(3)–Os(1)–C(2)	137.1(3)	C(3)–Os(2)–C(6)	95.1(4)	C(7)–Os(3)–C(9)	91.3(4)	Os(3)–C(9)–O(9)	178.9(10)
P–Os(1)–O(10)	93.4(2)	C(4)–Os(2)–C(5)	93.5(4)	C(8)–Os(3)–C(9)	95.8(4)	P–C(12)–C(13)	117.1(8)
P–Os(1)–C(1)	89.1(3)	C(4)–Os(2)–C(6)	94.3(4)	Os(1)–P–C(10)	114.9(4)	P–C(12)–C(17)	120.3(7)
P–Os(1)–C(2)	96.3(3)	C(5)–Os(2)–C(6)	165.6(4)	Os(1)–P–C(11)	113.8(3)	C(13)–C(12)–C(17)	122.3(10)
O(10)–Os(1)–C(1)	171.3(3)	Os(1)–Os(3)–Os(2)	60.5(0)	Os(1)–P–C(12)	114.1(3)	C(12)–C(13)–C(14)	117.2(11)
O(10)–Os(1)–C(2)	96.8(3)	Os(1)–Os(3)–O(10)	49.1(1)	C(10)–P–C(11)	105.6(5)	C(13)–C(14)–C(15)	122.3(13)
C(1)–Os(1)–C(2)	91.3(4)	Os(1)–Os(3)–C(7)	120.9(3)	C(10)–P–C(12)	103.5(5)	C(14)–C(15)–C(16)	121.6(12)
Os(1)–Os(2)–Os(3)	59.4(0)	Os(1)–Os(3)–C(8)	113.6(3)	C(11)–P–C(12)	103.6(4)	C(15)–C(16)–C(17)	119.1(13)
Os(1)–Os(2)–C(3)	160.0(4)	Os(1)–Os(3)–C(9)	133.9(3)	Os(1)–O(10)–Os(3)	82.4(2)	C(12)–C(17)–C(16)	117.4(11)
Os(1)–Os(2)–C(4)	98.5(3)						

[$Os_3H(CO)_{10}(CH_2{=}CCOMe)$], compound (2), as a yellow solid (0.002 g) which was characterised by its i.r. spectrum.

Thermolysis of [$Os_3H(CO)_{10}$(*trans*-CH=CHCOMe)], (1). A solution of compound (1) in octane was heated under reflux. After 10 min the i.r. spectrum of the solution (*ca.* 2 000 cm^{-1}) showed complete conversion into compound (3) together with a little [$Os_3(CO)_{12}$].

Thermolysis of [$Os_3H(CO)_{10}(CH_2{=}CCOMe)$], (2). A similar treatment of compound (2) in refluxing octane led to complete conversion into compound (3) after 7 min.

Thermolysis of [$Os_3H(CO)_{10}$(*cis*-CH=CHCOMe)], (3). A solution of compound (3) (0.109 g) in light petroleum (b.p. 120—160 °C) was heated under reflux for 15 min by which time i.r. absorptions of the starting material were no longer observable. Removal of the solvent *in vacuo* and separation of the residue by t.l.c. (SiO_2; pentane–diethyl ether, 19 : 1 v/v, as eluant) gave a main yellow band which gave [$Os_3H(CO)_9$(*cis*-CH=CHCOMe)], compound (4), as an oil, which could not be crystallised and obtained analytically pure, but was characterised by its i.r. and ^1H n.m.r. spectra.

Reaction of [$Os_3H(CO)_{10}$(*cis*-CH=CHCOMe)], (3), *with carbon tetrachloride.* A solution of compound (3) in CCl_4 in an n.m.r. tube was allowed to stand for 48 h. Over this time the ^1H n.m.r. hydride signal disappeared and a signal due to $CHCl_3$ appeared approximately quantitatively. The product [$Os_3Cl(CO)_{10}$(*cis*-CH=CHCOMe)], compound (5), was isolated as yellow crystals in *ca.* 90% yield (Found: C, 17.4; H, 0.7; Cl, 4.2. $C_{14}H_5ClO_{11}Os_3$ requires C, 17.6; H, 0.5; Cl, 3.7%).

Reaction of [$Os_3H_2(CO)_{10}$] *with pent-3-en-2-one.* A solution of the dihydride (0.100 g) and the pentenone (0.05 cm^3) in cyclohexane was warmed at *ca.* 40 °C for 2 min. Removal of solvent and work-up as above gave [$Os_3H(CO)_{10}(MeC{=}CHCOMe)$], compound (6), as yellow crystals (0.056 g, 51%) from hexane (Found: C, 19.3; H, 0.85. $C_{15}H_8O_{11}Os_3$ requires C, 19.25; H, 0.95%). These crystals were used for the *X*-ray structural determination.

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with pent-3-en-2-one.* A solution of the bis(acetonitrile) complex (0.190 g) and the ketone (0.1 cm^3) in benzene (50 cm^3) was heated under reflux for 7 min by which time the i.r. spectrum indicated complete reaction. Removal of the solvent *in vacuo* and t.l.c. on SiO_2 (hexane–dichloromethane, 4 : 1 v/v, as eluant) gave one major yellow band yielding compound (6) as yellow crystals (0.069 g, 36%) (Found: C, 19.4; H, 1.0%).

