Reactions of Co-ordinated Ligands. Part 46.[1] Formation of $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}CCH{=}CMe_2)(CO)_{10}]$ by Carbon–Carbon σ-Bond and Carbon–Hydrogen Activation of 3,3-Dimethylcyclopropene; Crystal and Molecular Structure of $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$† and Evidence for its Facile Rearrangement to $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHCHMe_2)(CO)_{10}]$

Michael Green,* A. Guy Orpen, and Colin J. Schaverien
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with 3,3-dimethylcyclopropene leads to both carbon–carbon σ-bond and carbon–hydrogen activation and formation of $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ (**1**) and $[Os_3(\mu\text{-}H)(\mu\text{-}CCH{=}CMe_2)(CO)_{10}]$ (**2**). The former was characterised in solution by ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy and in the solid state by single-crystal *X*-ray crystallography. The $\mu\text{-}CCH_2CHMe_2$ and μ-H groups bridge the Os(1)–Os(2) bond almost symmetrically. Significantly, the alkylidyne carbon also interacts with the $Os(CO)_4$ unit. Reaction of $[Os_3(\mu\text{-}D)_2(CO)_{10}]$ with 3,3-dimethylcyclopropene leads to deuterium incorporation only into the Os(μ-D)Os and $Os(\mu\text{-}CCHDCHMe_2)Os$ sites, there being no deuterium incorporation into the vinyl-substituted μ-carbyne complex; mechanisms are discussed. Thermolysis of complex (**1**) leads to the sequential formation of $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHCHMe_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)_2(\mu\text{-}C{=}CHCHMe_2)(CO)_9]$. Photolysis of (**1**) directly affords the latter. The mechanism of the thermal reaction is discussed in terms of a 1,2-hydrogen shift process, which does not involve the metal centres.

Various transition-metal species are known[2,3] to promote ring-opening reactions of cyclopropenes. We have previously observed that 3,3-dimethylcyclopropene reacts with the unsaturated dinuclear complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ to form, *via* 2,3 σ-bond cleavage a cisoid μ-allylidene $[Mo_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$,[4,5] whereas reaction with $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ gives[6,7] the transoid μ-allylidene $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$. The formally unsaturated Group 8 complexes $[M^1M^2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ ($M^1 = M^2 =$ Rh or Co; $M^1 =$ Rh, $M^2 =$ Co; $M^1 =$ Ir, $M^2 =$ Co; $M^1 =$ Rh, $M^2 =$ Ir) also react with 3,3-dimethylcyclopropene, but in contrast with the Mo_2 and Re_2 systems the alkene carbon to carbon double bond is broken and the resulting intermediate undergoes a carbonyl insertion reaction to form $[M^1M^2(\mu\text{-}CO)(\mu\text{-}COCHCMe_2CH)(\eta\text{-}C_5Me_5)_2]$.[8] In order to try and understand more fully this chemistry the reaction of 3,3-dimethylcyclopropene with the 46-electron trinuclear complex $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ was explored. This unsaturated molecule reacts with a range of donor ligands[9–12] including alkenes and alkynes[13–16] corresponding to the presence of a low-lying unoccupied molecular orbital[17,18] in $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.

Results and Discussion

Addition of an excess of 3,3-dimethylcyclopropene to a purple solution of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ in hexane led to a slow colour change from purple to yellow-orange. Work-up by removal of the volatiles followed by recrystallisation of the reaction mixture afforded the major product (**1**),[19] which was isolated as yellow crystals. Elemental analysis and mass spectroscopy indicated that (**1**) was a 1:1 adduct. The ^1H n.m.r. spectrum displayed resonances characteristic of an isopropyl group as well as a two-proton doublet [^3J(HH) 5.61 Hz] at 4.51 and a one-proton singlet at −16.73, the latter being in a region characteristic of a hydride bridging an Os–Os single bond. The proton-coupled ^{13}C n.m.r. spectrum was also revealing in structure elucidation. At room temperature a quaternary carbon resonance at low field (319.4 p.p.m.) appeared as a pseudo-quintet [^2J(CH) 5.4, ^2J(CH) 5.0 Hz]. This chemical shift is characteristic[20] of an alkylidyne-type carbon atom. Selective heteronuclear developing of the hydride resonance at −16.73 p.p.m. resulted in the collapse of the carbon resonance at 319.4 p.p.m. to a triplet [^2J(CH) 5.4 Hz]. These data, together with the existence of a saturated methylene carbon resonance at low field [73.1 p.p.m., ^1J(CH) 128 Hz] suggested that (**1**) was a hydridotriosmium, isobutyl-substituted edge-bridged methylidyne complex. The presence of only four carbonyl resonances at 300 K infers that there is an effective plane of symmetry perpendicular to the bridged Os–Os bond, and therefore the hydride must bridge the same Os–Os bond as does the alkylidyne unit. In order to confirm this a single crystal *X*-ray diffraction study was performed on complex (**1**). This established the molecular geometry shown in the Figure, selected bond lengths and angles being listed in Table 1.

The three osmium atoms define an approximate equilateral triangle [Os(1)–Os(2) 2.871(2), Os(1)–Os(3) 2.827(2), and Os(2)–Os(3) 2.861(2) Å]. The μ-alkylidyne group CCH_2CHMe_2 bridges the Os(1)–Os(2) bond almost symmetrically with Os(1)–C(11) 2.018(24) and Os(2)–C(11) 1.967(22) Å. Significantly the alkylidyne carbon also apparently interacts with the $Os(CO)_4$ unit, the Os(3) $\cdots$ C(11) distance is 2.639(25) Å and the dihedral angle between the triosmium and the Os(1)–C(11)–Os(2) planes is acute at 82.1°. This compares with the corresponding parameters in $[Os_3(\mu\text{-}H)(\mu\text{-}CH)(CO)_{10}]$[21] (2.35 Å,

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Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

* *Present address:* Department of Chemistry, King's College London, Strand, London WC2R 2LS.

† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-hydrido-1,2-μ-(3′-methylbutylidyne)-*triangulo*-triosmium.

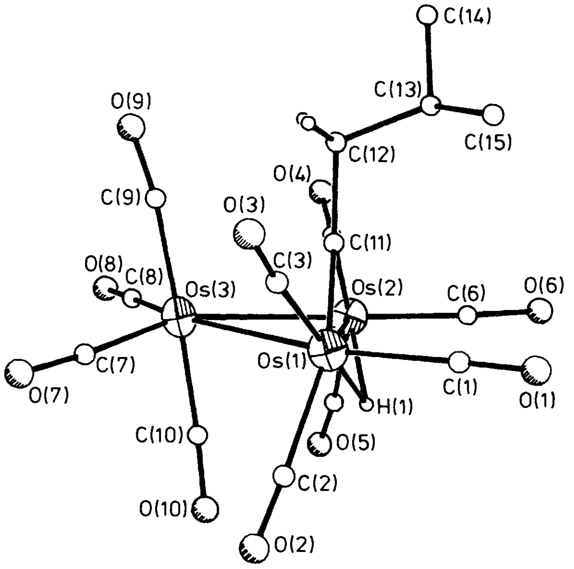


Figure. Molecular structure of complex (**1**) showing the atom-labelling scheme. Methyl and methyne group hydrogens have been omitted for clarity

