Reactions of Allene with Triosmium and Triruthenium Clusters including Coupling and Oxidative Addition: *X*-Ray Structure of the Coupled Allene Compound $[Os_3(C_6H_8)(CO)_{10}]$ †

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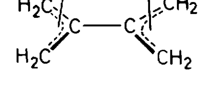
Allene ($CH_2=C=CH_2$) reacts with $[Os_3(CO)_{11}(MeCN)]$ to give the known compound $[Os_3(\mu\text{-}C_3H_4)(CO)_{11}]$ and with $[Os_3(CO)_{10}(MeCN)_2]$ to give $[Os_3(\mu_3\text{-}C_6H_8)(CO)_{10}]$, the single-crystal *X*-ray structure of which shows an open chain of metal atoms [Os–Os–Os 136.8(1)°] with the C_6H_8 ligand, formed by end-to-centre allene coupling, bridging three Os atoms through μ, η^2-vinyl and η^3-allyl linkages. U.v. photolysis of $[Os_3(\mu\text{-}C_3H_4)(CO)_{11}]$ gives mainly $[Os_3H(\mu_3\text{-}\sigma,\eta^2,\eta^2\text{-}CH=C=CH_2)(CO)_9]$ which isomerises thermally to $[Os_3H(\mu_3\text{-}\sigma,\sigma,\eta^3\text{-}CHCHCH)(CO)_9]$. In contrast, thermolysis of $[Os(\mu\text{-}C_3H_4)(CO)_{11}]$ gives mainly $[Os_2(\mu\text{-}\sigma,\eta^3\text{-}C_3H_4)(CO)_7]$ (92%; reaction under CO). Thus photolysis leads to Os–CO and C–H cleavages and thermolysis to Os–Os cleavages. Reaction of $[Ru_3(CO)_{11}(MeCN)]$ with allene at 0 °C gives $[Ru_2(\mu,\sigma,\eta^3\text{-}C_3H_4)(CO)_7]$ with no evidence for trinuclear products. Tetramethylallene reacts slowly with $[Os_3(CO)_{11}(MeCN)]$ to give $[Os_3(C_3Me_4)(CO)_{10}]$ of unknown structure.

Allene ($CH_2=C=CH_2$) frequently couples on reaction with transition-metal carbonyls and there are relatively few compounds with simple allene co-ordination. For example, $[Fe_2(CO)_9]$ reacts with allene in an autoclave at 50 °C to give $[Fe_2(C_6H_8)(CO)_6]$ (**1**) and $[Fe_2(C_3H_4)(CO)_7]$ (**2**),[1] and the *X*-ray structure of the derivative $[Fe_2(C_3H_4)(CO)_6(PPh_3)]$ has been determined.[2] In the cluster area, $[Os_3(CO)_{11}(MeCN)]$ reacts with allene to give $[Os_3(\mu\text{-}\sigma,\eta^3\text{-}C_3H_4)(CO)_{11}]$ (**3**) (Scheme 1), also of known *X*-ray crystal structure.[3] Both (**2**) and (**3**) contain σ,η^3-allene bridges but only in (**2**) is the bridge associated with a metal bond. We have further explored the chemistry of allene with triosmium and triruthenium clusters and find primarily that the bis(acetonitrile) cluster $[Os_3(CO)_{10}(MeCN)_2]$, in contrast to the monoacetonitrile cluster above, reacts to give $[Os_3(C_6H_8)(CO)_{10}]$ with a μ_3 ligand formed by end-to-centre coupling of allene molecules. Thermolysis and photolysis of $[Os_3(\mu\text{-}\sigma,\eta^3\text{-}C_3H_4)(CO)_{11}]$ lead to totally different products.



