Metal–Metal Bond Fission and the Formation of Triosmium–Alkene Complexes *via* the Reaction of $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ with Nucleophiles; A Complete Model for the Catalytic Reduction of an Alkyne to an Alkene by a Cluster

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The reaction of $[Os_3H_2(CO)_{10}]$ with hexafluorobut-2-yne gives the complex $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ in 88% yield. The reactions of this complex with a variety of nucleophiles have been investigated and have led to the preparation of a series of stable fluoro-alkene complexes $[Os_3\{CF_3(H)C{=}C(H)CF_3\}(CO)_{10}Y]$ ($Y = PEt_3$, CO, Cl^-, Br^-, I^-, or H^-). For $Y = PEt_3$ and CO both the *cis*- and *trans*-fluoro-alkene complexes are formed in approximately equimolar proportions, but the other nucleophiles give only a single fluoro-alkene complex which, for $Y = Br^-$, is the *trans* product. The major product of the reaction with $Y = PEt_3$ results from metal–metal bond cleavage to give the complex $[Os_3H\{\mu\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}(PEt_3)]$ which contains a bent chain of Os atoms and a terminal Os–H ligand. The reactions of $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ with nucleophiles are compared with those of the unsubstituted vinyl complex $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$, and a model is proposed for the catalytic reduction of an alkyne to an alkene by a trinuclear osmium cluster.

The reaction of $[Os_3H_2(CO)_{10}]$ with alkynes has been well studied and leads to a wide variety of products, the nature of which depends upon the particular alkyne employed.[1,2] With acetylene itself the μ-vinyl complex $[Os_3(\mu\text{-}H)\{\mu\text{-}\eta^2\text{-}CH{=}CH_2\}(CO)_{10}]$ (1) is formed in high yield at r.t. under 1 atm (*ca.* 10^5 Pa) of HC≡CH.[1,3] Subsequent treatment of (1) with CO in refluxing CH_2Cl_2 gives $[Os_3(CO)_{12}]$ and, presumably, C_2H_4, *via* transfer of the remaining hydride ligand to the organic moiety, although no intermediate alkene complex was isolated.[1] This is, perhaps, hardly surprising in view of the reported thermal instability of $[Os_3(CO)_{11}(C_2H_4)]$, prepared from the reaction of $[Os_3(CO)_{11}(NCMe)]$ with C_2H_4.[4]

Reaction of (1) with nucleophiles other than CO has not been widely studied but, with certain organophosphines, attack at the β-carbon atom of the organic ligand, rather than at the metal atoms, takes place.[5,6] A heteropolar ylide ligand is generated and the complexes may be formulated as $[Os_3(\mu\text{-}H)(\mu\text{-}\bar{C}HCH_2{}^+PR_3)(CO)_{10}]$ [*e.g.*, $PR_3{=}PMe_2Ph$ (2)].

Co-ordination of C=C double bonds is known to activate them towards nucleophilic attack, although previous work with mononuclear complexes suggests that either a positive charge on the complex or a strong nucleophile is required.[7] Indeed complexes of type (2) are stable only for $PR_3 = PMe_2Ph$ and, in an attempt to prepare an analogue of (1) with enhanced susceptibility towards nucleophilic attack, we have investigated the reaction of $[Os_3H_2(CO)_{10}]$ with the fluoro-alkyne $CF_3C{\equiv}CCF_3$. Thus, at room temperature, an essentially quantitative yield of the complex $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (3) is obtained and this has a stoicheiometry which suggests that it is analogous to (1). An *X*-ray structure determination[8] has revealed, however, that the organic ligand is μ_3- rather than μ-bonded to the metal-atom triangle (Figure). In this paper we report in detail the synthesis of this complex and its reactions with a wide variety of nucleophiles. These reactions have led to the preparation of a series of stable cluster alkene complexes in addition to other products which reveal a contrasting chemistry to that exhibited by (1). Apart from the complexes $[Os_3(CO)_{11}(C_2H_4)]$[4] and $[Os_3(CO)_9(C_2H_4)(SMe)]$[9] the alkene complexes now described are the first simple cluster alkene complexes to have been reported. Preliminary accounts of part of this work have appeared.[8,10-12]

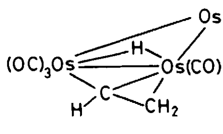
Results and Discussion

(*a*) *Preparation of* $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (3).—When an excess of hexafluorobut-2-yne is sealed into a glass tube with a hexane solution of $[Os_3H_2(CO)_{10}]$, the purple mixture becomes completely yellow within 12 h at r.t. and pale yellow crystals of a single complex are deposited on the sides of the tube. A mass spectrum of the crystalline product reveals a parent ion at *m/z* 1 020 corresponding to the formulation $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (3) and both ^1H and ^{19}F n.m.r. data were consistent with (3) having an analogous structure to (1). The i.r. spectra of (1) and (3) in the ν(CO) region, however, display significant differences and an *X*-ray diffraction study of (3) subsequently revealed the μ_3-bonding mode of the organic ligand in (3) (Figure).[8]

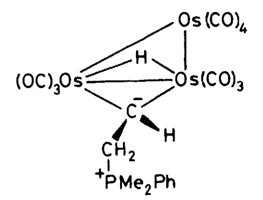
The structural differences between (1) and (3) may be rationalised by considering the effect of substituting CF_3 groups for two of the H atoms on the vinyl ligand in (1). This presumably increases the susceptibility of the β-carbon atom to nucleophilic attack and hence leads, in the absence of other electron donors, to the formation of a bond between the β-carbon atom and the $Os(CO)_4$ group, acting as a weak nucleophile, as is found in (3). A valence-bond description of (3) is shown in the figure to illustrate the formal relationship between this complex and those of type (2). An alternative description of (3) may be given in terms of dative metal–metal bonds, which are required in order that the effective atomic number (e.a.n.) rule may be obeyed by each individual metal atom.