Reaction of [$Os_3H_2(CO)_{10}$] *with 4-phenylbut-3-en-2-one.* No reaction was observed between these two reagents after 2 h in refluxing n-heptane. However, a solution of [$Os_3H_2(CO)_{10}$] (0.232 g), the ketone (0.3 g), and diphenylacetylene (0.2 g) in n-heptane (60 cm^3) was allowed to stand at room temperature for 24 h by which time the purple solution had become orange. Reducing the volume of the solution *in vacuo* to 5 cm^3 and cooling to −20 °C gave orange crystals of [$Os_3H(CO)_{10}(PhC{=}CHCOMe)$], compound (7) (0.211 g, 78%), which were washed with methanol and dried (Found: C, 24.6; H, 1.0. $C_{20}H_{10}O_{11}Os_3$ requires C, 24.1; H, 1.0%).

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with but-3-yn-2-one.* The bis(acetonitrile) compound (0.210 g) was treated in chloroform (70 cm^3) with the alkyne (0.025 cm^3) at room temperature for 30 min. Removal of the solvent and t.l.c. of the residue on SiO_2 (hexane–chloroform, 1 : 4 v/v, as eluant) gave many bands. The major yellow band gave [$Os_3(CO)_{10}(CH{=}CCOMe)$] (0.022 g, 11%) as orange crystals, characterised by its ^1H n.m.r. and i.r. spectra.

Reaction of [$Os_3H_2(CO)_9(PMe_2Ph)$] *with but-3-en-2-one.* A solution of the dihydride (0.160 g) and $CH_2{=}CHCOMe$ (0.15 cm^3) in n-heptane was heated under reflux for 10 min. Removal of the solvent *in vacuo* and t.l.c. of the residue SiO_2 [light petroleum (b.p. 40—60 °C)–CH_2Cl_2, 3 : 2 v/v, as eluant] gave one main yellow band which gave [$Os_3H(OH)(CO)_9(PMe_2Ph)$], compound (8), as yellow crystals (0.083 g, 51%) from chloroform–hexane at −20 °C (Found: C, 20.8; H, 1.5. $C_{17}H_{13}O_{10}Os_3P$ requires C, 20.9; H, 1.3%). These crystals were used for the *X*-ray structural determination.

Crystallographic Studies.—Crystal data. Compound (6): $C_{15}H_8O_{11}Os_3$, $M = 934.8$, monoclinic, $a = 17.377(2)$, $b = 14.293(2)$, $c = 16.476(2)$ Å, $\beta = 91.79(3)°$, $U = 4\,090.3$ Å^3, space group $C2/c$, $Z = 8$, $D_c = 3.04$ g cm^{-3}, $F(000) = 3\,312$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 186.7 cm^{-1}.

Compound (8): $C_{17}H_{13}O_{10}Os_3P$, $M = 978.9$, monoclinic, $a = 17.535(2)$, $b = 9.500(1)$, $c = 14.326(2)$ Å, $\beta = 101.86(1)°$, $U = 2\,335.4$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 2.78$ g cm^{-3}, $F(000) = 1\,748$, Mo-K_α radiation, μ(Mo-K_α) = 164.2 cm^{-1}.

Data collection. For both structures, unit-cell parameters and intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω—2θ scan procedure.[18]

For compound (6), 4 786 data ($1.5 \leqslant \theta \leqslant 27°$) were measured of which 4 454 were unique and 2 906 were considered observed [$I \geqslant 1.5\sigma(I)$]. The mounting of the crystal did not allow the measurement of azimuthal ψ scan data for a semi-empirical absorption correction.[19] For compound (8), 5 594 data ($1.5 \leqslant \theta \leqslant 27°$) were measured of which 5 081 were unique and 3 474 were considered observed [$I \geqslant 1.5\sigma(I)$]. A semi-empirical absorption correction using normalised and averaged ψ-scan measurements from three reflections was applied to the data; the maximum and minimum transmission was 99.9 and 38.8%, respectively.

Structure solution and refinement. The heavy-atom method was used to determine the positions of the three Os atoms in both compounds and difference-Fourier syntheses were used to locate the remaining non-hydrogen atoms. After isotropic refinement of all the non-hydrogen atoms, the DIFABS method of absorption correction [20] was applied. Refinement using anisotropic thermal parameters for all atoms failed to reveal the location of any hydrogen atoms in compound (8), and only that of H(13) attached to C(13) in compound (6). The full-matrix least-squares refinement was carried out with unit weights and the final R factor values, $\Sigma|\Delta F|/\Sigma|F_o|$, were 0.034 for compound (6) and 0.041 for compound (8). All computations were made using programs in the Enraf–Nonius SCP package on a DEC PDP 11/34 computer. Final atomic co-ordinates are given in Tables 2 and 5, bond lengths in Tables 3 and 6, and bond angles in Tables 4 and 7, for compounds (6) and (8) respectively.

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