Journal of

The Chemical Society,

Chemical Communications

NUMBER 14/1980

Formation of Cluster Alkene Complexes by Nucleophilic Attack on a Vinyl Hydride Cluster: *X*-Ray Crystal Structures of $[(Ph_3P)_2N]\ [Os_3(CO)_{10}\{CF_3(H)C{:}C(H)CF_3\}Br]$ and $[Os_3(CO)_{10}\{CF_3(H)C{:}C(H)CF_3\}(PEt_3)]$

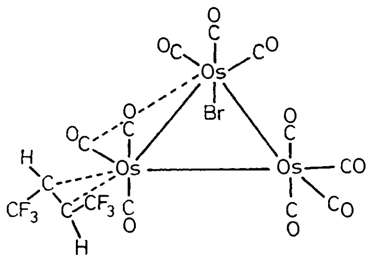
By ZAIN DAWOODI, MARTIN J. MAYS,* and PAUL R. RAITHBY
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)
and KIM HENRICK
(*Department of Chemistry, Polytechnic of North London, Holloway, London* N7 8DB)

Summary $[Os_3H(CO)_{10}\{CF_3CCHCF_3\}]$ reacts with certain 2-electron donor ligands, L, to give cluster alkene complexes $[Os_3(CO)_{10}\{CF_3(H)C{:}C(H)CF_3\}L]$; the *X*-ray structures of two of these complexes ($L = Br^-$, PEt_3) are reported.

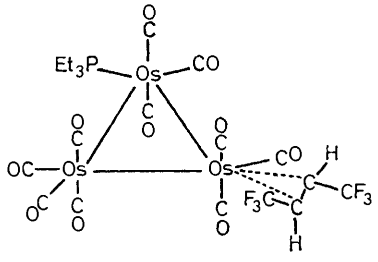
THE reaction of ethylene with $[Os_3(CO)_{12}]$ to give $[Os_3H_2(CO)_9(C_2H_2)]$[1] is of considerable interest in that it may provide a model for the dissociative adsorption of ethylene onto a metal surface.[2] A mechanism has been proposed for this reaction which involves initial formation of $[Os_3(CO)_{11}(C_2H_4)]$ (**1**), followed by hydrogen transfer from carbon to metal and loss of a CO group to give the vinyl hydride intermediate $[Os_3H(CO)_{10}(CHCH_2)]$ (**2**). Further hydrogen transfer from carbon to metal and loss of CO then gives the observed product.[3] Of the intermediates required by this scheme, (**1**) has been isolated, but not structurally characterised,[4] while (**2**), which is relatively more stable, has been prepared from the reaction between $[Os_3H_2(CO)_{10}]$ and C_2H_2.[5]

We now report that, for the related vinyl hydride complex, $[Os_3H(CO)_{10}(CF_3CCHCF_3)]$ (**3**),[6] attack by a range of nucleophiles gives a series of stable cluster alkene complexes. Apart from $[Os_3(CO)_{11}(C_2H_4)]$, only one cluster alkene complex, $[Os_3H(CO)_9(C_2H_4)SMe]$, has been reported previously.[7]

Thus, treatment of (**3**) in CH_2Cl_2 with a slight excess of $[Et_4N]Br$ at room temperature under N_2 gave an immediate reaction which was complete after 2 h. The solution was taken to dryness and the residue taken up in the minimum of methanol. Addition of 1·5 equiv. of $[(Ph_3P)_2N]Cl$ in small aliquots, over several hours, then gave bright amber cube-shaped crystals of $[(Ph_3P)_2N]\ [Os_3(CO)_{10}\{CF_3(H)C{:}C(H)CF_3\}Br]$ (**4**). The reaction is essentially quantitative and the final yield of crystals was *ca.* 75%.