The analogy between (3) and the complexes of type (2) suggested to us that displacement of the weak nucleophile $Os(CO)_4$ by stronger nucleophiles might be possible, and the reactions of (3) with a wide range of nucleophiles have therefore been investigated.

(*b*) *Reaction of* (3) *with Nucleophiles*.—(*i*) *Triethylphosphine*. Treatment of a slurry of (3) in hexane at r.t. with an equimolar quantity of PEt_3 leads to dissolution within a few minutes to give a bright yellow solution. Separation of the reaction mixture by t.l.c. revealed the formation of at least five complexes with one pale yellow complex in major yield. This was extracted and crystallised from warm hexane to give pale



(1)*



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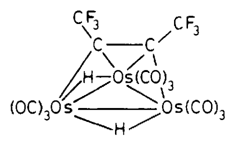

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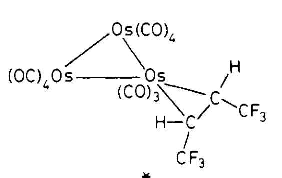

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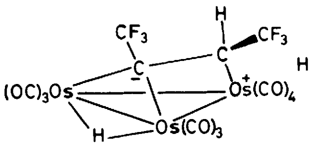

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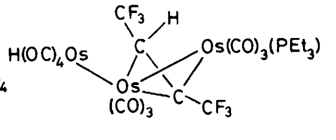

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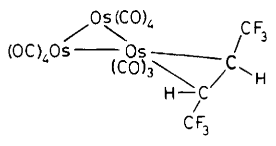

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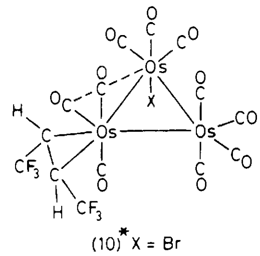
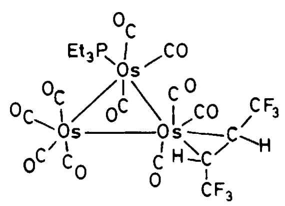


(10)* X = Br
(11) X = I
(12) X = Cl



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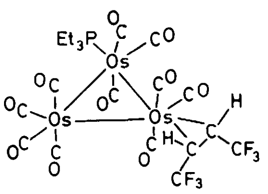

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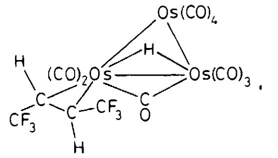


(13)

Figure. Proposed structures for some substituted triosmium carbonyl complexes; those indicated by an asterisk have been confirmed by an *X*-ray study (references given in text)

yellow blocks in 60% yield. Its stoicheiometry was shown by mass spectroscopy to correspond to the formula $[Os_3H\{\mu\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}(PEt_3)]$ (4) and suggested initially that a complex analogous to those of type (2) had been formed. The ^1H n.m.r. spectrum of (4) (Table 1), however, showed a singlet resonance at $\delta - 9.72$ p.p.m. indicative of a terminal rather than a bridging Os-H ligand, and the i.r. spectrum of (4) in the ν(CO) region did not bear any resemblance to those of the complexes (2).[5,6] An *X*-ray structure determination was therefore undertaken [10] which showed that (4) has the structure shown in the Figure. The triethylphosphine ligand is co-ordinated to an Os atom, rather than to the organic ligand as in (2), and the triangular arrangement of Os atoms has opened out to form a bent chain.

The reaction of (3) with PEt_3 to give a product arising from metal-metal bond cleavage is clearly very unusual when compared to other reactions of trinuclear osmium complexes with two-electron donor ligands which have previously been studied.[13] It can formally be regarded as a reduction reaction, in the sense that two electrons have been added to the cluster. Such reductions are more common for higher nuclearity clusters,[13] as in the reaction of MeCN with $[Ru_5C(CO)_{15}]$ to give $[Ru_5C(CO)_{15}(NCMe)]$ [14] or RNC with $[Os_6(CO)_{18}]$ to give $[Os_6(CO)_{18}(CNR)_2]$.[15] Both these reactions take place at r.t. and in each case the number of metal-metal bonds is clearly reduced. The triangular array of metal atoms present in $[Os_3(CO)_{12}]$ is, however, one of the most stable cluster units known and usually remains intact in reactions of $[Os_3(CO)_{12}]$ and related trinuclear osmium complexes with other molecules such as PR_3 and RNC.[16,17] The fact that a metal-metal bond is broken in the reaction of (3) with PEt_3 lends some support to our suggestion that dative metal-metal bonds are present in (3) since dative or heteronuclear metal-metal bonds are, in general, more easily broken than non-polar bonds in reactions of this type.[18,19]

