Electron Rich Acetylide Clusters; Molecular and Electronic Structure and Reactions of Os₃(CO)₇(μ₂-η²-C≡CR)₂(μ-PPh₂)₂ (R = Ph, Prⁱ); 50-electron Species with Expanded Metal Frameworks

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The reactivity of the 50-electron acetylide clusters $Os_3(CO)_7(\mu_2-\eta^2-C\equiv CR)_2(\mu-PPh_2)_2$ [(**1a**) R = Ph; (**1b**) R = Prⁱ] which have unusual expanded Os_3 frameworks, is dominated by nucleophilic addition at the metals: the molecular structures of $Os_3(CO)_7(\mu_2-\eta^2-C\equiv CPr^i)_2(\mu-PPh_2)_2$ and the ethylamine adduct of (**1a**), $Os_3(CO)_6(\mu_2-\eta^2-C\equiv CPh)(\eta^1-C\equiv CPh)(\mu-PPh_2)_2(EtNH_2)_2$ (**2a**) have been determined by X-ray diffraction and their electronic structures probed by EHMO calculations.

The chemistry and physical properties of terminal[1] and polynuclear[2] acetylides and polyacetylides are now undergoing extensive investigation for several substantive reasons: (i) –C≡CR, –C≡C–, and –(C≡C)ₙ–R groups are unmatched among hydrocarbyls in their co-ordinating versatility and their ability to link metal centres in chains or clusters; (ii) with σ-donor/π-acceptor capabilities,[3] and a high degree of unsaturation, acetylides permit extended delocalisation through metal centres, attractive features for new materials with unusual electrical or non-linear optical properties;[4] (iii) co-ordinated acetylides can be converted to an extensive array of other hydrocarbyls making them useful synthons in organometallic chemistry. In documenting the structural features, electronic properties, and chemical behaviour of multiply bound acetylides we[5] and others[6] have shown that edge (μ₂-η²-) and face (μ₃-η²-) bridging –C≡C–R groups in electron precise 34- or 48-electron polymetallics are excep-

tionally electrophilic. Theoretical studies suggest that nucleophilic attack at carbon in Ru_3 acetylide systems may be charge controlled.[7] We have synthesised a new series of electron rich clusters $Os_3(CO)_7(\mu_2-\eta^2-C\equiv CR)_2(\mu-PPh_2)_2$ [(**1a**) R = Ph, (**1b**) R = Prⁱ] with unusual expanded Os_3 cores. The clusters (**1**) undergo nucleophilic attack uniquely at the metal centres, with conversion of μ₂-η²- to terminal η¹-acetylides and/or CO displacement leading to molecules with highly elongated metal–metal bonds. Such facile μ₂-η²- to η¹-displacements and unique patterns of cluster expansion have not been previously documented, to our knowledge, for trinuclear clusters.