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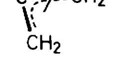

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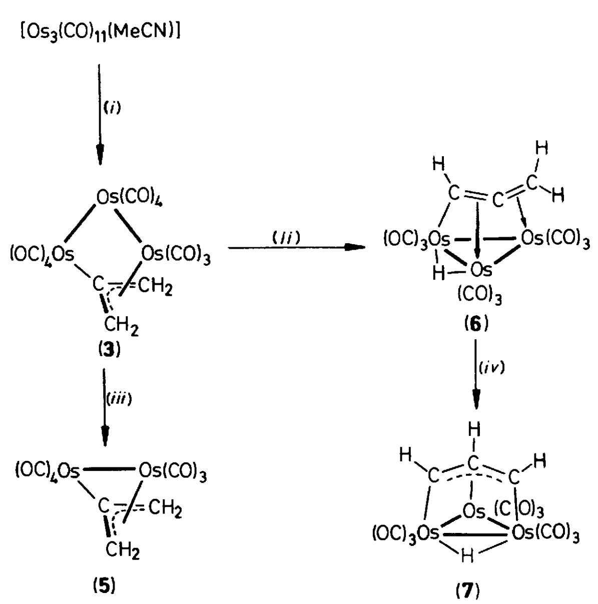
Results and Discussion

The reaction of $[Os_3(CO)_{11}(MeCN)]$ with an excess of allene at room temperature is reported to give good yields of the allene cluster $[Os_3(C_3H_4)(CO)_{11}]$ (**3**), which was shown to contain a four-electron-donating allene bridge and hence two Os–Os bonds.[3] Thermolysis of (**3**) at 125 °C leads to reformation of the cluster to yield $[Os_4(CHCMe)(CO)_{12}]$ (**4**) as the only reported product in 50% yield.[3] A 1,3-hydrogen-atom shift has produced a μ_4-propyne compound of known type.[4] However, we now find that thermolysis in refluxing octane (125 °C) affords a mixture which by careful chromatographic work-up gives as the main product a colourless dinuclear compound (*ca.* 60%) which we have characterised by mass, i.r., and ^1H n.m.r. spectroscopy (Table 1) as $[Os_2(C_3H_4)(CO)_7]$ (**5**), Scheme 1. The previously reported compound (**4**) is only a very minor product while low



Scheme 1. (*i*) $CH_2=C=CH_2$; (*ii*) u.v. irradiation; (*iii*) heat, CO; (*iv*) heat

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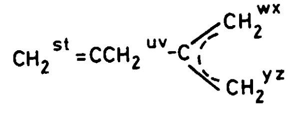
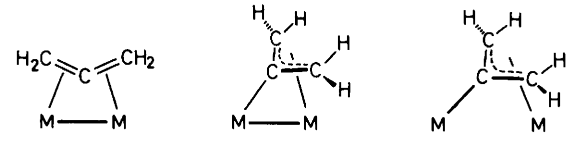
† *catena*-1,1,1,1,2,2,2,3,3,3-Decacarbonyl-μ_3-[2′-methylenepent-4′-en-1′,4′-diyl-$C^{1',2',2'}(Os^3)C^{4'}(Os^{1,2})C^{5'}(Os^1)$]-triosmium.

