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Preliminary communication

Reactions of carbonyl clusters with potentially tridentate thioethers: crystal and molecular structures of $[Os_4(CO)_{13}([12]aneS_3)]$ and $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)([12]aneS_3)]$ $[([12]aneS_3) = \{(CH_2)_3S\}_3]$

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Abstract

The reaction of $[Os_3(CO)_{12}]$ with $[12]aneS_3$ ($[12]aneS_3 = \{(CH_2)_3S\}_3$) in octane for 6 h, under reflux, led to isolation of two products $[Os_3(CO)_{11}([12]aneS_3)]$ (**1**) and $[Os_4(CO)_{13}([12]aneS_3)]$ (**2**), while with $[Ru_3(CO)_{12}]$ under similar conditions, in THF, a number of products were obtained, including $[Ru_4(CO)_{11}([12]aneS_3)]$ (**3**), $[Ru_5(CO)_{13}([12]aneS_3)]$ (**4**), and $[Ru_6(CO)_{16}([12]aneS_3)]$ (**5**). An X-ray diffraction study of **2** shows that the macrocycle is coordinated to the 'wingtips' of an Os_4 butterfly through the two electron pairs on one sulphur atom, while in **5** all three sulphur atoms of the macrocycle coordinate to two of the Ru atoms in a spiked edge-bridged tetrahedral metal framework.

It is well established that transition metal cluster complexes tend to undergo degradative fragmentation reactions when subjected to the forcing reaction conditions common to catalytic processes [1]. One method that has been employed to help retain the integrity of the cluster has been to "clamp" the metal atoms together by means of bridging or capping ligands which contain main group "bridgehead" atoms, such as nitrogen, phosphorus or sulphur [2]. The bulk of this work has been concentrated on the use of fairly simple bridging ligands such as PR_2, PR, SR, S, AsR_2, AsR, *etc.*, and there have been relatively few studies where polydentate ligands have been "tailored" to coordinate to triangular or rectangular faces of a cluster. However, there have been a number of reports of triangular and tetrahedral metal clusters being "clamped" by tripod phosphorus donor ligands [3] or by small sulphur containing macrocycles [4]. We recently reported the use of a novel tris-isocyanide ligand as a "clamp" for a triosmium cluster [5], and this has prompted us to investigate other polydentate ligand systems which might have

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appropriate "bites" to coordinate to faces of metal clusters. Studies on thioether macrocycles [6] have indicated that these could prove to be useful ligands in the design of "ligand stabilised" clusters since the "soft" sulphur donor atoms are appropriate for coordination to second and third row transition metals, and macrocycles with a range of ring sizes are readily available and this would facilitate changes in the ligand "bite". We, therefore, undertook some preliminary experiments to establish whether thioether ethers would indeed coordinate to clusters and what bonding modes they would adopt. If these ligands do coordinate over cluster faces we plan to carry out an extensive study comparing the reactivity and stability of these clusters with those of the parent carbonyls. We now report the preliminary results of our studies of the reaction of ([12]aneS$_3$) [([12]aneS$_3$) = {(CH$_2$)$_3$S}$_3$] with [Os$_3$(CO)$_{12}$] and [Ru$_3$(CO)$_{12}$].

The reaction of [Os$_3$(CO)$_{12}$] with ([12]aneS$_3$) in octane, under reflux, for 6 h, afforded two products after purification by TLC using a 2 : 1 ratio of hexane : CH$_2$Cl$_2$ as eluent. The first yellow band was characterised as [Os$_3$(CO)$_{11}$([12]aneS$_3$)] (**1**) from spectroscopic and mass spectral data *. In this complex it is assumed that the thioether coordinates to one site on the metal triangle through a single sulphur atom. The two sharp signals in the ratio 2:1 in the room temperature ^{1}H NMR spectrum is consistent with a fluxional process which either involves pyramidal inversion of the coordinated sulphur or a reversal in conformation of the coordinated ligand as has been observed for a number of mononuclear complexes with coordinated thioether macrocycles [7]. The second band was red-brown, and was formulated as [Os$_4$(CO)$_{13}$([12]aneS$_3$)] (**2**) from spectroscopic and mass spectra data. This assignment was confirmed by a single crystal X-ray study **.