(4)



(5)

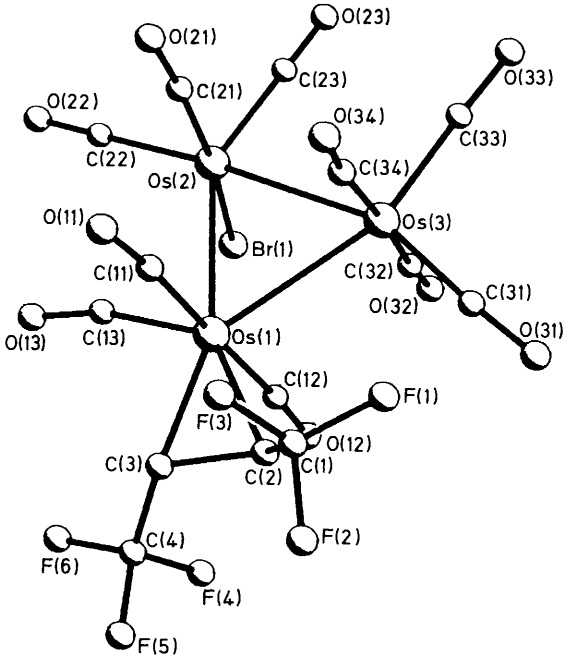


FIGURE 1 The molecular structure of $[Os_3(CO)_{10}\{CF_3(H)C C(H)CF_3\}Br]^-$ Bond lengths Os(1)–Os(2), 2 901(2), Os(1)–Os(3), 2 892(2), Os(2)–Os(3) 2 853(2), Os(2)–Br(1), 2 628(2), Os(1)–C(2), 2 17(2), Os(1)–C(3), 2 12(2), C(2)–C(3), 1 49(3) Å

The molecular structure of (**4**) has been determined by a single-crystal *X*-ray analysis† and is shown in Figure 1 together with some important bond parameters The structure is derived from that of $[Os_3(CO)_{12}]^8$ with an axial carbonyl ligand on one metal atom replaced by a bromine ligand, and an equatorial carbonyl on another osmium atom replaced by the fluoro-alkene group The C=C bond axis lies in the plane of the Os_3 triangle and the CF_3 groups are *trans* with respect to each other There is also an incipient bridging carbonyl group spanning the Os(1)–Os(2) edge with Os(1)–C(13) 1·93(2) Å and Os(2)–C(13) 2 73(2) Å This presumably helps to reduce the electron deficiency on Os(2) which formally has only 17 electrons if the negative charge is delocalised over the cluster ‡

The ^1H n m r spectrum of (**4**) (CD_2Cl_2) at −60 °C shows that the alkene ligand is non-fluxional at this temperature Two separate resonances at δ 2 60 (q, $^3J_{HF}$ 8 6 Hz) and δ 2 88 (q, $^3J_{HF}$ 8·2 Hz) are observed for the non-equivalent alkene protons These resonances coalesce at *ca* 10 °C and an averaged signal is observed at + 40 °C

The driving force for the transformation (**3**)→(**4**) is presumably provided by the transfer of hydrogen from the metal atom framework to the vinyl ligand This reduces the total electron count by two and allows co-ordination of the incoming nucleophile without metal–metal bond fission or ligand dissociation For some nucleophiles metal–metal bond fission is a competing process and in the reaction of (**3**) with Et_3P this gives rise to the major product[9] A minor product of this reaction is, however, the alkene complex $[Os_3(CO)_{10}\{CF_3(H)C\colon C(H)CF_3\}(PEt_3)]$ (**5**) which has now also been characterised by a single crystal *X*-ray analysis §

