Decarboxylation of Vinylene Carbonate at Triosmium Clusters; *X*-Ray Crystal Structure of the μ_3-Formylmethylidene Compound $[Os_3(CHCHO)(CO)_{10}]$ †

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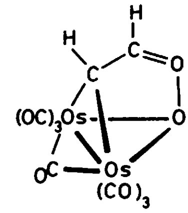
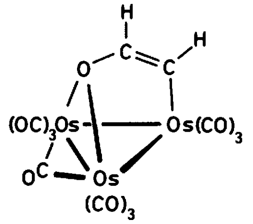
Vinylene carbonate $\overline{OCH{=}CHOCO}$ reacts at room temperature with $[Os_3H_2(CO)_{10}]$ to give a good yield of the vinyloxy cluster $[Os_3H(OCH{=}CH_2)(CO)_{10}]$ (**1**). A similar decarboxylation occurs on reaction with $[Os_3(CO)_{10}(MeCN)_2]$ to give the formylmethylidene cluster $[Os_3(\mu_3\text{-}CHCHO)(\mu\text{-}CO)(CO)_9]$ (**2**). The single-crystal *X*-ray structure of (**2**) is closely related to those of $[Os_3(\mu\text{-}CHR)(\mu\text{-}CO)(CO)_{10}]$ (R = H or $SiMe_3$) with two osmium atoms bridged both by CO and an alkylidene group. In (**2**) this group is part of a four-electron-donating μ_3 bridge. Hydrogenation of (**2**) or decarbonylation of (**1**) leads to the formylmethylidene compound $[Os_3H_2(CHCHO)(CO)_9]$ (**3**).

In a related study we have examined the reactions of ketene ($CH_2{=}C{=}O$) with triosmium clusters and found that it reacts with $[Os_3(CO)_{10}(MeCN)_2]$ by C=C cleavage to give $[Os_3(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_{10}]$,[1] a compound also synthesised by successive treatment of $[Os_3(CO)_{12}]$ with a source of hydride then proton,[2,3] or by reacting $[Os_3(CO)_{11}(MeCN)]$ with CH_2N_2.[4,5] A by-product of our reaction of ketene with the bis(acetonitrile) compound was the allene compound $[Os_3(CO)_{11}(C_3H_4)]$, previously reported to be formed directly from allene and $[Os_3(CO)_{11}(MeCN)]$.[5] In trying to establish the origin of allene in our synthesis we examined various reactions between ketene or its precursor diketene, $CH_2{=}\overline{COCOC}H_2$, with triosmium clusters. We concluded, not unexpectedly, that allene as an impurity in the ketene generated on cracking diketene is the source of the allene complex, but in one experiment we showed that diketene reacts with $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing benzene (much below the diketene cracking temperature of 550 °C) to give a low yield of $[Os_3(CO)_{11}(C_3H_4)]$ (18%) by decarboxylation of diketene. This led us to explore the use of lactones and related cyclic species that might, by decarboxylation, give small organic fragments as ligands in triosmium clusters. Most lactones we used required high temperatures for reaction with $[Os_3(CO)_{10}(MeCN)_2]$ or $[Os_3H_2(CO)_{10}]$ and gave no products in reasonable yield. However, the related cyclic carbonate, vinylene carbonate $\overline{OCH{=}CHOCO}$, reacted smoothly at room temperature with these triosmium clusters to give good yields of decarboxylation products, the subject of this paper and a previous communication.[1] Unfortunately this is not a reaction of general value since ethylene carbonate $\overline{OCH_2CH_2OCO}$ or *o*-phenylene carbonate $\overline{OC_6H_4OCO}$ do not react under these mild conditions and reaction of the latter compound with $[Os_3H_2(CO)_{10}]$ or $[Os_3(CO)_{10}(MeCN)_2]$ gave only $[Os_3(CO)_{12}]$ in refluxing octane. This is particularly surprising because the product of decarboxylation of *o*-phenylene carbonate would be the cyclohexadienonediyl ligand C_6H_4O which we have previously identified as a ligand in a product from the high-temperature reaction of phenol and $[Os_3(CO)_{12}]$,[6,7] *i.e.*, the product would be stable if the decarboxylation had occurred.



