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Reactions of the isomers methoxyallene and methyl propargyl ether with triosmium and triruthenium clusters: crystal structure of the methoxyallene cluster $[\text{Os}_3(\text{CO})_{11}(\mu, \eta^1, \eta^3\text{-CH}_2\text{CCHOMe})]$

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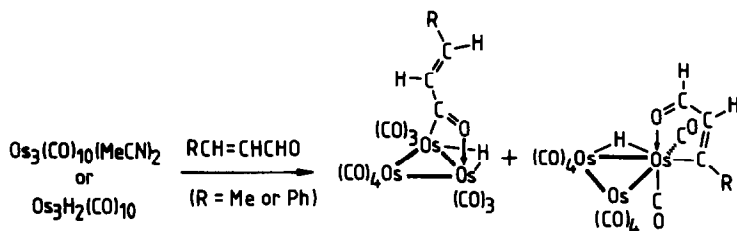
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Abstract

The clusters $[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]$ and $[\text{Ru}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ react with methoxyallene ($\text{CH}_2=\text{C}=\text{CHOMe}$) to give two isomers of $[\text{Os}_3(\text{CO})_{11}(\mu\text{-C}_3\text{H}_3\text{OMe})]$ (**1a** and **1b**) and the dinuclear compounds $[\text{M}_2(\text{CO})_7(\mu\text{-C}_3\text{H}_3\text{OMe})]$ (**2a**, M = Os, and **2b**, M = Ru). The X-ray crystal structure of cluster **1a** shows it to contain a four-electron donating allene bridge which is σ -bonded through the central carbon atom to one Os atom and η^3 -bonded to another. There is no Os–Os bond associated with this bridge and there are only two Os–Os bonds as expected. The MeO group is *syn* in **1a** and we believe that it is *anti* in **1b**. The clusters $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$, $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ and $[\text{Ru}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ react with the isomeric methyl propargyl ether ($\text{CH}\equiv\text{CCH}_2\text{OMe}$) to afford the compounds $[\text{M}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-alkyne})]$ (**3a**, M = Os, and **3b**, M = Ru), $[\text{M}_3\text{H}(\mu_3, \eta^2\text{-C}\equiv\text{CCH}_2\text{OMe})(\text{CO})_9]$ (**4a**, M = Os, and **4b**, M = Ru), $[\text{Os}_3(\text{CO})_9(\text{RCCHCOCH}=\text{CR})]$, **5**, and $[\text{Os}_3(\text{CO})_9\{(\text{RC}_2\text{H})_2\text{CO}\}]$ (**6**, R = CH_2OMe), where the last two are alkyne-coupled products.

Introduction

We have been interested in the coordination and rearrangement of small oxygen-containing organic ligands within trinuclear clusters in view of the importance of oxy-ligands of various sorts in the chemical modification of CO in clusters and on surfaces. Previously we have reported studies on oxy-ligands derived from saturated [1] or unsaturated [2] aldehydes, unsaturated ethers [3], saturated or unsaturated



Scheme 1

ketones [4], unsaturated carboxylic acids [5] and formyl derivatives of heterocycles [6], among others.

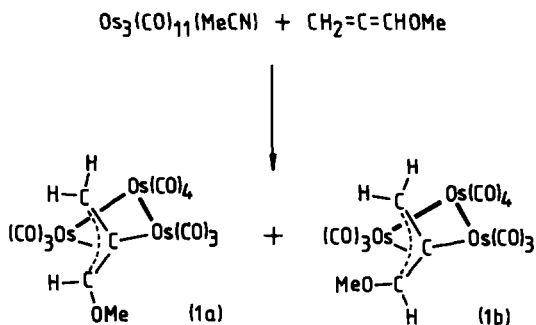
Organic oxy-ligands have been found to coordinate readily through oxygen atoms as part of a chelate ring or within a bridging system in triosmium clusters when this is geometrically favoured or even possible [2,3]. This is typified by unsaturated aldehydes, $\text{RCH}=\text{CHCHO}$, which react with triosmium clusters with competitive oxidative addition with cleavage of a vinylic C–H bond to give compounds of the type $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{RC}=\text{CHCHO})]$ or of the aldehydic C–H bond to give μ -acyl clusters of the type $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{RCH}=\text{CHCO})]$ (Scheme 1) [2]. In both cluster products the oxygen atoms of the organic carbonyl ligand are coordinated even though one could easily envisage alternative structures in which there is an η^2 -coordination though the available C=C bond. In general we have found that oxygen-coordination is a major aspect of this chemistry and plays a role in controlling metallation sites and structures of compounds.