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

Table 1. I.r. and ^1H n.m.r. data for allene-derived clusters

	Compound	$\tilde{\nu}(CO)^a/cm^{-1}$	^1H N.m.r.^{b}
(3)	$[Os_3(C_3H_4)(CO)_{11}]$	2 120m, 2 074vs, 2 043vs, 2 032vs, 2 017ms, 2 008m, 1 996m, 1 984m (sh), 1 975ms	3.09(m) 3.02(m) } AA′BB′
(5)	$[Os_2(C_3H_4)(CO)_7]$	2 113m, 2 054s, 2 029vs, 2 009vs, 1 984s, 1 951w	3.66(s) 3.62(s)
(6)	$[Os_3H^w(CH^x{=}C{=}CH_2{}^{y,z})(CO)_9]$	2 100m, 2 071s, 2 046s, 2 025s, 2 016ms, 2 002s, 1 993ms, 1 985w, 1 981w	9.1(d) x, J_{wx} 1.9 4.3(s) y 2.6(s) z −22.4(d) w, J_{xw} 1.9
(7)	$[Os_3H^x(CH^yCH^zCH^y)(CO)_9]$	2 100w, 2 072s, 2 051s, 2 021s, 2 010m, 2 004s, 1 990w, 1 979w	8.68(m)^c y J_{yz} 6.6 8.54(m)^c z −19.71(s) x J_{xz} 1.0
(8)	$[Ru_2(C_3H_4)(CO)_7]$	2 108m, 2 052s, 2 038 (sh), 2 021vs, 2 019s, 1 992s	3.44(s) 2.43(s)
(9)	$[Os_3(C_6H_8)(CO)_{10}]^d$  	2 105w, 2 060vs, 2 025m (sh), 2 016s, 1 997m, 1 980m, 1 960w, 1 942w	5.45(d) u J_{uv} 12.8 4.07(d) v 4.25(s) 3.23(m) 2.98(t) } s, t, w, x, y, z 2.60(s) 2.40(s)
(10)	$[Os_3(C_3Me_4)(CO)_{10}]$	2 114w, 2 061s, 2 046m, 2 027vs, 2 009w, 2 003w, 1 987w, 1 971vw	2.08(s) 2.02(s)

^{a} In cyclohexane. ^{b} In $CDCl_3$ or CD_2Cl_2 at 200 MHz at room temperature, *J* in Hz. ^{c} AB_2 part of an AB_2X spectrum. ^{d} N.m.r. signals each correspond to one H except that at δ 2.40 which is for two H atoms. Assignments uncertain except for the two doublets for u and v.



(A) **(B)** **(C)**

Figure 1. Different modes that have been established for allene bridges

yields of $[Os_3H(\mu_3\text{-}\eta^3\text{-}CH{=}C{=}CH_2)(CO)_9]$ (**6**) (see later) are also formed. We regard the dinuclear compound (**5**) as the primary product and this may be obtained in very high yields (92%) if the thermolysis of (**3**) is carried out while bubbling CO or C_3H_4 through the refluxing octane solution. Presumably these small molecules stabilise the $Os(CO)_4$ fragment lost and prevent CO dissociation from (**3**) to give (**6**), or $Os(CO)_4$ addition to a trinuclear cluster to give (**4**).

The structure of compound (**5**) is probably as shown. We could not get crystals suitable for *X*-ray diffraction analysis but the ν(CO) i.r. spectrum shows only terminal CO ligands and is quite similar to that of the analogous iron compound (**2**).[1] The ^1H n.m.r. spectrum consists of two singlets at δ 3.66 and 3.62, which do not vary over the temperature range 60 to −60 °C. Different modes of allene bridge have been identified: $\mu\text{-}\eta^2,\eta^2$-allene (**A**) (Figure 1) has been found for $[Mo_2(C_5H_5)_2(C_3H_4)(CO)_4]$,[5] $\mu\text{-}\sigma,\eta^3$-allene in $[Fe_2(C_3H_4)(CO)_6(PPh_3)]$[2] in which there is an Fe–Fe bond (**B**), and in $[Os_3(C_3H_4)(CO)_{11}]$[3] in which there is no associated Os–Os bond (**C**). In the di-iron compound the Fe–Fe distance is 2.65 Å whereas the bridged Os–Os separation in (**3**) is 3.860 Å. Clearly the σ,η^3-bridge can accommodate a good range of metal–metal distances with or without associated metal–metal bonds.

