

Synthesis of High Nuclearity Cluster Alkynes Under Mild Reaction Conditions; the X-Ray Crystal Structures of $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta\text{-CCEt})]$, $[\text{Os}_6(\text{CO})_{17}(\mu_4\text{-}\eta^2\text{-HCCEt})]$, and $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta\text{-MeCCEt})]$

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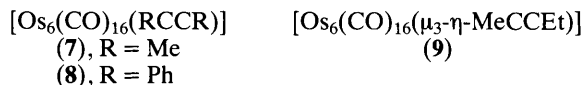
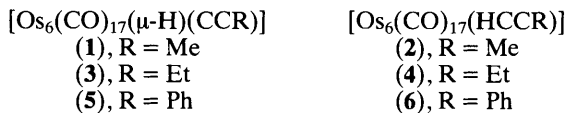
Reaction of the labilised cluster $[\text{Os}_6(\text{CO})_{17}(\text{NCMe})]$ with the terminal alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Me}$, Et , or Ph) affords the isomeric alkyne substituted clusters $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta\text{-CCR})]$ [$\text{R} = \text{Me}$ (**1**), Et (**3**), or Ph (**5**)] and $[\text{Os}_6(\text{CO})_{17}(\mu_4\text{-}\eta^2\text{-HCCR})]$ [$\text{R} = \text{Me}$ (**2**), Et (**4**), or Ph (**6**)], and under similar conditions the disubstituted alkynes $\text{RC}\equiv\text{CR}'$ ($\text{R} = \text{Me}$ or Ph ; $\text{R}' = \text{Me}$, Ph , or Et) give $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta\text{-RCCR}')]$ [$\text{R} = \text{R}' = \text{Me}$ (**7**); $\text{R} = \text{R}' = \text{Ph}$ (**8**); $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$ (**9**)] as the major product; the structures of complexes (**3**), (**4**), and (**9**) have been established by X-ray diffraction studies.

There is a useful analogy between the chemistry of alkyne substituted cluster complexes and the chemisorption of alkynes on metal surfaces.¹ However, developments in the area of alkyne cluster chemistry have been limited because of the vigorous conditions usually required for the synthesis of the appropriate cluster. Particularly in the case of higher nuclearity osmium cluster carbonyls, the preparation of alkene or alkyne containing derivatives has generally required the application of high temperatures or pressures.^{2,3} These conditions frequently result in carbon-carbon bond rupture within the organic species.³ With trinuclear osmium clusters the use of the activated complex $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$,⁴ containing the labile acetonitrile ligand, has considerably simplified the production of specific cluster complexes under mild reaction conditions.⁵ In this communication we report the synthesis of the complex $[\text{Os}_6(\text{CO})_{17}(\text{NCMe})]$, which contains the labile MeCN ligand, and its reactions with a

variety of substituted alkynes, which afford a series of osmium cluster alkyne complexes containing Os_6 units.

The reaction of $[\text{Os}_6(\text{CO})_{18}]$ with a slight excess of Me_3NO , in acetonitrile, affords the cluster $[\text{Os}_6(\text{CO})_{17}(\text{NCMe})]$ which was used in subsequent reactions without further purification. With the terminal alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Me}$, Et , or Ph), in toluene at 70 °C over a period of 1.5–2.5 h, two products, one purple the other orange-red, are obtained. Both exhibit the same molecular ion in their mass spectrum and show the same stepwise loss of seventeen carbonyl groups. However, they exhibit different i.r. spectra (Table 1), and while the purple product of the reaction with $\text{HC}\equiv\text{CEt}$ shows a ^1H n.m.r. resonance at $\delta -21.62$, which is consistent with the presence of a metal hydride, the red-orange product shows no hydride signals. On the basis of this spectroscopic evidence the products may be formulated as the isomers $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\text{CCR})]$ [$\text{R} = \text{Me}$ (**1**), Et (**3**), or Ph (**5**)] and

$[\text{Os}_6(\text{CO})_{17}(\text{HCCR})]$ [$\text{R} = \text{Me}$ (**2**), Et (**4**), Ph (**6**)]. This is consistent with the observation that the orange-red product $[\text{Os}_6(\text{CO})_{17}(\text{HCCR})]$ is converted into the purple product $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\text{CCR})]$ on heating in hexane or toluene at 40–45 °C for four days.