In this paper we describe the synthesis of several triosmium and triruthenium clusters derived from the reactive clusters $[\text{M}_3(\text{CO})_{12-x}(\text{CH}_3\text{CN})_x]$ ($\text{M} = \text{Ru}$ or Os and $x = 1$ or 2) with the isomeric unsaturated ethers, 2-methoxyprop-1-yne (methyl propargyl ether) and 1-methoxypropadiene (methoxyallene). We believed that the alkyne and allene functions would strongly bond to the clusters with the potential of donating four electrons and that might work against oxygen atom coordination, but ligand modifications within the clusters might allow oxygen-coordination subsequently.

For both $\text{CH}\equiv\text{CCH}_2\text{OMe}$ and $\text{CH}_2=\text{C}=\text{CHOMe}$, no coordination through oxygen atoms was observed, as expected for a weakly coordinating ether group in the presence of strongly coordinating alkyne and allene functions. This contrasts with our results reported earlier with methyl vinyl ether [3], which gives an insertion product $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-MeCHOMe})]$ with ether coordination. Only alkyne and coupled-alkyne products were obtained from $\text{CH}\equiv\text{CCH}_2\text{OMe}$ with triosmium clusters as far as we can establish. In the case of $\text{CH}_2=\text{C}=\text{CHOMe}$, two isomeric products were obtained by an insertion of the allene functions into an Os–Os bond; one of them was structurally characterised and the structure of the other inferred from that of the first.

Results and discussion

The cluster $[\text{Os}(\text{CO})_{11}(\text{MeCN})]$ reacts at room temperature with a 2-fold excess of methoxyallene ($\text{CH}_2=\text{C}=\text{CHOMe}$) in CH_2Cl_2 to afford two yellow compounds with the same molecular formula, $[\text{Os}_3(\text{CO})_{11}(\text{C}_4\text{H}_6\text{O})]$ (**1a** and **1b**) in around 80% total



Scheme 2

yield. These compounds depicted in Scheme 2 were characterised by IR, ^1H NMR and in the case of **1a** by X-ray diffraction. Both compounds have nearly identical IR spectra in the carbonyl region, spectra which are also very similar to that of the known allene compound $[\text{Os}_3(\text{CO})_{11}(\text{C}_3\text{H}_4)]$, which was obtained analogously by the reaction of allene with $[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]$ [7]. Almost certainly these compounds are closely related structurally so the question remaining was the origin of the isomerism in the methoxy case. The ^1H NMR spectra of **1a** and **1b** are quite distinct, as shown in Table 1. An obvious interpretation is that in both compounds, methoxyallene acts as a four-electron-donating bridge and hence only two Os–Os bonds are present as shown in the molecular structure of $[\text{Os}_3(\text{CO})_{11}(\text{C}_4\text{H}_6\text{O})]$, **1a** (Fig. 1) determined by a single-crystal X-ray structure determination. Selected bond lengths and angles are in Table 2.

