Chelation of Vinyl Acetate and Related Unsaturated Ketones: Molecular Structure of $[Os_3(CO)_{10}(CH_2{=}CHOCOMe)]$†

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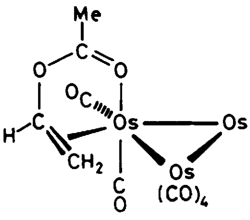
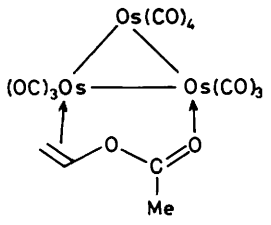
The cluster $[Os_3H_2(CO)_{10}]$ reacts with neat vinyl acetate at room temperature to give complexes $[Os_3H(CH{=}CH_2)(CO)_{10}]$ (5%) and $[Os_3(CO)_{10}(CH_2{=}CHOCOMe)]$ (**1**) (43%). Complex (**1**) has also been obtained (30%) from $[Os_3(CO)_{10}(MeCN)_2]$. The *X*-ray crystal structure of complex (**1**) has been determined. Crystals are monoclinic, space group $P2_1/n$, with a = 17.218(3), b = 13.407(3), c = 8.597(3) Å, β = 93.67(4)°, and Z = 4; the structure has been refined to R = 0.0565 for 2 562 observed reflections. The structure is related to that of $[Os_3(CO)_{12}]$ but with two carbonyl ligands at one osmium atom being replaced by a chelating vinyl acetate. The ester group is co-ordinated axially [ν(CO) 1 622 cm^{-1}] and the η^2-vinyl group equatorially. The triosmium cluster $[Os_3(CO)_{10}(CH_2{=}CMeCH_2COMe)]$ [ν(CO) 1 642 cm^{-1}] obtained from 4-methylpent-3-en-2-one and $[Os_3(CO)_{10}(MeCH{=}CHCH_2COMe)]$ [ν(CO) 1 640 cm^{-1}] obtained from hex-5-en-2-one have been shown by their i.r. and ^{1}H n.m.r. spectra to be isostructural with complex (**1**).

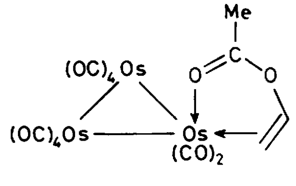
We have been interested in the chemistry of organic carbonyl compounds with triosmium clusters[1–7] and have reported[7] that the unsaturated ketones RCH=CHCOMe (R = H, Me, or Ph) undergo metallation at the β position on reaction with $[Os_3(CO)_{10}(MeCN)_2]$ to give $[Os_3H(RC{=}CHCOMe)(CO)_{10}]$ which adopts an open Os_3 chain when R = H but an approximately equilateral Os_3 triangle when R = Me or Ph. Although the vinyl group is activated in these reactions, there is co-ordination of the ketonic group in each case. We now report some reactions of unsaturated carbonyl compounds (esters and ketones) for which cyclometallation at the β site to give five-membered rings is not possible. Again we find that the carbonyl group is co-ordinated whenever possible and report the formation and the first *X*-ray structure determination of a chelating vinyl acetate complex.



(1)



(A)



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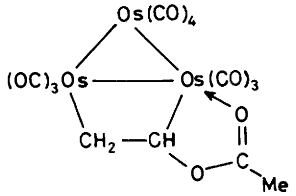

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Results and Discussion

The hydrido-cluster $[Os_3H_2(CO)_{10}]$ reacts in vinyl acetate as solvent at room temperature to give the yellow crystalline compound $[Os_3(CO)_{10}(CH_2{=}CHOCOMe)]$ (1) as the major product (43%) after chromatography. A very low yield of the known vinyl compound $[Os_3H(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$[8,9] is also obtained. This compound is also formed from the reaction of $[Os_3H_2(CO)_{10}]$ with ethylene, ethane being the other product;[8,10] in the reaction the initial insertion compound $[Os_3H(CH_2CH_3)(CO)_{10}]$ reacts with more ethylene to displace ethane and to give $[Os_3H(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ by oxidative addition.