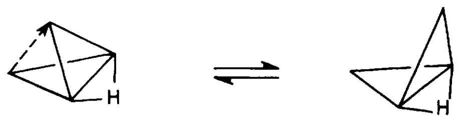
69.7°), $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}CPh)(CO)_{10}}]$[22] (2.59 Å, 78.2°), $[\mathrm{Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}}]$[23] (2.70 Å, 91°), and $[\mathrm{Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}}]$[24] (2.90 Å, 94.7°). The hydride ligand was not located in the final difference map, its position being calculated using the HYDEX program.[25] It was assigned to bridge the same Os–Os edge as the alkylidyne moiety (as was suggested by the ^{13}C n.m.r. data) at a distance set at *ca.* 1.855 Å. This value is close to the Os ··· H distances found for the symmetrically bridging hydrides in the neutron diffraction structures of $[\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}]$ and $[\mathrm{Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}}]$.[26] In complex (**1**) the metal–metal bond lengthening effect of a μ-hydride is effectively counterbalanced by the bond-shortening effect of the bridging alkylidyne, hence the osmium atoms describe an approximately equilateral triangle.

The $\mathrm{Os(CO)_4}$ unit is considerably tilted with respect to the triosmium plane [Os(1)–Os(3)–C(10) 82.6(8), Os(2)–Os(3)–C(10) 77.3(11), C(9)–Os(3)–C(10) 176.5(15), Os(1)–Os(3)–C(9) 97.1(7), and Os(2)–Os(3)–C(9) 105.6(9)°] although it still closely conforms to localised C_{2v} symmetry. This distortion presumably occurs because of the acute angle (82.1°) between the $\mathrm{Os_3}$ and Os(1)–C(11)–Os(2) planes and thus reduces the steric interaction of the isobutyl-substituted alkylidyne ligand with one of the axial carbonyls, C(9) on the $\mathrm{Os(CO)_4}$ unit. Symmetry in bonding is achieved by a shift of the other axial carbonyl C(10) towards the opposite face of the $\mathrm{Os_3}$ triangle [Os(1) ··· C(10) 3.204, Os(2) ··· C(10) 3.075 Å]. This distortion is similarly observed[23] in $[\mathrm{Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}}]$. There is clearly a difference in geometry between the alkyl- and heteroatom-substituted alkylidyne complexes. In the alkoxy and amino-alkylidyne compounds electron deficiency at the alkylidyne carbon is stabilised by π-donation from the heteroatom into the vacant unhybridised *p* orbital. This is confirmed by the observation of hindered rotation about the C–OMe[24,27] or $\mathrm{C\text{-}NMe_2}$[28] bond. In the case of the trinuclear complex (**1**) stabilisation is achieved by a donor interaction between the formally saturated (18e) $\mathrm{Os(CO)_4}$ group and the alkylidyne carbon; similar donations have been observed in the complexes $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}CH)(CO)_{10}}]$,[21] $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}CPh)(CO)_{10}}]$,[22] and $[\mathrm{Os_3(\mu\text{-}H)\{\mu\text{-}(\eta^2\text{-}CF_3CCHCF_3)\}(CO)_{10}}]$.[29]

Table 1. Bond lengths (Å) and inter-bond angles (°) for complex (**1**)

Os(1)–Os(2)	2.871(2)	Os(1)–Os(3)	2.827(2)
Os(1)–C(1)	1.965(27)	Os(1)–C(2)	1.972(30)
Os(1)–C(3)	1.879(41)	Os(1)–C(11)	2.018(24)
Os(1)–H(1)	1.854(1)	Os(2)–Os(3)	2.861(2)
Os(2)–C(4)	1.917(24)	Os(2)–C(5)	1.985(25)
Os(2)–C(6)	1.892(28)	Os(2)–C(11)	1.967(22)
Os(2)–H(1)	1.855(1)	Os(3)–C(7)	1.908(35)
Os(3)–C(8)	1.912(25)	Os(3)–C(9)	1.907(22)
Os(3)–C(10)	1.916(25)	Os(3) ··· C(11)	2.639(25)
O(1)–C(1)	1.105(33)	O(2)–C(2)	1.092(35)
O(3)–C(3)	1.191(49)	O(4)–C(4)	1.100(32)
O(5)–C(5)	1.085(30)	O(6)–C(6)	1.169(35)
O(7)–C(7)	1.145(47)	O(8)–C(8)	1.132(34)
O(9)–C(9)	1.137(30)	O(10)–C(10)	1.198(31)
C(11)–C(12)	1.525(28)	C(12)–C(13)	1.515(43)
C(13)–C(14)	1.436(38)	C(13)–C(15)	1.629(53)
Os(2)–Os(1)–Os(3)	60.3(1)	Os(2)–Os(1)–C(1)	104.8(7)
Os(3)–Os(1)–C(1)	164.7(7)	Os(2)–Os(1)–C(2)	121.0(8)
Os(3)–Os(1)–C(2)	95.4(8)	C(1)–Os(1)–C(2)	95.8(10)
Os(2)–Os(1)–C(3)	136.1(10)	Os(3)–Os(1)–C(3)	93.9(11)
C(1)–Os(1)–C(3)	95.6(13)	C(2)–Os(1)–C(3)	94.3(14)
Os(2)–Os(1)–C(11)	43.2(6)	Os(3)–Os(1)–C(11)	63.5(7)
C(1)–Os(1)–C(11)	103.8(9)	C(2)–Os(1)–C(11)	157.5(10)
C(3)–Os(1)–C(11)	94.7(12)	Os(2)–Os(1)–H(1)	39.3(1)
Os(3)–Os(1)–H(1)	81.5(1)	C(1)–Os(1)–H(1)	88.4(7)
C(2)–Os(1)–H(1)	88.2(9)	C(3)–Os(1)–H(1)	174.9(11)
C(11)–Os(1)–H(1)	81.4(7)	Os(1)–Os(2)–Os(3)	59.1(1)
Os(1)–Os(2)–C(4)	140.2(8)	Os(3)–Os(2)–C(4)	98.5(8)
Os(1)–Os(2)–C(5)	122.3(10)	Os(3)–Os(2)–C(5)	99.7(10)
C(4)–Os(2)–C(5)	91.9(11)	Os(1)–Os(2)–C(6)	102.7(8)
Os(3)–Os(2)–C(6)	161.3(8)	C(4)–Os(2)–C(6)	93.7(11)
C(5)–Os(2)–C(6)	93.9(12)	Os(1)–Os(2)–C(11)	44.6(7)
Os(3)–Os(2)–C(11)	63.1(8)	C(4)–Os(2)–C(11)	96.9(10)
C(5)–Os(2)–C(11)	161.7(13)	C(6)–Os(2)–C(11)	101.5(11)
Os(1)–Os(2)–H(1)	39.3(1)	Os(3)–Os(2)–H(1)	80.5(1)
C(4)–Os(2)–H(1)	179.0(9)	C(5)–Os(2)–H(1)	88.2(9)
C(6)–Os(2)–H(1)	87.2(8)	C(11)–Os(2)–H(1)	82.8(7)
Os(1)–Os(3)–Os(2)	60.6(1)	Os(1)–Os(3)–C(7)	94.9(9)
Os(2)–Os(3)–C(7)	152.8(9)	Os(1)–Os(3)–C(8)	154.7(9)
Os(2)–Os(3)–C(8)	94.1(9)	C(7)–Os(3)–C(8)	109.3(13)
Os(1)–Os(3)–C(9)	97.1(7)	Os(2)–Os(3)–C(9)	105.6(9)
C(7)–Os(3)–C(9)	87.9(13)	C(8)–Os(3)–C(9)	91.3(10)
Os(1)–Os(3)–C(10)	82.6(8)	Os(2)–Os(3)–C(10)	77.3(11)
C(7)–Os(3)–C(10)	88.6(13)	C(8)–Os(3)–C(10)	90.4(11)
C(9)–Os(3)–C(10)	176.5(15)	Os(1)–Os(3)–C(11)	43.2(5)
Os(2)–Os(3)–C(11)	41.7(5)	C(7)–Os(3)–C(11)	127.4(10)
C(8)–Os(3)–C(11)	119.1(10)	C(9)–Os(3)–C(11)	72.4(9)
C(10)–Os(3)–C(11)	109.3(10)	Os(1)–C(1)–O(1)	178.7(15)
Os(1)–C(2)–O(2)	175.2(26)	Os(1)–C(3)–O(3)	174.6(31)
Os(2)–C(4)–O(4)	178.8(27)	Os(2)–C(5)–O(5)	174.0(31)
Os(2)–C(6)–O(6)	176.6(21)	Os(3)–C(7)–O(7)	174.9(25)
Os(3)–C(8)–O(8)	179.1(28)	Os(3)–C(9)–O(9)	172.3(29)
Os(3)–C(10)–O(10)	175.7(33)	Os(1)–C(11)–Os(2)	92.2(8)
Os(1)–C(11)–Os(3)	73.4(8)	Os(2)–C(11)–Os(3)	75.2(7)
Os(1)–C(11)–C(12)	134.5(18)	Os(2)–C(11)–C(12)	132.9(19)
Os(3)–C(11)–C(12)	117.6(16)	C(11)–C(12)–C(13)	112.6(21)
C(12)–C(13)–C(14)	109.8(27)	C(12)–C(13)–C(15)	112.9(27)
C(14)–C(13)–C(15)	109.7(26)	Os(1)–H(1)–Os(2)	101.4(1)

