Bridging Methylene and π-Allylic Bonding Modes in Tetranuclear Osmium Clusters; the *X*-Ray Crystal Structures of [Os$_4$H$_2$(CO)$_{12}$CHCH$_2$Ph] and [Os$_4$H$_2$(CO)$_{11}$MeCCPhCHPh]

By BRIAN F. G. JOHNSON, JOHN W. KELLAND, JACK LEWIS,* ALASTAIR L. MANN, and PAUL R. RAITHBY
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary [Os$_4$H$_3$(CO)$_{11}$CH:CHR] reacts with CO under pressure to give edge bridging methylenic compounds [Os$_4$H$_2$(CO)$_{12}$CHCH$_2$R] and, when R=H, with acetylenes, R′C$_2$R″, to give π-allylic derivatives of the form [Os$_4$H$_2$(CO)$_{11}$MeCCR′CHR″]; the structures of these two compounds have been confirmed by *X*-ray diffraction analyses.

PHOTOCHEMICAL or thermal reaction of [Os$_4$H$_4$(CO)$_{12}$] with alkenes or alkynes gives [Os$_4$H$_3$(CO)$_{11}$CR^1:CHR^2] (**1**) and [Os$_4$H$_2$(CO)$_{11}$R^{1}C:CR^2] (**2**) respectively.[1] These molecules may be considered as models for the modes of co-ordination of organic groups on metal surfaces. Of particular importance in catalysis is the ability to form additional C–C bonds once an organic group is co-ordinated to the metal surface thus forming large organic species. In this communication we report the reactions of (**1**) and (**2**) with CO, R′C:CR″, and P(OMe)$_3$.

The complexes [Os$_4$H$_3$(CO)$_{11}$CR^1:CHR^2] (R^1=H, R^2=Me, Ph; R^1=R^2=Ph; R^1+R^2 = –[CH$_2$]$_4$–) show no reaction with CO under mild conditions, but at elevated temperatures and pressures react in high yield (>80%) by uptake of CO and internal rearrangement to give [Os$_4$H$_2$(CO)$_{12}$R^{1}CCH$_2$R^2]. These reactions may be viewed as α-addition of Os and β-addition of H to the olefin. In the case of R^1=H, R^2=Ph the product may be recrystallised from hexane–dichloromethane and its structure has been confirmed by a single crystal *X*-ray analysis.

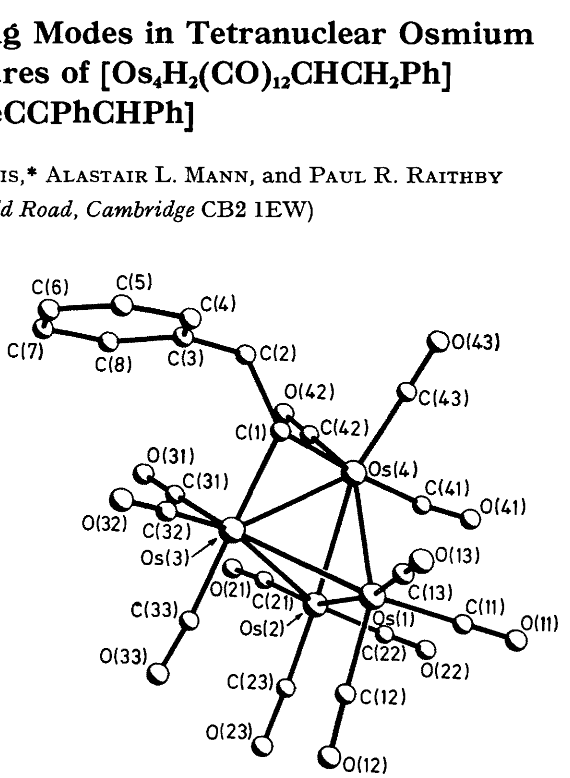


FIGURE 1. The molecular structure of [Os$_4$H$_2$(CO)$_{12}$CHCH$_2$Ph] including the atom numbering scheme. Bond lengths: Os(1)–Os(2), 2·801(2), Os(1)–Os(3), 2·964(2); Os(1)–Os(4), 2·948(2); Os(2)–Os(3), 2·825(2); Os(2)–Os(4), 2·835(2); Os(3)–Os(4), 2·755(2); Os(3)–C(1), 2·11(2); Os(4)–C(1), 2·15(2); C(1)–C(2), 1·60(3) Å; bond angles: Os(3)–C(1)–Os(4), 80·6(7)°.

