Syntheses of Linked Ruthenium and Osmium Carbonyl Clusters containing a Bridging Oxalato Ligand: X-ray Structures of $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(C_2O_4)]$ and $[\{Ru_5(\mu\text{-}H)C(CO)_{14}\}_2(C_2O_4)]$

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The reaction of oxalic acid ($H_2C_2O_4$) with 2 equivalents of $[Os_3(CO)_{10}(MeCN)_2]$ in CH_2Cl_2 yields yellow crystals of $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(C_2O_4)]$ **1** in good yield, while treatment of $[Ru_5C(CO)_{15}]$ with 2 equivalents of oxalic acid affords $[\{Ru_5(\mu\text{-}H)C(CO)_{14}\}_2(C_2O_4)]$ **2** in low yield; the structures of **1** and **2** have been established by X-ray crystallography.

The chemistry of mononuclear transition metal oxalato complexes has been extensively studied.[1–4] In these compounds the oxalato ion exhibits a range of different coordination modes ranging from unidentate to quadridentate.[5] It also functions as a bridging group linking two or more metal atoms to form polynuclear species.[6] This latter observation prompted us to investigate the possibility of linking some ruthenium and osmium carbonyl clusters by oxalate ion as a method of generating high nuclearity species. Herein we report the syntheses and full characterization of decaruthenium and hexaosmium clusters containing a bridging quadridentate oxalate group.

The reaction of oxalic acid with 2 equivalents of $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing CH_2Cl_2 for 2 h gives the yellow air-stable cluster $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(C_2O_4)]$ **1** in 60% yield after chromatography on silica. Single crystals of **1** suitable for X-ray analysis were grown from slow evaporation of a CH_2Cl_2 solution. This analysis revealed that the compound **1** contains two $HOs_3(CO)_{10}$ moieties bridged by an oxalato ligand. The molecular structure is shown in Fig. 1, together with some important bond parameters.† The molecule possesses approximate C_{2h} symmetry. The midpoint of the C–C bond of the bridging oxalato ligand coincides with the crystallographic centre of symmetry and only half of the molecule is in the asymmetric unit. Each molecule contains two triangular triosmium cores arranged in parallel fashion with a plane-to-plane separation of 6.79 Å.

Similar structural arrangement has been found in the group IB (11) metal bridging triosmium clusters $[\{HOs_3(CO)_{10}\}_2M]^-$, M = Ag,[7] Au.[8] The quadridentate oxalato group is essentially planar (maximum deviation 0.02 Å) and occupies two axial positions of each triosmium cluster. This type of coordination of a carboxylato group to a triosmium structural unit has been previously observed in $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}O_2CH)]$,[9] $[Os_3(\mu\text{-}H)(CO)_{10}{\cdot}O_2C{\cdot}Os_6(CO)_{17}]^-$,[10] and $[Os_3(\mu\text{-}H)(CO)_{10}{\cdot}O_2C{\cdot}Os_6(CO)_{20}]^-$.[11] The distribution and orientations of the carbonyl ligands are virtually identical to those in $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}O_2CH)]$.[9] The spectroscopic data‡ are totally consistent with this formulation and structure.

The corresponding reaction of $[Ru_5C(CO)_{15}]$ with 2 equivalents of oxalic acid in refluxing CH_2Cl_2 for *ca.* 20 h affords two yellow products in low yields after TLC on silica with CH_2Cl_2–n-hexane (3 : 2) as eluent. The first yellow product is found to be $[\{Ru_5(\mu\text{-}H)C(CO)_{14}\}_2(C_2O_4)]$ **2** in 15% yield, on the basis of spectroscopic data‡ and single crystal X-ray analysis†. The molecular structure of **2** is shown in Fig. 2. In this crystal structure, the asymmetric unit contains two independent, but structurally similar, $[Ru_5C(CO)_{14}]$ moieties bridged by a quadridentate oxalato group. The molecule exhibits an approximate C_2 symmetry with the 2-fold axis along the C–C bond of the oxalato ligand. The five ruthenium atoms in the two Ru_5 units form a distorted bridged butterfly arrangement where the bridging Ru atom is chelated by two oxygen atoms of the oxalato group. Each ruthenium atom is attached to three terminal carbonyls, except for Ru(1) and Ru(6) which are ligated by two terminal CO groups. The average Ru–Ru bond lengths are 2.86(1) Å (hinge) and 2.85(1) Å (hinge to wing-tip). The Ru(1)–Ru(2) and Ru(6)–Ru(8) distances [2.919(1), 2.945(1) Å] are slightly longer than the rest. All bond parameters are within the range normally observed for other Ru_5 carbido clusters with a bridged-butterfly metal core.[12,13]

