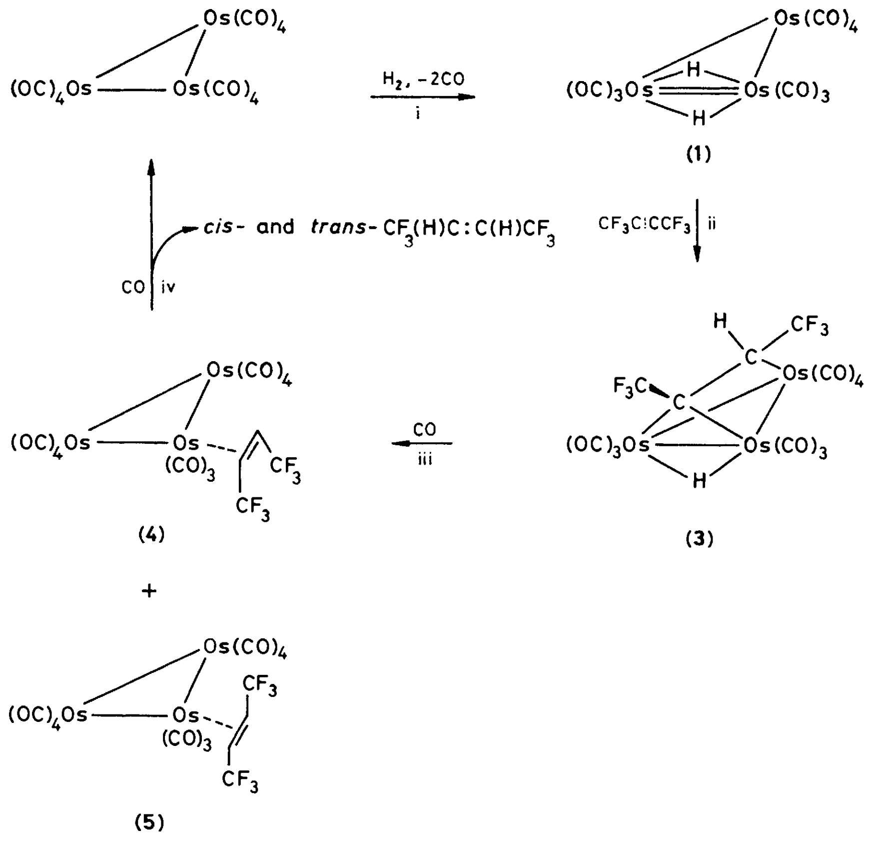
A Complete Model for the Catalytic Reduction of an Alkyne to an Alkene by a Trinuclear Osmium Cluster: the *X*-Ray Crystal Structure of *cis*-$[Os_3(CO)_{11}\{CF_3(H)C{:}C(H)CF_3\}]$

Zain Dawoodi,[a] Kim Henrick,[b] and Martin J. Mays*[a]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *Department of Chemistry, Polytechnic of North London, Holloway, London N7 8DB, U.K.*

$[HOs_3(CO)_{10}\{CF_3C{:}C(H)CF_3\}]$ reacts with carbon monoxide to give the complexes *cis*- and *trans*-$[Os_3(CO)_{11}$-$\{CF_3(H)C{:}C(H)CF_3\}]$, which react further with CO to liberate free alkenes and generate $[Os_3(CO)_{12}]$; an *X*-ray diffraction study of the *cis*-isomer is the first for a mono-substituted alkene derivative of a binary metal carbonyl cluster.

Although many cluster complexes which may be considered as intermediates in catalytic reduction schemes have been prepared,[1-3] few such complexes can be reduced further to give the free, reduced organic species together with the initial cluster. A rare example is provided by the reaction of $[Os_3H_2(CO)_{10}]$ (**1**) with C_2H_2 to give $[Os_3H(CH{:}CH_2)(CO)_{10}]$ (**2**)[4,5] which, on subsequent treatment with H_2 gives ethylene or ethane and (**1**).[4] Compound (**2**) was the only intermediate



Scheme 1. *Reagents and conditions:* i, octane, 125 °C, 1.5 h;[11] ii, hexane, room temp., 12 h; iii, CH_2Cl_2, 45 °C, 2 h; iv, octane, 125 °C, 1.5 h.

isolated, however, leaving the reaction pathways open to speculation.[6,7] We now present a complete cycle of reactions in which each of the proposed steps in the reduction of an alkyne to an alkene by molecular hydrogen and a metal cluster is defined by the isolation of an intermediate complex.