In order to establish the molecular geometry of these products the X-ray crystal structures of the ethyl-alkyne derivatives $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\text{CCEt})]$ (**3**) and $[\text{Os}_6(\text{CO})_{17}(\text{HCCEt})]$ (**4**) were determined. The structure of (**3**)[†] is illustrated in Figure 1 which includes some important bond parameters. The metal framework consists of a tetrahedron,

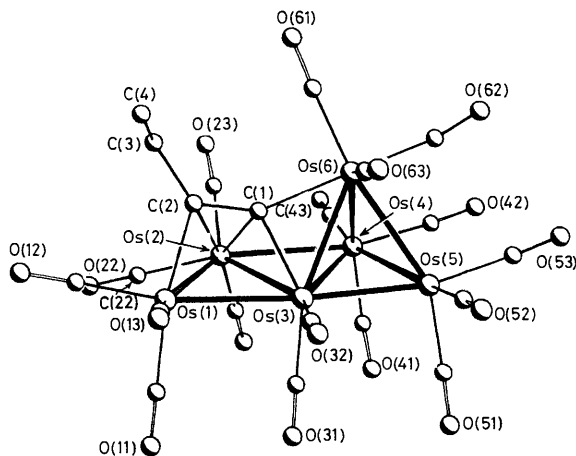


Figure 1. The molecular structure of $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta\text{-CCEt})]$ (**3**). Bond lengths: Os(1)–Os(2), 2.791(1); Os(1)–Os(3), 2.877(1); Os(2)–Os(3), 2.733(1); Os(2)–Os(4), 2.938(1); Os(3)–Os(4), 2.793(1); Os(3)–Os(5), 2.651(1); Os(3)–Os(6), 2.812(1); Os(4)–Os(5), 2.936(1); Os(4)–Os(6), 2.902(1); Os(5)–Os(6), 2.861(1); Os(2)–C(1), 2.28(3); Os(3)–C(1), 2.04(2); Os(6)–C(1), 2.09(2); Os(1)–C(2), 2.11(2); Os(2)–C(2), 2.35(2); C(2)–C(3), 1.51(3); C(3)–C(4), 1.48(4) Å. Bond angles: Os(2)–C(1)–Os(3), 72.8(8); Os(2)–C(1)–Os(6), 124(1); Os(2)–C(1)–Os(6), 85.9(7); Os(2)–C(1)–C(2), 76(1); Os(3)–C(1)–C(2), 123(2); Os(6)–C(1)–C(2), 150(2); Os(1)–C(2)–Os(2), 77.3(7); Os(1)–C(2)–C(1), 100(1); Os(2)–C(2)–C(1), 70(1); Os(1)–C(2)–C(3), 130(1); Os(2)–C(2)–C(3), 123(1); C(1)–C(2)–C(3), 130(2)°.

[†] *Crystal data:* (**3**), $[\text{C}_{21}\text{H}_6\text{O}_{17}\text{Os}_6] \cdot \text{CH}_2\text{Cl}_2$, $M = 1756.33$, triclinic, space group $P1$ (No. 2), $a = 9.485(4)$, $b = 11.012(6)$, $c = 16.686(4)$ Å, $\alpha = 88.87(2)$, $\beta = 84.20(2)$, $\gamma = 69.36(3)^\circ$, $U = 1622.3$ Å³, $Z = 2$, $D_c = 3.59$ g cm⁻³, $F(000) = 1532$, $\mu(\text{Mo-K}\alpha) = 236.31$ cm⁻¹. Data recorded on a Stoe 4-circle diffractometer using graphite monochromated Mo-K α radiation; 2θ range 5–50°. 4368 unique observed [$F > 4\sigma(F)$] absorption corrected reflections, $R = 0.049$, $R_w = 0.048$.

