Acid-induced Isomerisations of Osmium and Ruthenium Clusters involving Hydroxide Transfer from Carbon to Metal Atoms. *X*-Ray Crystal Structure of Nonacarbonyl-μ_3-(3,3-diphenylallene-1,1-diyl)-μ-hydrido-μ-hydroxo-triosmium(2 *Os–Os*)

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The complexes $[M_3H(CO)_9(\mu_3\text{-}C{\equiv}CCPh_2OH)]$ (M = Ru or Os) were prepared by reaction of $[M_3(CO)_{12}]$ with $HOCPh_2C{\equiv}CCPh_2OH$ in saturated hydrocarbon at 130 °C for M = Os or in refluxing cyclohexane from M = Ru. In the latter case the yield of cluster is low and there is some 1,1,4,4-tetraphenylbutadiene formed. Treatment of the trinuclear clusters in chloroform with trifluoroacetic acid leads to isomerisation with migration of the OH group from carbon to metal atoms. This was confirmed by an *X*-ray structure determination for the osmium product $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_9(\mu_3\text{-}C{=}C{=}CPh_2)]$. The crystals are monoclinic, space group $P2_1$, a = 10.569(1), b = 20.259(3), c = 12.287(2) Å, β = 95.66(1)°, and Z = 4. The structure was refined to R = 0.0621 for 4 112 observed reflections. There are two independent molecules (A and B) in the unit cell with very closely similar structures. Spectroscopically, an OH group was identified and another hydrogen bound to osmium but neither hydrogen atom was located by *X*-ray diffraction. The OH group bridges two non-bonded osmium atoms separated by 3.374(5) Å in molecule A [3.372(5) Å in B], while the μ-H was deduced to be across the longer Os–Os bond [2.905(5) *versus* 2.861(5) Å for molecule A and 2.902(5) *versus* 2.869(5) Å for molecule B]. The 3,3-diphenylallene-1,1-diyl ligand is bonded through two Os–C σ bonds and a 1,2-η^2-co-ordination to the other osmium atom and is bent about the central atom [145(3)° for molecule A and 144(3)° for B]. The orientation of the phenyl substituents at the non-co-ordinated allene carbon atom agrees with this interpretation of the bonding.

We have been interested in introducing hydroxy- or amino-substituted alkynes into triruthenium and triosmium clusters so that the alkyne is bound to the metal atoms while the hydroxy- or amino-function is free.[1-4] We had in mind various uses for the free function such as linking the cluster to other metal atoms or to metal oxide supports, but firstly we wished to learn what influence the hydroxy- or amino-group and the metal cluster had on each other.

In this paper we describe an acid-induced migration of a non-co-ordinated hydroxy-group from carbon to metal, a reaction which may be regarded as an intramolecular oxidative addition of an alcohol but with a C–O rather than the more usual O–H cleavage.

Results and Discussion

Syntheses.—We have already described how the diol $HOCPh_2C{\equiv}CCPh_2OH$ reacts with $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ according to reaction (i).[1] We used this interesting C–C

$$[M_3(CO)_{12}] + HOCPh_2C_2CPh_2OH \longrightarrow [M_3H(CO)_9(C{\equiv}CCPh_2OH)] + Ph_2CO + 3\,CO \quad \text{(i)}$$