With the establishment of the structure of (**1**) in the solid state it is possible to return to the question of the solution n.m.r. spectra. The ^{13}C n.m.r. spectrum showed carbonyl resonances at 174.6, 174.3, 174.0, and 169.7 p.p.m. in a 4:2:2:2 ratio. Because the last three resonances showed couplings to the bridging hydride of 3.4, 11.2, and 2.9 Hz respectively, these are assigned to the carbonyls *cis*, *trans*, and *cis* to the bridging hydride. The resonance at 174.6 p.p.m. showed zero coupling to the bridging hydride and appears as a sharp singlet at room temperature collapsing to a broad signal at −50 °C. This equivalency can be explained in terms of a polytopal rearrangement.[24,27] More interestingly the ^{13}C chemical shift of the alkylidyne carbon is temperature dependent, moving to higher



(1a) **(1b)**

μ-CR	Os ⋯ C/Å	Fold angle/°	δ(^{13}C)/p.p.m.
μ-CH	2.35	69.7	219
μ-CPh	2.59	78.2	304
μ-CCH$_2$CMe$_2$	2.63	82.1	312
μ-COMe	3.02	96	346

Scheme 1.

frequency as the temperature is raised: δ 312.0 (−80), 314.0 (−50), 317.05 (−20), 317.95 (0), 319.5 (22), and 320.54 (40 °C). Similar behaviour was noted[22] for [Os$_3$(μ-H)(μ-CPh)(CO)$_{10}$] where the alkylidyne carbon shifted from δ 304 at 158 K to 315 at 290 K. It is suggested that in solution the alkylidyne moiety in (**1**) is in equilibrium between a geometry where the angle between the Os$_3$ and Os$_2$ (μ-C) planes is acute, as in the crystal structure, and an open geometry as observed in the heteroatom-substituted alkylidyne complexes (Scheme 1). At low temperatures, (**1a**) is thermodynamically favoured, where electron deficiency at the alkylidyne carbon is stabilised by its electrophilic interaction with the saturated Os(CO)$_4$ group. As the temperature is increased the equilibrium shifts in favour of (**1b**). Electron donation from the saturated Os(CO)$_4$ unit is reduced and the alkylidyne carbon resonance moves to higher frequency. This argument is supported by the monotonic relationship between the ^{13}C chemical shifts for the μ-alkylidyne carbon and the Os⋯C distance or fold angle for the complexes [Os$_3$(μ-H)(μ-CR)(CO)$_{10}$], implying the 'average' Os–C distance rises with temperature in the μ-CPh and μ-CCH$_2$CHMe$_2$ cases.

There is a second product (**2**) in the reaction of 3,3-dimethylcyclopropene with [Os$_3$(μ-H)$_2$(CO)$_{10}$], which can be separated by repeated recrystallisations and obtained as yellow crystals in yields of *ca.* 10%. Elemental analysis, mass spectrometry (m.s.), and ^{1}H and ^{13}C n.m.r. spectroscopy showed that the trinuclear complex was the dimethylvinyl-substituted μ-alkylidyne complex [Os$_3$(μ-H)(μ-CCH=CMe$_2$)(CO)$_{10}$]. The presence of a vinyl group was indicated from the presence of a slightly broadened singlet in the ^{1}H spectrum at 8.42 as well as methyl singlets at 2.13 and 2.05 with the bridging hydride resonating at −16.26. The carbonyl region of the ambient temperature proton-coupled ^{13}C spectrum shows resonances at 176.6 (s, 2 C), 175.7 (s, 4 C), 174.1 [d, 2 C, ^2J(CH) 9.8], and 169.8 (s, 2 C), indicating that the molecule possesses a time-averaged plane of symmetry and thus the cluster as a whole conforms to C_s symmetry, as in (**1**). The alkylidyne carbon resonates at higher frequency (332.3 p.p.m.), and in contrast to that of (**1**) is not temperature dependent. Presumably, the lack of electron donation from the Os(CO)$_4$ unit in complex (**2**) is partially compensated for by π interaction with the vinyl moiety, although there is free rotation about the alkylidyne carbon–vinyl substituent bond on the low-temperature n.m.r. time-scale.