The new cluster (**1a**) (R = Ph) was prepared from the disubstituted osmium carbonyl $Os_3(CO)_{10}(Ph_2PC\equiv CPh)_2$ upon heating in decalin for 3 h at 125 °C followed by chromatography on Florisil. Yellow–orange crystals were obtained (68%). Pyrolysis of $Os_3(CO)_{10}(Ph_2PC\equiv CPr^i)_2$ simi-
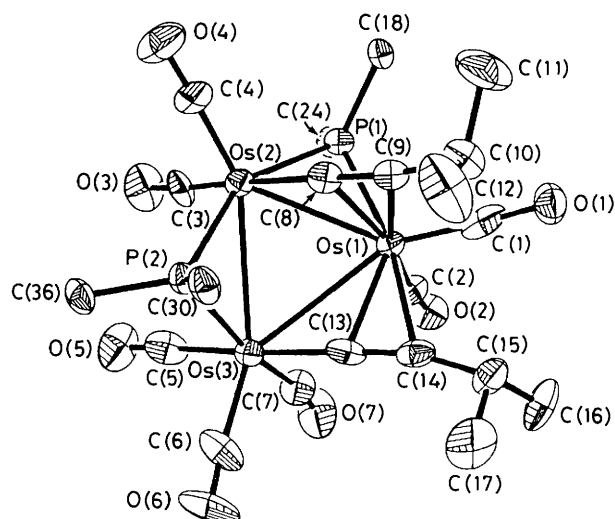
Figure 1. A perspective view of the molecular structure of Os$_3$(CO)$_7$(μ_2-η^2-C≡CPr^i)$_2$(μ-PPh$_2$)$_2$ (**1b**) showing the atomic numbering. Important bond lengths (Å) and angles (°) are: Os(1)–Os(2) 2.972(1), Os(1)–P(1) 2.338(6), Os(2)–Os(3) 3.101(1), Os(2)–P(2) 2.347(6), Os(2)–P(1) 2.356(6), Os(2)–C(8) 2.064(21), Os(3)–P(2) 2.389(7), C(8)–C(9) 1.227(32), Os(3)–C(13) 2.018(28), Os(1)–C(8) 2.343(24), C(13)–C(14) 1.253(38), Os(1)–C(13) 2.290(21), Os(1)–C(9) 2.519(22), Os(1)–C(14) 2.407(24); Os(2)–C(8)–C(9) 165.7(10), C(8)–C(9)–C(10) 167.4(14), Os(3)–C(13)–C(14) 173.4(11), C(13)–C(14)–C(15) 162.2(16).

larly gave (**1b**) (25%).† An X-ray analysis of (**1b**)‡ revealed the structure shown in Figure 1. The molecule consists of a triangle of osmium atoms with one edge [Os(1)–Os(2)] bridged by both μ-PPh$_2$ and μ$_2$-η^2-C≡CPr^i groups and the remaining edges bridged by either diphenylphosphido [Os(2)–
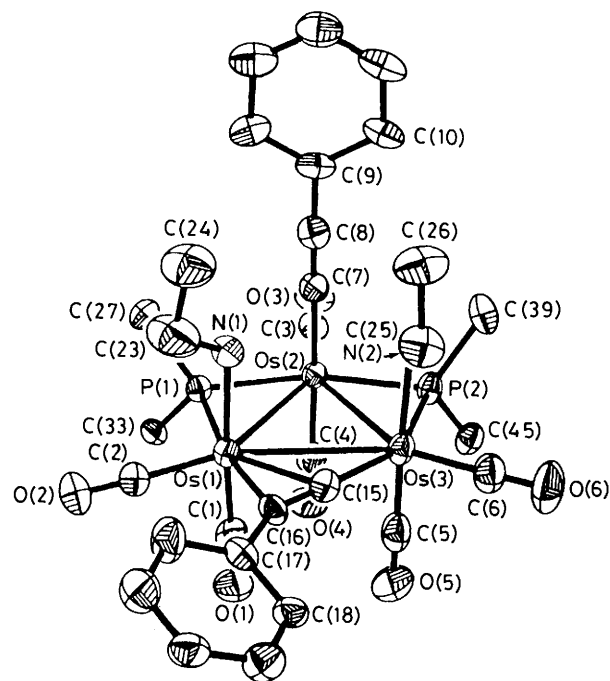
Figure 2. An ORTEP plot of the structure of Os$_3$(CO)$_6$(μ-η^2-C≡CPh)(η^1-C≡CPh)(μ-PPh$_2$)$_2$(NH$_2$Et)$_2$ (**2a**). Pertinent bond lengths (Å) and angles (°) are: Os(1)–Os(2) 3.2456(6), Os(1)–P(1) 2.340(3), Os(2)–P(1) 2.335(3), Os(2)–P(2) 2.352(3), Os(3)–P(2) 2.354(3), Os(1)–N(1) 2.204(10), Os(3)–N(2) 2.221(11), Os(3)–C(15) 2.060(13), Os(2)–C(7) 2.075(12), Os(1)–C(15) 2.286(12), Os(1)–C(16) 2.362(12), Os(3)–C(15)–C(16) 175.5(6), Os(2)–C(7)–C(8) 178.3(6), C(7)–C(8)–C(9) 178.5(8), C(15)–C(16)–C(17) 153.3(8).