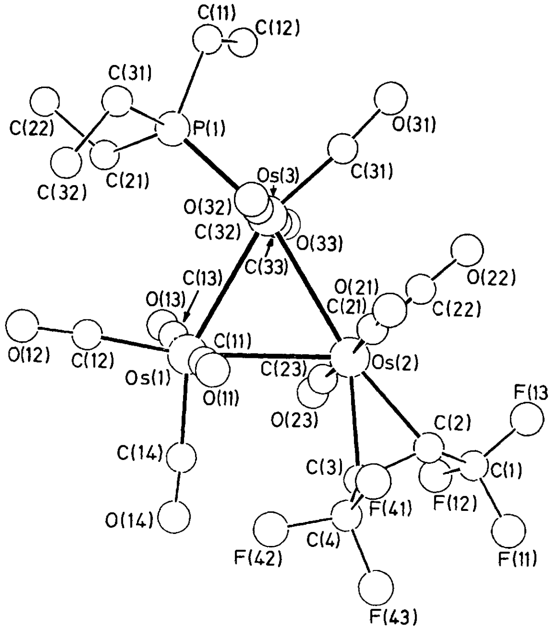


FIGURE 2 The molecular structure of $[Os_3(CO)_{10}(CF_3(H)C C(H)CF_3)(PEt_3)]$ Bond lengths Os(1)–Os(2), 2 911(2) Os(1)–Os(3), 2 874(2), Os(2)–Os(3) 2 951(2) Os(3)–P(1) 2 352(9), Os(2)–C(2), 2 15(3), Os(2)–C(3), 2 22(3), C(2)–C(3), 1 36(4) Å

The molecular structure of (**5**) is shown in Figure 2 which includes some important bond lengths The major difference between this structure and that of (**4**) is that in this case the incoming nucleophile is substituted in an equatorial position Each metal atom obeys the 18-electron rule and there is no evidence of incipient carbonyl bridge bonding

Other nucleophiles which give alkene complexes on

---

† *Crystal Data* $[C_{36}H_{30}NP_2]$ $[C_{14}H_2BrF_6O_{10}Os_3]$, *M* 1633 21, monoclinic, $P2_1/c$, a = 15 521(4), b = 8 863(3) c = 37 497(11) Å, β = 95·11(2)°, U = 5137 7 Å^3, Z = 4, D_c = 2 11 g cm^{-3}, μ(Mo-K_α) = 82 76 cm^{-1} 8854 intensities were recorded on a Stoe 4-circle diffractometer and merged to give 5650 unique observed reflections $[F > 4\sigma(F)]$ The residuals are R = 0 047 and R_w $[= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|]$ = 0 048 The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least-squares

‡ The atomic co ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

§ *Crystal Data* $C_{20}H_{17}F_6O_{10}Os_3P$, *M* 1132 92, triclinic $P1$, a = 9 169(3), b = 10 520(2), c = 14 577(4) Å α = 96 48(3) β = 92 55(2), γ = 93 51(3)°, U = 1392 6 Å^3, Z = 2, D_c = 2 71 g cm^{-3}, μ(Mo-K_α) = 132 4 cm^{-1} 3833 intensities were recorded on a Phillips PW1100 4-circle diffractometer and merged to give 3616 unique observed reflections $[F > 6\sigma(F)]$ The residuals are R = 0 071 and $R_w[= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|]$ = 0 072 The structure was solved by a combination of Patterson and Fourier difference techniques, and refined by full-matrix least-squares reaction with (**3**) are CO, Cl^-, I^-, and H^-. The H-atom transfer from metal to ligand which gives rise to these alkene complexes, although known,[10] is not a common process in cluster chemistry.

We thank Johnson Matthey Ltd. for the loan of OsO_4 and the S.R.C. for financial support.

(*Received*, *18th April* 1980; *Com.* 397.)

[1] R. P. Ferrari, G. A. Vaglio, O. Gambino, M. Valle, and G. Cetini, *J. Chem. Soc., Dalton Trans.*, 1972, 1998.
[2] E. L. Muetterties, *Bull. Soc. Chim. Belg.*, 1975, **84**, 959; *Science*, 1977, **196**, 389.
[3] J. Lewis and B. F. G. Johnson, *Gazz. Chim. Ital.*, 1979, **109**, 271.
[4] B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.*, 1978, **145**, C4.
[5] A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1974, 1415 and references therein.
[6] M. Laing, P. Sommerville, Z. Dawoodi, M. J. Mays, and P. J. Wheatley, *J. Chem. Soc., Chem. Commun.*, 1978, 1035.
[7] B. F. G. Johnson, J. Lewis, D. Pippard, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1978, 551.
[8] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.
[9] Z. Dawoodi, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1979, 721.
[10] R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, 1977, **99**, 5225; C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1974, 1013.