Two of the minor products of the reaction of (3) with PEt_3 were identified as $[Os_3(CO)_{10}(PEt_3)_2]$ and $[Os_3(CO)_9(PEt_3)_3]$ by comparison of their i.r. spectra with those of authentic samples.[20] The remaining two low-yield products exhibited parent ions in their mass spectra of identical mass (m/z 1 138 for ^{192}Os) to that observed for the major product (4). However, the mass multiplets for the parent ions were weak and were accompanied by a fragmentation pattern indicative of a ligand of m/z 164 being lost first, this mass loss corresponding to the alkene $CF_3(H)C{=}C(H)CF_3$. The ^1H n.m.r. spectra of both complexes (Table 1) show the absence of any metal-hydride resonance and reveal a quartet signal in the C-H region at δ 3.45 p.p.m. [^3J(HCCF) = 7.27 Hz] due, presumably, to the protons on such an alkene ligand. An *X*-ray analysis of one of the complexes was undertaken and shows that it is indeed the alkene complex $[Os_3\{$*trans*-$CF_3(H)C{=}C(H)CF_3\}(CO)_{10}(PEt_3)]$ (5),[10] the structure of which is shown in the Figure. The structure is derived from that of $[Os_3(CO)_{12}]$ [21] with two mutually *trans* equatorial CO ligands on adjacent Os atoms being substituted by the $CF_3(H)C{=}C(H)CF_3$ and PEt_3.ligands. The minor product (6) with the same stoicheiometry as (5) and almost identical spectroscopic properties could be related to (5) in a number of ways. The two most likely possibilities are (*a*) that (6) contains the *trans* alkene substituted in an axial site or (*b*) that (6) contains the *cis* alkene substituted in an equatorial position. Since the reaction of (3) with CO also gives two isomeric alkene complexes (see later) one of which has been shown by an *X*-ray study to contain the *cis* alkene substituted in an equatorial position,[12] (*b*) seems the more likely possibility. In any event, although axial/equatorial isomers have been identified in solution by n.m.r.,[17] such isomers are not in general separable, whereas neither (5) nor (6) shows any tendency to isomerise. Complex (6) is therefore formulated as $[Os_3\{$*cis*-$CF_3(H)C{=}C(H)(CF_3)\}(CO)_{10}(PEt_3)]$.

Table 1. Mass spectroscopic, infrared, and ^1H n.m.r. data (δ/p.p.m.) for the new complexes

Compound	$m/z(^{192}Os)$	$\nu(CO)/cm^{-1}$ [a]	^1H N.m.r. [b]
(3) $[Os_3(\mu-H)\{\mu_3-\eta^2-CF_3C=C(H)CF_3\}(CO)_{10}]$	1 020	2 097(sh), 2 091vs, 2 088vs, 2 077w, 2 059w, 2 047s, 2 040s, 2 028(sh), 2 020m, 2 015(sh), 2 001w [c]	2.9 (m, 1 H, CH), −13.4 (s, 1 H, OsH)
(4) $[Os_3H\{\mu-\eta^2-CF_3C=C(H)CF_3\}(CO)_{10}(PEt_3)]$	1 138	2 119m, 2 088m, 2 079w, 2 057m, 2 041(sh), 2 034(sh), 2 027s, 2 018s, 2 013s, 1 992m [d]	4.42 [q, ^3J(HF) 11, $CHCF_3$], 2.20 (m, 6 H, CH_2), 1.18 (m, 9 H, Me), −9.72 (s, 1 H, OsH)
(5) $[Os_3\{$*trans*-$CF_3(H)C=C(H)CF_3\}(CO)_{10}(PEt_3)]$	1 138	2 105w, 2 055m, 2 035m, 2 026s, 2 014m, 2 003(sh), 1 996w, 1 986w, 1 976w, 1 971w	3.45 [q, ^3J(HF) 7.27, 2 H, CH], 2.10 (m, 6 H, CH_2), 1.14 (m, 9 H, Me)
(6) $[Os_3\{$*cis*-$CF_3(H)C=C(H)CF_3\}(CO)_{10}(PEt_3)]$	1 138	2 106w, 2 055s, 2 035s, 2 026vs, 2 015s, 2 011(sh), 2 003(sh), 1 996m, 1 984m, 1 973m [e]	3.45 [q, ^3J(HF) 7.27, 2 H, CH], 2.10 (m, 6 H, CH_2), 1.14 (m, 9 H, Me)
(7) $[Os_3(\mu-H)_2(\mu_3-\eta^2-CF_3C=CCF_3)(CO)_9]$	992	2 122w, 2 096vs, 2 075vs, 2 068m, 2 047(sh), 2 043vs, 2 036(sh), 2 029s, 2 025s, 2 014m, 2 000m	−21.1 (s, 1 H, OsH), −18.0 (s, 1 H, OsH)
(8) $[Os_3\{$*cis*-$CF_3(H)C=C(H)CF_3\}(CO)_{11}]$	1 048	2 129w, 2 079vs, 2 065s, 2 044vs, 2 040vs, 2 027s, 2 022s, 2 010m, 1 997w, 1 992(sh) [f]	3.1 (q, 2 H, CH)
(9) $[Os_3\{$*trans*-$CF_3(H)C=C(H)CF_3\}(CO)_{11}]$	1 048	2 128w, 2 077vs, 2 064s, 2 043vs, 2 039s, 2 025m, 2 021m, 2 009w, 1 996w, 1 990(sh)	3.1 (q, 2 H, CH)
(10) $[N(PPh_3)_2][Os_3\{$*trans*-$CF_3(H)C=C(H)CF_3\}(CO)_{10}Br]$	—	2 097w, 2 044s br, 2 008s br, 1 985(sh), 1 962(sh), 1 829w br	2.88 [q, ^3J(HF) 8.2, 1 H, CH], 2.60 [q, ^3J(HF) 8.6, 1 H, CH]
(11) $[N(PPh_3)_2][Os_3\{CF_3(H)C=C(H)CF_3\}(CO)_{10}I]$	—	2 098, 2 044s br, 2 009s br, 1 985(sh), 1 961(sh), 1 828w br	
(12) $[N(PPh_3)_2][Os_3\{CF_3(H)C=C(H)CF_3\}(CO)_{10}Cl]$	—	2 097w, 2 045s br, 2 009s br, 1 985(sh), 1 962(sh), 1 828w br	
(13) $[N(PPh_3)_2][Os_3(\mu-H)(\mu-CO)\{CF_3(H)C=C(H)CF_3\}(CO)_9]$	—	2 078m, 2 032s br, 1 989s br, 1 964(sh), 1 791w br	2.58 [q, ^3J(HF) 6.1, 2 H, CH], −20.0 (s, 1 H, OsH)

