An Unusual Carbon–Carbon σ-Bond Cleavage Reaction on attempted Methylation of the Anionic Alkene Cluster $[Os_3H(\mu\text{-}CO)\{CF_3(H)C{=}C(H)CF_3\}(CO)_9]^-$; *X*-Ray Crystal Structure of $[Os_3H(\mu_3\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCF_3)(CO)_9]$†

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Attempted methylation of the anionic fluoroalkene cluster $[Os_3H(\mu\text{-}CO)\{CF_3(H)C{=}C(H)CF_3\}(CO)_9]^-$ (1) with $[Me_3O][BF_4]$ at room temperature gives four neutral products, $[Os_3H\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (2), $[Os_3H(\mu_3\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCF_3)(CO)_9]$ (4), $[Os_3H_2\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}CCF_3\}(CO)_9]$ (5), and an uncharacterised complex (6). The formation of (4), a major product of the reaction, necessitates the cleavage of a carbon–carbon σ-bond and an *X*-ray analysis of (4), confirming its structure, is presented. Crystals of (4) are triclinic, space group $P\bar{1}$, with a = 14.354(2), b = 9.510(1), c = 6.714(1) Å, α = 103.21(2), β = 93.81(2), γ = 90.66(2)°, and Z = 2. 2 645 Unique observed data [$F \geqslant 6\sigma(F_o)$, $3 \leqslant \theta \leqslant 25°$] refined to an R value of 0.028.

Carbon–hydrogen bond cleavage in metal cluster chemistry is a commonly observed reaction and often takes place under mild reaction conditions.[1] Carbon–carbon bond cleavage is much rarer and, although there are examples in the literature of the breaking of C=C [2,3] and C–C [4,5] bonds, relatively forcing conditions are generally required.

We have previously reported the preparation of the anionic cluster alkene complex $[Os_3H(\mu\text{-}CO)\{CF_3(H)C{=}C(H)CF_3\}(CO)_9]^-$ (1) from the reaction of $[Os_3H\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (2), with $[NBu^n_4]F$.[6,7] Complex (1) may be regarded as an alkene-substituted analogue of $[Os_3H(CO)_{11}]^-$ (3).[8]

Complex (3) reacts with methylating agents to give the *O*-methylated complex $[Os_3H(\mu\text{-}COMe)(CO)_{10}]$ [9] and it therefore seemed of interest to attempt the methylation of (1) to ascertain the preferred site of methylation, in view of the additional possibility of attack at the alkene ligand. The results presented below show that the reaction of (1) with $[Me_3O][BF_4]$, even at room temperature, is much more complex than had been anticipated, and that none of the four neutral products isolated is formed as the result of simple incorporation of an Me^+ group into (1). Instead the major product of the reaction has been identified by an *X*-ray study as $[Os_3H(\mu_3\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCF_3)(CO)_9]$ (4), the formation of which must involve a C–C bond cleavage reaction in addition to the loss of a CO ligand and the dehydrogenation of (1).

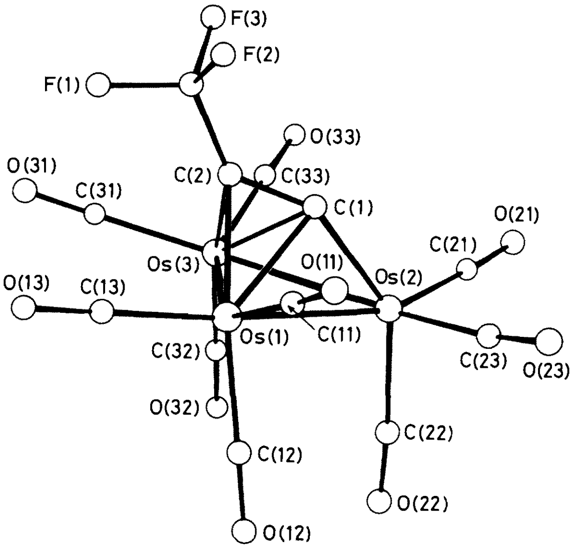

Figure. Molecular structure of $[Os_3H(\mu_3\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCF_3)(CO)_9]$ (4) including the atom numbering scheme