The structure is based on an open chain of osmium atoms. The $\text{C}_4\text{H}_6\text{O}$ ligand is bridging two metal atoms and acting as a four-electron donor, so that cluster **1a** is a 48-valence system and hence there are only two Os–Os bonds: distances Os(1)–Os(3) = 2.9516(8) Å and Os(2)–Os(3) = 2.9204(9) Å. The non-bonded Os–Os distance is 3.888(1) Å. The allene ligand bridges by forming a σ -bond to Os(2) and the

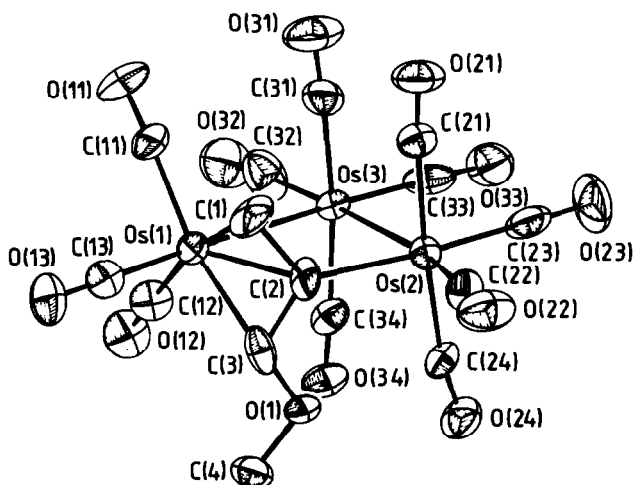
Fig. 1. Molecular structure of $[\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2\text{CCHOMe})]$, **1a**.

Table 1

Some spectroscopic data for compounds **1** to **7**

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	$^1\text{H NMR}^b$
[Os ₃ (CO) ₁₁ (CH ₂ ^{xy} CCH ^z OMe ^w)] (1a) (<i>syn</i>)	2123mw 2075s 2046sh	4.6(m,z) J_{xy} 2.7
	2040vs 2036vs 2018m	3.4(s,w) J_{xz} 0.7
	2011m 1999m 1990m	2.9(dd,x) J_{yz} 0.9
	1973m 1967m	2.7(dd,y)
[Os ₃ (CO) ₁₁ (CH ₂ ^{xy} CCH ^z OMe ^w)] (1b) (<i>anti</i>)	2123mw 2075s 2052sh	6.0(dd,x) J_{xy} 2.0
	2044s 2034vs 2020m	4.0(dd,z) J_{xz} 0.6
	2010mw 1997m 1979mw	3.56(dd,y) J_{yz} 1.1
	1970w	
[Os ₂ (CO) ₇ (CH ₂ ^{xy} CCH ^z OMe ^w)] (2a)	2117m 2075s 2032vs	5.9(dd,x) J_{xy} 2.4
	2011s 1987s	4.8(m,br,z) J_{xz} 0.5
[Ru ₂ (CO) ₇ (CH ₂ ^{xy} CCH ^z OMe ^w)] ^c (2b)	2107m 2051vs 2040sh	5.9(dd,x) J_{xy} 2.3
	2026vs 2021vs 1992m	3.6(m,br,z) J_{xz} 0.5
		3.5(dd,y)
		3.3(s,w)
[Os ₃ (CO) ₁₀ (CH ^x CCH ₂ ^{yz} OMe ^w)] (3a)	2100m 2061vs 2055vs	9.3(s,x) J_{yz} 14.0
	2020s 2004m 1848m	4.1(d,y)
		3.5(d,z)
		3.3(s,w)
[Ru ₃ (CO) ₁₀ (CH ^x CCH ₂ ^{yz} OMe ^w)] ^d (3b)	2096w 2058vs 2052vs	8.3(s,x) J_{yz} 1.7
	2026s 2006m 1880	3.8(s,yz)
		3.3(s,w)
		3.4(d,y)
		4.0(d,z)
[Os ₃ H ^z (CO) ₉ (C ₂ CH ₂ ^z OMe ^y)] (4a)	2100m 2075s 2054s	5.0(s,x)
	2020vs 2013vs 1982m	3.6(s,y)
[Ru ₃ H ^z (CO) ₉ (C ₂ CH ₂ ^z OMe ^y)] (4b)	2102m 2082s 2066s	4.6(s,x)
	2036vs 2006m 1975w	3.5(s,y)
[Os ₃ (CO) ₉ (Me ^x OCH ₂ ^{yz} C=CH ^p - OCCH ^q CCH ₂ ^z OMe ^w)] (5)	2096m 2060vs 2032vs	8.9(s,q) J_{yz} 12.0
	2026sh 2011m 1990m	7.2(s,p) J_{yz} 4.0
	1846	4.8,4.2(d,yz)
		4.6,4.4(d,yz)
		3.5,3.4(s,x)
[Os ₃ (CO) ₉ {(CH ^x =CCH ₂ ^z - OMe ^w) ₂ CO}] (6)	2094m 2060vs 2050vs	6.1(s,x) J_{yz} 15.0
	2021s 2012m 2000m	4.6,3.9(d,yz)
	1978w 1635	3.5(s,w)
[Os ₄ (CO) ₁₂ (Me ^x C ₂ OMe ^y)] (7)	2100w 2072vs 2047vs	4.1(s,x)
	2038vs 2015m 2000m	3.4(s,y)
	1974w	