Presumably ethyl acetate is a by-product of the reaction with vinyl acetate but we have not confirmed this; great care would be needed to establish the formation of a few milligrams of ethyl acetate in 10 cm^3 of vinyl acetate. The remarkable observation is that oxidative addition of vinyl acetate to give $[Os_3H(\mu\text{-}\eta^2\text{-}CH{=}CHOCOMe)(CO)_{10}]$ does not occur. The vinyl acetate ligand stabilises compound (1) by acting as a four-electron donor. The low i.r. frequency for the ester function (1 622 cm^{-1}) confirms that it is co-ordinated. The vinyl resonances in the ^{1}H n.m.r. spectrum (Table 1) do not clearly establish its mode of bonding; the three signals at δ 6.30, 2.35, and 1.65 confirm that the vinyl group is co-ordinated but the three coupling constants are all *ca.* 6 Hz which is unexpected for a vinyl group. We could

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† 1,1,1,1,2,2,2,2,3,3-Decacarbonyl-3-(η^2-3′-oxapent-4′-en-2′-one-$C^{4',5'}$,*O*)-*triangulo*-triosmium.

Supplementary data available (No. SUP 56519, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. I.r. and ^{1}H n.m.r. data for compounds (**1**)—(**4**)

Compound	ν(CO)^a/cm^{-1}			^{1}H N.m.r.^{b} (δ)	
(**1**) $[Os_3(CO)_{10}(CH_2{}^{w,x}{=}CH^yOCOMe^z)]$	2 109w, 2 022 (sh), 1 985w, 1 622w	2 058m, 2 005m, 1 977w,	2 025s, 1 991w, 1 943vw,	1.65 (t) (w), 6.30 (t) (y), J_{wx} 6.3, J_{xy} 5.4	2.35 (dd) (x), 2.09 (s) (z), J_{wy} 5.7,
(**2**) $[Os_3(CO)_{10}(CH_2{}^{u,v}{=}CMe^wCH_2{}^{x,y}COMe^z)]$	2 102w, 2 013m, 1 978w, 1 642w	2 052m, 1 999m, 1 971w,	2 020s, 1 985w, 1 934w,	1.58 (d) (u), 2.23 (s) (w), 3.76 (d) (y), J_{uv} 3.2,	2.92 (d) (v), 3.11 (d) (x), 2.28 (s) (z),^{c} J_{xy} 21.6
(**3**) $[Os_3(CO)_{10}(Me^uCH^v{=}CH^wCH_2{}^{x,y}COMe^z)]$	2 102w, 2 013m, 1 969w,	2 052m, 2 000m, 1 936w,	2 021s, 1 981w, 1 640w	2.02 (d) (u), 3.35 (dd) (w), 3.01 (dd) (y), J_{uv} 5.8, J_{wy} 5.7,	2.20 (dq) (v), 3.81 (d) (x), 2.32 (s) (z), J_{vw} 9.4, J_{xy} 20.8
(**4**) $[Os_3H^z(CH^u{=}CH^vCH_2{}^wCH_2{}^xCOMe^y)(CO)_{10}]$	2 103w, 2 020vs, 1 992m, 1 954vw,	2 058s, 2 010s, 1 984w, 1 726w	2 050s, 2 000w, 1 978w,	7.10 (dd) (u), 2.19 (dt) (w), 2.18 (s) (y), J_{uv} 13.7, J_{vw} 6.2,	4.29 (dt) (v), 2.68 (t) (x), −18.96 (t) (z), J_{uz} 1.6, J_{wx} 7.2

^{a} Recorded in cyclohexane. ^{b} Recorded in $CDCl_3$ at 200 MHz at 20 °C; *J* values in Hz. ^{c} This absorption was absent from a sample of (**2**) prepared from $Me_2C{=}CHCOCD_3$; other signals unchanged.