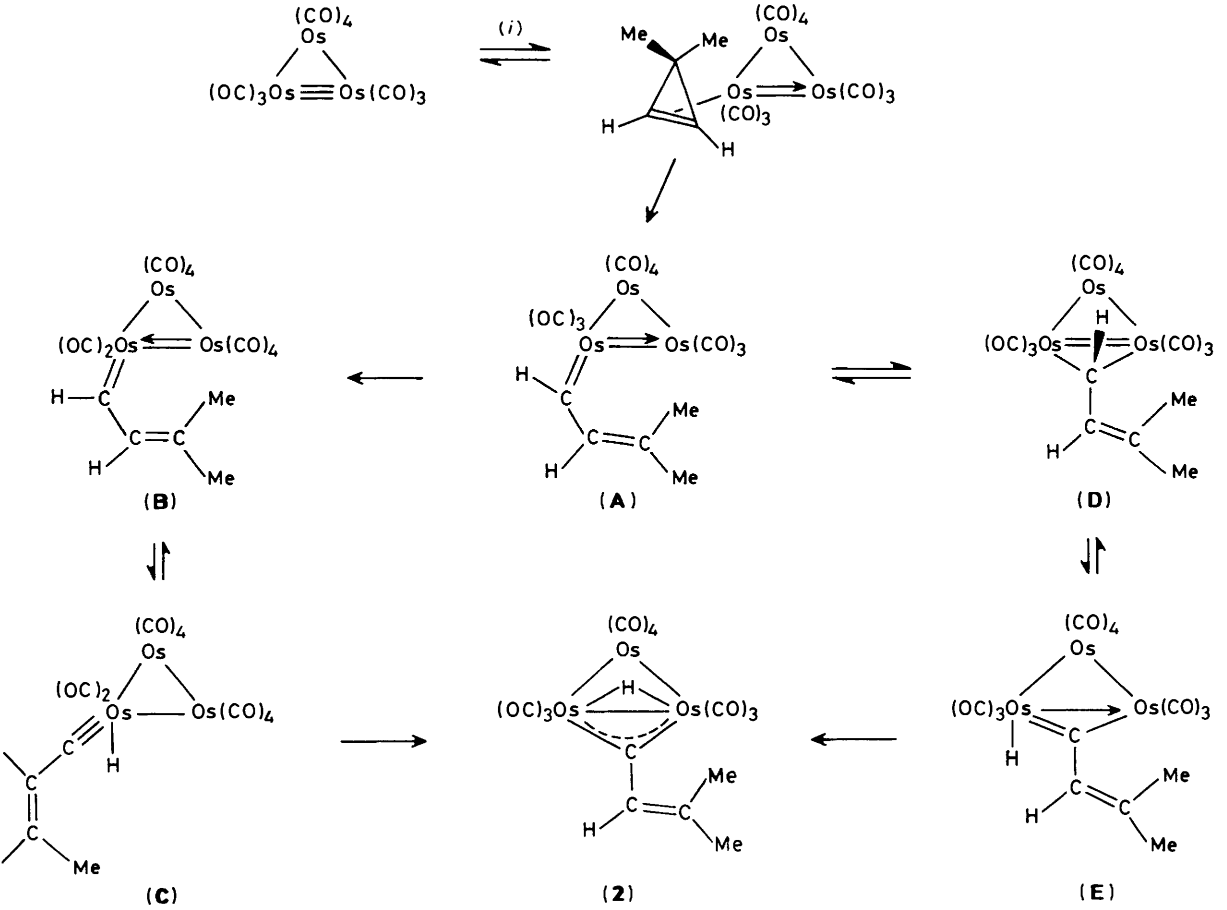
The formation of complexes (**1**) and (**2**) under mild conditions is unusual in that both carbon–carbon σ bond and alkene C–H bond cleavage occurs. In order to elucidate the reaction paths followed in the formation of (**1**) and (**2**) the reaction of [Os$_3$(μ-D)$_2$(CO)$_{10}$] with 3,3-dimethylcyclopropene was studied. The reaction is regioselective in that deuterium incorporation occurs only into the Os(μ-D)Os and Os(μ-CCHDCHMe$_2$)Os sites of (**1**) as determined by ^{1}H, ^{2}D, and ^{13}C-{^{1}H} n.m.r. spectroscopy. Significantly, there is no H incorporation into the bridging site (< 2%) and no Os(μ-CCH$_2$CHMe$_2$)Os is formed. This suggests that H/D site exchange does not occur on the triosmium framework. Consequently hydrogen migration from a formerly alkene C–H bond of the cyclopropene (to create the alkylidyne carbon) to the CMe$_2$ group (to produce the isopropyl group) must either be non-metal assisted or else occur before the CMe$_2$ group becomes attached to the Os$_3$ core, otherwise deuterium incorporation into the isopropyl group would seem inevitable, as facile H/D site exchange would be expected to occur. The absence of any protons in the bridging site implies that if the proton does migrate *via* the metal selective C–H insertion occurs at a rate significantly faster than H/D site exchange. In comparison it is interesting that there is a marked preference for H in bridging sites on reaction of [Os$_3$(μ-H)$_2$(CO)$_{10}$] with CD$_2$N$_2$,[26] and secondly H/D site exchange is facile in the complex [Os$_3$(μ-H)(μ-D)(μ-C=CH$_2$)(CO)$_9$].[30]

There is no deuterium incorporation into complex (**2**), suggesting that this is formed by capture of a [Os$_3$(CO)$_{10}$] fragment, which is generated by competing deuteriation of 3,3-dimethylcyclopropene. In agreement, analysis of the volatile reaction products by ^{2}D n.m.r. spectroscopy shows only a singlet a 0.36 p.p.m., a chemical shift characteristic of cyclopropane-type protons. This evidence is supported by the observation that (**2**) is also formed by displacement of methane by 3,3-dimethylcyclopropene from the equilibrating species [Os$_3$(μ-H)(μ-CH$_3$)(CO)$_{10}$] and [Os$_3$(μ-H)$_2$(μ-CH$_2$)(CO)$_{10}$], a reaction which in a sense parallels the formation[31] of [Os$_3$(CO)$_{10}$(PMe$_2$Ph)] from PMe$_2$Ph and [Os$_3$(μ-H)(μ-CH$_3$)(CO)$_{10}$]. This reaction to form (**2**) requires more forcing conditions (refluxing hexane) and proceeds less cleanly, however the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of the reaction mixture are characteristic of the starting material together with minor decomposition products, and the major product (**2**).