^a Cyclohexane solutions. ^b 100 MHz spectra at room temperature in CDCl₃, except for **1a** and **3b** which are in CD₂Cl₂ (multiplicities and assignments in parentheses, J in Hz). ^c J_{yz} not resolved. ^d Recorded at -73°C.

Os(2)-C(2) bond length [2.12(2) Å] is shorter, as expected, than the three Os-C contacts in the η^3 -allyl interaction with Os(1) [Os(1)-C(1) 2.26(2), Os(1)-C(2) 2.29(2), and Os(1)-C(3) 2.30(2) Å]. The η^3 -allyl is not significantly unsymmetrical although the end with the longer Os-C bond (that substituted by OMe) is associated with the shorter C-C bond. The Os-CO bond lengths vary from 1.90(2) to

Table 2

Selected bond lengths (Å) and angles (°) for $[\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2\text{CCHOMe})]$, **1a**

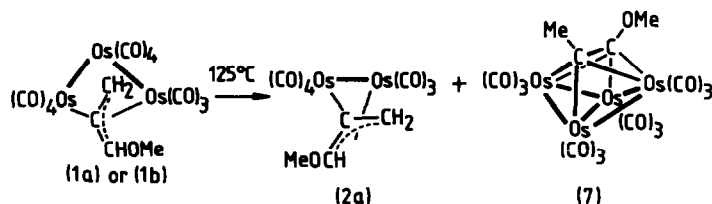
Os(1)–Os(3)	2.9516(8)	Os(2)–Os(3)	2.9204(9)
Os(1)–C(1)	2.26(2)	Os(1)–C(2)	2.29(2)
Os(1)–C(3)	2.30(2)	Os(2)–C(2)	2.12(2)
C(1)–C(2)	1.48(3)	C(2)–C(3)	1.41(2)
O(1)–C(4)	1.42(2)	O(1)–C(3)	1.39(2)
Os(1)–Os(3)–Os(2)	82.92(2)	Os(3)–Os(2)–C(2)	78.4(4)
Os(3)–Os(1)–C(1)	95.7(6)	Os(3)–Os(1)–C(2)	75.3(3)
Os(3)–Os(1)–C(3)	94.0(4)	Os(2)–C(2)–C(1)	122(1)
Os(2)–C(2)–C(3)	127(1)	C(1)–C(2)–C(3)	111(2)
Os(1)–C(2)–Os(2)	123.3(6)	C(3)–O(1)–C(4)	114(1)
O(1)–C(3)–C(2)	115(1)		

1.96(2) Å. The longer ones are those of the axial ligands as in $[\text{Os}_3(\text{CO})_{12}]$ but in this case the differences are barely significant.