Table 2. Fractional atomic co-ordinates for $[Os_3(CO)_{10}(CH_2{=}CHOCOMe)]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.080 91(5)	0.193 82(7)	0.329 60(11)	C(14)	−0.002 3(13)	0.134 9(23)	0.425 7(30)
Os(2)	0.002 56(5)	0.244 17(6)	0.034 64(11)	O(14)	−0.051 8(14)	0.098 0(16)	0.485 7(31)
Os(3)	0.163 00(5)	0.290 18(6)	0.095 53(11)	C(21)	−0.018 5(14)	0.373 4(18)	0.114 8(28)
O(1)	0.197 9(8)	0.144 8(11)	0.009 7(18)	O(21)	−0.037 2(11)	0.453 8(13)	0.155 5(26)
O(2)	0.308 3(10)	0.227 9(12)	−0.037 0(28)	C(22)	0.039 3(12)	0.120 5(16)	−0.058 8(27)
C(1)	0.262 3(8)	0.136 0(12)	−0.044 7(28)	O(22)	0.056 3(11)	0.051 8(13)	−0.125 8(24)
C(2)	0.298 5(17)	0.048 7(17)	−0.112 1(34)	C(23)	−0.026 0(12)	0.292 5(18)	−0.165 3(26)
C(3)	0.286 6(14)	0.291 0(18)	0.067 2(27)	O(23)	−0.044 6(13)	0.312 9(15)	−0.292 2(26)
C(4)	0.270 9(17)	0.276 4(24)	0.239 0(29)	C(24)	−0.090 0(14)	0.189 1(19)	0.096 0(30)
C(11)	0.058 3(16)	0.328 7(19)	0.401 5(29)	O(24)	−0.148 5(11)	0.153 5(14)	0.132 9(29)
O(11)	0.046 5(13)	0.404 2(14)	0.453 6(24)	C(31)	0.150 1(15)	0.416 4(24)	0.161 1(28)
C(12)	0.108 2(15)	0.065 5(19)	0.237 8(28)	O(31)	0.147 7(14)	0.500 6(12)	0.200 2(27)
O(12)	0.126 3(12)	−0.010 6(12)	0.195 1(25)	C(32)	0.151 2(17)	0.330 9(19)	−0.120 5(32)
C(13)	0.161 5(20)	0.182 2(29)	0.487 1(30)	O(32)	0.142 3(16)	0.358 2(17)	−0.242 4(31)
O(13)	0.209 1(19)	0.167 7(23)	0.577 8(30)				

Table 3. Bond lengths (Å) for $[Os_3(CO)_{10}(CH_2{=}CHOCOMe)]$ (**1**)

Os(1)–Os(2)	2.875(1)	Os(1)–Os(3)	2.843(1)	O(1)–C(1)	1.236(1)	O(2)–C(1)	1.464(1)
Os(1)–C(11)	1.96(3)	Os(1)–C(12)	1.96(3)	O(2)–C(3)	1.304(1)	C(1)–C(2)	1.463(1)
Os(1)–C(13)	1.88(3)	Os(1)–C(14)	1.873(23)	C(3)–C(4)	1.531(1)	C(11)–O(11)	1.13(3)
Os(2)–Os(3)	2.846(1)	Os(2)–C(21)	1.909(24)	C(12)–O(12)	1.14(3)	C(13)–O(13)	1.11(3)
Os(2)–C(22)	1.965(22)	Os(2)–C(23)	1.873(21)	C(14)–O(14)	1.14(3)	C(21)–O(21)	1.18(3)
Os(2)–C(24)	1.864(25)	Os(3)–O(1)	2.182(14)	C(22)–O(22)	1.134(25)	C(23)–O(23)	1.15(3)
Os(3)–C(3)	2.158(22)	Os(3)–C(4)	2.17(3)	C(24)–O(24)	1.18(3)	C(31)–O(31)	1.18(3)
Os(3)–C(31)	1.80(3)	Os(3)–C(32)	1.93(3)	C(32)–O(32)	1.11(3)		

not discriminate between bonding modes with bridging vinyl acetate (**A**), chelating ligand (**B**), or some other mode of bonding such as (**C**) which would have analogies in compounds of type $[Os_3(CO)_8(\mu\text{-}\sigma,\sigma\text{-alkanediyl})]$.[11]

A single-crystal *X*-ray structure determination has resolved the problem. The molecular structure of compound (**1**) is shown in Figure 1. The atomic co-ordinates are in Table 2 while bond lengths and selected angles are given in Tables 3 and 4 respectively. The structure of (**1**) relates directly to that of $[Os_3(CO)_{12}]$[12] except that the chelating vinyl acetate has replaced two CO ligands at Os(3). The η^2-vinyl group occupies an equatorial position with the C–C bond lying slightly out of the Os_3 plane on the same side as the rest of the ligand [deviations: C(3) −0.66 and C(4) −0.20 Å].