Results and Discussion

Treatment of a dichloromethane solution of (1) with a large excess of $[Me_3O][BF_4]$ at room temperature gave, after 16 h, at least four neutral products. Two of these products, present in approximately equal quantities, together accounted for 70% of the reaction yield. Of these one was identified, on the basis of i.r., mass, and ^1H n.m.r. data as (2), the precursor of (1), originally obtained from the reaction of $[Os_3H_2(CO)_{10}]$ with $CF_3C{\equiv}CCF_3$.[7,10]

The nature of the second major product (4) proved more difficult to determine. A mass spectrum showed a parent ion at m/z 922 (^{192}Os), but the loss of a molecule of $CF_3(H)C{=}C(H)CF_3$, characteristic of other fluoroalkene–triosmium complexes,[7] was not observed. An i.r. spectrum (see Experimental section) of a Nujol mull of the complex contained three strong sharp absorptions in the region 1 300—1 000 cm^{-1} confirming the presence of a C–F fragment; the pattern of bands assignable to ν(C–F) was, however, relatively simple compared to previously prepared fluoroalkene complexes.[7] Crystals as colourless blocks were obtained from hexane and an *X*-ray analysis (see below) showed the compound to be $[Os_3H(\mu_3\text{-}\sigma{:}\eta^2\text{-}C{\equiv}CCF_3)(CO)_9]$ in which the $C{\equiv}CCF_3$ ligand

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† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-hydrido-μ$_3$-σ:1′—2′-η-3′,3′,3′-trifluoropropynyl-$C^{1'}(Os^3)C^{1'-2'}(Os^1,Os^2)$-*triangulo*-triosmium.

Supplementary data available (No. SUP 23922, 21 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Bond lengths (Å)

Os(1)–Os(2)	2.872(1)	Os(1)–Os(3)	2.828(1)	Os(3)–C(2)	2.181(9)	C(11)–O(11)	1.127(12)
Os(1)–C(11)	1.934(11)	Os(1)–C(12)	1.934(11)	C(12)–O(12)	1.116(13)	C(13)–O(13)	1.158(13)
Os(1)–C(13)	1.895(11)	Os(1)–C(1)	2.262(10)	C(21)–O(21)	1.137(13)	C(22)–O(22)	1.122(13)
Os(1)–C(2)	2.179(10)	Os(2)–Os(3)	2.874(1)	C(23)–O(23)	1.103(13)	C(31)–O(31)	1.133(12)
Os(2)–C(21)	1.905(11)	Os(2)–C(22)	1.946(11)	C(32)–O(32)	1.141(13)	C(33)–O(33)	1.151(12)
Os(2)–C(23)	1.941(12)	Os(2)–C(1)	1.937(10)	C(1)–C(2)	1.331(13)	C(2)–C(3)	1.464(14)
Os(3)–C(31)	1.921(11)	Os(3)–C(32)	1.941(12)	C(3)–F(1)	1.332(12)	C(3)–F(2)	1.333(12)
Os(3)–C(33)	1.918(11)	Os(3)–C(1)	2.271(10)	C(3)–F(3)	1.318(12)		

Table 2. Bond angles (°)