[‡] The atomic co-ordinates for structures (**3**), (**4**), and (**9**) 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.

one edge of which is bridged by one Os atom, and the triangle thus formed is bridged by a second Os atom. The Os(1)Os(2)Os(3)Os(4)Os(5) unit shows some deviation from planarity [maximum deviation of 0.16 Å for Os(3)], but this fragment resembles part of the hexagonal packed array in $[\text{Os}_6(\text{CO})_{17}(\text{P}(\text{OMe})_4)_4]$,⁶ or the basal hexametal unit in the $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ anion.⁷ An edge-bridged tetrahedral metal geometry has been observed previously in the structure of $[\text{Os}_5\text{H}_2(\text{CO})_{16}]^8$ and a number of its derivatives.⁹ The alkyne ligand caps the Os(1)Os(2)Os(3) triangle, forming σ -bonds to Os(1) and Os(3) and a π -bond to Os(2). This mode of bonding has been observed for an alkyne co-ordinating to a trinuclear cluster in a wide range of systems.² However, in (**3**) the alkyne hydrogen has transferred to the cluster framework, and has been shown, by potential energy calculations,¹⁰ to bridge the Os(4)–Os(6) edge, while the alkyne carbon C(1) is σ -bonded to Os(6). The angles at the acetylenic carbons in (**3**) are similar to those observed in $[\text{Os}_3(\text{CO})_{10}(\text{PhCCPh})]$ ¹¹ which suggests that the bonding of the alkyne in the two molecules is not significantly different. Another similarity between the two structures is the presence of incipient bridging carbonyls which may help to relieve the electronic imbalance within the molecule. In (**3**) the Os(1) ··· C(22) distance is 2.74(2) Å and the Os(2)–C(22)–O(22) angle is 169(2)°. These data are indicative of electron donation to the formally electron-poor Os(1) atom (17 electrons) from the electron-rich Os(2) atom (19 electrons). There is also a relatively short contact of 3.08(2) Å between Os(5) and C(62) which again may reflect

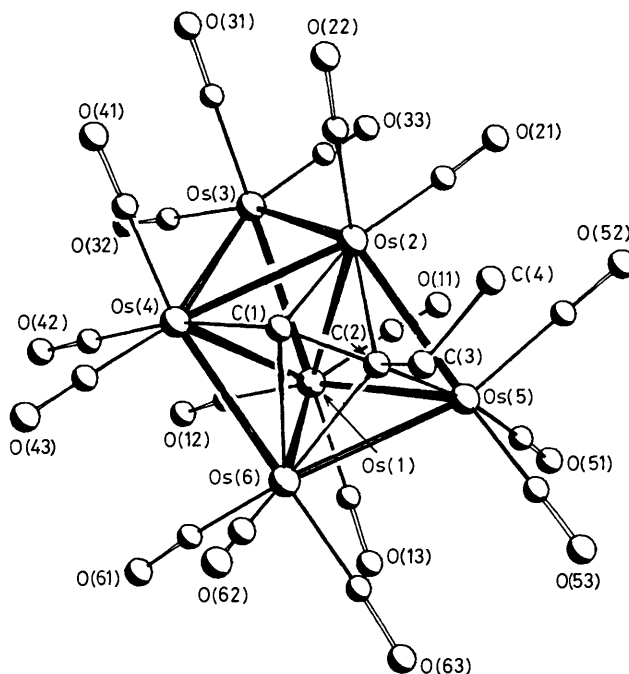


Figure 2. The molecular structure of $[\text{Os}_6(\text{CO})_{17}(\mu_4\text{-}\eta^2\text{-HCCEt})]$ (**4**). Bond lengths: Os(1)–Os(2), 2.861(1); Os(1)–Os(3), 2.881(1); Os(1)–Os(4), 2.849(1); Os(1)–Os(5), 2.906(1); Os(1)–Os(6), 2.865(1); Os(2)–Os(3), 2.635(1); Os(2)–Os(4), 2.837(1); Os(2)–Os(5), 2.822(1); Os(3)–Os(4), 2.911(1); Os(4)–Os(6), 2.859(1); Os(5)–Os(6), 2.929(1); Os(2)–C(1), 2.23(1); Os(4)–C(1), 2.16(2); Os(6)–C(1), 2.34(2); Os(2)–C(2), 2.43(1); Os(5)–C(2), 2.15(2); Os(6)–C(2), 2.32(2); C(1)–C(2), 1.45(2); C(2)–C(3), 1.53(3); C(3)–C(4), 1.44(3) Å. Bond angles: Os(2)–C(1)–Os(4), 80.4(5); Os(2)–C(1)–Os(6), 106.0(7); Os(4)–C(1)–Os(6), 78.8(6); Os(2)–C(1)–C(2), 79.5(9); Os(4)–C(1)–C(2), 137(4); Os(6)–C(1)–C(2), 71.4(9); Os(2)–C(2)–Os(5), 75.8(5); Os(2)–C(2)–Os(6), 100.4(6); Os(5)–C(2)–Os(6), 81.7(6); Os(2)–C(2)–C(1), 64.7(7); Os(5)–C(2)–C(1), 127(1); Os(6)–C(2)–C(1), 72.5(9); C(1)–C(2)–C(3), 114(1)°.