There are only a few cases of η^2-alkene Os_3 clusters because of a strong tendency to undergo oxidative addition and it is interesting that the ester co-ordination in (**1**) is sufficiently robust to prevent this happening. The structure of $[Os_3(CO)_{11}(C_2H_4)]$ has not been determined,[13] but in $[Os_3H(SMe)(CO)_9(C_2H_4)]$[14] and $[Os_3Br(CF_3CH{=}CHCF_3)(CO)_{10}]^-$ and related fluorocarbon compounds[15] the alkene ligands lie approximately in the Os_3 plane. The alkene co-ordination in (**1**) is symmetrical, with Os(3)–C(3) and Os(3)–C(4) bond lengths of 2.16(3) and 2.17(3) Å respectively.

Table 4. Bond angles (°) for [$Os_3(CO)_{10}(CH_2$=CHOCOMe)] (**1**)

Os(3)–Os(1)–Os(2)	59.7(1)	C(11)–Os(1)–Os(2)	88.3(8)	C(4)–Os(3)–Os(1)	90.3(6)	C(4)–Os(3)–Os(2)	150.6(6)
C(11)–Os(1)–Os(3)	85.5(7)	C(12)–Os(1)–Os(2)	87.8(7)	C(4)–Os(3)–O(1)	82.6(9)	C(4)–Os(3)–C(3)	41.4(4)
C(12)–Os(1)–Os(3)	88.3(6)	C(12)–Os(1)–C(11)	173.8(9)	C(31)–Os(3)–Os(1)	97.4(7)	C(31)–Os(3)–Os(2)	97.1(8)
C(13)–Os(1)–Os(2)	159(1)	C(13)–Os(1)–Os(3)	100(1)	C(31)–Os(3)–O(1)	170.7(8)	C(31)–Os(3)–C(3)	100(1)
C(13)–Os(1)–C(11)	90(1)	C(13)–Os(1)–C(12)	92(1)	C(31)–Os(3)–C(4)	91(1)	C(32)–Os(3)–Os(1)	141.4(9)
C(14)–Os(1)–Os(2)	99.2(8)	C(14)–Os(1)–Os(3)	158.9(8)	C(32)–Os(3)–Os(2)	81.0(9)	C(32)–Os(3)–O(1)	86.7(8)
C(14)–Os(1)–C(11)	94(1)	C(14)–Os(1)–C(12)	91(1)	C(32)–Os(3)–C(3)	86(1)	C(32)–Os(3)–C(4)	127(1)
C(14)–Os(1)–C(13)	101(1)	Os(3)–Os(2)–Os(1)	59.6(1)	C(32)–Os(3)–C(31)	92(1)	C(1)–O(1)–Os(3)	119(1)
C(21)–Os(2)–Os(1)	89.1(8)	C(21)–Os(2)–Os(3)	86.6(7)	C(3)–O(2)–C(1)	114(2)	O(2)–C(1)–O(1)	113(1)
C(22)–Os(2)–Os(1)	91.0(6)	C(22)–Os(2)–Os(3)	85.6(6)	C(2)–C(1)–O(1)	130(2)	C(2)–C(1)–O(2)	117(2)
C(22)–Os(2)–C(21)	171.0(9)	C(23)–Os(2)–Os(1)	166.3(7)	O(2)–C(3)–Os(3)	114(2)	C(4)–C(3)–Os(3)	70(1)
C(23)–Os(2)–Os(3)	106.8(6)	C(23)–Os(2)–C(21)	88(1)	C(4)–C(3)–O(2)	131(3)	C(3)–C(4)–Os(3)	69(1)
C(23)–Os(2)–C(22)	89(1)	C(24)–Os(2)–Os(1)	91.1(8)	O(11)–C(11)–Os(1)	175(2)	O(12)–C(12)–Os(1)	175(2)
C(24)–Os(2)–Os(3)	150.6(8)	C(24)–Os(2)–C(21)	94(1)	O(13)–C(13)–Os(1)	175(4)	O(14)–C(14)–Os(1)	179(3)
C(24)–Os(2)–C(22)	95(1)	C(24)–Os(2)–C(23)	103(1)	O(21)–C(21)–Os(2)	174(2)	O(22)–C(22)–Os(2)	173(2)
Os(2)–Os(3)–Os(1)	60.7(1)	O(1)–Os(3)–Os(1)	89.6(4)	O(23)–C(23)–Os(2)	173(2)	O(24)–C(24)–Os(2)	179(2)
O(1)–Os(3)–Os(2)	91.7(4)	C(3)–Os(3)–Os(1)	128.4(8)	O(31)–C(31)–Os(3)	174(2)	O(32)–C(32)–Os(3)	176(2)
C(3)–Os(3)–Os(2)	158.9(5)	C(3)–Os(3)–O(1)	70.8(6)				