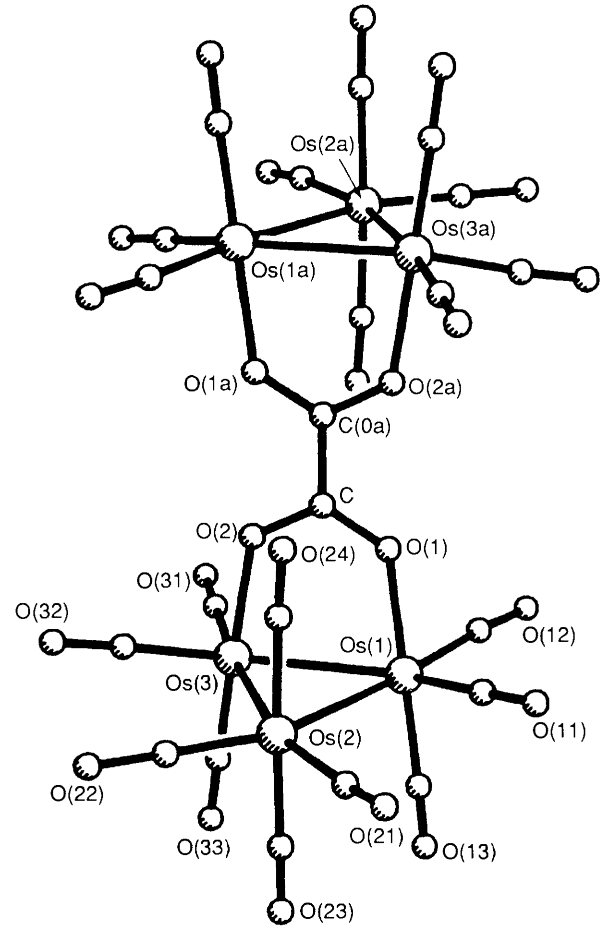

Fig. 1 The molecular structure of $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(C_2O_4)]$ **1**. Principal bond distances (Å): Os(1)–Os(2), 2.871(2); Os(1)–Os(3), 2.918(2); Os(2)–Os(3), 2.879(2); Os(1)–O(1), 2.15(1); Os(3)–O(2), 2.15(1); C–O(1), 1.27(2); C–O(2), 1.25(2); C–C(a), 1.49(3). Principal bond angles (°): Os(2)–Os(1)–Os(3), 59.6(1); Os(1)–Os(2)–Os(3), 61.0(1); Os(1)–Os(3)–Os(2), 59.4(1); O(1)–C–O(2), 126(1); O(1)–C–C(a), 118(2); O(2)–C–C(a), 116(2).

There has been a change in geometry of the parent $[Ru_5C(CO)_{15}]$ cluster from 74 electron, square-based pyramid, to 76 electron, bridged-butterfly, in **2** by the oxidative addition of oxalic acid. Similar structural change is also observed in the mercury-linked cluster $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$[14] in which the linking involved the 'hinge' Ru–Ru bond. The ^1H NMR spectrum of **2** shows a singlet at δ −22.5 which has been assigned to the metal hydride atoms in an indentical environment from both $[Ru_5(\mu\text{-}H)C(CO)_{14}]$ structural units. That the hydride atoms are bridging the 'hinge' edge of the bridged-butterfly is indicated by potential energy calculations.[15] The second yellow product from this reaction has not been fully characterised. It is of interest to note that in these two linked clusters **1** and **2** the oxalato bridge adopts a different linking mode but in both cases involves the formation of a five-membered ring.

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† *Crystal data* for **1**: $C_{22}H_2O_{24}Os_6$, M = 1791.4, triclinic, space group $P\bar{1}$ (No. 2), a = 8.410(3), b = 8.473(4), c = 14.196(6) Å, α = 72.38(1), β = 76.29(1), γ = 66.50(1)°, U = 876.3(6) Å^3, Z = 1, D_c = 3.395 g cm^{-3}, F(000) = 782, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 217.88 cm^{-1}, 1784 observed diffractometer data [$F > 3\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Os and atoms of oxalato group anisotropic) to R = 0.039, R_w = 0.042.