Os(3)–Os(1)–Os(2)	60.5	C(11)–Os(1)–Os(2)	96.2(3)	C(33)–Os(3)–Os(1)	145.4(3)	C(33)–Os(3)–Os(2)	94.8(3)
C(11)–Os(1)–Os(3)	145.2(3)	C(12)–Os(1)–Os(2)	88.1(3)	C(33)–Os(3)–C(31)	94.6(5)	C(33)–Os(3)–C(32)	91.7(4)
C(12)–Os(1)–Os(3)	110.4(3)	C(12)–Os(1)–C(11)	92.9(5)	C(1)–Os(3)–Os(1)	51.3(2)	C(1)–Os(3)–Os(2)	42.2(3)
C(13)–Os(1)–Os(2)	168.7(3)	C(13)–Os(1)–Os(3)	108.2(3)	C(1)–Os(3)–C(31)	128.3(4)	C(1)–Os(3)–C(32)	132.7(4)
C(13)–Os(1)–C(11)	93.7(4)	C(13)–Os(1)–C(12)	96.7(5)	C(1)–Os(3)–C(33)	94.1(4)	C(2)–Os(3)–Os(1)	49.5(2)
C(1)–Os(1)–Os(2)	42.3(3)	C(1)–Os(1)–Os(3)	51.5(2)	C(2)–Os(3)–Os(2)	75.5(2)	C(2)–Os(3)–C(31)	93.9(4)
C(1)–Os(1)–C(11)	93.7(4)	C(1)–Os(1)–C(12)	130.4(4)	C(2)–Os(3)–C(32)	159.8(4)	C(2)–Os(3)–C(33)	103.7(4)
C(1)–Os(1)–C(13)	131.7(4)	C(2)–Os(1)–Os(2)	75.5(2)	C(2)–Os(3)–C(1)	34.7(3)	O(11)–C(11)–Os(1)	176(1)
C(2)–Os(1)–Os(3)	49.6(2)	C(2)–Os(1)–C(11)	102.2(4)	O(12)–C(12)–Os(1)	176(1)	O(13)–C(13)–Os(1)	179.6(7)
C(2)–Os(1)–C(12)	158.7(4)	C(2)–Os(1)–C(13)	97.2(4)	O(21)–C(21)–Os(2)	177(1)	O(22)–C(22)–Os(2)	175(1)
C(2)–Os(1)–C(1)	34.8(3)	Os(3)–Os(2)–Os(1)	59.0	O(23)–C(23)–Os(2)	173(1)	O(31)–C(31)–Os(3)	178(1)
C(21)–Os(2)–Os(1)	159.5(4)	C(21)–Os(2)–Os(3)	103.4(4)	O(32)–C(32)–Os(3)	176.3(9)	O(33)–C(33)–Os(3)	178(1)
C(22)–Os(2)–Os(1)	98.9(3)	C(22)–Os(2)–Os(3)	98.9(3)	Os(2)–C(1)–Os(1)	85.9(4)	Os(3)–C(1)–Os(1)	77.2(3)
C(22)–Os(2)–C(21)	94.0(5)	C(23)–Os(2)–Os(1)	100.1(3)	Os(3)–C(1)–Os(2)	85.7(4)	C(2)–C(1)–Os(1)	69.2(6)
C(23)–Os(2)–C(3)	157.0(3)	C(23)–Os(2)–C(21)	95.0(5)	C(2)–C(1)–Os(2)	147.5(8)	C(2)–C(1)–Os(3)	68.9(6)
C(23)–Os(2)–C(22)	93.3(5)	C(1)–Os(2)–Os(1)	51.8(3)	Os(3)–C(2)–Os(1)	80.9(3)	C(1)–C(2)–Os(1)	76.0(6)
C(1)–Os(2)–Os(3)	52.0(3)	C(1)–Os(2)–C(21)	110.0(5)	C(1)–C(2)–Os(3)	76.3(6)	C(3)–C(2)–Os(1)	133.6(7)
C(1)–Os(2)–C(22)	145.1(4)	C(1)–Os(2)–C(23)	108.8(5)	C(3)–C(2)–Os(3)	133.2(7)	C(3)–C(2)–C(1)	133.9(9)
Os(2)–Os(3)–Os(1)	60.5	C(31)–Os(3)–Os(1)	107.3(3)	F(1)–C(3)–C(2)	111.6(8)	F(2)–C(3)–C(2)	113.4(9)
C(31)–Os(3)–Os(2)	167.2(3)	C(32)–Os(3)–Os(1)	110.9(3)	F(2)–C(3)–F(1)	105.7(9)	F(3)–C(3)–C(2)	113.5(9)
C(32)–Os(3)–Os(2)	90.5(3)	C(32)–Os(3)–C(31)	97.8(5)	F(3)–C(3)–F(1)	105.9(9)	F(3)–C(3)–F(2)	106.2(9)

acts as a five-electron donor. Related complexes containing non-fluorinated ligands are known for both ruthenium[11–14] and osmium.[14,15]