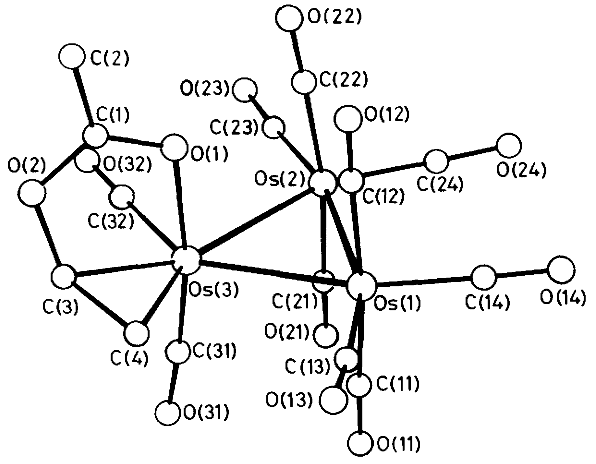
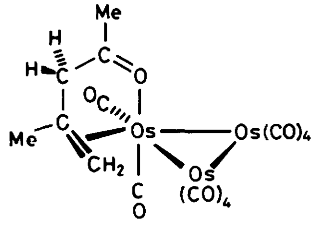


Figure 1. Molecular structure of [$Os_3(CO)_{10}(CH_2$=CHOCOMe)] (**1**)

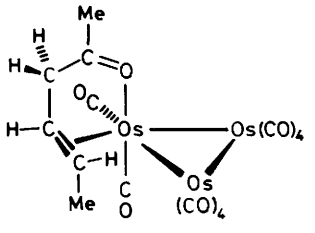
In contrast, the alkene in the vinyl alcohol and vinyl ether complexes [PtCl(acac)(CH_2=CHOH)] (acac = acetylacetonate)[16] and [$PtCl_2(PhCHMeNH_2)(CH_2$=$CHOCHMeCMe_3$)][17] respectively are unsymmetrically bonded with the terminal carbon atom closer to the metal atom.

In the reported structure of [$Os_3(CO)_{12}$] the axial Os–CO bond lengths [mean 1.946(6) Å] are longer than the equatorial [mean 1.912(7) Å].[12] This difference, which may be explained by the mutual competition of the *trans* carbonyl ligands for available metal π-electron density, is also noticeable for the $Os(CO)_4$ units in the molecule of (**1**). Within these units the axial Os–CO lengths [mean 1.948(25) Å] are significantly longer than the equatorial ones [mean 1.873(23) Å]. It is consistent with this behaviour that the Os–CO bond in (**1**) which is *trans* to the ester oxygen atom, Os(3)–C(31) 1.80(3) Å, is the shortest in the structure even though it is in an axial position. There is no π-acceptor ligand *trans* to it.

The structure of compound (**1**) suggests that there should be stable mononuclear compounds of type [$M(CO)_3(CH_2$=CHOCOMe)] (M = Fe, Ru, or Os) or of type [$M(CO)_4(CH_2$=CHOCOMe)] (M = Cr, Mo, or W), for example, with chelating vinyl acetate but none of these has been reported. In fact we have been unable to find any examples of authentic stable vinyl acetate complexes except perhaps [Ni(bipy)(CH_2=CHOCOMe)] (bipy = 2,2′-bipyridine).[18]



(**2**)



(**3**)