(**2a**)



(**2b**)

Results and Discussion

Vinylene carbonate in excess reacts with a dichloromethane solution of $[Os_3H_2(CO)_{10}]$ at room temperature to give a good yield (76%) of the vinyloxy species $[Os_3H(OCH{=}CH_2)(CO)_{10}]$ (**1**). This compound was previously obtained in lower yield (40%) by reaction of ketene with the dihydride cluster.[8,9] The dihydride $[Os_3H_2(CO)_{10}]$ is known to co-ordinate to alkenes which insert reversibly into the Os–H bond, and a similar addition and insertion also seems likely for vinylene carbonate since its saturated form $\overline{OCH_2CH_2OCO}$ does not react at all under these conditions. Insertion would give the σ-bonded compound $[Os_3H(\overline{OCHCH_2OCO})(CO)_{10}]$ which subsequently undergoes ring opening with C–O bond cleavage followed by decarboxylation to give cluster (**1**).

The reaction of vinylene carbonate with $[Os_3(CO)_{10}(MeCN)_2]$ under mild conditions (refluxing dichloromethane) gives a moderate yield (56%) of the red complex $[Os_3(C_2H_2O)(CO)_{10}]$ (**2**). The compound has a bridging CO ligand [ν(CO) 1 863 cm^{-1}] and might reasonably be formulated either as $[Os_3(\mu\text{-}CHCH{=}O)(\mu\text{-}CO)(CO)_9]$ (**2a**) or its valence tautomer $[Os_3(\mu\text{-}OCH{=}CH)(\mu\text{-}CO)(CO)_9]$ (**2b**). Certain spectroscopic details (see Table 1) supported (**2a**): ν(CO) for the co-ordinated formyl group at 1 500 cm^{-1} and a ^1H n.m.r. doublet at δ 10.68 for the formyl group. The value of J_{HH} of 4 Hz seems too low for the formulation (**2b**).

A single-crystal *X*-ray structure determination of compound (**2**) confirms the formulation (**2a**) (Figure 1). Selected bond lengths and angles are given in Table 2. There is a molecular but not crystallographic mirror plane through the μ_3-ligand atoms C(11), C(12), O(11), and Os(3) and the μ-carbonyl ligand C(10)O(10). The metal–metal distances not associated with the

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† 1,2-μ-carbonyl-1,1,1,2,2,2,3,3,3-nonacarbonyl-μ_3-formylmethylidene-*C*(Os^{1,2})*O*(Os^3)-*triangulo*-triosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Spectroscopic data for compounds (**2**) and (**3**)

Compound	$\nu(CO)^a/cm^{-1}$	^1H N.m.r.^{b}	
		δ	J_{HH}
(**2**) $[Os_3(CHCHO)(CO)_{10}]$	2 102w, 2 059s, 2 020m, 2 006w, 1 988w, 1 863w, 1 500vw	10.68(d) 3.43(d)	4.0
(**3**) $[Os_3H_2(CHCHO)(CO)_9]$	2 112m, 2 084s, 2 056s, 2 027s, 2 014ms, 2 002s, 1 983ms, 1 953vw, 1 500s	11.59(d) 4.39(d) −12.55(d) −14.42(d)	4.0 2.0

^{a} In cyclohexane. ^{b} Recorded at 200 MHz at room temperature in $CDCl_3$; J in Hz.