(1) M = Ru
(2) M = Os

cleavage reaction to synthesise the compounds (1) and (2) containing hydroxy-substituted μ_3-alkynyl ligands which are the subject of this paper. The yield of (2) from refluxing hydrocarbon at 130 °C is good (70%) and no other products were identified. In contrast the yield of (1) from refluxing cyclohexane is quite low (10%). Most of the dodecacarbonyltriruthenium converts to an inadequately characterised material, most likely of the type $[Ru_2(CO)_6(alkyne)_2]$, which did not elute on silica. The only other product identified was an organic yellow solid giving a mass spectrum corresponding to a parent molecule $C_{28}H_{22}$ (that is, with two oxygen atoms less than the parent diol). Hydrogen-1 and ^{13}C n.m.r. spectra were used to identify it as $Ph_2C{=}CHCH{=}CPh_2$ [^1H n.m.r. ($CDCl_3$), δ 7.15—7.50 (m, 10 H), δ 6.75 p.p.m. (s, 1 H); ^{13}C n.m.r. ($CDCl_3$), several overlapping doublets and singlets in the range δ 125.4—144.0 p.p.m.]. The simplicity of the ^1H n.m.r. spectrum and the lack of ^{13}C signals above δ 125.4 rule out other structures such as $Ph_2CHC{\equiv}CCHPh_2$. The deoxygenation of $HOCPh_2C{\equiv}CCPh_2OH$ might relate to chemistry occurring in the reactions of related diols, including $HOCH_2C{\equiv}CCH_2OH$, with iron carbonyls to give butatriene complexes such as $[Fe_2(CO)_6(CH_2{=}C{=}C{=}CH_2)]$,[5] although the mechanisms of these deoxygenations are unknown.

On adding two drops of trifluoroacetic acid to a solution of $[Os_3H(CO)_9(C{\equiv}CCPh_2OH)]$ (2), in $CDCl_3$ in an n.m.r. tube, the almost colourless solution became immediately bright orange. In spite of this very distinct colour change there was no immediate change in the ^1H n.m.r. spectrum, but the hydride signal at δ −23.55 disappeared over about 15 min with the associated growth of a new signal at δ −11.26 (Table 1). A similar treatment of the ruthenium complex (1) with CF_3CO_2H gave related changes in the ^1H n.m.r. spectrum. There were also qualitatively similar changes in both cases in

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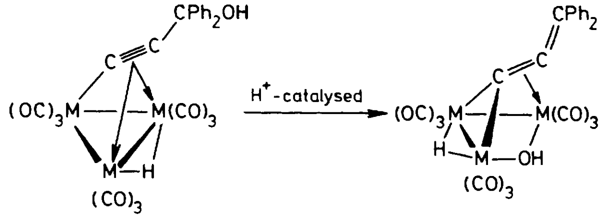
Supplementary data available (No. SUP 23320; 25 pp.); observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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

Compound	ν(CO) (cyclohexane)/cm^{-1}	^1H n.m.r. ($CDCl_3$) δ/p.p.m.	Assignment
(1) $[Ru_3H(CO)_9(C{\equiv}CCPh_2OH)]$	2 101m, 2 076vs, 2 056vs, 2 026s, 1 990m	7.8m 7.3m 2.9s −20.8s	4 H } Ph$_2$ 6 H } Ph$_2$ OH RuH
(2) $[Os_3H(CO)_9(C{\equiv}CCPh_2OH)]$	2 103w, 2 078s, 2 054vs, 2 023s, 2 018m, 1 986 (sh), 1 982m, 1 949vw	7.77m 7.34m 2.72s −23.55s	4 H } Ph$_2$ 6 H } Ph$_2$ OH OsH
(3) $[Ru_3H(OH)(CO)_9(C{=}C{=}CPh_2)]$ [a]		7.5m −11.27s	Ph$_2$ RuH
(4) $[Os_3H(OH)(CO)_9(C{=}C{=}CPh_2)]$ [b]	2 104w, 2 085s, 2 062s, 2 027s, 2 016 (sh), 2 014s, 2 008s, 1 988w	7.48m −11.26s	Ph$_2$ OsH

[a] Not isolated but observed by ^1H n.m.r. in $CDCl_3$ and characterised by comparison with data for compound (4). [b] ν(OH) at 3 618 cm^{-1} (Nujol).