[a] I.r. spectra recorded in hexane for neutral complexes and in CH_2Cl_2 for anions. [b] Recorded in CD_2Cl_2 solution except for (3) which was recorded in $(CD_3)_2CO$ solution. All spectra at 298 K except for (10) for which the 213 K spectrum is given. *J* Values are in Hz; q = quartet, m = multiplet. [c] ν(CF) (Nujol mull): 1 115m and 1 105m cm^{-1}. [d] ν(CF) (Nujol mull): 1 132s, 1 118vs, 1 110vs, and 1 042m cm^{-1}. [e] ν(CF) (Nujol mull): 1 255s br and 1 140s br cm^{-1}. [f] ν(CF) (Nujol mull): 1 256w, 1 150w, 1 135s br, and 1 125(sh) cm^{-1}.

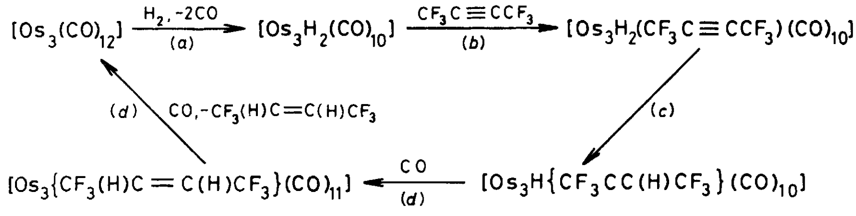
(*ii*) *Carbon monoxide.* When CO gas is bubbled through a refluxing CH_2Cl_2 solution of (3) no starting material is detected by t.l.c. after 2 h. The reaction mixture comprises three complexes, separated by t.l.c., in addition to *ca.* 30% $[Os_3(CO)_{12}]$. The fastest eluting band, present in approximately 10% yield, contained two metal–hydride singlets at δ − 18.0 and −21.1 in its ^1H n.m.r. spectrum (Table 1) and the highest peak in the mass spectrum was at *m/z* 992 (^{192}Os) corresponding to the formulation $[Os_3(\mu-H)_2(\mu_3-\eta^2-CF_3C=CCF_3)(CO)_9]$ (7). The probable structure of this complex (Figure) is proposed on the basis of the spectroscopic data and by analogy with $[Os_3H_2(HC=CH)(CO)_9]$.[1] It presumably results from the thermolytic dissociation of a CO ligand from the starting material.

The remaining two complexes, present in approximately equal quantities, together account for *ca.* 60% of the reaction yield. They exhibit identical mass spectra, showing initial loss of a fragment of *m/z* 164 followed by sequential carbonyl loss. The highest mass multiplet for both complexes is at *m/z* 1 048 (^{192}Os) corresponding to the formulation $[Os_3\{CF_3(H)C=C(H)CF_3\}(CO)_{11}]$ and, as expected, no metal hydrides are found in the ^1H n.m.r. spectrum of either complex, although the now characteristic alkene proton quartet appears at *ca.* δ 3.1 in the spectrum of both. There seems to be little doubt, therefore, that the two products are isomeric $CF_3(H)C=C(H)CF_3$-substituted derivatives of $[Os_3(CO)_{12}]$, and the structure of one isomer, $[Os_3\{$*cis*-$CF_3(H)C=C(H)CF_3\}(CO)_{11}]$ (8) (Figure) has been confirmed by an *X*-ray study.[12] The structure is based on that of $[Os_3(CO)_{12}]$ [21] with an equatorial carbonyl group substituted by a *cis*-$CF_3(H)C=C(H)CF_3$ ligand acting as a two-electron donor. The C=C bond lies in the plane of the Os_3 triangle with both C–CF_3 bonds pointing upwards out of this plane. The other isomer is formulated, on the basis of spectroscopic data and according to the arguments presented earlier for the PEt_3-substituted analogues, as $[Os_3\{$*trans*-$CF_3(H)C=C(H)CF_3\}(CO)_{11}]$ (9).