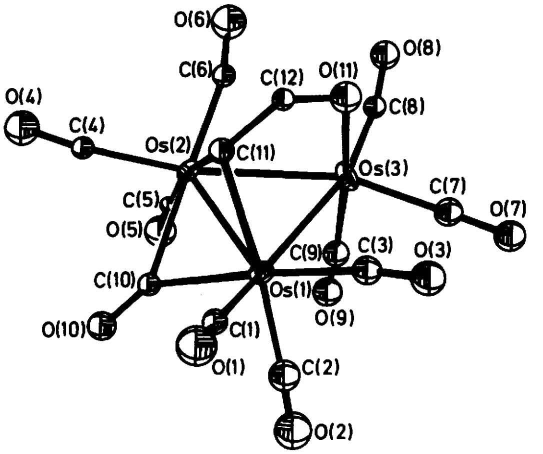


Figure 1. Molecular structure of $[Os_3(\mu_3\text{-}CHCHO)(\mu\text{-}CO)(CO)_9]$ (**2**)

μ-CO bridge are similar [Os(1)–Os(3) 2.818(1) and Os(2)–Os(3) 2.810(1) Å] and longer than the double-bridged osmium–osmium bond [Os(1)–Os(2) 2.725(1) Å]. The atoms Os(1) and Os(2) are bridged by single carbon atoms and the shorter distance between them is probably necessary to accommodate these smaller first-row atoms. The formylmethylidene ligand shows a typical methylidene-type bridge between Os(1) and Os(2) with a distorted tetrahedral geometry at C(11). The C(12)–O(11) distance of 1.254(15) Å is consistent with a double bond but the short C(11)–C(12) distance of 1.338(17) Å implies multiple bonding. This may be a consequence of the necessarily small Os(1)–C(11)–Os(2) angle of 74.9(4)° and the state of hybridisation at C(11) which allows p_π–p_π bonding between this atom and the formyl group.

Table 2. Selected bond distances (Å) and angles (°) for the cluster $[Os_3(\mu_3\text{-}CHCHO)(\mu\text{-}CO)(CO)_9]$ (**2**)

Os(1)–Os(2)	2.725(1)	Os(2)–C(5)	1.856(10)
Os(1)–Os(3)	2.818(1)	Os(2)–C(6)	1.904(13)
Os(1)–C(1)	1.985(12)	Os(2)–C(10)	2.259(12)
Os(1)–C(2)	1.973(16)	Os(2)–C(11)	2.262(14)
Os(1)–C(3)	1.951(14)	Os(3)–C(7)	1.941(13)
Os(1)–C(10)	2.091(12)	Os(3)–C(8)	1.768(14)
Os(1)–C(11)	2.222(14)	Os(3)–C(9)	1.967(17)
Os(2)–Os(3)	2.810(1)	Os(3)–O(11)	2.176(11)
Os(2)–C(4)	1.918(10)		