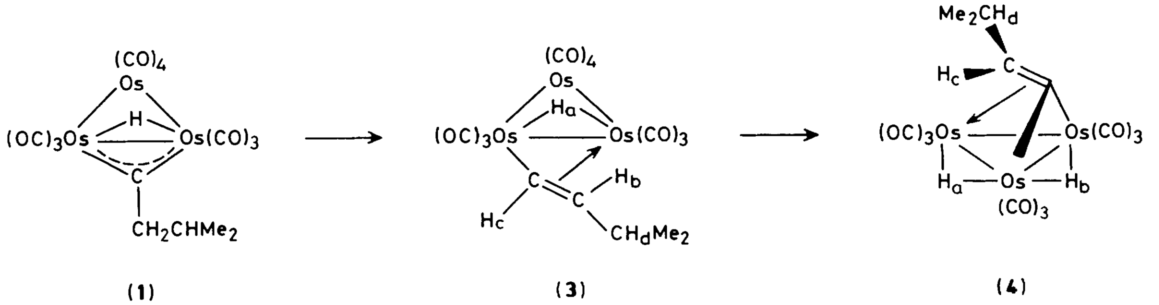
Since the evidence indicates that complex (**2**) is formed by initial capture of [Os$_3$(CO)$_{10}$] by 3,3-dimethylcyclopropene, it is reasonable to suggest that a 2,3 σ-bond cleavage reaction occurs similar to that observed with the Mo$_2$[4,5] and Re$_2$[6,7] systems, and discussed in the Introduction. Thus, as is shown in Scheme 2, η^2 co-ordination of the cyclopropene to one of the osmium centres could lead to formation of the vinylcarbene complex (**A**). There are now, as is illustrated in Scheme 2, two possible pathways available to (**2**). The first involves carbonyl transfer allowing access to (**B**), where a vinylcarbene ligand is terminally bonded onto a 16-electron osmium centre. Since certain carbene complexes carrying an α-hydrogen are known[32] reversibly to rearrange to hydridoalkylidynes it is reasonable to suggest the intervention of the equilibrium (**B**) $\rightleftharpoons$ (**C**), which provides a path to the bridged hydridoalkylidyne complex (**2**). The alternative route to (**2**) requires two metal centres and involves the transformation, possibly *via* a μ-allylidene, of (**A**) into the μ-vinylcarbene complex (**D**). This is followed by an α-hydrogen elimination reaction giving (**E**), which can then rearrange to (**2**).

The formation of the main product (**1**) is more difficult to explain. The regioselective incorporation of deuterium into the Os(μ-D)Os and Os(μ-CCHDCHMe$_2$)Os sites implies a relatively complex and selective sequence of reactions.

With the availability of the bridged carbyne complex (**1**) it was obviously interesting to begin to examine its reaction chemistry. Thermolysis of (**1**) in refluxing octane–hexane (1:1) (100 °C) resulted in the formation of two triosmium complexes. These proved to be inseparable using silica gel column chromatographic techniques, and therefore a work-up procedure was adopted which involved removal of solvent and recrystallisation from hexane. This allowed the isolation of [Os$_3$(μ-H)(μ-CH=CHCHMe$_2$)(CO)$_{10}$] (**3**) and [Os$_3$(μ-H)$_2$(μ-C=CHCHMe$_2$)(CO)$_9$] (**4**) as a mixture, and they were characterised by i.r., ^{1}H and ^{13}C-{^{1}H} n.m.r. spectroscopy (see Experimental section). When the thermolysis reaction was monitored by ^{1}H n.m.r. it was observed that the singlet at − 16.73 due to (**1**) is replaced by a hydride resonance due to (**3**) at −18.95 [d, H$_a$,



Scheme 2. (*i*) + 3,3-dimethylcyclopropene

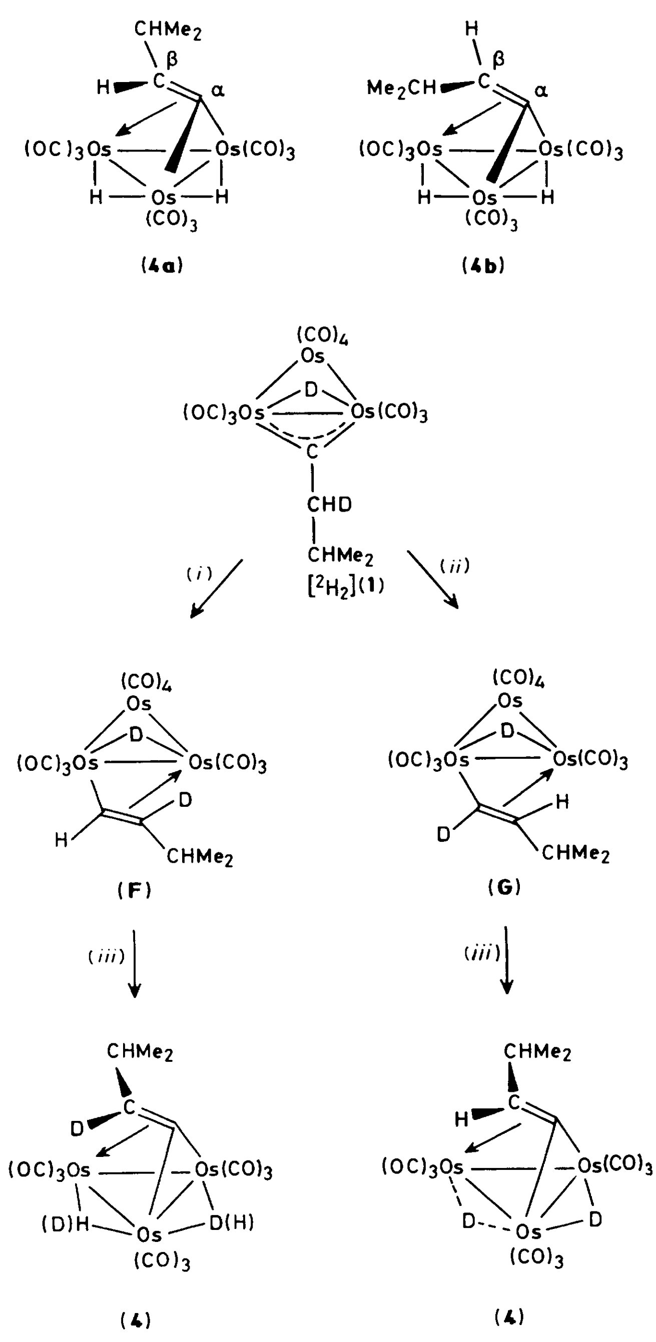


Complex	Product ratios		
	0 h	4 h	16 h
(**1**)	1.0	0.42	—
$[Os_3(\mu\text{-}H)_2(CO)_{10}]$	—	—	0.1
(**3**)	—	0.48	0.30
(**4**) major	—	0.10	0.47
minor	—	—	0.11

Scheme 3.

$^3J(H_aH_c)$ 1.7 Hz]. Subsequently resonances due to (**4**) at -18.27 (d, H_b) and -21.35 [d, H_a, $^2J(H_aH_b)$ 1.28 Hz] were observed with concomitant disappearance of (**3**). As is shown in Scheme 3 the relative proportion of complex (**4**) compared to (**3**) as determined by ^1H n.m.r. spectroscopy increases with time, indicating that (**4**) is produced from (**3**) by the known[33] rearrangement of μ-vinyl to μ-vinylidene complexes rather than directly from (**1**). Presumably some $[Os_3(CO)_{12}]$ is also produced in the thermolysis due to capture of the CO liberated in the conversion of (**3**) into (**4**), then reductive elimination of the organic fragment. However, the origin of the $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ is not apparent.