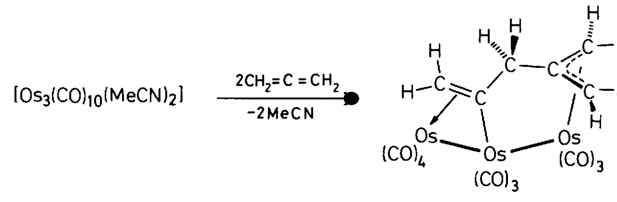
Whereas thermolysis of $[Os_3(C_3H_4)(CO)_{11}]$ (**3**) gave the dinuclear compound $[Os_2(C_3H_4)(CO)_7]$ (**5**), u.v. photolysis of the same compound gave $[Os_3H(\mu_3\text{-}\sigma,\eta^2,\eta^2\text{-}CH{=}C{=}CH_2)(CO)_9]$ (**6**) (80%). This was only formed as a very minor product in the thermolysis. Compound (**6**) was characterised by comparison of its i.r. and ^1H n.m.r. data (Table 1) with those of closely related compounds, such as $[Os_3H(MeC{=}C{=}CH_2)(CO)_9]$,[6] which are spectroscopically very similar indeed. The isomeric compound $[Os_3H(\mu_3\text{-}\sigma,\sigma,\eta^3\text{-}CHCHCH)(CO)_9]$ (**7**) was obtained (89%) readily by the thermal treatment of compound (**6**) at 125 °C. Compounds (**6**) and (**7**) are the lowest homologues of these known types of compounds[6,7] and are reported for the first time. Thus we have a clear example of thermal and photochemical reactions being substantially different; photolysis gives predominantly Os–CO and thermolysis predominantly Os–Os cleavage. The loss of CO would lead to the species $[Os_3(C_3H_4)(CO)_{10}]$. This compound would be electron-precise if an Os–Os bond were created, but apparently oxidative addition of allene to give the allenyl derivative follows the loss of a second CO ligand.

Ruthenium clusters generally break down and reform more easily than osmium ones and, consistent with this, $[Ru_3(CO)_{11}(MeCN)]$[8] reacts with allene at room temperature or below to give $[Ru_2(C_3H_4)(CO)_7]$ (**8**) in moderate yields (50%). Compound (**8**) is believed on spectroscopic evidence (Table 1) to be isostructural with (**2**) and (**5**), the iron and osmium analogues. No evidence was found in this reaction for $[Ru_3(\mu_3\text{-}\sigma,\eta^3\text{-}C_3H_4)(CO)_{11}]$ or any other triruthenium cluster products. Breakdown to the dinuclear compound occurs as with osmium but under very much milder conditions.

Attempting to prepare $[Os_3(C_3H_4)(CO)_{10}]$ which we believed might be an intermediate in the decarbonylation of cluster (**3**) and would be like (**3**) except that it would contain three Os–Os bonds instead of two, we treated $[Os_3(CO)_{10}(MeCN)_2]$ with allene. Instead we obtained as the main product (69%) the cluster $[Os_3(C_6H_8)(CO)_{10}]$, (**9**), Scheme 2. The ^1H n.m.r. spectrum of cluster (**9**) is quite complex so we could not obtain any unambiguous evidence for its structure nor the nature of the allene coupling that we believed had occurred. All

Table 2. Selected bond lengths (Å) and angles (°) for the compound $[Os_3(C_6H_8)(CO)_{10}]$, (9)

Os(1)–Os(2)	2.848(4)	Os(3)–C(16)	2.288(18)
Os(2)–Os(3)	2.882(4)	C(11)–C(12)	1.423(22)
Os(1)–C(11)	2.306(17)	C(12)–C(13)	1.521(23)
Os(1)–C(12)	2.350(16)	C(13)–C(14)	1.602(23)
Os(2)–C(12)	2.060(16)	C(14)–C(15)	1.395(22)
Os(3)–C(14)	2.276(16)	C(14)–C(16)	1.437(22)
Os(3)–C(15)	2.337(19)		
Os(1)–Os(2)–Os(3)	136.8(1)	Os(1)–C(12)–C(11)	70.5(10)
Os(2)–Os(1)–C(12)	45.5(3)	Os(1)–C(12)–Os(2)	80.1(6)
Os(1)–Os(2)–C(12)	54.4(5)	Os(2)–C(12)–C(11)	124.9(12)
Os(2)–Os(3)–C(14)	83.3(5)	Os(2)–C(12)–C(13)	118.3(11)
Os(2)–Os(3)–C(15)	100.7(5)	C(11)–C(12)–C(13)	116.7(14)
Os(2)–Os(3)–C(16)	96.3(5)	C(12)–C(13)–C(14)	105.6(13)
C(11)–Os(1)–C(12)	35.6(5)	C(13)–C(14)–C(15)	117.0(14)
Os(1)–C(11)–C(12)	73.9(10)	C(13)–C(14)–C(16)	121.3(14)
		C(15)–C(14)–C(16)	121.2(15)