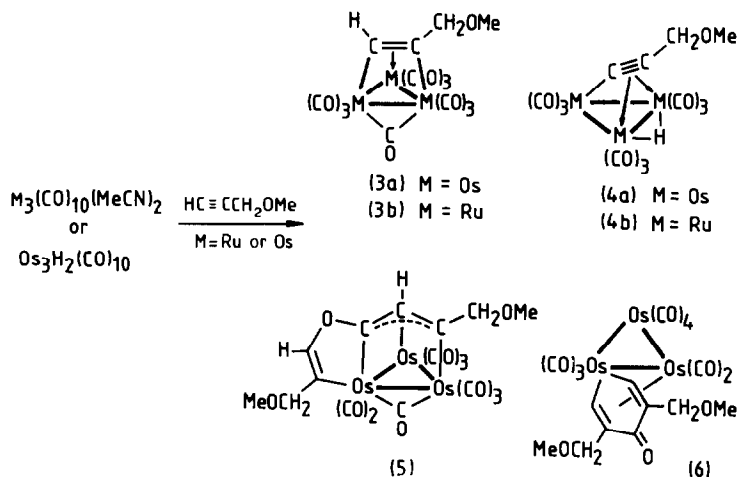
The structure of **1a** is closely related to that of $[\text{Os}_3(\text{CO})_{11}(\text{C}_3\text{H}_4)]$ [7] which also has a μ_2, η^1, η^3 -allene bridge unlike $[\text{Mo}_2(\text{C}_5\text{H}_5)_2(\text{CO})_4(\text{C}_3\text{H}_4)]$ which contains a μ_2, η^2, η^2 -allene bridge [8]. This difference seems to be controlled by electronic requirements of the individual metal centres. We predicted that $[\text{Os}_3(\text{CO})_{10}(\text{C}_3\text{H}_4)]$ would have three Os–Os bonds and the allene coordinated as in the Mo_2 compound but we were unable to obtain this compound or the MeO-substituted analogue by decarbonylation (see below).

By analogy with **1a**, the structure of compound **1b** is probably as shown in Scheme 2. The IR spectra of **1a** and **1b** around 2000 cm^{-1} are so closely similar that they must be close to isostructural and the simplest interpretation is that these are related as *syn* and *anti* isomers. Unfortunately we were unable to get suitable crystals for X-ray diffraction analysis to confirm our assessment.

Thermal treatment of **1a** or **1b** in *n*-octane under nitrogen affords $[\text{Os}_2(\text{CO})_7(\text{C}_4\text{H}_6\text{O})]$ (**2a**) and $[\text{Os}_4(\text{CO})_{12}(\text{CH}_3\text{C}_2\text{OCH}_3)]$ (**7**) both in reasonable yields (Scheme 3), and in the case of **1b** some **1a** is also obtained. However, thermolysis of **1a** does not give any **1b**, thus compound **1a** must be thermodynamically more stable than **1b**. At room temperature **1a** and **1b** do not interconvert since there is no easy route for *syn*–*anti* exchange as found for some mononuclear η^3 -allyl complexes. The simplest analysis of the formation of **2a** and **7** is a loss of an $\text{Os}(\text{CO})_4$ unit intramolecularly from **1a** or **1b** to give **2a** directly and that this mononuclear unit reacts rapidly with compounds **1** to give the tetrameric compound **7**.