electron donation from an electron-rich centre, Os(6) (19 electrons), to an electron-poor one, Os(5) (17 electrons). The cluster as a whole is an 88 electron system, consistent with the presence of ten Os–Os bonds, with the 'CCET' fragment donating five electrons and the hydride donating one electron.

The molecular structure†§ of the second isomeric product $[\text{Os}_6(\text{CO})_{17}(\text{HCCEt})]$ (**4**) is shown in Figure 2 together with some important bond parameters. The metal framework may be described as a capped, square-based pyramid, a geometry which has been observed previously in a number of hexosmium clusters.^{3,12} The four metal atoms in the square base, Os(2)Os(4)Os(5)Os(6), show slight deviations from planarity (maximum 0.16 Å). The alkyne ligand caps this square with the C(1)–C(2) bond lying approximately parallel to the Os(4)–Os(5) vector. The alkyne co-ordinates *via* σ -bonds to Os(4) and Os(5) and *via* π -bonds to Os(2) and Os(6). This mode of alkyne co-ordination has been observed in the mixed-metal clusters $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R}')] (R = R' = \text{Et, Ph; R = Ph, R}' = \text{CO}_2\text{R})$,¹³ and is similar in some respects to the bonding of the HCCEt ligand to the Os₄ butterfly framework in $[\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-HCCEt})]$.¹⁴ Although not located directly, a hydrogen is bonded to C(1).

The capped, square-based pyramidal metal framework geometry observed in (**4**) is normally associated with an 86 electron system. This is two electrons fewer than were assigned to the isomeric complex (**3**). The metal framework geometry in (**3**) may be derived from that of (**4**) by formally breaking a metal–metal bond. The cleavage of either the Os(2)–Os(5) or the Os(4)–Os(6) bond in (**4**) would give the same metal framework as in (**3**), but to obtain the same orientation of the alkyne would require a more complex migratory sequence. As in (**3**) the carbonyl distribution over the metal centres in (**4**) is asymmetric with two carbonyls bonded to Os(2) and three to each of the other five Os atoms.

Table 1. Spectroscopic data for the hexanuclear cluster alkynes.

Compound	m/z^a	i.r. ν_{CO} cm^{-1} (CH_2Cl_2 solvent)
(1)	1668	2104(vw), 2069(s, br.), 2056(s), 2040(w), 2025(m), 1998(w)
(2)	1668	2104(vw), 2071(s, sh.), 2055(vw) 2035(m), 2008(w), 1925(vw)
(3)	1682	2104(vw), 2070(vs, br), 2057(s), 2040(w), 2025(m), 1998(w)
(4)	1682	2104(vw), 2070(s, sh), 2050(w), 2036(m), 2007(w), 1925(vw)
(5)	1730	2105(vw), 2071(s, sh), 2059(s), 2041(w), 2026(m), 1999(w)
(6)	1730	2106(vw), 2073(s, br), 2038(m), 2010(w), 1999(w), 1925(vw)
(7)	1654	2098(vw), 2068(vs), 2057(s), 2023(vs), 2003(w)
(8)	1778	2099(vw), 2070(vs), 2054(s) 2037(w), 2025(vs), 1985(vw)
(9)	1668	2100(w), 2068(vs), 2055(vs), 2030(s), 2023(s), 2002(w)

^a Based on ¹⁹²Os.