(9)

Scheme 2.

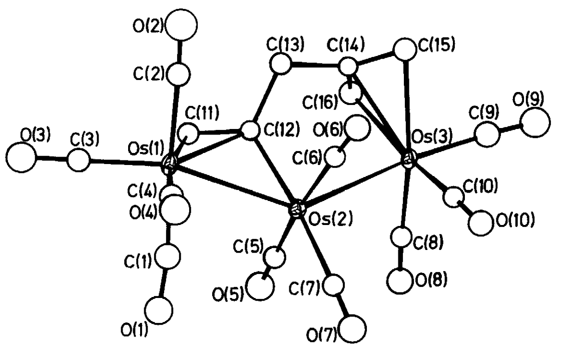


Figure 2. Molecular structure of $[Os_3(C_6H_8)(CO)_{10}]$, (9)

we could deduce was that the complexity of the ^1H n.m.r. spectrum seemed to rule out a structure related to that of the C_6H_8 compound (**1**).

The single-crystal *X*-ray structure of cluster (**9**) is shown in Figure 2 and selected bond lengths and angles are in Table 2. The structure is based on an open chain of osmium atoms [Os(1)–Os(2)–Os(3) 136.8(1)°] with each osmium atom adopting octahedral geometry within constraints imposed by the organic ligand. There is another chain, in this case of carbon atoms, running roughly parallel to the Os_3 chain with bonds between each metal atom and the carbon chain. The C_6H_8 ligand results from end-to-centre coupling of two allene molecules, in contrast to the centre-to-centre coupling that gave $[Fe_2(C_6H_8)(CO)_6]$, (**1**).[1] The C_6H_8 ligands in both (**1**) and (**9**) are six-electron donors so that cluster (**9**) is a 50-valence-electron system and hence there are only two Os–Os bonds: Os(1)–Os(2) 2.848(4) and Os(2)–Os(3) 2.882(4) Å. The hydrogen atoms were not located but the C–C bond lengths indicate that there has been a simple C–C bond formation between two allene molecules without any H-atom shifts. Thus the representation of cluster (**9**) in Scheme 2 is accurate. The ligand donates three electrons to atoms Os(1) and Os(2) together through a μ-σ,η^2-vinyl bridge and three electrons to Os(3) through an η^3-allyl group. The σ-Os(2)–C(12) bond is 2.060(16) Å but the other Os–C contacts which are part of η^2 or η^3 systems are longer, ranging from 2.276(16) to 2.350(16) Å. All eight hydrogen atoms are different and we have made probable assignments of the seven observed ^1H n.m.r. signals in Table 1. The Os–CO bond lengths vary from 1.877(20) to 1.989(20) Å. The longest are Os(1)–C(1) and Os(1)–C(2) [1.968(21) and 1.989(20) Å respectively] which are for CO ligands *trans* to each other, while the shortest are those *trans* to metal–metal bonds, Os(1)–C(3) and Os(3)–C(9) [1.877(20) and 1.890(21) Å respectively]. These variations are probably significant and reflect changes in π bonding in the metal–carbonyl bonds, for example CO ligands *trans* to each other are known to have a mutually M–CO bond-weakening effect.