Os(2)–Os(1)–Os(3)	60.9(0)	C(5)–Os(2)–C(6)	96.3(5)
Os(2)–Os(1)–C(1)	124.7(3)	C(5)–Os(2)–C(10)	89.6(5)
Os(2)–Os(1)–C(2)	117.9(4)	C(5)–Os(2)–C(11)	167.8(5)
Os(2)–Os(1)–C(3)	131.4(4)	C(6)–Os(2)–C(10)	173.9(5)
Os(2)–Os(1)–C(10)	54.0(3)	C(6)–Os(2)–C(11)	93.9(5)
Os(2)–Os(1)–C(11)	53.2(4)	C(10)–Os(2)–C(11)	80.1(5)
Os(3)–Os(1)–C(1)	158.1(4)	Os(1)–Os(3)–Os(2)	57.9(1)
Os(3)–Os(1)–C(2)	102.2(4)	Os(1)–Os(3)–C(6)	93.6(3)
Os(3)–Os(1)–C(3)	76.2(4)	Os(1)–Os(3)–C(7)	99.2(4)
Os(3)–Os(1)–C(10)	109.9(3)	Os(1)–Os(3)–C(8)	165.3(4)
Os(3)–Os(1)–C(11)	76.0(4)	Os(1)–Os(3)–C(9)	88.2(4)
C(1)–Os(1)–C(2)	93.1(6)	Os(1)–Os(3)–O(11)	81.6(3)
C(1)–Os(1)–C(3)	87.9(5)	Os(2)–Os(3)–C(6)	39.0(3)
C(1)–Os(1)–C(10)	86.1(5)	Os(2)–Os(3)–C(7)	157.1(4)
C(1)–Os(1)–C(11)	91.2(5)	Os(2)–Os(3)–C(8)	108.1(4)
C(2)–Os(1)–C(3)	91.3(6)	Os(2)–Os(3)–C(9)	88.8(4)
C(2)–Os(1)–C(10)	87.5(6)	Os(2)–Os(3)–O(11)	85.2(3)
C(2)–Os(1)–C(11)	170.9(6)	C(6)–Os(3)–C(7)	160.4(5)
C(3)–Os(1)–C(10)	173.8(5)	C(6)–Os(3)–C(8)	71.7(5)
C(3)–Os(1)–C(11)	96.9(5)	C(6)–Os(3)–C(9)	106.4(5)
C(10)–Os(1)–C(11)	84.8(5)	C(6)–Os(3)–O(11)	73.8(4)
Os(1)–Os(2)–Os(3)	61.2(0)	C(7)–Os(3)–C(8)	94.8(6)
Os(1)–Os(2)–C(4)	118.2(4)	C(7)–Os(3)–C(9)	88.9(6)
Os(1)–Os(2)–C(5)	116.2(3)	C(7)–Os(3)–O(11)	93.4(5)
Os(1)–Os(2)–C(6)	126.9(4)	C(8)–Os(3)–C(9)	96.2(6)
Os(1)–Os(2)–C(10)	48.5(3)	C(8)–Os(3)–O(11)	93.6(5)
Os(1)–Os(2)–C(11)	51.9(4)	C(9)–Os(3)–O(11)	169.7(6)
Os(3)–Os(2)–C(4)	165.8(3)	Os(1)–C(10)–Os(2)	77.5(4)
Os(3)–Os(2)–C(5)	101.2(3)	Os(1)–C(10)–O(10)	144.9(11)
Os(3)–Os(2)–C(6)	72.6(4)	Os(2)–C(10)–O(10)	135.7(10)
Os(3)–Os(2)–C(10)	105.2(3)	Os(1)–C(11)–Os(2)	74.9(4)
Os(3)–Os(2)–C(11)	75.6(3)	Os(1)–C(11)–C(12)	112.7(9)
C(4)–Os(2)–C(5)	91.6(5)	Os(2)–C(11)–C(12)	114.4(10)
C(4)–Os(2)–C(6)	100.3(5)	C(11)–C(12)–O(11)	128.4(13)
C(4)–Os(2)–C(10)	80.6(5)	Os(3)–O(11)–C(12)	114.7(9)
C(4)–Os(2)–C(11)	93.0(5)		

Compound (**2**) is an isomer of $[Os_3(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_{10}]$ and has a rather similar structure.[10] Since the CH_2 complex shows a disordered distribution of μ-CH_2 and μ-CO ligands, a better comparison of structures is made with $[Os_3(\mu\text{-}CHSiMe_3)(\mu\text{-}CO)(CO)_{10}]$ (Figure 2).[11] The CHCHO and CH_2 complexes are formally related by a CO ligand in $[Os_3(CH_2)(CO)_{11}]$ inserting into a C–H bond. This is a hypothetical transformation since we have no evidence for their interconversion; at high temperatures each converts to different compounds by decarbonylation so there is evidence that they do not interconvert up to their decomposition temperatures. The main geometric differences are apparent from the dihedral angles between the Os_2C and Os_3 planes given in Figure 2. In cluster (**2**) co-ordination of the formyl group to Os(3) pulls the methylidene carbon so that the Os(1)Os(2)C(11) and Os(1)Os(2)Os(3) planes are at 94.0°, compared with 66.9° in the $CHSiMe_3$ compound. In the methylidene complex the $CHSiMe_3$ and CO ligands are very similarly disposed with respect to the metal atoms; the structure is closely related to that of $[Fe_3(CO)_{12}]$. The structural differences seen in Figure 2 are also apparent in the CO positions. As C(11) in cluster (**2**) is pulled away from the metal plane, the bridging and terminal CO ligands relocate relative to the corresponding positions in the