$[Os_3H(CH:CH_2)(CO)_{10}]$

(2)

Insertion of $CF_3C:CCF_3$ into (1) was previously shown to give $[Os_3H\{CF_3CC(H)CF_3\}(CO)_{10}]$ (3)[8] and this complex was found to react further with nucleophiles to give alkene clusters of the type $[Os_3(CO)_{10}\{CF_3(H)C:C(H)CF_3\}Y]$ (Y = PEt_3, Cl^-, Br^-, I^-).[9] We have now found that reaction of CO with (3) (reflux, CH_2Cl_2) gives two products (each in yield of *ca.* 30%) identified spectroscopically as isomers of formula $[Os_3\{CF_3(H)C:C(H)CF_3\}(CO)_{11}]$ [(4) and (5)]. The structure of the *cis*-isomer (4) was determined by an *X*-ray analysis† and is the first such study for a simple mono-substituted alkene derivative of a binary metal carbonyl cluster. The molecular structure is shown in Figure 1, together with some important bond parameters. It is derived from the structure of $[Os_3(CO)_{12}]$[10] by replacing an equatorial carbonyl group with the *cis*-1,2-bis(trifluoromethyl)ethylene ligand and the C=C bond axis lies in the plane of the Os_3 triangle. Compound (5) gives virtually identical spectroscopic data to (4) and is believed

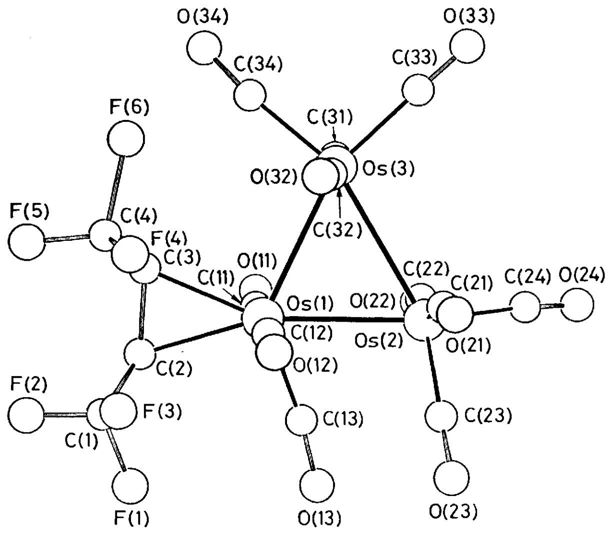


Figure 1. The structure of the complex cis-$[Os_3(CO)_{11}\{CF_3(H)C:C(H)CF_3\}]$ (4). Relevant molecular dimensions are Os(1)–Os(2) 2.760(2), Os(1)–Os(3) 2.906(1), Os(2)–Os(3) 3.045(2), Os(1)–C(2) 2.192(23), Os(1)–C(3) 2.185(26), C(2)–C(3) 1.509(35), mean Os–C 1.954, and mean C–O 1.131 Å; Os–C–O 172°.

---

† *Crystal data:* $C_{15}H_2F_6O_{11}Os_3$, M_r = 1042.8, monoclinic, $P2_1/c$, a = 11.091(2), b = 10.151(3), c = 18.796(4) Å, β = 93.65(5)°, U = 2111.7 Å^3, Z = 4, D_c = 3.279 g cm^{-3}, μ(Mo-K_α) = 173.95 cm^{-1}, $F(000)$ = 1848. The structure was solved from diffractometer data by the heavy atom method and refined to an R of 0.0409, R_w = 0.0404 for 1944 observed reflections having $F > 6\sigma(F)$. 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.

to contain the *trans*-alkene ligand.‡ The cycle of reduction is completed by treatment of each of the complexes (**4**) and (**5**) separately with CO (reflux, octane, 125 °C) to generate [$Os_3(CO)_{12}$] in quantitative yield in 1.5 h, with loss of the corresponding alkene.

The model thus provided by this sequence of reactions for the reduction of an alkyne to an alkene by molecular hydrogen in the presence of a metal cluster is shown in Scheme 1. Overall there is no loss or gain of CO and the model is well supported by experimental evidence in that each step takes place in good yield and is defined by the isolation of a fully characterised intermediate.

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

Received, 31st March 1982; Com. 364

---

‡ Selected spectroscopic data (i.r. measured in hexane and ^1H n.m.r. in CD_2Cl_2 at −80 °C) are as follows: compound (**4**), ν_{CO} 2129w, 2079vs, 2065s, 2044vs, 2040vs, 2027s, 2022s, 2010m, 1997w, and 1992sh cm^{-1}; ^1H n.m.r. δ 3.10(2H, m, CH); *m/z* 1048. Compound (**5**), ν_{CO} 2128w, 2077vs, 2064s, 2043vs, 2039s, 2025m, 2021m, 2009w, 1996w, and 1990sh cm^{-1}; n.m.r. δ 3.10(2H, m, CH); *m/z* 1048.

References

1 R. D. Adams, D. A. Katahira, and L. W. Yang, *J. Organomet. Chem.*, 1981, **219**, 85, and references therein.
2 Z. Dawoodi, M. J. Mays, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **219**, 103.
3 M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, **101**, 7255.
4 A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
5 M. Tachikawa, J. R. Shapley, and C. G. Pierpoint, *J. Am. Chem. Soc.*, 1975, **97**, 7172.
6 J. Lewis and B. F. G. Johnson, *Gazz. Chim. Ital.*, 1979, **109**, 271.
7 A. J. Deeming, in 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley–Interscience, Chichester, New York, Brisbane, and Toronto, 1980, p. 391.
8 M. Laing, P. Somerville, Z. Dawoodi, M. J. Mays, and P. Wheatley, *J. Chem. Soc., Chem. Commun.*, 1978, 1035.
9 Z. Dawoodi, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Chem. Commun.*, 1980, 641.
10 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.
11 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.