(*iii*) *Halide ions.* $[NEt_4]Br$. Treatment of a CH_2Cl_2 solution of (3) with a slight excess of $[NEt_4]Br$ at r.t. results in an immediate reaction which is complete after 2 h. The solution turns from pale yellow to amber and an ionic, hydrocarbon-insoluble solid is obtained on removal of the solvent. Dissolution in the minimum of methanol followed by the careful addition of 1.5 mol equiv. of $[N(PPh_3)_2]Cl$ over several hours then gives bright amber cube-shaped crystals of a single complex in essentially quantitatively yield (*ca.*75%). The molecular structure of this complex has been determined by *X*-ray analysis [11,22] and shows the molecular formula to be $[N(PPh_3)_2][Os_3\{$*trans*-$CF_3(H)C=C(H)CF_3\}(CO)_{10}Br]$ (10). The structure is again derived from that of $[Os_3(CO)_{12}]$ with an axial carbonyl on one metal atom replaced by a bromine ligand, and an equatorial carbonyl group on another osmium replaced by the fluoro-alkene group (Figure).

The ^1H n.m.r. spectrum of (10) at −60 °C indicates that the structure found in the solid state is also that adopted by the complex in solution at this temperature. Thus two quartet resonances for the non-equivalent C–H protons of the alkene group at δ 2.60 and 2.88 are observed. The quartets begin to broaden above 0 °C and coalescence takes place at 20 °C. Above 40 °C a single broad quartet resonance at δ 2.66 is observed, indicating that the alkene protons have become equivalent on the n.m.r. time-scale. This suggests that rotation of the alkene ligand is occurring about an axis lying along the alkene–osmium bond perpendicular to the C=C. Rotation about an axis lying along the C=C and perpendicular to the alkene–osmium bond may be rejected, as such a rotation, on its own, would maintain the inequivalence of the C–H protons.

The factors which cause the PEt_3 ligand to co-ordinate in an



Scheme. Model for the catalytic hydrogenation of an alkyne to an alkene. Reagents and conditions: (*a*) octane, 125 °C, 1.5 h (S. A. R Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942); (*b*) hexane, r.t., 12 h; (*c*) CH_2Cl_2, 45 °C, 2 h; (*d*) octane, 125 °C, 1.5 h

equatorial position in (6), whereas the bromide ligand in (10) occupies an axial site, presumably involve the relative steric requirements of the two nucleophiles. Studies of the substitution products, $[Os_3(CO)_{11}L]$ (L = two-electron donor ligand), indicate that substitution of axial CO groups is electronically preferred but that the use of bulky ligands (*e.g.* Bu^tNC or PPh_3) results exclusively in the formation of adducts substituted in the less crowded equatorial position.[17]

A further interesting point concerning the reaction of (3) with Br^- is that it leads exclusively to a *trans*-alkene derivative whereas the reactions with PEt_3 and CO give comparable amounts of *cis*- and *trans*-alkene complexes. Discussion of this point is deferred until the reactions of (3) with other anionic nucleophiles (which also lead to a single alkene product) have been considered.

$[NBu^n_4]I$, $[NBu^n_4]Cl$, *and* $[NBu^n_4]F$. The reaction between (3) and a slight excess of $[NBu^n_4]I$ proceeds more slowly but in a similar manner to the reaction with $[NEt_4]Br$. Yellow crystals of $[N(PPh_3)_2][Os_3\{CF_3(H)C{=}C(H)CF_3\}(CO)_{10}I]$ (11) were isolated from a methanol solution after the slow addition of 1.5 mol equiv. of $[N(PPh_3)_2]Cl$. The identical nature of the ν(CO) region of the i.r. spectrum of (10) and (11) suggests that the structures of these complexes are analogous.

When an excess of $[NBu^n_4]Cl$ is added to a CH_2Cl_2 solution of (3) and the $[N(PPh_3)_2]^+$ salt of the product is isolated, a ν(CO) i.r. spectrum reveals the presence of two complexes in comparable yields. Of these, one exhibits a spectrum identical to the Br^- and I^- analogues and is presumably the similar chloride product $[N(PPh_3)_2][Os_3\{CF_3(H)C{=}C(H)CF_3\}(CO)_{10}Cl]$ (12). The nature of the second product was more difficult to ascertain, since attempted separation of the mixture by fractional crystallisation was unsuccessful. This second product was, however, formed exclusively in 85% yield when (3) was treated with a tetrahydrofuran (thf) solution of $[NBu^n_4]F$, and clearly it does not therefore contain the halide ion. The ν(CO) i.r. spectrum of the complex contains a weak broad band at 1 791 cm^{-1} characteristic of an edge-bridging carbonyl ligand and the ^1H n.m.r. shows, in addition to the resonance expected for the $[N(PPh_3)_2]^+$ cation, a quartet due to alkene protons at δ 2.58 and an Os–H resonance at δ −20.0. Elemental analysis confirmed that the fluorine content of the complex could be fully accounted for by that present in the organic group and, on the basis of the spectroscopic data, the complex is formulated as $[N(PPh_3)_2][Os_3(\mu\text{-}H)(\mu\text{-}CO)\{CF_3(H)C{=}C(H)CF_3\}(CO)_9]$ (13). A proposed structure for this complex, formulated by analogy with that of $[Ru_3H(CO)_{11}]^-$,[23] is shown in the Figure.