Scheme 3



Scheme 4

The alkyne $\text{CH}\equiv\text{CCH}_2\text{OMe}$ reacts with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ and $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ to give compounds **3** to **6** (Scheme 4). The structures are based on IR $\{\nu(\text{CO})\}$ and ^1H NMR spectra which are quite characteristic of these known types of compounds [9]. Compounds **3a** and **3b** adopt the usual bridging CO structure ($\nu(\text{CO})$ 1850 and 1880 cm^{-1} respectively) and ready decarbonylation of these compounds in refluxing cyclohexane affords compounds **4a** and **4b** almost quantitatively. Compound **4b** is unstable in solution and in air. The ^1H NMR spectra of compounds **3a** and **3b** require that there is mobility of the alkyne ligand with respect to the metal framework leading to exchange of diastereotopic CH_2 protons. The osmium compound **3a** shows separate signals for these protons (an AB quartet) at room temperature, but this is well above the coalescence temperature for the ruthenium compound **3b** and in this case an AB quartet is only observed for the CH_2 group at -73°C . The process giving this exchange is an enantiomerisation involving rotation of the alkyne (in conjunction with CO migration) with the plane of the ligand passing through an angle orthogonal to the metal plane of the ligand and back into the tilted orientation. See reference 9 for related cases.

The structures of compounds **5** and **6**, depicted in Scheme 4 are based on IR and ^1H NMR spectroscopic data (Table 1) which were compared with those of analogous compounds obtained from the reactions of $[\text{Os}_3(\text{CO})_{12}]$ with $\text{PhC}\equiv\text{CH}$ [10] and $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ with $\text{RC}\equiv\text{CH}$ [11].

Experimental

The clusters $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ [12], $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ [13], $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ [14] and $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ [15] were prepared as reported previously.

Reactions of methoxyallene ($\text{CH}_2=\text{C}=\text{CHOMe}$) with $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$

A solution of $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ (0.200 g) and $\text{CH}_2=\text{C}=\text{CHOMe}$ (0.030 cm^3 , two-fold excess) in CH_2Cl_2 (40 cm^3) under nitrogen was stirred at room temperature for 3 h, after which time the IR spectrum showed no more change. After

removal of the solvent under reduced pressure, the yellow residue was separated by TLC [SiO_2 , eluant: petroleum ether (b.p. 40–60 °C)/diethyl ether, 10/1 by volume] to give two pale-yellow bands, both characterised with the formula $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2\text{CCHOMe})]$, the first one being **1a** (0.088 g, 43%) and the second one **1b** (0.074 g, 36%) in order of elution.

Thermolysis of isomer 1a

The solution of $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2\text{CCHOMe})]$, **1a**, (0.040 g) in n-octane (30 cm³) was refluxed under nitrogen for 20 min by which time complete conversion of the starting material had apparently occurred (IR evidence). Removal of the solvent and TLC [eluant: petroleum ether (b.p. 40–60 °C)] gave $[\text{Os}_2(\text{CO})_7(\text{CH}_2\text{CCHOMe})]$, **2a**, (0.011 g, 40%) and $[\text{Os}_4(\text{CO})_{12}(\text{MeC}\equiv\text{COMe})]$, **7** (0.015 g, 31%) both as pale yellow solids.

Thermolysis of isomer 1b

A solution of $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2\text{CCHOMe})]$ (**1b**) (0.050 g) in n-octane (40 cm³) was heated under reflux under nitrogen for 20 min after which time the IR spectrum showed no more change. Removal of the solvent and TLC [eluant: petroleum ether (b.p. 40–60 °C)] gave $[\text{Os}_2(\text{CO})_7(\text{CH}_2\text{CCHOMe})]$, **2a** (0.013 g, 38%) as a pale yellow solid, $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2\text{CCHOMe})]$, **1a** 0.013 g, 26% and $[\text{Os}_4(\text{CO})_{12}(\text{MeC}\equiv\text{COMe})]$, **7** (0.017 g, 28%) as a yellow solid.