(1) M = Ru (3) M = Ru

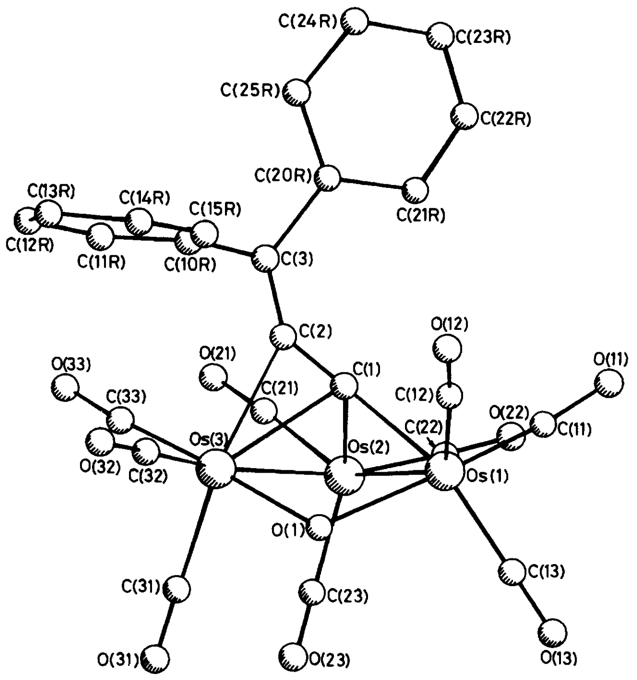
(2) M = Os (4) M = Os

the phenyl region of the spectrum (δ 7—8). We will show that the new clusters formed are compounds (3) and (4), but only in the case of osmium could we isolate this new complex by removing the solvent and chromatography of the residue on silica. This particular treatment decomposed the ruthenium complex.

On the basis of analytical data, complex (4) is isomeric with (2) and although no ^1H n.m.r. signal could be assigned to an OH group its presence was inferred from an ν(OH) absorption at 3 618 cm^{-1} (Nujol mull). We considered the possibility of an OH transfer from the 3-position to the 1- or 2-positions of the ligand or even to the metal atoms but, thinking that no spectroscopic evidence would establish this point adequately, a single-crystal *X*-ray structure determination for (4) was carried out.

The structure confirms that compound (4) is isomeric with compound (2) and that the hydroxy-group is no longer attached to the 3-position of the ligand (the 3-carbon atom is now planar) but is bridging two osmium atoms. There are two independent molecules A and B of compound (4) in the unit cell, both with very similar overall structure and bond lengths and angles. We presume that the minor differences observed are due to packing effects. In the following discussion, data are given for molecule A with those for B in parentheses. Selected bond lengths and angles for the two molecules are given in Tables 2 and 3 respectively; a diagram of molecule A is given in the Figure.

Each of the three non-equivalent osmium atoms is bound to three terminal CO groups of which one is best regarded as axial and the other two equatorial. There are two clearly detected bridging groups, a μ_3-Ph_2C_3 ligand and an oxygen atom bridging Os(1) and Os(3) out of the Os_3 plane opposite the hydrocarbon bridge. Hydrogen atoms were not located but their positions may be inferred. Apart from those of the C_6H_5 groups, one hydrogen atom is bound to osmium atoms and the other to oxygen (^1H n.m.r. and i.r. spectral evidence). The hydroxo-bridge is approximately symmetrical, having Os–O distances of 2.14 (2.13) and 2.07 (2.16) Å. The distance between the osmium atoms linked by the hydroxy group is 3.374 (3.372) Å, much longer than the other two metal–metal distances of 2.905 (2.902) and 2.861 (2.869) Å. In triosmium clusters most Os–Os bond lengths are in the range 2.8—3.0 Å with lengths at the upper end of this range usually found only for hydrogen-bridged Os–Os contacts. We believe therefore that there is no direct Os(1)–Os(3) bond. If the complex contains a four-electron-donor hydrocarbon bridge, a three-electron-donor hydroxy-bridge, and a one-electron-donor hydride, then a naive application of the 18-electron rule would require only two Os–Os bonds consistent with our observations. Other carbonyl clusters with hydroxy-bridges are



Molecular structure of $[Os_3H(OH)(CO)_9(C{=}C{=}CPh_2)]$ (4), showing the atom numbering