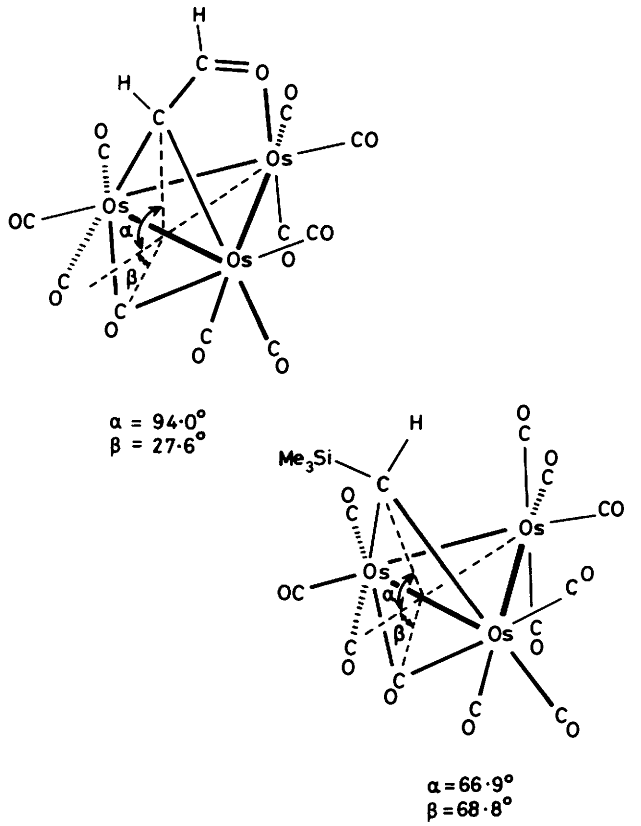


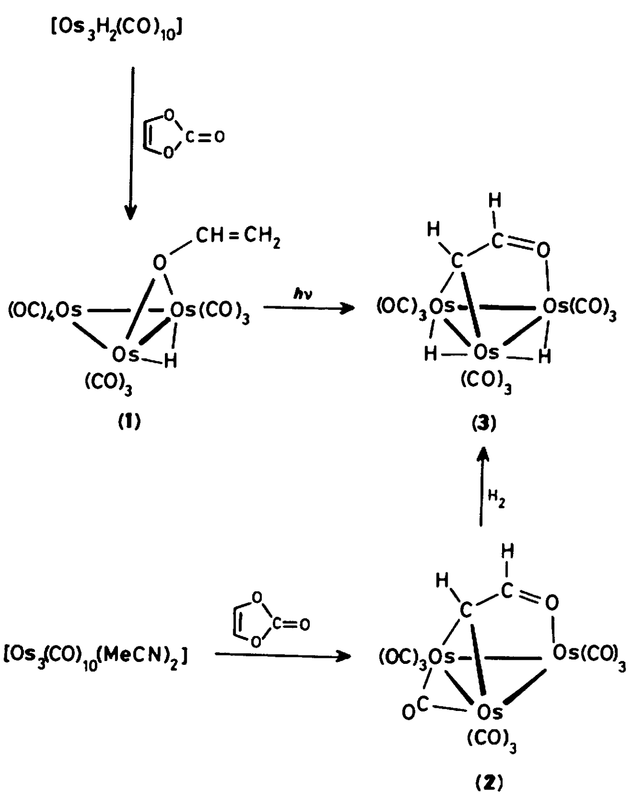
Figure 2. A comparison of the structures of compound (2) and $[Os_3(\mu\text{-}CHSiMe_3)(\mu\text{-}CO)(CO)_{10}]^{11}$ showing their similarities, but also the dihedral angles between the Os_3 plane and the Os_2C planes associated with the bridging ligands

$CHSiMe_3$ compound so as to maintain octahedral geometries at the metal atoms, if one ignores the Os(1)–Os(2) vector which should not be considered as a metal–ligand direction. Thus the μ-CO ligand is more closely in the metal plane in (2) and the terminal ligands more clearly either axial or equatorial in this compound relative to the $CHSiMe_3$ compound.