We have not observed any monoallene derivatives in the reaction of allene with $[Os_3(CO)_{10}(MeCN)_2]$ that might be intermediates leading to the coupled-allene product (**9**). Presumably $[Os_3(\mu$-σ,η^3-$C_3H_4)(CO)_{10}(MeCN)]$ analogous to (**3**) is formed first but this must be reactive towards allene which displaces the MeCN ligand leading to (**9**). There is, however, no substantiating evidence for this mechanism or for why end-to-centre rather than centre-to-centre coupling occurs.

Finally we tried to develop a chemistry of substituted allenes with triosmium and have so far found that tetramethylallene (C_3Me_4) reacts much slower with $[Os_3(CO)_{11}(MeCN)]$ than allene itself. Refluxing dichloromethane was used as the solvent and the product obtained was $[Os_3(C_3Me_4)(CO)_x]$ (x = 10 or 11). The i.r. spectrum around 2 000 cm^{-1} is sufficiently unlike that of (**3**) to show that these are not isostructural. Analytical data favour x = 10 so at present we propose a compound $[Os_3(\mu$-$C_3Me_4)(CO)_{10}]$ with three osmium–osmium bonds and a four-electron-donating tetramethylallene ligand.

Experimental

The clusters $[Os_3(CO)_{11}(MeCN)]$,[9] $[Os_3(CO)_{10}(MeCN)_2]$,[10] and the ruthenium analogues[8] were prepared as reported previously.

Synthesis of $[Os_3(C_3H_4)(CO)_{11}]$ (**3**).—This method has been communicated by others without experimental details.[3] Allene was bubbled at atmospheric pressure for 60 s at 20 °C through a stirred solution of $[Os_3(CO)_{11}(MeCN)]$ (0.341 g) in dry CH_2Cl_2 (75 cm^3). The reaction vessel was closed and the solution stirred for 2 h, that is until the i.r. spectrum indicated that there was no starting cluster remaining. Removal of the solvent gave a yellow residue which was purified by t.l.c. [SiO_2; eluant, light petroleum (b.p. < 40 °C)] to give a single band yielding the product as pale yellow crystals (0.286 g, 84%) (Found: C, 18.5; H, 0.4, $C_{14}H_4O_{11}Os_3$ requires C, 18.3; H, 0.45%).

Synthesis of $[Os_3H(\mu_3$-σ,η^2,η^2-$CH{=}C{=}CH_2)(CO)_9]$ (**6**).—A solution of $[Os_3(C_3H_4)(CO)_{11}]$ (**3**) (0.250 g) in dried cyclohexane was photolysed by a medium-pressure mercury lamp at room temperature for 20 min. Chromatographic work-up as above afforded the allenyl compound (**6**) as colourless crystals (0.200 g, 80%) (Found: C, 17.0; H, 0.4. $C_{12}H_4O_9Os_3$ requires C, 16.7; H, 0.45%) and some of the dinuclear compound $[Os_2(C_3H_4)(CO)_7]$ (**5**) as colourless crystals (0.043 g, 17%) characterised by its electron-impact (e.i.) mass spectrum (parent molecular ion observed) and data in Table 1.

Thermal Isomerisation of $[Os_3H(CH{=}C{=}CH_2)(CO)_9]$ **(6)**.—A solution of the cluster **(6)** (0.035 g) in n-octane (10 cm^3) was refluxed for 1 h by which time complete isomerisation had occurred (i.r. evidence). Removal of the solvent and t.l.c. [SiO_2; eluant, light petroleum (b.p. <40 °C)] gave only one band yielding $[Os_3H(\mu_3\text{-}\eta^3\text{-}CHCHCH)(CO)_9]$ **(7)** as colourless crystals (0.031 g, 89%) (Found: C, 16.5; H, 0.4. $C_{12}H_4O_9Os_3$ requires C, 16.7; H, 0.45%).