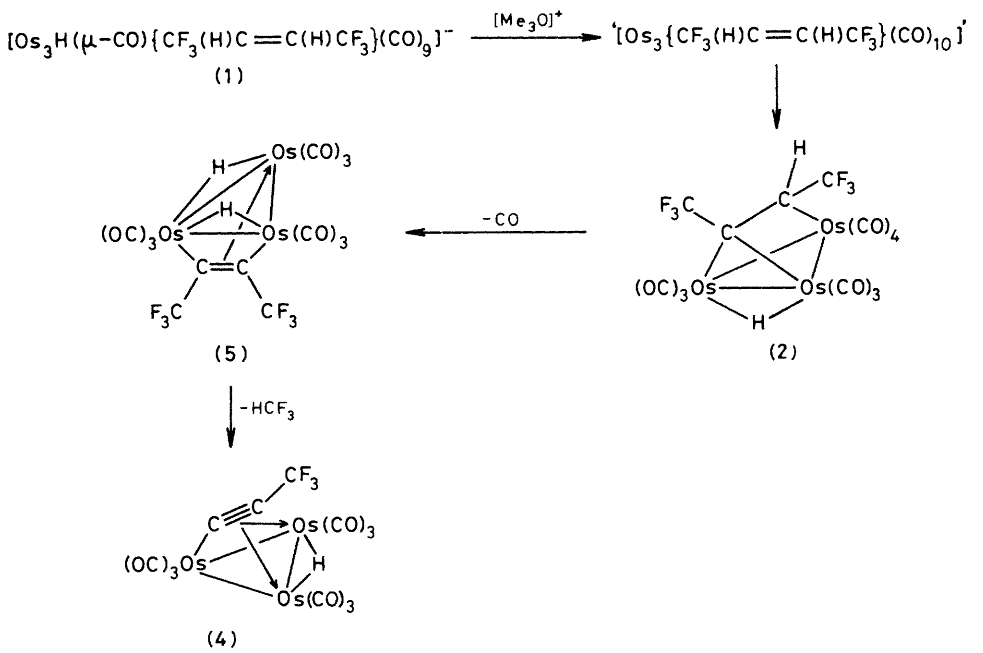
The molecular structure of (4) is shown in the Figure, and selected interatomic distances and angles are given in Tables 1 and 2 respectively. The structure of the complex is closely related to that found for the t-butylethynyl cluster $[Ru_3H(\mu_3\text{-}\eta^2\text{-}C{\equiv}CCMe_3)(CO)_9]$ (7)[11,12] and for the cluster $[Ru_3H\{\mu_3\text{-}\eta^2\text{-}C{\equiv}CC({=}CH_2)Ph\}(CO)_9]$ (8).[13] The position of the hydrido-atom was not located in (4) but the corresponding H atom was located by neutron diffraction in the structure of (7).[11] Whereas in (7) the Ru–Ru H-bridged distance of 2.792(3) Å is little different to the non-bridged Ru–Ru distances of 2.795 and 2.799 Å, in both (4) and (8) the M–M H-bridged distance is significantly shorter than the other two metal–metal bonds with an H-bridged Os(1)–Os(3) distance of 2.828(1) Å in (4) [H-bridged Ru–Ru in (8) of 2.791 Å] and non-bridged values of 2.872(1) and 2.874(1) Å [2.810, 2.812 Å in (8)]. The acetylenic $C{\equiv}CCF_3$ ligand in (4) shows similar σ-C–Os and π-C–Os bond lengths to those found for both (7) and (8). The C(1)–C(2) distance of 1.331(13) Å is significantly longer than the corresponding distance of 1.272 Å in (8), with the C(1)–C(2)–C(3) angle of 133.9(9)° being smaller than that in (8) (145.9°).