The formation of (13) rather than a halide-containing complex in the reactions of (3) with $[NBu^n_4]Cl$ and $[NBu^n_4]F$ is presumably associated with the hygroscopic nature of these salts. In the case of the fluoride the equilibrium $F^- + H_2O \rightleftharpoons HF + OH^-$ would give OH^- ions, which could then attack a CO group, with elimination of CO_2 being responsible for the formation of the Os–H ligand. In a separate experiment it was shown that (13) is also formed in good yield when $[NBu^n_4]OH$ is employed, lending some support to this suggestion.

(*iv*) *Metal–carbonyl anions.* The high reactivity of (3) towards anionic nucleophiles suggested that the preparation of mixed-metal complexes *via* the reaction of (3) with metal–carbonyl anions might be feasible. To explore this possibility (3) was treated, in separate experiments, with the salts $[N(PPh_3)_2][FeH(CO)_4]$, $[N(PPh_3)_2][Os_3H(CO)_{11}]$, and $Na[Mn(CO)_5]$ in thf solution. In each case, however, the trinuclear osmium hydrido-anion $[Os_3H(\mu\text{-}CO)\{CF_3(H)C{=}C(H)CF_3\}(CO)_9]^-$ was the only osmium-containing species which could be isolated from solution.

(*c*) *A Comparison of the Reactivity of* (1) *and* (3) *towards Nucleophiles.*—The reaction of two-electron donor ligands with triosmium carbonyl clusters containing an organic ligand can follow several different routes, which accounts for the complexity of such reactions and the wide variety of products which may be obtained in any given case. If the effective atomic number rule for the cluster as a whole is to be obeyed, then attachment of a single nucleophile must be accompanied by one or more of the following processes: (*i*) carbonyl ligand substitution; (*ii*) a reduction (by one) in the number or the order of the metal–metal bonds; (*iii*) loss of the organic ligand; (*iv*) a rearrangement in the mode of bonding of the organic ligand (and/or other non-carbonyl ligands which may be present) to the cluster. Processes (*i*), (*ii*), and (*iii*) are invariably accompanied by attachment of the incoming nucleophile to the metal, but process (*iv*) may, as an alternative, involve the attachment of the nucleophile to the organic ligand. The situation is further complicated by the possibility that a 1 : 1 reaction may not occur, even when the reactants are present in this ratio.

The difficulties inherent in predicting the course of a given reaction are nicely illustrated by a comparison of the reactivity of $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ (1) and $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (3) towards nucleophiles. Thus the reaction of (1) with PR_3 results in attachment of the nucleophile to the organic ligand [process (*iv*)] whereas the reaction of (3) leads principally to a reduction in the number of metal–metal bonds [process (*ii*)] although process (*iii*) and process (*iv*), with attachment of the nucleophile to the metal, are competing reactions. This outcome is contrary to what might have been expected solely on the basis of the relative electrophilicity of the organic ligands in (1) and (3). With carbon monoxide both (1) and (3) presumably react in the first instance *via* process (*iv*) although, in the case of (1), this mode of reaction is followed by displacement of the modified organic ligand [process (*iii*)] by a second molecule of the nucleophile. The complexes $[Os_3\{CF_3(H)C{=}C(H)CF_3\}(CO)_{11}]$ [*cis*-(8) and *trans*-(9)] undergo this subsequent reaction only under relatively forcing conditions and (8) is recovered essentially unchanged after reflux in hexane under CO gas

Table 2. ^{19}F N.m.r. data for complexes (3), (4), (5), and (10)

Compound	$\delta(^{19}F)$/p.p.m.*
(3)	59.51 (m, 3 F, $CHCF_3$), 57.93 [q, $^5J(FF)$ 9, 3 F, CCF_3]
(4)	56.87 (s, 3 F, CCF_3), 48.29 [d, $^3J(FH)$ 11, 3 F, $CHCF_3$]
(5)	60.35 [d, $^3J(FH)$ 7.46, 3 F, $CHCF_3$], 58.51 [d, $^3J(FH)$ 8.36, $CHCF_3$]
(10)	59.34 [d, $^3J(FH)$ 7.64, 3 F, $CHCF_3$], 58.50 [d, $^3J(FH)$ 7.64, 3 F, $CHCF_3$]

* Recorded at 298 K in CD_2Cl_2 for (3), (4), and (10) and in $CDCl_3$ for (5). In p.p.m. to high field of CCl_3F as internal reference. *J* Values are in Hz; d = doublet, q = quartet.

for 16 h, illustrating the relatively high stability of the fluoro-alkene complexes. Complex (8) may, however, be converted quantitatively to $[Os_3(CO)_{12}]$ by reflux in octane solution under CO. This completes the cycle shown in the Scheme, which may be regarded as a model for the catalytic hydrogenation of an alkyne to an alkene by a cluster. $[Os_3H_2(CO)_{10}]$ is not, however, a good catalyst for the hydrogenation of hexafluorobut-2-yne since, as described earlier, step (*c*) in the Scheme does not proceed quantitatively.