§ *Crystal data:* (**4**), $\text{C}_{21}\text{H}_6\text{O}_{17}\text{Os}_6$, $M = 1671.46$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.525(2)$, $b = 17.311(3)$, $c = 16.310(4)$ Å, $\beta = 95.81(2)^\circ$, $U = 2956.4$ Å³, $D_c = 3.75$ g cm⁻³, $Z = 4$, $F(000) = 2896$, $\mu(\text{Mo-K}\alpha) = 257.61$ cm⁻¹. Data recorded on a Stoe 4-circle diffractometer using graphite-monochromated Mo-K α radiation, 2θ range, 5–50°. 4304 unique observed [$F > 5\sigma(F)$] absorption corrected reflections, $R = 0.049$, $R_w = 0.049$.

In this case, however, there are no short Os \cdots C contacts under 3 Å which suggests that incipient carbonyl bridge bonding is absent.

In contrast to the reactions with terminal alkynes, the disubstituted alkynes $\text{RC}\equiv\text{CR}'$ ($R = \text{Me}$ or Ph ; $R' = \text{Me}$, Ph , or Et) react with $[\text{Os}_6(\text{CO})_{17}(\text{NCMe})]$ in toluene at 60–70 °C over a 3–4 h period, to give a green-brown complex in good yield (60%); $[\text{Os}_6(\text{CO})_{18}]$ (20%) was also isolated. The molecular ion of the major product was consistent with its formulation as $[\text{Os}_6(\text{CO})_{16}(\text{RCCR})]$ [$R = \text{Me}$ (**7**), Ph (**8**)] and the mass spectrum showed the stepwise loss of 16 carbonyl groups (Table 1). The i.r. spectrum indicated the presence of terminal carbonyls and no resonances in the metal hydride region were observed in the ¹H n.m.r. spectrum. Suitable crystals of an asymmetrically disubstituted analogue $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta\text{-MeCCEt})]$ (**9**)‡¶ were obtained and an X-ray analysis was carried out to determine the molecular structure.

The geometry of (**9**) is illustrated in Figure 3, which also includes some important bond parameters. The six Os atoms define a bicapped tetrahedron, a metal geometry observed previously in $[\text{Os}_6(\text{CO})_{18}]$ ¹⁵ and a number of its derivatives.¹⁶