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† *Selected spectroscopic data*: IR (C$_6$H$_{12}$) ν(CO), (**1a**) 2080s, 2020vs, 2000wsh, 1995m, 1954s; (**1b**) 2076s, 2016vs, 2009ssh, 1994s, 1949s; (**2a**) 2042vs, 2005s, 1983w, 1953m, 1941s, 1929vs cm^{-1}; ^{31}P{^{1}H} NMR (CDCl$_3$), (**1a**) δ (85% H$_3$PO$_4$) 48.7 p.p.m. (d, $^2J_{P–P}$ 125.8 Hz, μ-PPh$_2$), 47.6 p.p.m. (d, μ-PPh$_2$); (**1b**) 46.3 p.p.m. (d, $^2J_{P–P}$ 146.8 Hz, μ-PPh$_2$), 45.6 p.p.m. (d, μ-PPh$_2$); (**2a**) ^{1}H NMR (CDCl$_3$) δ 8.44—5.91 (m, Ph–H), 2.31 (q, $^3J_{H–H}$ 7.0 Hz, CH$_2$), 1.57 (br. s, N–H), 0.21 (t, $^3J_{H–H}$ 7.0 Hz, Me); ^{31}P{^{1}H} (CDCl$_3$) δ (85% H$_3$PO$_4$), 44.3 p.p.m. (s, μ-PPh$_2$, 300 k), 48.7 p.p.m. (d, $^2J_{P–P}$ 110.9 Hz, μ-PPh$_2$, 213 K), 39.5 p.p.m. (d, $^2J_{P–P}$ 110.9 Hz, μ-PPh$_2$).

‡ *Crystal data* for (**1b**)_Os$_3$P$_2$O$_7$C$_{41}$H$_{34}$: yellow crystals, M = 1271.3, triclinic, space group $P\bar{1}$, a = 10.783(1), b = 10.990(2), c = 18.955(4) Å, α = 90.91(1), β = 102.02(1), γ = 108.41(1)°, U = 2076.5(6) Å^3, Z = 2, D_c = 2.033 g cm^{-3}, F(000) = 1188, μ(Mo-$K_α$) = 98.62 cm^{-1}. The structure solution (heavy atom methods) was based on 3604 observed [$I \geq 3\sigma(I)$] diffractometer (Syntex $P2_1$) data and refined to R and R_w values of 0.051 and 0.060 by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. For (**2a**) Os$_3$P$_2$O$_6$N$_2$C$_{50}$H$_{44}$, 0.66 CHCl$_3$: M = 1481.1, monoclinic, space group $P2_1/n$, a = 12.762(2), b = 22.849(3), c = 18.377(2) Å; β = 93.35(1)°, U = 5350(1), Z = 4, D_c = 1.839 g cm^{-3}, F(000) = 2650.67, μ(Mo-$K_α$) = 77.66 cm^{-1}. Data were collected on a Syntex $P2_1$ diffractometer using graphite monochromated Mo-$K_α$ radiation. Of 6591 measured reflections 4505 with $I \geq 3\sigma(I)$ were used in the structure solution (heavy atom methods) and refinement (full-matrix least-squares). With all non-hydrogen atoms anisotropic R and R_w values were 0.035 and 0.040. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Os(3)] or acetylide [Os(1)–Os(3)] ligands. One osmium atom [Os(1)] is co-ordinated to both η^2-acetylides. The most remarkable structural features are the elongated Os–Os bonds. In comparison to the Os–Os bond length in Os$_3$(CO)$_{12}$ [2.877(3) Å][8] all three of the Os–Os distances are long with the Os(1)–Os(3) value [3.247(1) Å] being particularly notable. In other 50-electron clusters such as Os$_3$(CO)$_9$(μ$_3$-η^2-C≡CPr^i)(μ-PPh$_2$)[9] and Os$_3$(CO)$_9$(μ$_3$-η^2-C≡CPh)(μ$_2$-η^2-C≡CPh),[10] the pattern of Os–O sdistances (two short, one long) indicates that only two direct metal–metal bonds are present. In (**1b**) the effect of the additional electron pair above the 48-electron closed shell configuration is manifest not in bond cleavage but in an overall expansion of the metal core.