Hydrogenation of cluster (2) in refluxing octane gave the known dihydride $[Os_3H_2(\mu_3\text{-}CHCHO)(CO)_9]$ (3) (56%),[1,9] and the same dihydride is obtained in lower yield (18%) simply by heating compound (2) in refluxing octane in the absence of hydrogen. Compound (3) is also obtained (42%) by u.v. photolysis of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (1) at room temperature. We have previously reported that thermolysis of (1) in refluxing cyclohexane gave substantial amounts of $[Os_3H_3(\mu_3\text{-}CH)(CO)_9]$ but only traces of compound (3) (3.5%).[9] The formation of the CH compound presumably requires conversion of the $\mu\text{-}OCH{=}CH_2$ cluster into its $\mu\text{-}CH_3CO$ isomer and this is achieved thermally, whereas photolysis leads to CO dissociation and metallation at the β site of the vinyl group. Compound (3) is very similar spectroscopically, and presumably structurally, to the phenol derivative $[Os_3H_2(\mu_3\text{-}C_6H_4O)(CO)_9]$ which is known to contain the closely related cyclohexadienonediyl ligand.[6,7] The formation of compounds (1)—(3) is summarised in the Scheme.

Experimental

Vinylene carbonate (Aldrich) was used without purification. Hydrogen-1 n.m.r. spectra were recorded on a Varian XL200 spectrometer and i.r. spectra on a Perkin-Elmer 983 spectrometer. The complexes $[Os_3H_2(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ were prepared as reported previously.[12,13]



Scheme.

Preparation of $[Os_3H(OCH{=}CH_2)(CO)_{10}]$ (1).—A solution of vinylene carbonate (0.20 g) and $[Os_3H_2(CO)_{10}]$ (0.201 g) in dichloromethane (50 cm^3) turned from purple to orange-yellow over 24 h. The solvent was removed under vacuum and the solid residue purified by thin-layer chromatography (t.l.c.) [SiO_2; light petroleum (b.p. 30—40 °C)–diethyl ether; 10:3, v/v] to give the product as yellow crystals (0.160 g, 76%) (Found: C, 16.5; H, 0.55. $C_{12}H_4O_{11}Os_3$ requires C, 16.1; H, 0.45%).

Preparation of $[Os_3(CHCHO)(CO)_{10}]$ (2).—A solution of vinylene carbonate (0.25 g) and freshly prepared $[Os_3(CO)_{10}(MeCN)_2]$ (0.326 g) in dichloromethane (75 cm^3) was heated under reflux for 14 h, by which time the yellow solution had become red. The solvent was removed under reduced pressure and the red-orange solid residue purified by t.l.c. [SiO_2; light petroleum (b.p. 30—40 °C)] to give a deep yellow band which yielded red crystals of $[Os_3(CHCHO)(CO)_{10}]$ (2) (0.183 g, 56%) (Found: C, 16.5; H, 0.3. $C_{12}H_2O_{11}Os_3$ requires C, 16.2; H, 0.25%).

Hydrogenation of Compound (2).—Hydrogen was bubbled through a solution of compound (2) (0.126 g) in refluxing octane (40 cm^3) for 2 h. The deep yellow solution turned paler and the i.r. spectrum showed significant change. The solvent was removed under reduced pressure to give a pale yellow solid which was purified by t.l.c. [SiO_2; light petroleum (b.p. 30—40 °C)–dichloromethane, 5:1, v/v] to give $[Os_3H_2(CHCHO)(CO)_9]$ (3) as a pale yellow solid (0.070 g, 56%) (Found: C, 15.8; H, 0.6. $C_{11}H_4O_{10}Os_3$ requires C, 15.2; H, 0.45%).