Crystal data: C$_{20}$H$_{10}$O$_{12}$Os$_4$, M 1 203·08, monoclinic, a = 10·154(2), b = 17·197(4), c = 14·535(4) Å, β = 98·54(2)°, U = 2 509·9 Å^3, Z = 4, D_c = 3·18 g cm^{-3}; μ(Mo-K_α) =

202·37 cm^{-1}, space group $P2_1/n$. Intensities were recorded on a Syntex $P2_1$ diffractometer using graphite monochromated Mo-K_α radiation. 2 236 unique observed intensities were used in refinement. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by block-cascade least squares to $R = 0·037$.†

The molecular structure of $[Os_4H_2(CO)_{12}HCCH_2Ph]$ is shown in Figure 1 which includes some of the important bond parameters. The Os atoms define a distorted tetrahedron, and from the distribution of the terminal carbonyl groups the two hydrides on the cluster are thought to bridge the two long Os(1)–Os(3) and Os(1)–Os(4) edges. The methylene carbon C(1) bridges the short Os(3)–Os(4) edge. The long C(1)–C(2) bond length and the C(1)–C(2)–C(3) angle of 111(1)° show that this bond is single, and that C(2) is not co-ordinated to the cluster. Electron counting shows that Os(1) and Os(2) do not obey the '18 electron rule,' though this may be overcome by use of a metal-dative bond between the two atoms as in $Os_6(CO)_{18}$.[2] This is reflected by the incipient carbonyl bridge bonding to the electron deficient Os(2) atom with Os(2)–C(33) and Os(2)–C(41) contacts of 2·927 and 2·931 Å, respectively. These two carbonyl groups show significant distortions from linearity with an Os(3)–C(33)–O(33) angle of 167·1° and an Os(4)–C(41)–O(41) angle of 170·4°.

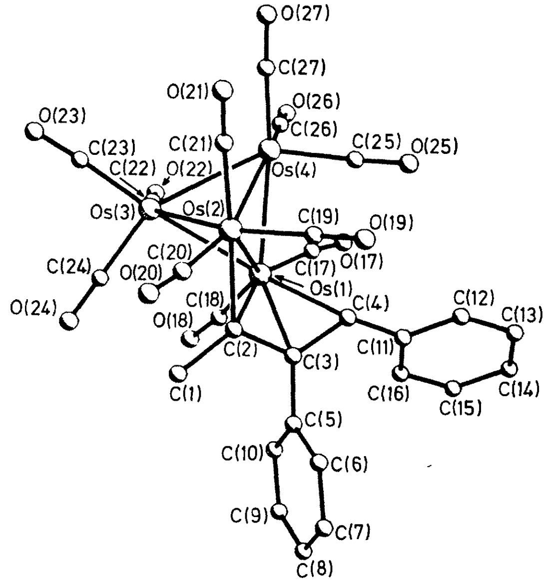
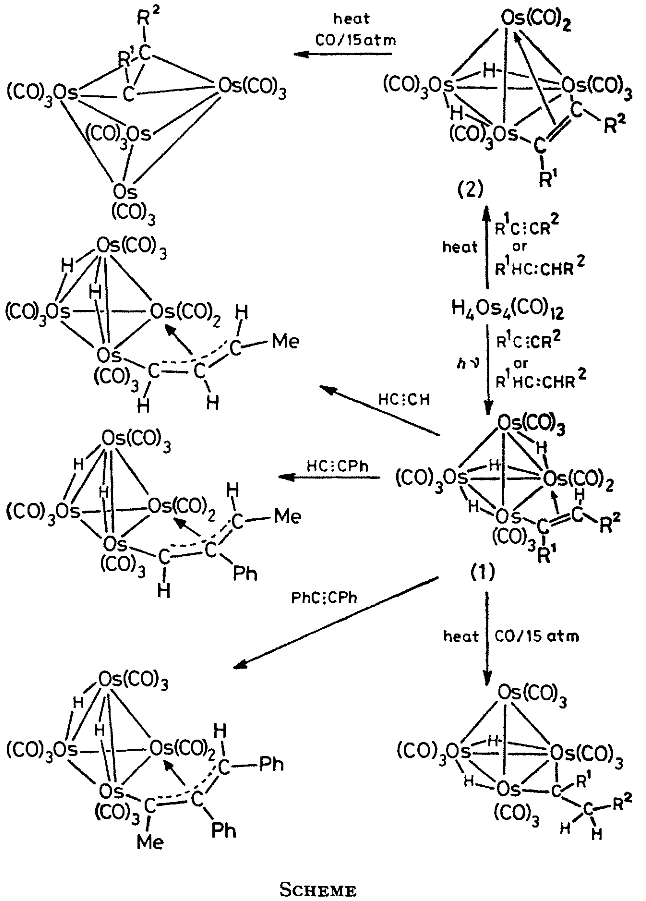


FIGURE 2. The molecular structure of $[Os_4H_2(CO)_{11}MeCCPhCHPh]$, hydrogen atoms have been omitted for clarity. Bond lengths: Os(1)–Os(2), 2·798(2); Os(1)–Os(3), 2·798(2); Os(1)–Os(4), 2·747(2); Os(2)–Os(3), 3·006(2); Os(2)–Os(4), 2·876(2); Os(3)–Os(4), 2·893(2); Os(1)–C(2), 2·16(2); Os(1)–C(3), 2·26(2); Os(1)–C(4), 2·32(1); Os(2)–C(2), 2·24(2); C(1)–C(2), 1·51(3); C(2)–C(3), 1·44(2); C(3)–C(4), 1·45(3) Å.