We have also synthesised two Os_3 derivatives of unsaturated ketones which are directly related to compound (**1**). Interaction of 4-methylpent-3-en-2-one (Me_2C=CHCOMe) with [$Os_3(CO)_{10}(MeCN)_2$] at room temperature gave the cluster [$Os_3(CO)_{10}(CH_2$=$CMeCH_2COMe$)] (**2**) as yellow microcrystals (15%). The same compound was obtained in variable, sometimes better, yield from reaction with [$Os_3H_2(CO)_{10}$] or [$Os_3(CO)_{10}$(*cis*-H_2C=CHCH=CH_2)] at elevated temperatures. The cluster [$Os_3(CO)_{10}(MeCN)_2$] also reacts with hex-5-en-2-one (CH_2=$CHCH_2CH_2COMe$) at room temperature to give two isolable products in this case. The major one, [$Os_3H(\mu$-η^2-CH=$CHCH_2CH_2COMe)(CO)_{10}$] (**4**) (30%), results from oxidative addition but the minor one, [$Os_3(CO)_{10}$(MeCH=$CHCH_2COMe$)] (**3**) (5%), directly relates to compound (**2**). The i.r. spectra of compounds (**2**) and (**3**) around 2 000 cm^{-1} are so close to that of compound (**1**) that the three must be isostructural (Figure 2). The ^1H n.m.r. spectra of compounds (**2**) and (**3**) (Table 1) unambiguously support the structures given and carbonyl absorptions at 1 642 and 1 640 cm^{-1} respectively confirm that these groups are co-ordinated. It is interesting that, even though compounds (**2**) and (**3**) are formed under conditions allowing double-bond migration, the less stable β,γ-unsaturated ketones are stabilised in the Os_3 clusters, rather than the conjugated α,β-unsaturated carbonyl ligands which are found to be η^4-co-ordinated in mononuclear compounds such as [$Fe(CO)_3(\eta^4$-PhCH=CHCHO)].[19]

Experimental

Reactions were carried out under nitrogen but chromatographic separations were in air. Vinyl acetate (containing 4 p.p.m. hydroquinone as a stabilizer) (Aldrich), 4-methylpent-3-en-2-one (mesityl oxide) (BDH), and hex-5-en-2-one (Aldrich) were used as purchased.

Reaction of [$Os_3H_2(CO)_{10}$] *with Vinyl Acetate*.—A solution of [$Os_3H_2(CO)_{10}$] (0.10 g) in vinyl acetate (10 cm^3) was stirred

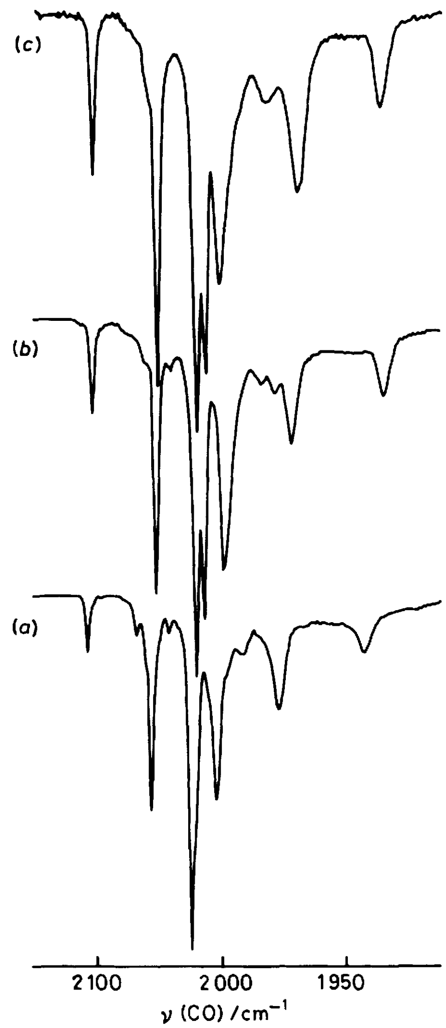


Figure 2. I.r. [ν(CO)] spectra of cyclohexane solutions of (*a*) [$Os_3(CO)_{10}(CH_2$=CHOCOMe)] (**1**), (*b*) [$Os_3(CO)_{10}(CH_2$=CMeCH$_2$COMe)] (**2**), and (*c*) [$Os_3(CO)_{10}$(MeCH=CHCH$_2$COMe)] (**3**)

at ambient temperature for 2.5 h. After removal of solvent, the residue was purified by t.l.c. [SiO_2; eluant: light petroleum (b.p. <40°C)–dichloromethane (10:1 v/v)] to give two yellow bands yielding [$Os_3(CO)_{10}(CH_2$=CHOCOMe)] (**1**) as yellow crystals (0.047 g, 43%) and [Os_3H(CH=CH$_2$)(CO)$_{10}$] as yellow crystals (0.005 g, 5%).