Synthesis of $[Os_2(\mu\text{-}\sigma,\eta^3\text{-}C_3H_4)(CO)_7]$ **(5)**.—A yellow solution of compound **(3)** (0.075 g) in n-octane (35 cm^3) was refluxed with CO bubbling through it for 2 h. The resulting colourless solution was taken to dryness and the white solid purified as above by t.l.c. to give colourless crystals of compound **(5)** (0.069 g, 92%).

Action of Allene on $[Os_3(C_3H_4)(CO)_{11}]$ **(3)**.—In an attempt to couple allene ligands, allene was bubbled for 6 min through a refluxing solution of compound **(3)** (*ca.* 0.005 g) in n-octane (10 cm^3). The colourless solution so formed was shown by its i.r. spectrum to contain the dinuclear compound **(5)** as the only metal carbonyl product.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with Allene*.—Allene was bubbled through a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.175 g) in dried CH_2Cl_2 (50 cm^3) for 2 min at room temperature. The solution was stirred in a stoppered flask for 2 h and t.l.c. work-up as in the above experiments gave one main yellow band yielding orange crystals (0.120 g, 69%) characterised as $[Os_3(C_6H_8)(CO)_{10}]$ **(9)** (Found: C, 20.6; H, 0.9. $C_{16}H_8O_{10}Os_3$ requires C, 20.6; H, 0.85%). Crystals suitable for *X*-ray single-crystal structure determination were obtained from pentane. A minor red band on the t.l.c. plate was not characterised.

Synthesis of $[Ru_2(\mu\text{-}\sigma,\eta^3\text{-}C_3H_4)(CO)_7]$ **(8)**.—A suspension of $[Ru_3(CO)_{11}(MeCN)]$ (0.100 g) in CH_2Cl_2 (30 cm^3) at 0 °C was degassed with nitrogen. A slow stream of allene was passed through this stirred solution which became pale yellow after 15 min. The solution was taken to dryness under vacuum and the pale yellow residue separated by chromatography (t.l.c. as above) to give $[Ru_2(C_3H_4)(CO)_7]$ **(8)** as colourless crystals (0.050 g, 50%) (Found: C, 27.95; H, 1.05. $C_{10}H_4O_7Ru_2$ requires C, 27.4; H, 0.9%).

Action of Tetramethylallene (2,4-*Dimethylpenta*-2,3-*diene*) *on* $[Os_3(CO)_{11}(MeCN)]$.—A solution of $[Os_3(CO)_{11}(MeCN)]$ (0.065 g) in dried CH_2Cl_2 (25 cm^3) was treated with an excess of the allene (0.10 cm^3) and the mixture was refluxed for 4 h by which time no starting cluster remained. The solution was taken to dryness and the residue separated by t.l.c. as above. The main yellow band gave $[Os_3(C_3Me_4)(CO)_{10}]$ **(10)** 0.048 g, 74%) as yellow crystals (Found: C, 22.0; H, 1.25. $C_{17}H_{12}O_{10}Os_3$ requires C, 21.55; H, 1.3%).

X-Ray Crystal Structure Determination of Compound **(9)**.—*Crystal data.* $C_{16}H_8O_{10}Os_3$, $M = 930.83$, monoclinic, space group $C2/c$ (no. 15), $a = 28.330(7)$, $b = 11.594(2)$, $c = 13.784(2)$ Å, $\beta = 118.43(2)°$, $U = 3\,981(2)$ Å^3, $Z = 8$, $D_c = 3.106$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $F(000) = 3\,296$, $\mu(Mo\text{-}K_\alpha) = 191.8$ cm^{-1}, crystal size $0.50 \times 0.23 \times 0.10$ mm.