When $[Os_4H_2(CO)_{11}CR^1{:}CR^2]$ (**2**) (R^1=H, R^2=Ph; R^1=R^2=Ph) is treated similarly the products include $[Os_4(CO)_{12}CR^1CR^2]$ (in about 20% yield). This known[3] compound has the four Os atoms in a 'butterfly' configuration with the organic group sitting above the open cluster bonding to all four metals. A similar reaction has been observed when $P(OMe)_3$ is used instead of CO, though proceeding under milder conditions.

$[Os_4H_3(CO)_{11}CH{:}CH_2]$ reacts with acetylenes HC_2H, HC_2Ph, and PhC_2Ph in hexane at 25 °C over 50 h to give (stoicheiometrically) addition products in *ca.* 50% yield. For all acetylene complexes the mode of bonding of the organic fragment to the metal cluster is the same; however, the positions of the substituents in the case of the PhC_2Ph complex differs from the other two. This has been confirmed by *X*-ray crystallography and n.m.r. decoupling experiments, respectively: $H_2Os_4(CO)_{11}CHCHCHMe$: τ −0·37 (ddd, 1H), 3·78 (dd, 1H), 6·52 (ddq, 1H), 7·81 (d,3H), 24·65 (d, 1H), and 30·22 (dd, 1H); $H_2Os_4(CO)_{11}CHCPhCHMe$: τ −0·25 (dd, 1H), 2·59 (m, 5H), 6·44 (dq, 1H), 7·83 (d, 3H), and 24·88 (d, 1H); $H_2Os_4(CO)_{11}CMeCPhCHPh$: τ 2·4—3·2 (m, 10H), 5·24 (br s, 1H), 7·26 (br s, 3H), 25·12 (s, 1H), and 30·13 (s, 1H).

Crystal data: $C_{27}H_{15}O_{11}Os_4$, M 1 276·19, triclinic, $a = 9·539(2)$, $b = 9·600(3)$, $c = 18·556(5)$ Å, $\alpha = 91·46(2)$, $\beta = 97·56(2)$, $\gamma = 117·26(2)°$, $U = 1\,490·3$ Å^3, $Z = 2$, $D_c = 2·85$ g cm^{-3}; μ(Mo-K_α) = 170·44 cm^{-1}, space group $P\bar{1}$.



SCHEME

---

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

The structure was solved by a combination of direct methods and Fourier difference techniques and refined by block cascade least squares to $R = 0{\cdot}050$.†

Figure 2 shows the molecular structure of $[Os_4H_2(CO)_{11}$-MeCCPhCHPh] and includes some of the important bond parameters. The distribution of the carbonyl ligands around the distorted tetrahedron of Os atoms indicates that the two hydrides on the cluster bridge the Os(2)–Os(3) and the Os(3)–Os(4) edges. The organic fragment σ-bonds to Os(2) and forms a π-allylic bond to Os(1). The planar C(2), C(3), C(4) fragment is tilted w.r.t. the Os(1), Os(2), Os-(3) triangle, and the Os(1)–C(2) bond is significantly shorter than the Os(1)–C(4) bond. The acetylene in this complex has formally added on to the existing C_2 unit while in the other two cases (Scheme) the acetylene has formally inserted between the metallic cage and the organic side chain.

The methylene bridged species is related to the intermediates observed by Shapley[4] in the reaction of the triosmium methyl derivative to yield the carbon capped species. The ready formation of bridged methylene complexes has also been observed by Deeming for co-ordinated alkyl phosphine[5] derivatives. This may be viewed as an α-hydrogen elimination reaction. The presence of a second metal centre thus allows a similar four-centre transition state involved for β-elimination in mononuclear species (Figure 3). The facility for both α- and β-hydrogen elimination in metal alkyl derivatives emphasises the enhanced potential reactivity of polynuclear metal species over their mononuclear counterparts.

FIGURE 3

We thank the S.R.C. for financial support.

(*Received, 22nd February* 1980; *Com.* 197.)

---

[1] B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organomet. Chem.*, 1976, **113**, C42.
[2] R. Mason, D. M. P. Mingos, and R. M. Thomas, *J. Am. Chem. Soc.*, 1973, **95**, 3802.
[3] R. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, and S. W. Sankey, unpublished results.
[4] R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, 1977, **99**, 5226.
[5] A. J. Deeming, *J. Organomet. Chem.*, 1977, **128**, 63.