Compound (**1**) was recrystallised by dissolving in a minimum amount of dichloromethane and precipitating with diethyl ether (Found: C, 18.1; H, 0.7. $C_{14}H_6O_{12}Os_3$ requires C, 17.95; H, 0.65%).

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with Vinyl Acetate.*—A solution of [$Os_3(CO)_{10}(MeCN)_2$] (0.15 g) in vinyl acetate (10 cm^3) was stirred at ambient temperature for 5 h. Removal of the solvent and work-up as above gave compound (**1**) as the major product (0.046 g, 30%).

Reaction of [$Os_3H_2(CO)_{10}$] *with 4-Methylpent-3-en-2-one.*—A solution of [$Os_3H_2(CO)_{10}$] (0.20 g) and Me_2C=CHCOMe (0.1 g) in n-octane (20 cm^3) was heated at 100 °C for 3 h. Removal of the solvent under reduced pressure and chromatography of the residue [t.l.c. on SiO_2; eluant: pentane–dichloromethane (1:1 v/v)] gave several bands. The main yellow band yielded [$Os_3(CO)_{10}(CH_2$=CMeCH$_2$COMe)] (**2**) as yellow microcrystals (0.12 g, 54%) (Found: C, 19.9; H, 0.95. $C_{16}H_{10}O_{11}Os_3$ requires C, 20.25; H, 1.05%). The parent molecular ion was observed in the mass spectrum (*m*/*e* 954 based on ^{192}Os). The yields of this reaction are variable, that quoted being the highest obtained.

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with 4-Methylpent-3-en-2-one.*—A solution of [$Os_3(CO)_{10}(MeCN)_2$] (0.20 g) and Me_2C=CHCOMe (0.1 cm^3) in dichloromethane (30 cm^3) was refluxed for 16 h. Work-up by t.l.c. [SiO_2; eluant: light petroleum (b.p. <40 °C)–dichloromethane (10:1 v/v)] gave many unidentified bands. However, the band with the lowest R_f value was characterised as [$Os_3(CO)_{10}(CH_2$=CMeCH$_2$COMe)] (**2**) (0.03 g, 15%).

Reaction of [$Os_3(CO)_{10}$(*cis*-H_2C=CHCH=CH$_2$)] *with 4-Methylpent-3-en-2-one.*—A solution of [$Os_3(CO)_{10}$(*cis*-H_2C=CHCH=CH$_2$)] (0.20 g) and Me_2C=CHCOMe (0.2 cm^3) in cyclohexane (25 cm^3) was refluxed for 8 h. Although some unreacted *cis*-butadiene complex was still present (i.r. evidence), work-up as above gave several bands including some unreacted [$Os_3(CO)_{10}$(*cis*-H_2C=CHCH=CH$_2$)] and some of its isomer [$Os_3(CO)_{10}$(*trans*-H_2C=CHCH=CH$_2$)]. The band closest to the base was identified as compound (**2**) (0.014 g, 7%).

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with Hex-5-en-2-one.*—A solution of [$Os_3(CO)_{10}(MeCN)_2$] (0.16 g) and CH_2=CHCH$_2$CH$_2$COMe (1 cm^3) in dichloromethane (20 cm^3) was kept at room temperature for 8 h. Removal of the solvent and work-up by t.l.c. [SiO_2; eluant: light petroleum (b.p. <40 °C)–dichloromethane (4:1 v/v)] gave two bands. These bands gave yellow crystals which were characterised as [$Os_3(CO)_{10}$(MeCH=CHCH$_2$COMe)] (**3**) (0.008 g, 5%) and [$Os_3H(\mu$-η^2-CH=CHCH$_2$CH$_2$COMe)(CO)$_{10}$] (**4**) (0.049 g, 30%).