One of the low-yield products was identified on the basis of its mass, i.r., and ^1H n.m.r. spectra as $[Os_3H_2\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}CCF_3\}(CO)_9]$ (5), originally obtained by the thermal dissociation of a CO ligand from (2) when (2) is refluxed in CH_2Cl_2.[7]

The second of the two low-yield products has not been identified but appears, from its mass spectrum, to be related to (4). Thus although the highest peak in the mass spectrum of (6) is greater by *m/z* 57 than that observed for (4), both spectra are distinguished by the unusual feature of a fragment ion corresponding to an initial loss of a fragment of mass 20 (possibly HF).

A possible course for the reaction leading to the formation of (2), (4), and (5) from (1) is shown in the Scheme. It is suggested that the $[Me_3O][BF_4]$ acts as a hydride abstracting agent to give an electronically unsaturated intermediate, $[Os_3\{CF_3(H)C{=}C(H)CF_3\}(CO)_{10}]$, which then undergoes H-atom transfer from ligand to metal to give (2). Subsequent postulated loss of CO to give (5) and of HCF_3 to give (4) is not unreasonable in that the related non-fluorinated vinyl complex $[Os_3H(CH{=}CHMe)(CO)_{10}]$ gives $[Os_3H_2(CH{=}CMe)(CO)_9]$ and $[Os_3H(C{\equiv}CMe)(CO)_9]$ among the products of pyrolysis when it is refluxed in n-octane.[15] The reaction of the fluorinated complex (1) to give (2), (4), and (5) is, however, unique in that it takes place at room temperature with C–C rather than C–H bond cleavage as the final step in the sequence. This final step may be contrasted with the room-temperature reaction between Bu^{t}NC and $[Os_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)(CO)_9]$ which involves C–C bond *formation* at the α-carbon atom of the acetylide ligand.[16]

Unfortunately, the quantities of (1) available were insufficient for it to be possible to identify HCF_3 as a product of its reaction with $[Me_3O]^+$. The reaction pathways may, in any event, be more complex than is suggested in the Scheme, since a dichloromethane solution of (2) alone does not lose CO spontaneously at room temperature and addition of $[Me_3O][BF_4]$ to this solution gives $[Os_3\{CF_3(H)C{=}C(H)CF_3\}(CO)_{11}]$[6,7] [plus unreacted (2)] as the major products, with there being no evidence for the formation of (4) or (5). Further studies are clearly needed to elucidate the mechanism of the reaction.



Scheme. Suggested reaction pathway for the formation of (2), (4), and (5) from (1)

Table 3. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	−0.160 56(2)	0.336 05(4)	0.213 16(6)	O(23)	−0.065 7(6)	−0.072 9(10)	−0.206 5(15)
Os(2)	−0.237 64(3)	0.049 53(4)	−0.005 55(6)	C(31)	−0.411 5(7)	0.469 1(11)	0.291 7(16)
Os(3)	−0.356 48(2)	0.289 10(4)	0.171 46(6)	O(31)	−0.444 3(6)	0.575 7(9)	0.359 1(14)
C(11)	−0.047 8(7)	0.326 1(11)	0.068 7(17)	C(32)	−0.396 0(6)	0.179 5(12)	0.363 5(18)
O(11)	0.015 4(5)	0.321 6(10)	−0.023 2(14)	O(32)	−0.414 5(6)	0.116 0(10)	0.481 1(14)
C(12)	−0.104 8(7)	0.241 5(11)	0.416 3(18)	C(33)	−0.462 5(7)	0.219 3(12)	−0.016 0(17)
O(12)	−0.077 2(6)	0.186 2(10)	0.536 9(13)	O(33)	−0.524 8(5)	0.173 5(10)	−0.130 2(13)
C(13)	−0.134 5(7)	0.528 3(11)	0.363 5(16)	C(1)	−0.252 8(6)	0.245 1(10)	−0.075 2(15)
O(13)	−0.118 7(6)	0.646 0(9)	0.454 4(15)	C(2)	−0.264 9(6)	0.386 3(9)	−0.009 5(14)
C(21)	−0.322 6(8)	−0.080 0(12)	−0.174 8(19)	C(3)	−0.275 4(7)	0.506 2(10)	−0.111 8(15)
O(21)	−0.371 8(6)	−0.161 8(10)	−0.282 9(15)	F(1)	−0.284 4(6)	0.631 5(7)	0.022 3(11)
C(22)	−0.228 9(8)	−0.040 7(10)	0.217 0(17)	F(2)	−0.202 5(5)	0.525 5(8)	−0.216 6(12)
O(22)	−0.227 0(8)	−0.090 5(10)	0.353 3(15)	F(3)	−0.349 5(6)	0.491 7(8)	−0.242 6(13)
C(23)	−0.126 6(8)	−0.028 2(11)	−0.124 1(18)				

