

Reactions of Terminal Acetylenes with the 'Raft' Cluster $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})]$; X-Ray Crystal Structures of $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ and $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$

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The 'raft' cluster $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})]$ reacts with the terminal alkyne $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Me}, \text{Ph}$) to afford the organo-cluster $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{R}\}]$, which, on standing, loses the elements of an $\text{Os}(\text{CO})_5$ fragment to give the pentanuclear cluster $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{R}\}]$; the structures of the phenyl derivatives of these hexa- and penta-nuclear clusters have been established by X-ray analysis.

We recently reported the preparation of a series of hexanuclear carbonyl clusters¹⁻³ which bear a clear structural relationship to the exposed (111) plane of a metal surface.⁴ As a consequence we have been interested in the interaction of simple, unsaturated organic molecules with these 'raft' complexes. In this way it is hoped to establish metal-ligand bonding modes which may be of relevance to the organic/metal surface interaction.

Recent molecular orbital calculations⁵ have shown that in the Os_6 'raft' systems there is an empty low lying molecular orbital which indicates that they may be susceptible to nucleophilic addition reactions. In this communication, we report the reaction of the activated cluster $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})]$,³ with the alkyne $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Me}, \text{Ph}$). On addition of excess of $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Me}, \text{Ph}$) to a solution of $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})]$, in CH_2Cl_2 , at room temperature, a green solution is slowly formed. After purification by t.l.c., dark green crystals of the new cluster $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{R}\}]$ ($\text{R} = \text{Me}, \text{Ph}$) were obtained, and the complex initially

characterised by spectroscopic techniques (Table 1). In order to establish the overall geometry of the cluster and the mode of co-ordination of the organic group a single-crystal X-ray analysis was undertaken.

The molecular structure[†] of $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ is illustrated in Figure 1, together with some important bond parameters. Unlike the tri-edge-bridged triangular, planar Os_6 geometry observed in $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{OMe})_3\}_4]$ ¹ and its derivatives, the metal framework geometry in $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ consists of a chain of four triangles sharing three common edges. Three of these triangles, defined by atoms $\text{Os}(1)$ - $\text{Os}(5)$ are essentially coplanar, while the fourth triangle, defined by the atoms $\text{Os}(4)$, $\text{Os}(5)$, and $\text{Os}(6)$,

[†] Crystal Data: $\text{C}_{28}\text{H}_{16}\text{O}_{20}\text{Os}_6$, $M = 1803.53$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.759(2)$, $b = 16.442(3)$, $c = 18.704(2)$ Å, $\beta = 96.99(2)^\circ$, $U = 3589.4$ Å³, $D_c = 3.34$ g cm⁻³, $Z = 4$, $F(000) = 3160$, $\mu(\text{Mo-K}\alpha) = 212.31$ cm⁻¹; $F > 4\sigma(F)$, 2θ range 5-45°, $R = 0.058$, $R_w = 0.054$ for 3629 absorption corrected diffractometer data.

Table 1. Spectroscopic properties of $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{R}\}]$ (R = Ph, Me) and their derivatives.

Compound	I.r. spectrum (ν_{CO} , cm^{-1}) ^a	m/z	N.m.r. (δ) ^c
$[\text{Os}_6(\text{CO})_{20}\{\text{CC}(\text{H})\text{Ph}\}]$	2128(w), 2081(s), 2065(m), 2048(s), 2027(m), 2005(m), 1982(w), 1967(vw), 1950(vw)	1733 ^b	
$[\text{Os}_6(\text{CO})_{20}\{\text{CC}(\text{H})\text{Me}\}]$	2128(w), 2081(s), 2065(m), 2048(s), 2028(m), 2006(m), 1982(w), 1969(vw), 1950(vw)	1800 ^b	(Me)2.11(d) $^3J_{\text{HH}}$ 6 Hz (H)6.41(q) (3:1) ^d
$[\text{Os}_5(\text{CO})_{15}\{\text{CC}(\text{H})\text{Ph}\}]$	2103(w), 2072(s), 2053(s), 2022(m), 2010(s), 1980(vw)	1481	(Ph)7.11(m) (H)6.34(s) (5:1) ^d
$[\text{Os}_5(\text{CO})_{15}\{\text{CC}(\text{H})\text{Me}\}]$	2101(w), 2069(s), 2051(s), 2020(m), 2005(ms)	1420	(Me)2.23(d) $^3J_{\text{HH}}$ 6 Hz (H)4.70(q) (3:1) ^d

^a Recorded in CH_2Cl_2 . ^b Poor mass spectral data. ^c Recorded in CD_2Cl_2 . ^d Intensity ratio.