Table 2. Selected bond lengths (Å)

Molecule A		Molecule B	
Os(1)–Os(2)	2.905(5)	Os(5)–Os(6)	2.902(5)
Os(1)–Os(3)	3.374(5)	Os(4)–Os(6)	3.372(5)
Os(2)–Os(3)	2.861(5)	Os(4)–Os(5)	2.869(5)
Os(1)–C(1)	2.15(4)	Os(6)–C(4)	2.08(3)
Os(2)–C(1)	2.07(3)	Os(5)–C(4)	2.04(3)
Os(3)–C(1)	2.33(3)	Os(4)–C(4)	2.33(3)
Os(3)–C(2)	2.22(3)	Os(4)–C(5)	2.21(3)
C(1)–C(2)	1.32(5)	C(4)–C(5)	1.38(4)
C(2)–C(3)	1.32(5)	C(5)–C(6)	1.36(4)
Os(1)–O(1)	2.14(2)	Os(6)–O(2)	2.13(2)
Os(3)–O(1)	2.07(2)	Os(4)–O(2)	2.16(2)
Os–C(carbonyl) (average)	1.88(1)		1.92(1)

Table 3. Selected bond angles (°)

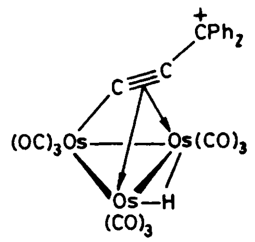
Molecule A		Molecule B	
Os(3)–Os(1)–Os(2)	53.6(1)	Os(4)–Os(6)–Os(5)	53.8(1)
Os(3)–Os(2)–Os(1)	71.6(1)	Os(4)–Os(5)–Os(6)	71.5(1)
Os(2)–Os(3)–Os(1)	54.8(1)	Os(5)–Os(4)–Os(6)	54.7(1)
Os(3)–O(1)–Os(1)	106(1)	Os(4)–O(2)–Os(6)	104(1)
Os(2)–C(1)–Os(1)	87(1)	Os(5)–C(4)–Os(6)	90(1)
Os(3)–C(1)–Os(1)	98(1)	Os(4)–C(4)–Os(6)	100(1)
Os(3)–C(1)–Os(2)	81(1)	Os(4)–C(4)–Os(5)	82(1)
C(3)–C(2)–C(1)	145(3)	C(6)–C(5)–C(4)	144(3)
C(20R)–C(3)–C(10R)	118(3)	C(40R)–C(6)–C(30R)	119(3)

known. $[Ru_4(OH)(C{=}CHPr^i)(PPh_2)(CO)_{10}]$ contains a μ_3-OH capping a metal–metal bonded triangle,[6] while a closer analogue to compound (4) is $[Os_4H_4(OH)(CO)_{12}]^+$ which contains an OH group bridging the two 'wing tips' of a butterfly-type Os_4 structure.[7] In this cation the non-bonded osmium atoms are rather further apart than in $[Os_3H(OH)(CO)_9(C{=}C{=}CPh_2)]$ [3.537 compared with 3.374 (3.372) Å] and the Os–O–Os angle is correspondingly larger.

The hydride ligand was not located but certainly bridges Os(1) and Os(2) [Os(5) and Os(6)] which have a longer metal–metal bond length than Os(2) and Os(3) [Os(4) and Os(5)]. Furthermore, there is a clear expansion of the Os–Os–C(carbonyl) angles at Os(1)–Os(2) [Os(5)–Os(6)] to accommodate the bridging hydride. Larger angles of this sort are associated with the axial carbonyl ligands at Os(1) and Os(2), 117 and 122° (119 and 125°), compared with those for the equatorial carbonyl ligands at these metal atoms, 98 and 96° (100 and 95°). We believe therefore that the hydride is close to the intersection of the C(21)–Os(2) and C(12)–Os(1) directions and is well out of the Os_3 plane on the side of the axial CO ligands.