With two edge bound acetylides (**1a,b**) might be expected to react readily at carbon with a nucleophile. However, treatment of (**1a**) with phosphines PR$^1_2$R^2 (R^1 = R^2 = Et; R^1 = Ph, R^2 = C$_2$Ph, C$_2$Pr^i, C$_2$Bu^t) at 25 °C afforded only Os$_3$(CO)$_6$(μ$_2$-η^2-C≡CPh)$_2$(μ-PPh$_2$)$_2$(PR$^1_2$R^2). Reaction with EtNH$_2$, a reagent which readily adds to μ$_2$-η^2-acetylides in 34-electron binuclear systems, afforded quantitative yields of a new cluster (**2a**) of stoicheiometry Os$_3$(CO)$_6$(C≡CPh)$_2$(μ-PPh$_2$)$_2$(NEtH$_2$)$_2$† whose structure was established by X-ray diffraction‡ (Figure 2). The reaction of (**1a**) with ethylamine has resulted in the addition of two amine ligands to Os(1) and Os(3) of the cluster with the loss of one CO group and the displacement of one η^2-bound acetylide from Os(1). The two amine ligands and the σ-bound acetylide on Os(2) are axially co-ordinated on one face of the metal triangle *trans* to three CO groups. The two μ-PPh$_2$ bridges and the remaining μ$_2$-η^2-acetylide on the Os(1)–Os(3) edge occupy equatorial

sites. The Os–Os distances in (2a) are even larger than in (1b), ranging from 3.1581(7) [Os(2)–Os(3)] to 3.2974(7) Å [Os(1)–Os(3)]. We are unaware of any other triangular Os$_3$ cluster in which all three Os–Os distances are so elongated. Although both (1) and (2) are 50-electron systems, it appears that the addition of two hard, non-π-acceptor EtNH$_2$ ligands results in cluster expansion rather than hydrocarbyl elaboration and the displacement of a CO and π-bound acetylide has led to a significant increase in electron density at the Os$_3$ core of (1), with a consequent expansion of the framework. Dynamic interchange of σ- and η-bound acetylide sites along the Os(1)–Os(3) edge renders the two μ-PPh$_2$ groups equivalent at 300 K in the ^{31}P NMR solution spectra, such that a plane of symmetry bisects the Os(1)–Os(3) bond and passes through Os(2) and the σ-bound acetylide [C(7)–C(8)]. The molecule is thus remarkable in that it possesses not only a terminal σ-bound acetylide with additional donor capabilities, a rarity in cluster chemistry, but also a dynamic σ-η-C≡CR group capable of creating a vacant reaction site. Such features are highly desirable in catalytic systems.

Extended Hückel molecular orbital (EHMO) calculations have been carried out on Os$_3$(CO)$_7$(μ$_2$-η^2-C≡CH)$_2$(μ-PH$_2$)$_2$ as a model for (1) based on the crystal structure co-ordinates for (1b). The HOMO of (1) is a 3-centre metal–metal bonding MO made up mainly of Os d orbitals with some p orbital contribution mixed in, such that lobes of the same phase point inwardly towards the centre of the Os$_3$ triangle. There is a striking resemblance between the frontier orbitals of 50-electron Os$_3$(CO)$_7$(μ$_2$-η^2-C≡CH)$_2$(μ-PPh$_2$)$_2$ and 44-electron [Pt$_3$(CO)$_3$(μ$_2$-PH$_2$)$_3$]$^+$ (ref. 11) and indeed these clusters can be shown to be isolobal. For (1) as for the Pt$_3$ system there are frontier MOs which are phosphido bridge-metal bonding but Os–Os antibonding and occupation of these MOs effects core expansion. The LUMO of (1) consists mainly of a d$_z{}^2$ and p$_z$ hybrid on Os(3) and a d–p hybrid on Os(1) with a node between, there being little contribution to the LUMO from the acetylide carbons. Reactions with nucleophiles would therefore be predicted to occur not at carbon but at Os(3) and Os(1), as observed experimentally.

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