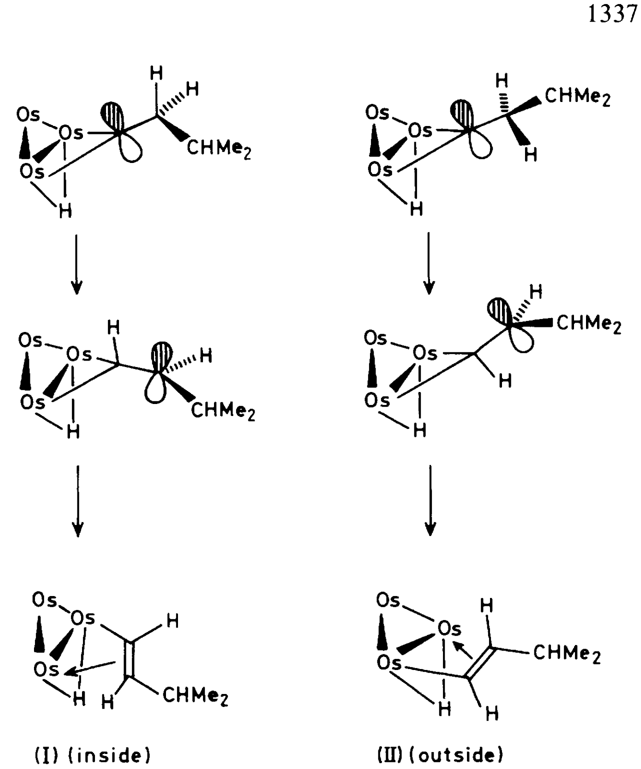
The presence of a minor isomer of (**4**) is surprising, and was indicated by the presence of singlets at -18.32 and -21.39 p.p.m. This is possibly due to two orientations of the μ-C=CHCHMe$_2$ moiety in (**4**). The presence of two sharp resonances for the inequivalent hydridic sites in the room-temperature ^1H n.m.r. spectrum of (**4**) implies that they are static at this



Scheme 4. (*i*) 1,2-H shift; (*ii*) 1,2-D shift; (*iii*) -CO. Note the μ-vinylidene complexes are shown as those formed before randomisation of H/D sites

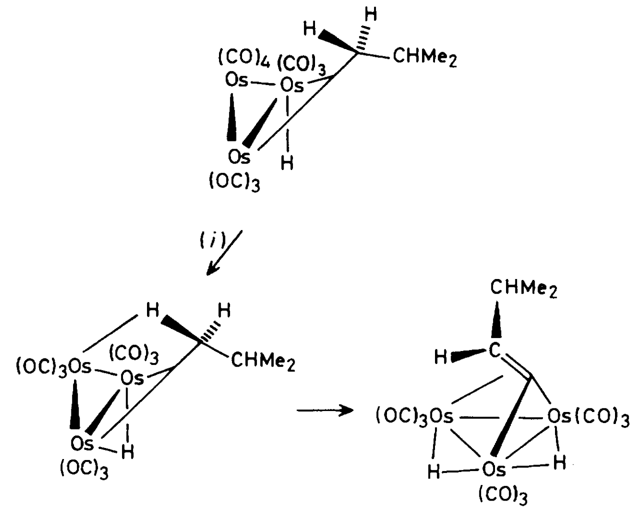
temperature, which suggests two geometries for the vinylidene fragment. Hydride fluxionality or rotation about the vinylidene carbon CHPr^i bond would effectively equivalence these conformations. In the μ-vinyl species (**4**) the prochiral methyl groups would be diastereotopic in a static structure. No evidence for anisochronicity was observed in the room-temperature ^{1}H n.m.r. spectrum indicating that the μ-vinyl group is undergoing a rapid σ/π-bond exchange process analogous to that observed in $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ and $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$.[34,35]

In order to examine more carefully the nature of the hydrogen-shift process involved in the transformation of (**1**) into (**3**), the thermolysis of $[Os_3(\mu\text{-}D)(\mu\text{-}CCHDCHMe_2)(CO)_{10}]$ was monitored by ^{1}H n.mr. spectroscopy. Complex $[^2H_2]$ (**1**) was dissolved in $[^2H_8]$toluene contained in a sealed n.m.r. tube and heated at 95 °C. It was then cooled and placed in the n.m.r. spectrometer probe at ambient temperature (22 °C), and spectra accumulated. Spectra were run periodically over a total time of 7.5 h at 95 °C. The initial spectrum ($t = 0$) showed essentially pure $[^2H_2]$(**1**) with impurities due to *ca.* 1% $[Os_3(\mu\text{-}CCH{=}CMe_2)(CO)_{10}]$ and a similar amount of $[Os_3(\mu\text{-}H)(\mu\text{-}CCHDCHMe_2)(CO)_{10}]$. On thermolysis the α- and β-methine proton resonances in the $[^2H_2]$μ-vinyl complexes, (**F**) and (**G**) (Scheme 4), were reduced to a singlet (7.24) and a doublet [4.40, ^3J(HH) 6.8 Hz] respectively, relative to $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHCHMe_2)(CO)_{10}]$ (**3**), indicating that no (*ca.* < 10%) μ-vinyl complex was formed with hydrogens in both vinylic positions. Secondly, integration of the two vinylic sites (which ought to show a combined total of one proton) *versus* the integration of μ-hydride resonance in (**F**) plus (**G**) shows approximately equal intensity. A ^{2}D n.m.r. spectrum of the reaction mixture after thermolysis for 7.5 h at 95 °C showed significant deuterium incorporation in both methine and methyl sites of the isopropyl group. There was no significant intermolecular H/D exchange between solvent and organometallic complexes. There was also no H/D scrambling in $[^2H_2]$(**1**) under the reaction conditions. Finally some $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and/or $[Os_3(\mu\text{-}H)(\mu\text{-}D)(CO)_{10}]$ is also produced.



Scheme 5. Terminal carbonyl ligands omitted for clarity

Thus, these observations are consistent with a mechanism for the conversion of complex (**1**) into (**3**) which involves a 1,2 shift by the protons of the methylene group $CC\mathit{H}_2CHMe_2$ to the electron-deficient carbyne carbon without direct assistance by the metal. In a sense such a process parallels a sigmatropic 1,2 H shift, a common rearrangement reaction in carbonium ion chemistry. There is also a relationship with the reported rearrangement of the dinuclear μ-carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CCH_2R)(CO)_2(\eta\text{-}C_5H_5)_2]$ into the μ-vinyl complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\eta^2\text{-}(E)\text{-}CH{=}CHR\}(CO)_2(\eta\text{-}C_5H_5)_2]$.[36–38] It is also interesting that in a recent theoretical analysis of these hydrogen-shift processes it was suggested[39] that the triosmium cluster reaction (**1**) $\longrightarrow$ (**3**) may be related to the observation[40] that when C_2H_4 is chemisorbed on surfaces of Rh(111), Pt(111),



Scheme 6. (*i*) U.v., –CO

and Pd(111) and then heat applied the metal surface becomes covered with a monolayer of the ethylidyne CMe. As can be seen in Scheme 5 there are in principle two possible pathways for the transformation (**1**) ⟶ (**3**) which differ in the sense that in path (I) the migrating hydrogen moves down the 'inside' of the folded array, whereas in path (II) the migrating hydrogen trajectory is on the 'outside.' Because the electron-deficient μ-carbyne carbon interacts with the $Os(CO)_4$ unit it is more likely that path (II) is preferred, where in a sense the migrating hydrogen is effectively displacing the $Os(CO)_4$ donor group by rear attack on the μ-carbyne carbon. At the reaction temperature, there would appear to be no significant primary deuterium isotope effect for the 1,2 shift, because of the approximately equal ratio of H and D observed in the α-carbon atom.