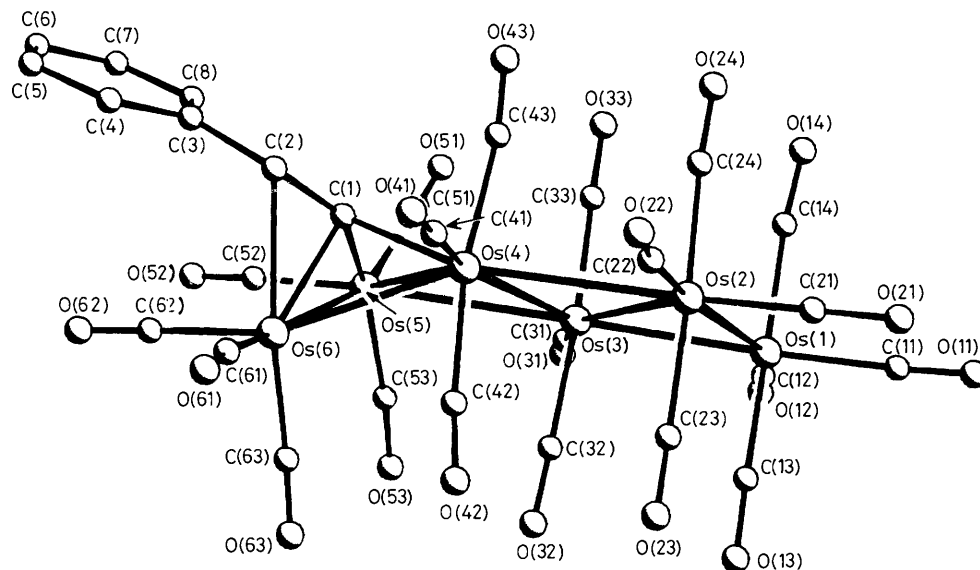


Figure 1. The molecular structure of $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$. Bond lengths: Os(1)–Os(2), 2.935(2); Os(1)–Os(3), 2.842(2); Os(2)–Os(3), 3.026(2); Os(2)–Os(4), 3.173(2); Os(3)–Os(4), 2.843(2); Os(3)–Os(5), 3.190(2); Os(4)–Os(5), 3.056(2); Os(4)–Os(6), 2.872(2); Os(5)–Os(6), 2.802(2); Os(4)–C(1), 2.161(3); Os(5)–C(1), 1.95(3); Os(6)–C(1), 2.09(3); Os(6)–C(2), 2.34(3); C(1)–C(2), 1.42(4); C(1)–C(2)–C(3), 124(3)^o, angle between Os(3), Os(4), Os(5) and Os(4), Os(5), Os(6) 34^o.

makes an angle of 34^o with the plane through the other three triangles. This fourth triangle is capped by an organic ligand, derived from an alkyne, which forms σ -bonds to Os(4) and Os(5) and π -bonds to Os(6). Although the hydrogen atom co-ordinated to C(2) was not located directly, its position may be inferred from the C(1)–C(2)–C(3) angle of 124(3)^o, and from its signal in the ^1H n.m.r. spectrum of $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Me}\}]$ [^1H δ 6.41(q), CH_3 δ 2.91(d)]. The bonding mode of this ligand is similar to that observed in the alkene-substituted clusters $[\text{Co}_2\text{Ru}(\text{CO})_9\{\text{C}=\text{C}(\text{H})\text{Me}\}]$,⁶ $[\text{Ru}_3(\text{CO})_9(\text{AuPPh}_3)_2\{\text{C}=\text{C}(\text{H})\text{Bu}^1\}]$,⁷ and $[\text{Os}_3(\text{CO})_9$

$\{\text{C}=\text{CH}_2\}]$.⁸ However, the synthesis of $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ represents the first example, in polynuclear osmium cluster chemistry, of the formation of a vinylidene-substituted cluster from a non-hydrido cluster and a terminal alkyne, which involves an apparent 1,2-hydrogen shift and where the transferred hydrogen originates from the alkyne. Similar alkyne–vinylidene rearrangements have been observed for mononuclear complexes of rhenium⁹ and tungsten¹⁰ with terminal alkynes, but in the previous examples from cluster chemistry^{8,11} the synthesis has required the presence of a metal hydride.