*Synthesis of $[\text{Ru}_2(\text{CO})_7(\text{CH}_2=\text{C}=\text{CHOMe})]$ (**2b**)*

To a solution of $\text{CH}_2=\text{C}=\text{CHOMe}$ (0.5 cm³) in CH_2Cl_2 (30 cm³) at room temperature was added to solid $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.075 g). The reaction vessel was closed and the solution stirred for 5 min. The orange residue was separated by TLC [eluant: petroleum ether (b.p. 40–60 °C)] to give several bands. The main one gave $[\text{Ru}_2(\text{CO})_7(\text{CH}_2\text{CCHOMe})]$, **2b** (0.018 g, 34%) as a colourless band. The other bands gave very small quantities of compounds which were not characterised.

Reaction of methyl propargyl ether with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

A solution of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.210 g) and $\text{CH}=\text{CCH}_2\text{OMe}$ (0.02 cm³) in CH_2Cl_2 (50 cm³) was stirred at room temperature for 5 h. After removal of the solvent under reduced pressure, the red–orange residue was separated by TLC [eluant: petroleum ether (b.p. 40–60 °C)/diethyl ether, 10/1 by volume] to give four bands. The main yellow band gave $[\text{Os}_3(\text{CO})_{10}(\text{CHCCH}_2\text{OMe})]$, **3a** (0.060 g, 30%) and the second orange-yellow band gave $[\text{Os}_3(\text{CO})_9(\text{MeOCH}_2\text{C}=\text{CHOCCHCCH}_2\text{OMe})]$, **5** (0.063 g, 20%). The other two bands gave very small quantities of compounds which were not characterised.

Reaction of methyl propargyl ether with $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$

The purified ether (0.05 cm³) was added to a yellow solution of $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.175 g) in CH_2Cl_2 (30 cm³) at –20 °C which became red in 5 min. Separation as above gave only two bands. The main one gave $[\text{Ru}_3(\text{CO})_{10}(\text{CHCCH}_2\text{OMe})]$, **3b** (0.084 g, 46%) as an orange solid and $[\text{Ru}_3(\text{CO})_{12}]$ (0.043 g, 25%).

Reaction of methyl propargyl ether with [Os₃H₂(CO)₁₀]

A solution of [Os₃H₂(CO)₁₀] (0.25 g) and the ether (0.5 cm³) in CH₂Cl₂ (50 cm³) was stirred at room temperature for 4 h. Removal of the solvent under reduced pressure and separation of the residue by TLC [eluant: petroleum ether (b.p. 40–60 °C)/diethyl ether, 10/1 by volume] gave several species of which only two were characterised as [Os₃(CO)₉{(HC₂CH₂OMe)₂CO}], **6** (0.180 g, 65%) as purple crystals and [Os₃(CO)₁₀(CHCCH₂OMe)], **3a** (0.068 g, 25%) as yellow crystals. Other products which increased in number on extended reaction time were not characterised.

Thermolysis of compound 3a

A solution of [Os₃(CO)₁₀(CH≡CCH₂OMe)], **3a** (0.05 g) in octane (20 cm³) was refluxed for 5 min. TLC work-up (eluant: pentane) gave on yellow crystalline compound [Os₃H(CO)₉(C≡CCH₂OMe)], **4a** (0.030 g, 75%).