The molecular structure of [Os$_4$(CO)$_{13}$([12]aneS$_3$)] (**2**) is shown in Fig. 1 which includes some important bond parameters. The four Os atoms adopt a "butterfly"

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* Spectroscopic data for **1**: IR ν(CO) (CH$_2$Cl$_2$): 2109m, 2055s, 2034s, 2019vs, 1988m cm^{-1}. FAB MS: M^+ (obs.) m/z 1106 (calc.) 1106. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.86 (q, 6H), 2.67 (t, 12H). **2**: IR ν(CO) (CH$_2$Cl$_2$): 2086m, 2048vs, 2035s, 2022m, 1986m, br. FAB MS: M^+ (obs.) m/z 1354 (calc.) 1354. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.87 (q, 2H), 2.23 (2, 4H), 2.71 (t, 4H), 2.91 (t, 4H), 3.68 (q, 4H). **3**: IR ν(CO) (CH$_2$Cl$_2$): 2071s, 2044vs, 2007vs, 1991vs, 1969m, 1942 cm^{-1}. FAB MS: M^+ (obs.): 934 (calc.) 934. ^{1}H NMR (CD$_2$Cl$_2$) δ 1.80–3.20 (m, br, 18H). **4**: IR ν(CO) (CH$_2$Cl$_2$): 2074m, 2041vs, 2028sh, 2002s, 1975w. FAB MS: M^+ (obs) 1091 (calc.) 1091. ^{1}H NMR (CD$_2$Cl$_2$) δ 1.80–3.30 (m,br, 18H). **5**: IR ν(CO) (acetone): 2061s, 2037vs, 2016s, 2005s, 1994m, 1970m. IR (KBr disc): 2068s, 2042vs, 2000s, 1985s, 1626s, 1559m, 1422m, 1385w. FAB MS: M^+ (obs.) 1276 (calc.) 1276. ^{1}H NMR (acetone) δ 1.80–3.20 (m, br, 18H).

** Crystal data for **2**: C$_{22}$H$_{18}$O$_{13}$Os$_4$S$_3$, $M = 1347.34$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), $a = 12.132(2)$, $b = 17.729(2)$, $c = 14.590(1)$ Å, $\beta = 93.66(2)°$, $U = 3131.7$ Å^3, $Z = 4$, $D_c = 2.857$ g cm^{-3}, $F(000) = 2424$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 166.1 cm^{-1}, 3374 observed diffractometer data [$F > 5\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by blocked full-matrix least-squares analysis (Os, S, O, anisotropic) to $R = 0.086$, $R_w = 0.084$. Crystal structure for **5**: C$_{25}$H$_{18}$O$_{16}$S$_3$Ru$_6$, $M = 1277.0$, monoclinic, space group $P2/c$ (No. 13), $a = 19.340(21)$, $b = 8.697(5)$, $c = 21.314(22)$ Å, $\beta = 107.76(8)°$, $U = 3414(5)$ Å^3, $Z = 4$, $D_c = 2.484$ g cm^{-3}, $F(000) = 2432$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 27.87 cm^{-1}, 1873 observed diffractometer data [$F > 4\sigma(F)$]. Structure solved by direct methods and subsequent Fourier difference techniques, refined by full-matrix least-squares analysis (Ru, S and O) anisotropic to $R = 0.076$, $R_w = 0.075$. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre.