In contrast to the thermolysis of complex (**1**) u.v. photolysis (15 min, 20 °C) led to the facile formation of (**4**) directly. This is presumably due to photochemical-induced CO loss from the $Os(CO)_4$ unit, then abstraction of a hydrogen from the methylene group to stabilise the electron-deficient osmium centre (Scheme 6). Hydrogen abstraction from the methylene rather than the methyl groups presumably occurs due to the steric bulk of the isopropyl group, its non-bonding interactions with the carbonyls on Os(3) preventing its coming into close proximity.

Experimental

The ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra were recorded on a JEOL FX 90Q or FX200 spectrometer as appropriate. Data are given for room-temperature measurements, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference, $SiMe_4$ for ^{13}C and ^1H. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Reaction of 3,3-*Dimethylcyclopropene with* $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.—3,3-Dimethylcyclopropene (0.3 cm^3) was added to a solution of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (0.7 g, 0.82 mmol) in degassed hexane (100 cm^3) contained in a tube fitted with a Westof stopcock. After 16 h at room temperature the volatiles were removed *in vacuo* and the residue extracted with hexane (2 × 10 cm^3) and filtered through a Celite pad (3 × 3 cm). Removal of the solvent followed by recrystallisation (–20 °C) from hexane–diethyl ether gave orange crystals of complex (**1**) which were slightly contaminated with $[Os_3(\mu\text{-}H)(\mu\text{-}CCH{=}CMe_2)(CO)_{10}]$ (**2**). The former was obtained pure by recrystallisation, (**1**) (0.65 g, 86%) (Found: C, 20.0; H, 1.1%; *M* 922. $C_{15}H_{10}O_{10}Os_3$ requires C, 19.6; H, 1.1%; *M* 922), ν_{CO}(hexane) 2 105w, 2 059vs, 2 023m, 2 013s, 2 001m, and 1 989s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), δ 4.51 [d, 2 H, CH_2, ^3J(HH) 5.6], 1.79 [t of septets, 1 H, $CHMe_2$, ^3J(HH) 5.6, 6.6], 1.15 [d, 6 H, 2 × Me, ^3J(HH) 6.6], and –16.73 (s, 1 H, μ-H); ^{13}C (CD_2Cl_2, ^1H coupled), δ 319.5 [dt, CCH_2CHMe_2, ^2J(CH) 5.4, 5], 174.6 (s, 4 CO), 174.3 [d, 2 CO, ^2J(CH) 3.4], 174.0 [d, 2 CO, ^2J(CH) 11.2], 169.7 [d, 2 CO, ^2J(CH) 2.9], 73.1 [t, CCH_2CHCMe_2, ^1J(CH) 128], 36.8 [d, CCH_2CHCMe_2, ^1J(CH) 128], and 23.4 p.p.m. [q, $CHMe_2$, ^1J(CH) 128]. The chemical shift of the alkylidyne carbon resonance is temperature dependent: δ 312.0 (–80), 314.4 (–50), 317.05 (–20), 318.0 (0), 319.5 (22), and 320.54 p.p.m. (40 °C). Recrystallisation of the mother-liquors afford yellow *crystals* of (**2**)* (0.07 g, 10%) (Found: C, 19.2; H, 1.0%; *M* 919. $C_{15}H_8O_{10}Os_3$ requires C, 19.6; H, 0.9%; *M* 919), ν_{CO}(hexane) 2 105w, 2 058vs, 2 021 (sh), 2 015s, and 1 989s cm^{-1}. N.m.r.: ^1H($CDCl_3$), δ 8.42 (br s, 1 H, CH), 2.13 (s, 3 H, Me), 2.05 (s, 3 H, Me), and –16.26 (s, 1 H, μ-H); ^{13}C-$\{^1H\}$ (CD_2Cl_2), δ 332.3 (μ-C), 176.6 (2 CO), 175.7 (4 CO), 174.1 [2 CO, ^2J(CH) 10], 169.8 (2 CO), 152.5 [CH, ^1J(CH) 150], 148.9 (CMe_2), 28.8 (Me), and 20.6 p.p.m. (Me).

Preparation of $[Os_3(\mu\text{-}D)(\mu\text{-}CCHDCHMe_2)(CO)_{10}]$.—The complex $[Os_3(\mu\text{-}D)_2(CO)_{10}]$ was prepared from a D_2 purge and $[Os_3(CO)_{12}]$ in refluxing octane. Typical isotopic enrichment was 95% $[Os_3(\mu\text{-}D)_2(CO)_{10}]$, 4.9% $[Os_3(\mu\text{-}H)(\mu\text{-}D)(CO)_{10}]$, and 0.1% $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ by mass-spectral analysis. Reaction with 3,3-dimethylcyclopropene resulted in regioselective deuterium incorporation only in the Os(μ-D)Os and Os(μ-$CCHDCHMe_2$)Os sites of (**1**). The ^1H n.m.r. spectrum was identical to that of (**1**) except for the doublet at 4.51 p.p.m. [^3J(HH) 5.6 Hz], which had an integrated intensity relative to the methyl groups of one proton, and was broadened slightly due to unresolved deuterium coupling. The hydride region showed a peak of *ca.* 2% of the expected intensity at a chemical shift characteristic of (**1**). The ^{13}C n.m.r. spectrum was essentially identical to that of (**1**) except for the peak assignable to the methylene carbon at 73.1 p.p.m., which appeared as a 1:1:1 triplet [^1J(CD) 19.6 Hz]. The ^2D n.m.r. showed no deuterium incorporation into the isopropyl group.

Thermolysis of $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ (**1**).—A solution of complex (**1**) (0.3 g, 0.32 mmol) in octane–hexane (1:1) (120 cm^3) was heated under reflux. After 8 h, examination of the i.r. spectrum showed the reaction to be complete. The solvent was removed *in vacuo*, and the residue extracted into hexane (2 × 10 cm^3), filtered through a Celite pad (3 × 3 cm), and cooled (–78 °C) to give a crystalline mixture (0.2 g, 70%) of (**3**) and (**4**). N.m.r. data for (**3**): ^1H ($CDCl_3$), δ 7.25 [dddd, 1 H, H_c, $^3J(H_cH_b)$ 14, $^3J(H_cH_a)$ 1.7, $^4J(H_cH_d)$ 0.6], 4.39 [dd, 1 H, H_b, $^3J(H_bH_c)$ 14, $J(H_bH_d)$ 7.1], 1.8 (m, 1 H, H_d), 1.30 [d, 6 H, 2 × Me, $^3J(HH_d)$ 6.6], and –18.95 [d, 1 H, H_a, $^3J(H_aH_c)$ 1.7]; ^{13}C-$\{^1H\}$ (CD_2Cl_2, selected data), δ 112.5 [CH, ^1J(CH) 153], 95.8 [CH, ^1J(CH) 149], 39.8 ($CHMe_2$), and 23.6 p.p.m. (2 × Me). N.m.r. data for (**4**): ^1H ($CDCl_3$), δ 6.74 [d, 1 H, H_c, $^3J(H_cH_d)$ 9], 1.8 (m, 1 H, H_d), 1.18 [d, 6 H, 2 × Me, $^3J(HH_d)$ 6.8], –18.27 [d, 1 H, H_b, $^2J(H_bH_a)$ 1.28], and –21.35 [d, 1 H, H_a, $^2J(H_aH_b)$ 1.28]; ^{13}C-$\{^1H\}$ ($CDCl_3$), δ 201.7 ($C{=}CHCHMe_2$), 103.3 [CH, $CHMe_2$, ^1J(CH) 155], 43.8 ($CHMe_2$), 27.0 (Me), and 23.2 p.p.m. (Me).