The arrangement of the novel μ_3-Ph_2C_3 ligand is of most interest. It is bound to the metal atoms only through C(1) and C(2) [C(4) and C(5)]. The σ bonds linking C(1) to Os(1) and Os(2) are shorter than the C–Os distances in the η^2-link between Os(3) and C(1) and C(2), 2.04 and 2.08 (2.07 and 2.15) Å compared with 2.33 and 2.21 (2.33 and 2.22) Å. This is consistent with the allene-1,1-diyl description with bonding of the organic ligand to the cluster very similar to that in the vinylidene complex $[Os_3H_2(CO)_9(C{=}CH_2)]$.[8] The angle of bend may be compared with those of simple mononuclear η^2-allene complexes which are found in the range 142—158°.[9] Examples are $[Fe(C_5H_5)(CO)_2(Me_2C{=}C{=}CMe_2)][BF_4]$, 146°;[10] $[Rh(MeCOCHCOMe)(Me_2C{=}C{=}CMe_2)_2]$, 149, 147°;[11] $[Pt_2Cl_4(Me_2C{=}C{=}CMe_2)_2]$, 151°.[10] In polynuclear complexes both double bonds may be co-ordinated as in $[Ru_3H(CO)_9(EtC{=}C{=}CHMe)]$ (142° bend)[12] or in $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4(CH_2{=}C{=}CH_2)]$ (146° bend).[13] In compound (4), the C(3)-C(10R)C(20R) plane through the non-co-ordinated allene atom C(3) is perpendicular to the Os_3 plane as required for $p\pi$–$p\pi$ bonding between C(2) and C(3). The planes of the C_6 rings are almost perpendicular to each other and the parallel arrangement of the C(10) to C(15) ring with respect to the Os_3 plane seems necessary to prevent a clash with the equatorial CO ligands.

Transfer for hydrogen atoms from organic ligands to ruthenium or osmium atoms in clusters is very common but the transfer of other groups such as hydroxide has not been reported. Solutions of the osmium complex (2) are almost colourless and the deep orange colour instantly generated on addition of trifluoroacetic acid to a chloroform solution must be of an intensely coloured species in low concentrations since there is no immediate change in the ^1H n.m.r. spectrum. We believe that this coloured species is the carbocation (5) which is brightly coloured like other phenyl-substituted carbocations. A small rotation of the Ph_2C_3 ligand would allow the positive charge to be localised at the metal atoms as in (6) but then the cluster is unsaturated and nucleophilic addition of water would give (4). Since the introduction of a bridging OH^- group provides four electrons to the cluster, one Os–Os bond is cleaved.



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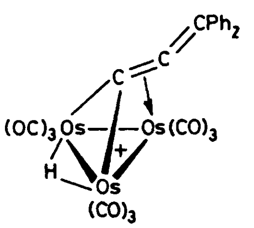

(6)

Experimental

Reaction of $HOCPh_2C{\equiv}CCPh_2OH$ *with* $[Ru_3(CO)_{12}]$.—A solution of the metal carbonyl (0.5 g) and the diol (0.2 g) in cyclohexane was heated at reflux under nitrogen for 8 h. The solvent was removed from the brown solution and the residue separated by t.l.c. on SiO_2, eluting with light petroleum (b.p. 40—60 °C)–diethyl ether (9 : 1 v/v). Some unreacted $[Ru_3(CO)_{12}]$ eluted first followed by a yellow band which gave 1,1,4,4-tetraphenylbutadiene (0.05 g). A very broad band below this gave a brown material which was recrystallised to give $[Ru_3H(CO)_9(C{\equiv}CCPh_2OH)]$ (1), as pale yellow crystals (0.05 g). The remaining material on the baseline was very poorly soluble in chloroform and probably contains dinuclear complexes but these were not characterised.