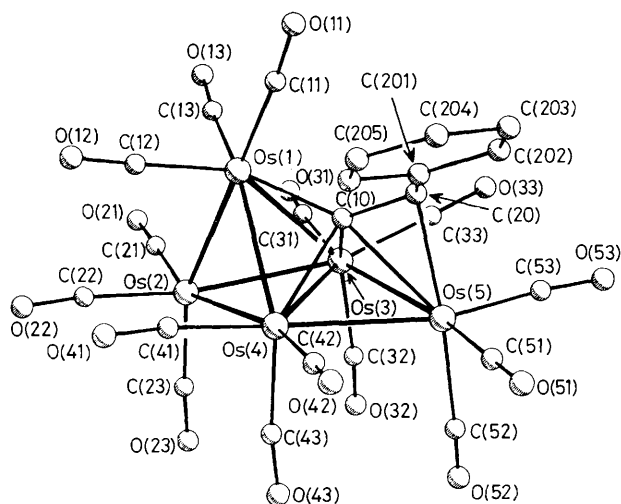


Figure 2. The molecular structure of $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$. Bond lengths: Os(1)–Os(2), 2.774(1); Os(1)–Os(3), 2.824(1); Os(1)–Os(4), 2.850(1); Os(2)–Os(3), 2.828(1); Os(2)–Os(4), 2.830(1); Os(3)–Os(4), 2.776(1); Os(3)–Os(5), 2.848(1); Os(4)–Os(5), 2.854(1); Os(1)–C(10), 2.033(1); Os(3)–C(10), 2.081(2); Os(4)–C(10), 2.171(2); Os(5)–C(10), 2.415(2); Os(5)–C(20), 2.265(2); C(10)–C(20), 1.51(3); C(10)–C(20)–C(201), 123(3)°.

In terms of electron counting $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ is a 92 electron system, having two more electrons than the 90 electron starting complex $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})]$. This difference in electron count may reflect the difference in metal framework geometry, although both complexes have the same number of 'formal' metal–metal bonds. In this context, it is interesting to note that a cyclic voltammogram of the alkyne-substituted complex shows two one-electron irreversible oxidation steps, confirming the ready loss of two electrons from the cluster. The chain of edge sharing Os_3 triangles in $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ may more readily accommodate the additional electron pair than the tri-edge-bridged triangular metal framework. The former geometry might be expected to be observed in the hypothetical anion ' $\text{Os}_6(\text{CO})_{21}^{2-}$ ' while the parent binary carbonyl, ' $\text{Os}_6(\text{CO})_{21}$ ', should exhibit the latter geometry observed in its phosphite derivatives.¹

When $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})]$ is treated with disubstituted alkynes under similar reaction conditions no reaction occurs, suggesting that the alkynyl terminal hydrogen plays an important role in the formation of the product. When this reaction is attempted at higher temperatures decomposition of the starting material occurs.

When $[\text{Os}_6(\text{CO})_{20}\{\text{C}=\text{C}(\text{H})\text{R}\}]$, in CH_2Cl_2 , is heated to reflux for 3 h, the complex decomposes to give an orange product in good yield. The mass spectrum, and ^1H n.m.r. and i.r. spectra of this complex (Table 1) are consistent with the formulation $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{R}\}]$ (R = Ph, Me). In order to establish the overall molecular geometry an X-ray analysis was undertaken on a crystal obtained from hexane solution.

The molecular structure[‡] of $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ is

[‡] Crystal Data: $\text{C}_{23}\text{H}_6\text{O}_{15}\text{Os}_5$, $M = 1473.20$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), $a = 17.984(11)$, $b = 11.643(6)$, $c = 13.565(9)$ Å, $\beta = 106.15(5)^\circ$, $U = 2728.5$ Å³, $D_c = 3.59$ g cm⁻³, $Z = 4$, $F(000) = 2576$, $\mu(\text{Mo-K}\alpha) = 247.33$ cm⁻¹; $F > 2\sigma(F)$, 2θ range 5–54°, $R = 0.065$, $R_g = 0.080$ for 4509 absorption corrected diffractometer data.

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.

illustrated in Figure 2, together with some important bond parameters. The metal atoms define an edge bridged tetrahedron with the organic ligand bonding Os(1), Os(3), and Os(4) through C(10) and via a π -interaction to Os(5). Again, the hydrogen atom bonded to C(20) was not located directly but the ^1H n.m.r. data (Table 1) and the C(10)–C(20)–C(201) angle of 123(3)° are consistent with this location. This bonding mode for the organic ligand has been observed previously in a number of tetra- and penta-nuclear clusters.¹² The overall structure is related to that of $[\text{Os}_5\text{H}_2(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$,¹³ which is a 76 electron complex and contains two more electrons than $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$. The additional electron pair in the dihydrido complex is consistent with the presence of one fewer formal metal–metal bonds, and the vector in $[\text{Os}_5\text{H}_2(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ ¹³ equivalent to the Os(3)–Os(4) bond in $[\text{Os}_5(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ is lengthened to 3.783(2) Å. The Os–C(10) distances in the two structures are not significantly different and the effect of the longer Os(3)–Os(4) separation in $[\text{Os}_5\text{H}_2(\text{CO})_{15}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ is to draw the organic carbons further inside the metal framework. This semi-interstitial position of the carbon is reminiscent of that observed in carbido-clusters, and Sappa *et al.*¹¹ have compared this class of compound to the 'butterfly' iron clusters which have been investigated as models for homogeneous catalysis in Fischer–Tropsch reactions.¹⁴

Alternatively, the closing up of the 'raft-like' cluster to the edge-bridged tetrahedral geometry may be considered as the formation of a 'stepped' metal surface. It has been emphasised that in the reactivity pattern on metal surfaces,⁴ 'steps' appear to show higher reactivity. It is clear from the above structures that the potential bonding mode of the α -carbon of the organic ligand to the three metal centres with a π -interaction to a fourth is more readily accommodated by such a 'step' geometry.

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