Crystal data for **2**: $C_{32}H_2O_{32}Ru_{10}$, M = 1909.04, monoclinic, space group $P2_1/c$, a = 16.931(2), b = 15.345(2), c = 19.140(3) Å, β = 97.35(2)°, U = 4932 Å^3, Z = 4, D_c = 2.570 g cm^{-3}, F(000) = 3560, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 29.81 cm^{-1}, 5180 observed diffractometer data [$F > 4\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by blocked full-matrix least-squares analysis (Ru and atoms of oxalato group anisotropic) to R = 0.040, R_w = 0.040. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *Spectroscopic data* for **1**: IR [ν(CO) cm^{-1}, CH_2Cl_2]: 2113w, 2078vs, 2067s, 2026vs, 2013s, 1985m; [$\nu(CO_2)$ cm^{-1}, KBr]: 1626vs, 1342s; ^1H NMR 250 MHz, CD_2Cl_2): δ −10.41 (s OsH); *m/z* 1791, with the expected Os_6 isotopic envelope pattern.

Spectroscopic data for **2**: IR [ν(CO) cm^{-1}, CH_2Cl_2]: 2105w, 2076s, 2068s, 2058m, 2043m, 2029m, 2006w, 1984w; [$\nu(CO_2)$ cm^{-1}, KBr]: 1615vs, 1262s; ^1H NMR (250 MHz, CD_2Cl_2): δ −22.5 (s, RuH); *m/z* 1880 (corresponds to $\{M-CO\}$).

Satisfactory elemental analyses were obtained for both complexes.

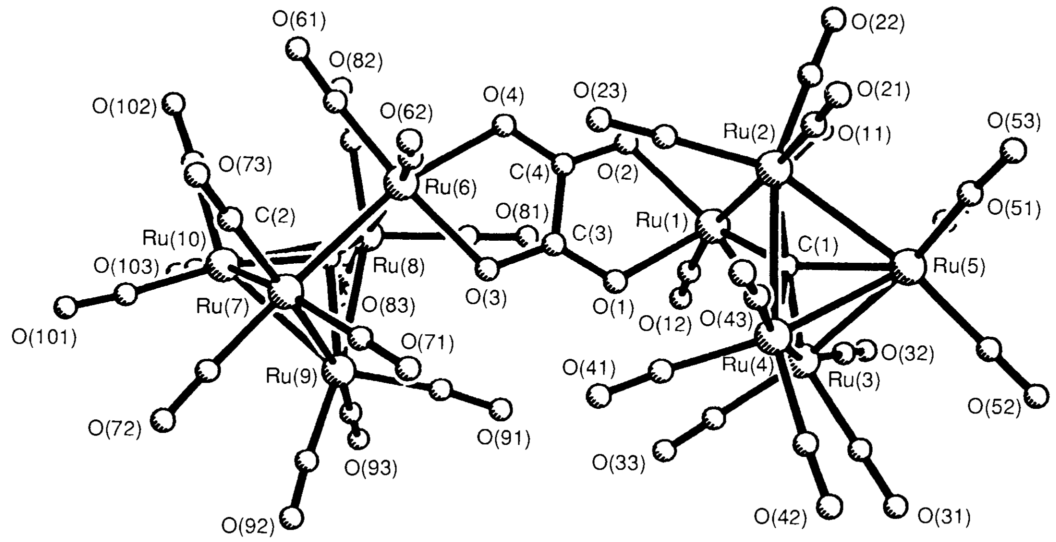

Fig. 2 The molecular structure of [{$Ru_5(\mu\text{-}H)C(CO)_{14}$}$_2(C_2O_4)$] **2**. Principal bond distances (Å): Ru(1)–Ru(2), 2.919(1); Ru(1)–Ru(3), 2.882(1); Ru(2)–Ru(4), 2.858(1); Ru(2)–Ru(5), 2.855(1); Ru(3)–Ru(4), 2.862(1); Ru(3)–Ru(5), 2.849(1); Ru(4)–Ru(5), 2.845(1); Ru(6)–Ru(7), 2.864(1); Ru(6)–Ru(8), 2.945(1); Ru(7)–Ru(9), 2.851(1); Ru(7)–Ru(10), 2.871(1); Ru(8)–Ru(9), 2.837(1); Ru(8)–Ru(10), 2.833(1); Ru(9)–Ru(10), 2.870(1); Ru(1)–O(1), 2.136(6); Ru(1)–O(2), 2.156(5); Ru(6)–O(3), 2.141(5); Ru(6)–O(4), 2.169(6); C(3)–C(4), 1.52(1); C(3)–O(1), 1.267(9); C(3)–O(3), 1.259(9); C(4)–O(2), 1.25(1); C(4)–O(4), 1.27(1).

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