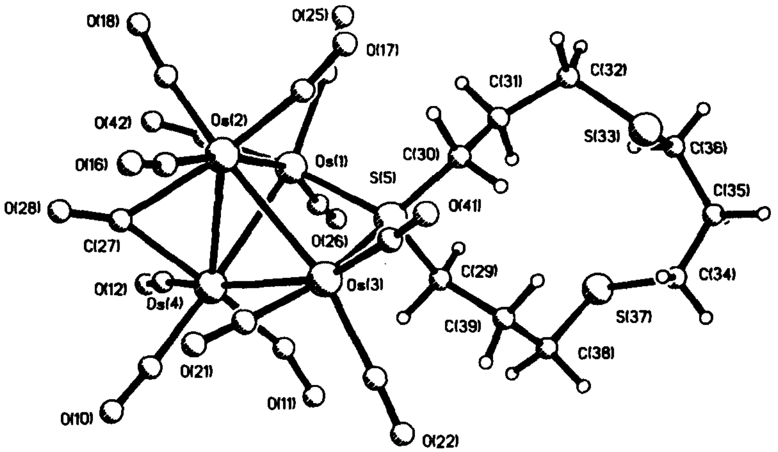

Fig. 1. The molecular structure of $[Os_4(CO)_{13}([12]aneS_3)]$ (2) showing the atom numbering scheme. Bond lengths: Os(1)–Os(2), 2.833(2); Os(1)–Os(4), 2.857(2); Os(2)–Os(3), 2.854(2); Os(2)–Os(4), 2.815(2); Os(3)–Os(4), 2.857(2); Os(1)–S(5), 2.396(8); Os(3)–S(5), 2.431(8); Os(2)–C(27), 2.28(4); Os(4)–C(27), 2.13(4); S(5)–C(29), 1.83(3); S(5)–C(30), 1.78(3) Å. Bond angles: Os(3)–S(5)–Os(1), 99.4(3); C(29)–S(5)–Os(1), 112.2(12); C(29)–S(2)–Os(3), 115.2(12); C(3)–S(5)–Os(1), 116.9(11); C(3)–S(5)–Os(3), 109.3(10); C(3)–S(5)–C(29), 104.3(15); Os(4)–C(27)–Os(2), 79.2(12)°.

geometry with a dihedral angle of 95.9° between the Os(1)–Os(2)–Os(4) and Os(2)–Os(3)–Os(4) "wings". Each Os atom is coordinated to three terminal carbonyls and the thirteenth carbonyl bridges the Os(2)–Os(4) "hinge" edge. One sulphur, S(5), of the thioether ring caps the two "wingtip" Os atoms, presumably bonding through its two lone-pairs and thus donating four electrons to the cluster framework; this would give the formal electron count of 62 to the cluster which is characteristic of the "butterfly" geometry. The conformation of the thioether ring does not deviate greatly from the favoured "square" conformation as defined by Dale [8], which is observed in the free ligand [6].

The structure of the cluster core is similar to that observed for $[Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2)]$ [9] and the related ruthenium cluster $[Ru_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2)]$ [10]. In the latter complex the dihedral angle between the two wings of the "butterfly" is 96°, while the two Ru–S distances (2.359(3) and 2.367(3) Å) are slightly shorter and show less asymmetry than those found in **2**.

The reaction $[Ru_3(CO)_{12}]$ with ([12]aneS_3) in tetrahydrofuran, under reflux, for 12 h, afforded four products after purification by column chromatography through silica using a 3 : 1 ratio of hexane : CH_2Cl_2 as eluent. The first two orange and red bands were characterised spectroscopically * as $[Ru_4(CO)_{11}([12]aneS_3)]$ (**3**) and $[Ru_5(CO)_{13}([12]aneS_3)]$ (**4**), respectively. If it is assumed that, in each case, thioether acts as a six electron donor, coordinating to a cluster *via* all three sulphur atoms as observed $[Rh_4(CO)_9(SCH_2SCH_2SCH_2)]$ [4], then the clusters **3** and **4** could have *closo*-tetrahedral and trigonal bipyramidal metal geometries. A third, low yield, brown band has not been characterised, but is thought to be a breakdown product which involves ligand fragmentation. The fourth black/brown band was the major product of the reaction, and was characterised spectroscopically * and crystallographically ** as $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)([12]aneS_3)]$ (**5**). The observation of the signals in the range 1600–1300 cm^{-1} in the IR spectrum indicated the presence of