Photolysis of Compound (1).—U.v. photolysis with a medium-pressure mercury lamp of a solution of compound (1) (0.098 g)

Table 3. Fractional atomic co-ordinates for the cluster $[Os_3(\mu_3\text{-}CHCHO)(\mu\text{-}CO)(CO)_9]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.853 56(5)	0.243 09(9)	0.126	C(1)	0.872(2)	0.299(2)	0.260(2)
Os(2)	0.879 95(5)	0.348 50(7)	−0.046 3(1)	C(2)	0.758(2)	0.210(3)	0.157(3)
Os(3)	0.874 60(6)	0.125 85(7)	−0.049 4(2)	C(3)	0.883(2)	0.104(3)	0.173(3)
O(1)	0.891(2)	−0.181(3)	−0.160(3)	C(4)	0.907(1)	0.494(2)	−0.038(3)
O(2)	0.704(2)	0.196(3)	0.172(3)	C(5)	0.805(1)	0.383(2)	−0.124(2)
O(3)	0.896(2)	0.028(2)	0.214(2)	C(6)	0.936(2)	0.302(3)	−0.153(2)
O(4)	1.074(1)	0.423(2)	−0.039(3)	C(7)	0.861(2)	−0.016(3)	0.003(3)
O(5)	0.755(2)	0.400(2)	−0.166(2)	C(8)	0.897(2)	0.083(3)	−0.170(3)
O(6)	0.967(2)	0.296(3)	−0.221(3)	C(9)	0.777(2)	0.135(3)	−0.075(3)
O(7)	0.851(1)	−0.099(2)	0.031(2)	C(10)	0.822(2)	0.397(2)	0.091(2)
O(8)	0.919(1)	0.066(2)	−0.256(2)	C(11)	0.954(2)	0.297(3)	0.072(3)
O(9)	0.777(1)	−0.354(2)	−0.089(2)	C(12)	0.995(1)	0.217(2)	0.046(2)
O(10)	0.714(1)	−0.038(2)	0.111(2)	O(11)	0.979(1)	0.133(2)	0.001(2)

in cyclohexane (100 cm^3) for 2.5 h at room temperature under nitrogen gave complete reaction; no compound (**1**) remained (i.r. evidence). Removal of solvent gave a pale brown residue which gave, on t.l.c. work-up as above, pale yellow crystals of $[Os_3H_2(CHCHO)(CO)_9]$ (**3**) (0.041 g, 42%).

X-Ray Crystal-structure Determination for $[Os_3(\mu_3\text{-}CHCHO)(\mu\text{-}CO)(CO)_9]$ (**2**).—All *X*-ray measurements were made on a crystal of dimensions 0.1 × 0.27 × 0.35 mm sealed in a thin-walled glass capillary using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation and procedures previously described in detail.[14]

Crystal data. $C_{12}H_2O_{11}Os_3$, $M = 892.74$, orthorhombic, $a = 19.714(16)$, $b = 12.610(24)$, $c = 13.488(11)$ Å, $U = 3\,354(12)$ Å^3, space group *Aba*2, $Z = 8$, $D_c = 3.54$ g cm^{-3}, μ(Mo-K_α) = 227.7 cm^{-1}, $F(000) = 3\,120$.

Data collection. Using ω–2θ scan mode, ω scan width 0.80 + 0.35tanθ, $1.5 \leqslant \theta \leqslant 30°$, 2 706 reflections measured, 1 782 observed $[I > 1.5\sigma(I)]$. The data were corrected for absorption empirically.[15]

Structure solution. The structure was solved by direct methods and developed and refined by standard Fourier and full-matrix least-squares methods. An additional absorption correction was made using DIFABS[16] at the isotropic stage. Only the Os atoms were eventually refined anisotropically since problems of non-positive definiteness were met when attempts were made to refine the lighter atoms anisotropically. Unit weights were used. The final values of *R* and *R′* were 0.046 and 0.053 respectively. All calculations were made using programs in the Enraf-Nonius SDP package. Final atomic co-ordinates are given in Table 3.

Acknowledgements

We thank the S.E.R.C. for support of the *X*-ray work and for a postdoctoral research assistantship (to A. J. A.).

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Received 17th September 1986; *Paper* 6/1842