Neither compound (**3**) nor compound (**4**) was obtained analytically pure but were characterised by the observation of parent molecular ions in their mass spectra and by data given in Table 1.

X-Ray Structure Determination of [$Os_3(CO)_{10}(CH_2$=CHOCOMe)] (**1**).—*Crystal data.* $C_{14}H_6O_{12}Os_3$, M = 936.70, monoclinic, a = 17.218(3), b = 13.407(3), c = 8.597(3) Å, β = 93.67(4)°, U = 1 980.47 Å^3, space group $P2_1/n$, D_c = 3.14 g cm^{-3}, Z = 4, $F(000)$ = 1 656, μ(Mo-K_α) = 185.03 cm^{-1}.

Data collection. Data were collected on a Philips PW1100 diffractometer using a crystal of dimensions *ca.* 0.13 × 0.11 × 0.09 mm. The method of data collection and absorption correction was similar to that reported previously.[20] A total of 360 azimuthal scan data were used in the absorption correction and the relative transmission factors ranged from 1.0 to 0.481.

Structure solution and refinement.[21] The three osmium atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from subsequent difference-Fourier syntheses. Full-matrix least-squares refinement with anistropic thermal parameters for all non-hydrogen atoms gave final R of 0.0565 and R' of 0.0570 with $w = 1/\sigma^2(F)$ for 2 562 reflections having $I\sigma(I) \geqslant 3.0$.

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References

1 K. A. Azam and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1977, 472.
2 K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *J. Chem. Soc., Chem. Commun.*, 1978, 1086.

3 K. A. Azam, A. J. Deeming, and I. P. Rothwell, *J. Organomet. Chem.*, 1979, **178**, C20.
4 K. A. Azam, A. J. Deeming, and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1981, 91.
5 A. J. Arce and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1982, 364.
6 A. J. Deeming, *J. Mol. Catal.*, 1983, **21**, 25.
7 A. J. Deeming, P. J. Manning, I. P. Rothwell, M. B. Hursthouse, and N. P. C. Walker, *J. Chem. Soc., Dalton Trans.*, 1984, 2039.
8 A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
9 A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Crystallogr., Sect. B*, 1978, **34**, 2466.
10 J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, 1975, **85**, C29.
11 K. M. Motyl, J. R. Norton, C. K. Schauer, and O. P. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 7325; M. R. Burke, J. Takats, F. W. Grevels, and J. G. A. Reuvers, *ibid.*, 1983, **105**, 4092.
12 M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.
13 J. Evans and G. S. McNulty, *J. Chem. Soc., Dalton Trans.*, 1984, 79 and refs. therein.
14 B. F. G. Johnson, J. Lewis, D. Pippard, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1978, 551; *Acta Crystallogr., Sect. B*, 1980, **36**, 703.
15 Z. Dawoodi, M. J. Mays, P. R. Raithby, K. Henrick, W. Clegg, and G. Weber, *J. Organomet. Chem.*, 1983, **249**, 149; M. Laing, P. Sommerville, Z. Dawoodi, M. J. Mays, and P. J. Wheatley, *J. Chem. Soc., Chem. Commun.*, 1978, 1035; Z. Dawoodi, M. J. Mays, and P. R. Raithby, *ibid.*, 1979, 721; Z. Dawoodi, K. Henrick, and M. J. Mays, *ibid.*, 1982, 696; Z. Dawoodi, M. J. Mays, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 1769; Z. Dawoodi and M. J. Mays, *ibid.*, p. 1931.
16 F. A. Cotton, J. N. Francis, B. A. Frenz, and M. Tsutsui, *J. Am. Chem. Soc.*, 1973, **95**, 2483.
17 F. Sartori, L. Leoni, R. Lazzoroni, and P. Salvadori, *J. Chem. Soc., Chem. Commun.*, 1974, 322.
18 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, New York, 1982; T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, 1971, **93**, 3350.
19 A De Cian and R. Weiss, *Acta Crystallogr., Sect. B*, 1972, **28**, 3273.
20 M. K. Cooper, P. A. Duckworth, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1981, 2357.
21 G. M. Sheldrick, SHELX Crystal Structure Solving Package, University of Cambridge, 1976.

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