One intriguing feature of the reactions of (3) leading to fluoro-alkene complexes is that attack of Br^- leads to exclusive formation of a *trans*-alkene complex, whereas attack of PEt_3 or CO leads to the *cis*- and *trans*-alkene complexes in approximately equimolar proportions. Anionic nucleophiles other than Br^- also gives rise to single isomers and, by analogy, these are probably *trans* alkene complexes although this has not been proven.

cis Alkenes are invariably formed as the first products in the hydrogenation of alkynes with metals and also with mononuclear complexes.[1] The use of polynuclear complexes also leads, in general, to the formation of *cis* alkenes although the selective formation of *trans* alkenes has recently been reported.[24] The key factor which determines whether *cis* or *trans* alkenes are obtained is the configuration of the μ-vinyl intermediate which is presumed to be involved.[24] For the majority of μ-vinyl complexes which have been structurally characterised [25] the alkyne substituents are mutually *cis*, but in the reactions of $[Rh_2(\mu\text{-}H)_2\{P(OPr^i)_3\}_4]$ and H_2 with alkynes leading to *trans* olefins a μ-vinyl complex with *trans* substituents has been isolated.[24]

The reactions leading to alkene complexes described in this paper represent a unique case, in that we have shown they proceed *via* a μ_3-vinyl rather than a μ-vinyl intermediate. In such a μ_3-vinyl complex, the stereochemical outcome of the further reaction leading to alkene formation is not predetermined. Alkene formation from (3) requires the breaking of two of the three Os–C bonds, and which bonds break will determine whether the CF_3 substituents are *cis* or *trans* in the alkene product. It is not, of course, possible to discover whether the Os–C bonds in (3) are broken synchronously or consecutively in the formation of alkenes, but the isolation of the μ-vinyl complex (4) (in which the CF_3 substituents are *trans*) in the reaction with PEt_3 suggests that a transformation from a μ_3-vinyl to a μ-vinyl complex (with the breaking of one Os–C bond) may be involved. Bond-breaking in (3) will clearly be influenced by the steric and electronic properties of the incoming nucleophile and it is tempting to attribute the different stereochemical outcome of the reactions of (3) with Br^- and with PEt_3 to the fact that the former takes up an axial and the latter an equatorial position in the alkene products. More detailed stereochemical studies on the reaction are required, however, before a firm conclusion can be reached.

Experimental

All reactions were performed under dry, oxygen-free nitrogen using freshly redistilled degassed solvents. Infrared spectra were recorded on Perkin-Elmer 257 or 577 spectrophotometers for dichloromethane or hexane solutions in 0.5-mm NaCl cells or, for Nujol mulls, between CsBr plates, and were calibrated with CO gas or polystyrene. Mass spectra were recorded on an AEI MS12 spectrometer using perfluoroheptyl-*s*-triazine introduced indirectly as calibrant. Hydrogen-1 n.m.r. spectra were recorded for CD_2Cl_2 solutions on Varian XL-100-12 and XL-100-15 spectrometers in the Fourier-transform mode and solvent resonances were used as secondary standards to calibrate spectra. Fluorine-19 n.m.r. spectra (Table 2) were recorded for CD_2Cl_2 solutions on a Varian XL-100-12 instrument in the continuous-wave mode with CCl_3F as internal standard. All chromatography was carried out on commercial Merck t.l.c. plates coated with a 0.25-mm layer of silica. Microanalyses were carried out at the Chemical Laboratory, University of Cambridge (percentage yields of complexes are given in parentheses).

(*i*) *Preparation of* $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}]$ (3).—Typically, an excess of $CF_3C{\equiv}CCF_3$ gas [188 cm^3, 10 cmHg ($\sim 1.33 \times 10^4$ Pa), 1.10 mmol] was sealed into a glass tube containing a solution of $[Os_3H_2(CO)_{10}]$ (0.20 g, 0.23 mmol) in hexane (30 cm^3). It was allowed to stand at r.t. overnight after which time a pale yellow solution was obtained in which yellow block-shaped crystals of (3) (0.21 g, 88%) had formed. The solution was decanted off and the crystals washed twice with pentane and then dried.

(*ii*) *Reaction of* (3) *with Nucleophiles*.—(*a*) PEt_3. To a slurry of (3) (0.26 g, 0.25 mmol) in hexane (25 cm^3) was added PEt_3 (0.04 cm^3, 0.27 mmol). The mixture immediately changed from pale to bright yellow and this colour change was accompanied by dissolution of the starting material. The colour deepened to amber overnight and a pale yellow precipitate formed. The mixture was taken to dryness under reduced pressure and the residue placed on t.l.c. plates. Several elutions with acetone–hexane (10 : 90) gave three main bands. The fastest and slowest moving bands were identified by their i.r. spectra respectively as $[Os_3(CO)_{10}(PEt_3)_2]$ and $[Os_3(CO)_9(PEt_3)_3]$. The middle band separated into three further bands on re-elution with CH_2Cl_2–hexane (15 : 85) and, of these, the band with the highest R_f value was extracted and crystallised by cooling a saturated hexane solution to −30 °C to give pale yellow blocks of $[Os_3H\{\mu\text{-}\eta^2\text{-}CF_3C{=}C(H)CF_3\}(CO)_{10}(PEt_3)]$ (4) (60%). The next band was crystallised by slow evaporation of a CH_2Cl_2 solution at r.t. to give yellow plates of $[Os_3\{trans\text{-}CF_3(H)C{=}C(H)CF_3\}(CO)_{10}(PEt_3)]$ (5) (*ca.* 10%). The band with the lowest R_f value was crystallised by slow cooling of a saturated hexane solution to give $[Os_3\{cis\text{-}CF_3(H)C{=}C(H)CF_3\}(CO)_{10}(PEt_3)]$ (6) (*ca.* 10%).