Table 3

Fractional atomic coordinates for [Os₃(CO)₁₁(μ-CH₂CCHOMe)], **1a**

	x	y	z
Os(1)	0.40198(7)	0.21638(5)	0.12194(4)
Os(2)	0.16544(6)	0.36389(5)	0.22407(3)
Os(3)	0.07660(6)	0.26254(5)	0.06493(4)
O(1)	0.422(1)	0.4595(9)	0.1592(7)
O(11)	0.315(2)	-0.005(1)	0.082(1)
O(12)	0.376(2)	0.278(1)	-0.0516(8)
O(13)	0.738(1)	0.176(1)	0.1739(9)
O(21)	0.108(2)	0.164(1)	0.2990(8)
O(22)	0.328(2)	0.454(1)	0.3939(9)
O(23)	-0.159(1)	0.419(1)	0.205(1)
O(24)	0.165(1)	0.571(1)	0.1440(8)
O(31)	0.053(2)	0.063(1)	0.1462(9)
O(32)	0.011(2)	0.158(1)	-0.0995(9)
O(33)	-0.253(1)	0.321(1)	0.025(1)
O(34)	0.161(1)	0.4528(9)	-0.0094(8)
C(1)	0.440(3)	0.213(1)	0.257(1)
C(2)	0.377(2)	0.314(1)	0.2247(9)
C(3)	0.474(1)	0.366(1)	0.1935(9)
C(4)	0.500(2)	0.499(1)	0.111(1)
C(11)	0.340(2)	0.077(1)	0.095(2)
C(12)	0.385(2)	0.255(1)	0.014(1)
C(13)	0.613(2)	0.191(1)	0.158(1)
C(21)	0.135(2)	0.235(1)	0.269(1)
C(22)	0.267(2)	0.423(1)	0.330(1)
C(23)	-0.040(2)	0.397(2)	0.209(1)
C(24)	0.175(2)	0.494(1)	0.1719(9)
C(31)	0.059(2)	0.138(1)	0.117(1)
C(32)	0.039(2)	0.194(2)	-0.037(1)
C(33)	-0.129(2)	0.297(1)	0.038(1)
C(34)	0.130(2)	0.384(1)	0.0208(9)

Thermolysis of compound 3b

A solution of $[\text{Ru}_3(\text{CO})_{10}(\text{CH}\equiv\text{CCH}_2\text{OMe})]$, **3b** (0.070 g) in C_6H_{12} (30 cm^3) was heated under reflux for 30 min. TLC separation as above gave $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}\equiv\text{CCH}_2\text{OMe})]$, **4b** (0.038 g, 55%) as a pale yellow solid.

X-Ray crystal structure determination of $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2\text{CCHOMe})]$ (**1a**)

A yellow prism of $\text{C}_{15}\text{H}_6\text{O}_{12}\text{Os}_3$ ($M = 948.81 \text{ g mol}^{-1}$) of size $0.63 \times 0.33 \times 0.25 \text{ mm}^3$ was mounted on a glass fibre on a goniometer of an Enraf-Nonius CAD4 diffractometer operating with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Monoclinic cell constants were obtained by least-squares refinement of 25 reflections with 2θ between 16 and 30° : $a = 9.550(1)$, $b = 13.203(3)$, $c = 17.529(3) \text{ \AA}$, $\beta = 111.88(1)^\circ$, $U = 2051(1) \text{ \AA}^3$, space group $P2_1/c$, $Z = 4$, $F(000) = 1680$, $D_c = 3.07 \text{ g cm}^{-3}$.

6408 unique intensity data were collected at 25°C (ω - 2θ mode) in a 2θ range up to 60° . Three check reflections were measured periodically and a decay correction applied as were Lorentz and polarisation corrections and empirical corrections based on psi-scans ($\mu = 186.3 \text{ cm}^{-1}$). A Patterson solution using SHELXS-86 [16] gave the Os atom positions. Other atoms were located and the structure was refined by successive least squares and Fourier syntheses using 4181 intensity data with $I_o > 1.5\sigma(I_o)$. All atoms in the model with 272 parameters were refined anisotropically although H-atoms were not included, and the model refined to give $R = 0.061$ and $R_w = 0.079$ minimising the function $\sum w(|F_o| - |F_c|)^2$ where the weight $w = 4F_o^2/[\sigma(F_o)^2]^2$. Scattering factors and $\Delta f'$ and $\Delta f''$ were taken from standard sources [17]. Maximum shift/e.s.d. = 0.05 and the largest peak in the final difference Fourier map was 1.90 e\AA^{-3} .

All calculations were performed on a MicroVax II computer using SDP/VAX [18]. Fractional atomic coordinates are in Table 3 while other standard data (anisotropic parameters, full lists of bond lengths and angles, observed and calculated structure factors) may be obtained from the authors.

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