Experimental

The compound $[N(PPh_3)_2][Os_3H(\mu\text{-}CO)\{CF_3(H)C{=}C(H)\text{-}CF_3\}(CO)_9]$ (1) was prepared as described previously.[7,10]

Reaction of (1) *with* $[Me_3O][BF_4]$.—A large excess of $[Me_3O][BF_4]$ (0.124 g, 0.84 mmol) was added to a solution of (1) (0.242 g, 0.16 mmol) in dichloromethane (20 cm^3). The mixture was stirred for 16 h at room temperature during which time it turned from yellow to amber. It was filtered, taken to dryness under reduced pressure, and placed on t.l.c. plates. One elution with CH_2Cl_2–hexane (1 : 9) gave four bands of which two were identified by mass, i.r., and ^{1}H n.m.r. spectroscopy as the known compounds (yields in parentheses) (2) [7,10] (35%) and (5) [7,14] (15%). Of the remaining two products, compound (4) (35%) [ν(CO)(hexane), 2 114m, 2 087s, 2 068s, 2 044s, 2 027vs, 2 008m, and 1 976vs cm^{-1}; ν(CF) (Nujol mull), 1 226s, 1 142s, and 1 121m cm^{-1}; ^{1}H n.m.r. (CD_2Cl_2 at −80 °C) δ −24.56 (s, 1 H, OsH)] was characterised by an *X*-ray study. The remaining low-yield product (6) (10%) was obtained as an orange powder on evaporation of the solvent [ν(CO) (hexane), 2 119w, 2 074vs, 2 068vs, 2 044m, 2 035s, 2 021m, 2 010m, and 1 996m cm^{-1}]. The order of elution of the complexes (decreasing R_f values) was (6), (4), (2), and (5).

Crystal Data.—$C_{12}HF_3O_9Os_3$, $M = 916.4$, triclinic, space group $P\bar{1}$, $a = 14.354(2)$, $b = 9.510(1)$, $c = 6.714(1)$ Å, $\alpha = 103.21(2)$, $\beta = 93.81(2)$, $\gamma = 90.66(2)°$, $U = 889.92$ Å^3, $Z = 2$, $D_c = 3.419$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 205.97$ cm^{-1}, $F(000) = 800$.

2 967 Reflections were recorded ($3.0 \leqslant \theta \leqslant 25.0°$) on a Philips PW1100 diffractometer, with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å) and a θ—2θ scan mode on a crystal of size 0.13 × 0.11 × 0.08 mm. Lorentz polarisation corrections were applied together with a semi-empirical absorption correction based on 356 azimuthal scan data with relative transmission factors ranging from 1.0 to 0.593 for the full data set. Equivalents were averaged to give 2 645 unique observed data $[F \geqslant 6\sigma(F_o)]$.

The Os atoms were located from a Patterson function and positions of all the non-hydrogen atoms were found from subsequent Fourier-difference syntheses. The structure was refined by full-matrix least squares with complex neutral-atom scattering factors from International Tables [17] and weights,

$w = 1/\sigma^2(F)$, with anisotropic thermal parameters. The refinement converged to $R = 0.028$ and $R' = 0.039$. The atomic co-ordinates are given in Table 3.

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