Reaction of $HOCPh_2C{\equiv}CCPh_2OH$ *with* $[Os_3(CO)_{12}]$.—A solution of the metal carbonyl (0.208 g) and the diol (0.094 g, 1.06 mol per mol Os_3) in light petroleum (b.p. 120—160 °C) was refluxed under nitrogen for 6.5 h. The solution on cooling and standing deposited unreacted $[Os_3(CO)_{12}]$ (0.069 g) as yellow crystals. The solvent was removed from the brown solution and the residue was separated by t.l.c. (SiO_2), eluting with n-pentane–toluene (6 : 4 v/v) to give several bands, most of which contained little material. One main band gave $[Os_3H(CO)_9(C{\equiv}CCPh_2OH)]$ (2), as off-white crystals (0.113 g, 72%

Table 4. Atom co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	1 400(1)	231(1)	−973(1)	Os(4)	2 960(1)	3 790(1)	5 354(1)
Os(2)	882(1)	0	1 274(1)	Os(5)	5 082(1)	3 228(1)	6 671(1)
Os(3)	−1 073(1)	−622(1)	−144(1)	Os(6)	5 491(1)	3 061(1)	4 386(1)
C(1)	1 140(31)	−636(18)	−6(19)	C(4)	5 167(24)	3 858(12)	5 385(20)
C(2)	658(23)	−1 209(17)	−353(23)	C(5)	4 564(28)	4 443(12)	5 071(31)
C(3)	912(26)	−1 789(16)	−771(21)	C(6)	4 758(26)	5 071(13)	4 729(20)
C(11)	3 032(47)	316(32)	−682(33)	C(41)	1 852(33)	3 118(17)	5 916(33)
C(12)	1 640(35)	−292(29)	−2 184(28)	C(42)	1 742(23)	4 184(13)	4 228(33)
C(13)	1 258(30)	1 085(17)	−1 619(26)	C(43)	2 611(33)	4 375(18)	6 468(28)
C(21)	698(31)	−663(19)	2 307(28)	C(51)	6 742(46)	2 994(25)	7 344(41)
C(22)	2 447(31)	295(19)	1 970(27)	C(52)	4 905(34)	3 876(17)	7 714(27)
C(23)	−193(42)	653(18)	1 932(28)	C(53)	4 311(37)	2 515(19)	7 425(26)
C(31)	−2 309(31)	13(14)	341(24)	C(61)	7 205(44)	3 041(26)	4 637(23)
C(32)	−2 135(28)	−1 064(16)	−1 260(23)	C(62)	5 580(28)	3 647(22)	3 123(31)
C(33)	−1 575(35)	−1 250(16)	791(24)	C(63)	5 458(30)	2 212(16)	3 608(26)
C(10R)	−63(31)	−2 232(17)	−1 297(30)	C(30R)	6 072(28)	5 341(20)	4 748(23)
C(11R)	−894(33)	−2 564(16)	−690(31)	C(31R)	7 157(35)	4 939(22)	5 118(30)
C(12R)	−1 842(39)	−2 973(17)	−1 273(48)	C(32R)	8 312(38)	5 217(23)	5 164(29)
C(13R)	−1 883(52)	−2 997(18)	−2 423(44)	C(33R)	8 515(54)	5 881(23)	4 878(38)
C(14R)	−1 033(40)	−2 633(18)	−2 954(34)	C(34R)	7 432(58)	6 293(26)	4 587(40)
C(15R)	−172(41)	−2 274(18)	−2 430(28)	C(35R)	6 243(36)	6 024(18)	4 544(28)
C(20R)	2 301(35)	−2 048(18)	−613(27)	C(40R)	3 658(40)	5 495(15)	4 287(40)
C(21R)	3 378(33)	−1 615(19)	−279(27)	C(41R)	3 019(49)	5 823(17)	5 177(47)
C(22R)	4 527(40)	−1 889(32)	−227(34)	C(42R)	2 000(68)	6 268(38)	4 456(108)
C(23R)	4 814(43)	−2 492(34)	−363(36)	C(43R)	1 819(107)	6 447(27)	3 254(143)
C(24R)	3 810(51)	−2 929(31)	−583(54)	C(44R)	2 527(57)	6 069(33)	2 781(47)
C(25R)	2 539(39)	−2 719(25)	−708(40)	C(45R)	3 521(41)	5 622(19)	3 113(38)
O(1)	−615(19)	93(12)	−1 246(16)	O(2)	3 470(20)	3 070(10)	4 173(18)
O(11)	4 233(25)	337(22)	−385(27)	O(41)	1 184(24)	2 740(12)	6 174(22)
O(12)	1 752(28)	−638(19)	−2 903(23)	O(42)	1 097(26)	4 477(17)	3 694(22)
O(13)	1 182(33)	1 604(17)	−1 940(30)	O(43)	2 347(29)	4 756(13)	7 133(22)
O(21)	568(32)	−1 030(17)	3 026(25)	O(51)	7 770(30)	2 866(21)	7 801(26)
O(22)	3 480(25)	443(13)	2 318(20)	O(52)	4 779(32)	4 283(14)	8 392(20)
O(23)	−771(26)	1 013(13)	2 363(23)	O(53)	3 827(29)	2 101(17)	7 849(23)
O(31)	−3 006(26)	384(16)	579(27)	O(61)	8 373(25)	3 048(19)	4 823(30)
O(32)	−2 825(23)	−1 338(16)	−1 939(23)	O(62)	5 592(28)	4 011(15)	2 458(22)
O(33)	−1 749(29)	−1 624(14)	1 545(24)	O(63)	5 405(31)	1 727(14)	3 126(23)