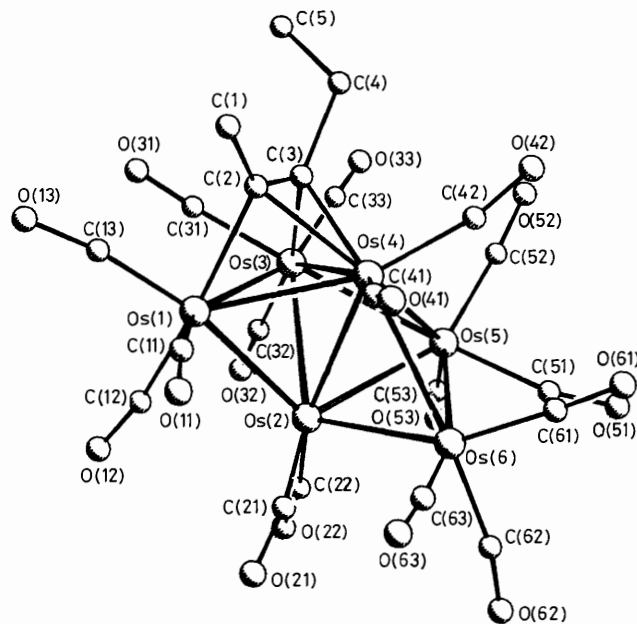


Figure 3. The molecular structure of $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta\text{-MeCCEt})]$ (**9**). Bond lengths: Os(1)–Os(2), 2.657(3); Os(1)–Os(3), 2.817(2); Os(1)–Os(4), 2.780(2); Os(2)–Os(3), 2.833(3); Os(2)–Os(4), 2.764(2); Os(2)–Os(5), 2.745(3); Os(2)–Os(6), 2.637(3); Os(3)–Os(4), 2.769(2); Os(3)–Os(5), 2.878(3); Os(4)–Os(5), 2.778(3); Os(4)–Os(6), 2.893(3); Os(5)–Os(6), 2.799(3); C(1)–C(2), 1.42(6); Os(1)–C(2), 2.25(4); Os(4)–C(2), 2.25(4); C(2)–C(3), 1.35(6); Os(3)–C(3), 2.16(4); Os(4)–C(3), 2.09(5); C(3)–C(4), 1.64(7); C(4)–C(5), 1.50(8) Å. Bond angles: Os(1)–C(2)–Os(4), 76(1); Os(1)–C(2)–C(1), 125(3); Os(4)–C(2)–C(1), 134(3); Os(1)–C(2)–C(3), 99(3); Os(4)–C(2)–C(3), 65(3); C(1)–C(2)–C(3), 133(4); Os(3)–C(3)–Os(4), 81(3); Os(3)–C(3)–C(2), 120(3); Os(4)–C(3)–C(2), 79(6); Os(3)–C(3)–C(4), 123(3); Os(4)–C(3)–C(4), 125(3); C(2)–C(3)–C(4), 115(4)°.

¶ *Crystal data:* (**9**), $\text{C}_{21}\text{H}_8\text{O}_{16}\text{Os}_6$, $M = 1657.47$, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, No. 14), $a = 9.947(2)$, $b = 19.511(2)$, $c = 15.313(3)$ Å, $\beta = 94.95(2)^\circ$, $U = 2960.8$ Å³, $Z = 4$, $D_c = 3.72$ g cm⁻³, $F(000) = 2872$, $\mu(\text{Mo-K}\alpha) = 257.19$ cm⁻¹. Data recorded on a Stoe 4-circle diffractometer using graphite-monochromated Mo-K α radiation, 2θ range 5–45°. 2998 unique observed [$F > 5\sigma(F)$] absorption corrected reflections, current $R = 0.088$, $R_w = 0.087$.

The alkyne ligand caps the Os(1)Os(3)Os(4) triangular face, forming σ -bonds to Os(1) and Os(3) and a π -bond to Os(4) in a bonding mode similar to that observed for a range of trinuclear clusters,² and related to that described for (3). As in [Os₆(CO)₁₈]¹⁵ the electron count for each Os atom shows that they exhibit different 'formal' oxidation states. In (9) Os(2) and Os(6) are formally associated with 17 electrons each, Os(1), Os(4), and Os(5) 18 electrons, and Os(3) 19 electrons. This electronic imbalance is partially compensated for by the presence of incipient bridging carbonyls; there are four Os...C contacts less than 3 Å [Os(2)...C(12), 2.73(5); Os(6)...C(21), 2.78(5); Os(1)...C(31), 2.84(5); Os(6)...C(51), 2.74(6) Å]. The Os–Os bond lengths in the bicapped tetrahedral frameworks also differ between [Os₆(CO)₁₈]¹⁵ and (9), with the Os(1)–Os(2) and Os(2)–Os(6) bonds in (9) being as much as ca. 0.2 Å shorter than the equivalent bonds in [Os₆(CO)₁₈].¹⁵

Overall, the cluster (9) is an 84 electron system, consistent with the existence of 12 metal–metal bonds. If one bond in the closed bicapped tetrahedral framework of (9) is broken the more open capped square-pyramidal geometry of (4) is obtained, in keeping with going from an 84 to an 86 electron system. It is therefore possible to consider the sequence where the formal addition of an electron pair to the metal framework of (9) results in the framework geometry of (4) and the addition of a second electron pair produces the framework geometry of (3). In this context, it is noteworthy that when (8) is heated to 130 °C in n-octane for 20 h the known complex [Os₆(CO)₁₆(μ_4 -CPh)(μ_3 -CPh)]¹⁷ is obtained. This molecule is an 86 electron system with a capped square-pyramidal Os framework. Under the reaction conditions the acetylenic C–C bond has ruptured, and the two resultant CPh groups each donate three electrons to the cluster, making a total of six from the organic fragment. Carbon–carbon bond rupture in an alkyne-cluster complex has been observed previously in [HOs₃W(CO)₁₀(μ_3 - η^2 -C₂R₂)(η^5 -C₅H₅)]¹⁸.

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