Data collection. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[11] using a CAD4 diffractometer operating in the ω—2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 3 899 reflections were collected ($3 \leqslant 2\theta \leqslant 52°$). The segment of reciprocal space scanned was h 0 to 35, k 0 to 14, l -17 to 17. The reflection intensities were corrected for absorption, using the azimuthal-scan method;[12] maximum transmission factor 1.00, minimum value 0.56.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for $[Os_3(C_6H_8)(CO)_{10}]$, **(9)**

Atom	*x*	*y*	*z*
Os(1)	8 685.3(2)	392.7(5)	10 161.0(5)
Os(2)	8 788.9(2)	2 322.0(5)	8 997.8(4)
Os(3)	8 718.7(2)	4 796.1(5)	9 091.5(4)
O(1)	8 152(6)	−263(12)	7 691(12)
O(2)	9 327(6)	902(16)	12 647(13)
O(3)	8 072(6)	−1 643(14)	10 459(13)
O(4)	9 666(6)	−886(15)	10 371(13)
O(5)	7 639(6)	2 303(12)	7 076(11)
O(6)	9 932(5)	2 764(11)	10 862(11)
O(7)	9 264(6)	1 959(13)	7 463(12)
O(8)	7 878(5)	4 653(11)	6 669(11)
O(9)	8 678(6)	7 405(14)	8 951(12)
O(10)	9 694(5)	4 598(10)	8 694(10)
C(1)	8 329(7)	88(16)	8 564(15)
C(2)	9 110(7)	732(15)	11 764(15)
C(3)	8 317(7)	−861(16)	10 346(14)
C(4)	9 281(7)	−441(15)	10 236(14)
C(5)	8 071(7)	2 310(14)	7 794(13)
C(6)	9 500(6)	2 609(13)	10 185(12)
C(7)	9 103(6)	2 102(13)	8 031(12)
C(8)	8 195(6)	4 657(13)	7 566(13)
C(9)	8 689(7)	6 424(16)	9 023(14)
C(10)	9 339(6)	4 672(13)	8 883(12)
C(11)	8 014(6)	1 672(14)	9 914(13)
C(12)	8 457(6)	2 355(12)	10 042(12)
C(13)	8 722(7)	3 105(14)	11 069(13)
C(14)	8 644(6)	4 408(12)	10 631(11)
C(15)	9 105(7)	5 082(15)	10 996(14)
C(16)	8 132(7)	4 818(14)	9 794(13)

Structure solution and refinement. The structure was solved by routine heavy-atom methods (SHELX 86[13]) and refined by full-matrix least squares (SHELX 76[14]). Only Os atoms were refined anisotropically, and H atoms were not included in the final model. The final residuals R and R' were 0.044 and 0.050 respectively for the 132 variables and 3 160 data for which $F_o > 6\sigma(F_o)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, being defined as $1/[\sigma^2(F_o) + 0.001\,F_o^2]$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 15 and 16 respectively. All computations were made on a DEC VAX-11/750 computer. Atomic co-ordinates are given in Table 3.

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References

1 R. Ben-Shoshan and R. Pettit, *Chem. Commun.*, 1968, 247.
2 R. E. Davis, *Chem. Commun.*, 1968, 248.
3 B. F. G. Johnson, J. Lewis, P. R. Raithby, and S. W. Sankey, *J. Organomet. Chem.*, 1982, **231**, C65.
4 R. Belford, H. P. Taylor, and P. Woodford, *J. Chem. Soc., Dalton Trans.*, 1972, 2425.
5 M. H. Chisholm, L. A. Rankel, W. I. Bailey, F. A. Cotton, and C. A. Murillo, *J. Am. Chem. Soc.*, 1977, **99**, 1261.
6 A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
7 B. E. Hanson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 1852; A. J. Deeming and P. J. Manning, *Philos. Trans. R. Soc. London, Ser. A*, 1982, **308**, 59.

8 G. A. Foulds, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1985, **294**, 123; **296**, 147.

9 P. A. Dawson, B. F. G. Johnson, J. Lewis, J. Puga, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 233.

10 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.

11 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

12 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

13 G. M. Sheldrick, SHELX 86 Program for Crystal Structure Solution, University of Göttingen, 1986.

14 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination and Refinement, University of Cambridge, 1976.

15 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

16 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

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