based on osmium carbonyl reacted) (Found: C, 27.9; H, 1.3. $C_{24}H_{12}O_{10}Os_3$ requires C, 27.95; H, 1.15%).

Treatment of $[Os_3H(CO)_9(C{\equiv}CCPh_2OH)]$ *with Trifluoroacetic Acid.*—On adding CF_3CO_2H (0.2 cm^3) to a solution of compound (2) (0.069 g) in chloroform (5 cm^3) the colour changed instantly from very pale yellow to orange-red. After 15 min at room temperature the solvent was removed under vacuum and the residue separated by t.l.c. (SiO_2), eluting with pentane–diethyl ether (1 : 1 v/v) to give a pale yellow band which was discarded followed by a bright yellow band which gave $[Os_3H(OH)(CO)_9(C{=}C{=}CPh_2)]$, (4), as an oil giving good orange crystals (0.033 g) from hexane (Found: C, 28.15; H, 1.45. $C_{24}H_{12}O_{10}Os_3$ requires C, 27.95; H, 1.15%).

X-*Ray Crystal Structure Determination.*—*Crystal data.* $C_{24}H_{12}O_{10}Os_3$, $M = 1\,030.69$, Monoclinic, $a = 10.569(1)$, $b = 20.259(3)$, $c = 12.287(2)$ Å, $\beta = 95.66(1)°$, space group $P2_1$, $Z = 4$, $D_c = 2.61$ g cm^{-3}, $U = 2\,617.89$ Å^3, $F(000) = 1\,856$, $\mu(\text{Mo-}K_\alpha) = 248.28$ cm^{-1}.

Data collection. This was carried out as in ref. 14 using a CAD4 diffractometer, $\omega/2\theta$ scan, ω scan width $= 0.85 + 0.35 \tan\theta$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $1.5 \leqslant \theta \leqslant 25°$, h, k, $\pm l$, max. measuring time = 60 s, crystal size 0.48 × 0.25 × 0.11 mm, faces $\{1\,0\,\bar{1}\}$, $\{0\,1\,0\}$, $\{1\,0\,1\}$, total data measured 5 155, unique 4 719, observed 4 112 $[I > 1.5\sigma(I)]$, absorption correction applied.

Structure solution and refinement. The heavy-atom method was used, with full-matrix least squares, with the weighting scheme $w = 1/[\sigma^2(F) + 0.0011_9(F_o)^2]$; $R = 0.0621$, $R' = 0.0613$. Programs, computers, and scattering factors were as in ref. 14. Atom co-ordinates are given in Table 4.

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