Thermolysis of $[Os_2(\mu\text{-}D)(\mu\text{-}CCHDCHMe_2)(CO)_{10}]$.—Thermolysis was performed in a refluxing hexane–octane mix-

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* The yield of (**2**) was not readily reproducible.

Table 2. Atomic co-ordinates (× 10^4) for complex (**1**)

Atom	x	y	z
Os(1)	3 499(1)	2 904(1)	1 791(1)
Os(2)	1 710(1)	735(1)	1 770(1)
Os(3)	2 973(1)	1 045(1)	3 498(1)
O(1)	3 404(25)	4 584(19)	−212(14)
O(2)	7 014(20)	1 965(23)	1 280(17)
O(3)	3 204(28)	5 666(25)	3 152(19)
O(4)	−1 259(25)	−52(26)	3 015(15)
O(5)	3 209(30)	−2 508(19)	1 151(18)
O(6)	603(26)	1 444(22)	−205(14)
O(7)	5 298(28)	1 858(29)	4 533(22)
O(8)	1 781(30)	−1 482(22)	4 672(16)
O(9)	635(28)	3 250(26)	5 148(19)
O(10)	5 690(24)	−1 135(22)	1 955(17)
C(1)	3 424(22)	3 992(22)	516(22)
C(2)	5 768(35)	2 354(29)	1 440(23)
C(3)	3 336(37)	4 552(47)	2 664(25)
C(4)	−184(26)	240(28)	2 553(20)
C(5)	2 676(35)	−1 351(28)	1 316(24)
C(6)	1 046(30)	1 129(26)	536(19)
C(7)	4 471(33)	1 560(30)	4 100(23)
C(8)	2 217(30)	−542(26)	4 230(19)
C(9)	1 444(36)	2 449(26)	4 485(17)
C(10)	4 604(38)	−318(30)	2 533(21)
C(11)	1 297(28)	2 720(23)	2 428(19)
C(12)	−174(25)	3 762(26)	3 061(19)
C(13)	−1 164(32)	4 476(33)	2 370(26)
C(14)	−2 715(35)	5 031(45)	3 009(30)
C(15)	−500(38)	5 791(44)	1 706(37)

ture as previously described in C_7D_8 at 95 °C. The final reaction mixture showed (^1H and ^2D n.m.r. spectroscopy) peaks attributable to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, $[Os_3(\mu\text{-}D)_2(CO)_{10}]$, $[Os_3(\mu\text{-}D)(\mu\text{-}CH{=}CDCHMe_2)(CO)_{10}]$, $[Os_3(\mu\text{-}D)(\mu\text{-}CD{=}CHCHMe_2)(CO)_{10}]$, $[Os_3(\mu\text{-}XY)(\mu\text{-}C{=}CHCHMe_2)(CO)_9]$, and $[Os_3(\mu\text{-}XY)(\mu\text{-}C{=}CDCHMe_2)(CO)_9]$ where XY = HD or D_2. By integration of the resonances at 7.27 and 4.48 p.p.m. in the ^2D n.m.r. spectra the ratio of $[Os_3(\mu\text{-}D)(\mu\text{-}CH{=}CDCHMe_2)(CO)_{10}]$ to $[Os_3(\mu\text{-}D)(\mu\text{-}CD{=}CHCHMe_2)(CO)_{10}]$ was found to be *ca.* 1.5:1.

Photolysis of $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$.—A solution of complex (**1**) (0.05 g, 0.054 mmol) in hexane (50 cm^3) was irradiated (250 W, u.v.) in a water-cooled quartz apparatus. Monitoring the reaction by i.r. spectroscopy showed that the reaction was complete after 15 min. The solvent was removed *in vacuo* and the residue dissolved in pentane (2 × 5 cm^3) and recrystallised (−78 °C) from pentane to give yellow crystals of complex (**4**) (0.042 g, 87%).

Structure Analysis of $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ (**1**).—*Crystal data.* $C_{15}H_{10}O_{10}Os_3$, $M = 920.6$, triclinic, space group $P\bar{1}$, $a = 9.226(3)$, $b = 9.333(5)$, $c = 13.136(7)$ Å, $\alpha = 89.70(4)$, $\beta = 74.18(4)$, $\gamma = 78.00(3)°$, $U = 1\,062.9(9)$ Å^3, $Z = 2$, $D_c = 2.48$ g cm^{-3}, $F(000) = 815.7$, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 179.6$ cm^{-1}.

All diffraction measurements were made on a Nicolet P3m diffractometer using graphite-monochromated Mo-K_α *X*-radiation. Unit-cell dimensions were determined from 15 centred reflections in the range $20.0 < 2\theta < 30.0°$. Data were collected at room temperature for a unique hemisphere of reciprocal space for $4 < 2\theta < 50°$ using a crystal of approximate dimensions 0.26 × 0.30 × 0.45 mm mounted under N_2 in a glass capillary. An absorption correction was applied on the basis of azimuthal scan data collected at 10° increments of the azimuthal angle for five reflections and their Friedel opposites. Transmission coefficients for the full data set (3 614 intensities) varied from 0.017 to 0.049. The structure was solved by conventional heavy-atom methods and refined by blocked-cascade least squares. Hydrogen atoms of the s-butyl group were constrained to ideal geometries (C–H 0.96 Å, H–C–H 109.5°) and the hydride hydrogen placed on the basis of HYDEX[25] calculations so as to have Os–H ≈ 1.85 Å; all hydrogens were assigned fixed isotropic displacement parameters. All other atoms were refined without positional constraints and with anisotropic displacement parameters. Refinement converged to final residual indices $R = 0.071$, $R' = 0.075$, $S = 1.34$* for 2 931 unique, observed $[I > 1.5\sigma(I)]$ data. Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$. Here $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.003$ was chosen to minimise the variation in S as a function of F_o. Final difference electron-density maps showed no features outside the range +2.7 to −3.2 e Å^{-3}, all the largest of these being close (within 1.0 Å) to the osmium atoms. Table 2 lists the final atomic positional parameters for the non-hydrogen atoms. All calculations were carried out on a Nicolet R3m/E structure determination system using programs of the SHELXTL package.[41] Complex neutral-atom scattering factors were taken from ref. 42.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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* $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, and $\Delta = |F_o| - |F_c|$ where N_o and N_v and the numbers of observables and variables respectively.

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