(*b*) CO. Carbon monoxide gas was passed through a solution of (3) (0.05 g, 0.05 mmol) in CH_2Cl_2 at r.t. for 10 min after which time the temperature was raised to reflux and maintained for 2 h. A yellow-amber solution was obtained which was evaporated under reduced pressure and extracted with a little CH_2Cl_2. The residue was $[Os_3(CO)_{12}]$ (*ca.* 30%) and the extract was separated by preparative t.l.c. using hexane–dichloromethane (90 : 10) as eluant. The order of elution was (decreasing R_f values, % yields in parentheses): $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}CF_3C{=}CCF_3)(CO)_9]$ (7) (*ca.* 10%), $[Os_3\{trans\text{-}CF_3(H)C{=}C(H)CF_3\}(CO)_{11}]$ (9) (30%), and $[Os_3\{cis\text{-}CF_3(H)C{=}$

C(H)CF$_3$}(CO)$_{11}$] (8) (25%). Complex (8) was crystallised by slow evaporation of a concentrated dichloromethane solution to give golden yellow blocks.

(*c*) [NEt$_4$]Br. To a solution of (3) (0.30 g, 0.29) mmol in dichloromethane (15 cm^3) was added a slight excess of [NEt$_4$]Br (0.077 g, 0.37 mmol). The mixture was stirred at r.t. for 2 h during which time the colour darkened from yellow to amber, and the solvent was then evaporated off. The residue was taken up in the minimum of warm methanol and the addition of an excess of [N(PPh$_3$)$_2$]Cl (0.26 g, 0.45 mmol) in small aliquots over several hours then gave amber cube-shaped crystals of [N(PPh$_3$)$_2$][Os$_3${*trans*-CF$_3$(H)C=C(H)CF$_3$}(CO)$_{10}$Br] (10) (75%) (Found: C, 36.9; H, 1.9; Br, 4.7; F, 7.4; N, 0.6. $C_{50}H_{32}BrF_6NO_{10}Os_3P$ requires C, 37.5; H, 2.0; Br, 5.0; F, 7.1; N, 0.9%).

(*d*) [NBu^n$_4$]I. Complex (3) (0.30 g, 0.29 mmol) and [NBu^n$_4$]I (0.14 g, 0.38 mmol) were used in an analogous procedure to (*c*) above giving [N(PPh$_3$)$_2$][Os$_3${CF$_3$(H)=C(H)CF$_3$}(CO)$_{10}$I] (11) (72%) (Found: C, 35.1; H, 2.0; F, 6.8; I, 7.2; N, 1.0. $C_{50}H_{32}F_6INO_{10}Os_3P$ requires C, 36.4; H, 1.9; F, 6.9; I, 7.7; N, 0.8%).

(*e*) [NBu^n$_4$]Cl. A slight excess of 85% [NBu^n$_4$]Cl–thf (0.18 g, 0.05 mmol approx.) was added to a solution of (3) (0.05 g, 0.049 mmol) in dichloromethane (8 cm^3). The mixture was taken up in the minimum of methanol and an excess of [N(PPh$_3$)$_2$]Cl (0.043 g, 0.075 mmol) was added. Overnight cooling at –50 °C gave yellow crystals (0.47 g) of a mixture of [N(PPh$_3$)$_2$][Os$_3${CF$_3$(H)C=C(H)CF$_3$}(CO)$_{10}$Cl] (12) and [N(PPh$_3$)$_2$][Os$_3$(μ-H)$_2$(μ-CO){CF$_3$(H)C=C(H)CF$_3$}(CO)$_9$] (13).

(*f*) [NBu^n$_4$]F. To a solution of (3) (0.40 g, 0.40 mmol) in dichloromethane (20 cm^3) was added a 1.0 mol dm^{-3} solution of [NBu^n$_4$]F in thf (0.4 cm^3, 0.4 mmol). A colour change from yellow to amber took place immediately and the mixture was stirred at r.t. for 1 h. It was then taken to dryness, taken up in the minimum of methanol and treated with an excess of [N(PPh$_3$)$_2$]Cl (0.342 g, 0.60 mmol). A crystalline amber solid was precipitated immediately and this was filtered off and crystallised from a saturated hot methanol solution to give amber needles of [N(PPh$_3$)$_2$][Os$_3$(μ-H)(μ-CO){CF$_3$(H)C=C(H)CF$_3$}(CO)$_9$] (13) (7.2%). Similar results were obtained using [NBu^n$_4$]OH, Na[Mn(CO)$_5$], [N(PPh$_3$)$_2$][FeH(CO)$_4$], or [N(PPh$_3$)$_2$][Os$_3$H(CO)$_{11}$] in place of the fluoride salt.

(*iii*) *Reaction of* (9) *with* CO.—(*a*) *At* 80 °C. The i.r. spectrum of a solution of (9) (0.01 g) in hexane (10 cm^3) showed no change after the solution had been refluxed under CO gas for 6 h. CO gas was then bubbled through the solution for a further 16 h; separation of the reaction mixture on t.l.c. plates showed unchanged (9) and a trace of [Os$_3$(CO)$_{12}$].

(*b*) *At* 125 °C. A solution of (9) (0.01 g) in n-octane (20 cm^3) was refluxed under CO for 1.5 h after which time *ca.* 90% conversion to [Os$_3$(CO)$_{12}$] had taken place. When the experiment was repeated with CO gas passing through the solution, complete conversion of (9) to [Os$_3$(CO)$_{12}$] was achieved.

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