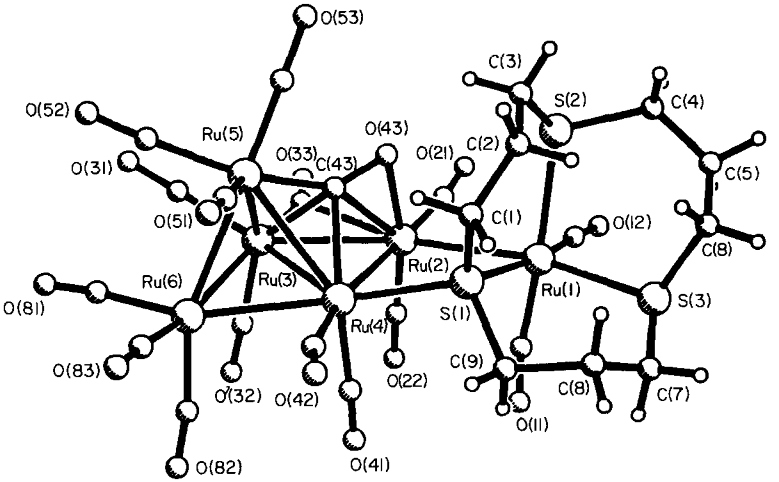

Fig. 2. The molecular structure of $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-CO})([12]aneS_3)]$ (**5**) showing the atom numbering scheme. Bond lengths: Ru(1)–Ru(2), 2.838(6); Ru(2)–Ru(3), 2.790(5); Ru(2)–Ru(4), 2.891(5); Ru(3)–Ru(4), 2.769(6); Ru(3)–Ru(5), 2.811(7); Ru(3)–Ru(6), 2.787(5); Ru(4)–Ru(5), 2.839(6); Ru(4)–Ru(6), 2.749(5); Ru(5)–Ru(6), 2.786(6); Ru(1)–S(1), 2.376(11); Ru(1)–S(2), 2.466(13); Ru(1)–S(3), 2.414(11); Ru(4)–S(1), 2.395(11), Ru(2)–C(43), 2.34(5); Ru(4)–C(43), 2.16(4); Ru(5)–C(43), 2.01(4); Ru(2)–O(43), 2.07(3); S(1)–C(1), 1.83(5); S(1)–C(9), 1.86(4); C(3)–S(2), 1.82(5); S(2)–C(4), 1.83(5); C(6)–S(3), 1.80(5); S(3)–C(7), 1.80(5) Å. Bond angles: Ru(1)–S(1)–Ru(4), 114.4(5); Ru(1)–S(1)–C(1), 119.3(12); Ru(4)–S(1)–C(1), 106.2(12); Ru(1)–S(1)–C(9), 107.8(12); Ru(4)–S(1)–C(9), 108.9(12); C(1)–S(1)–C(9), 98.7(19); Ru(1)–S(2)–C(3), 115.5(16); Ru(1)–S(2)–C(4), 110.6(17); C(3)–S(2)–C(4), 101.0(24); Ru(1)–S(3)–C(6), 111.7(4); Ru(1)–S(3)–C(7), 113.3(14); C(6)–S(3)–C(7), 102.1(22)°.

a carbonyl ligand in an uncommon bonding mode, and in order to establish the molecular geometry a full X-ray structure determination was undertaken.

The molecular structure of $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-CO})([12]aneS_3)]$ (**5**) is shown in Fig. 2 which includes some important bond parameters. The metal framework consists of an edge-bridged tetrahedron with the sixth metal atom, Ru(1), coordinated to the edge-bridging metal, Ru(2), and acting as a spike. This sixth metal atom has a *pseudo*-octahedral geometry, with one site occupied by the Ru–Ru bond, two by carbonyl ligands, and three sites by the three sulphur atoms of the thioether which adopt a *fac*-arrangement. One of these sulphur atoms, S(1), is also linked to the basal ruthenium atom, Ru(4), of the edge-bridged tetrahedron. The thioether conformation is similar to that found in the mononuclear ruthenium dication $[Ru([12]aneS_3)_2]^{2+}$ [11]. Of the other ruthenium atoms, Ru(3) and Ru(4) are each coordinated to two terminal carbonyls, and Ru(5) and Ru(6) are each coordinated to three carbonyls. The fifteenth carbonyl bridges the Ru(2)–Ru(3) edge, and the sixteenth carbonyl, C(43)–O(43), adopts the novel μ_4-η^2-bonding mode, bonding to Ru(3), Ru(4) and Ru(5) *via* C(43) and to Ru(2) through the C(43)–O(43) π-bond. This carbonyl bonding mode has been observed previously in hexaruthenium clusters $[Ru_6(\eta^2\text{-}\mu_4\text{-CO})_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$ and $[Ru_6H(\eta^2\text{-}\mu_4\text{-CO})(CO)_{13}(\eta^7\text{-}\mu_2\text{-}C_6H_3Me_2CH_2)]$ [12].

With the thioether acting as an eight electron donor, and the η^2-μ_4-CO acting as a four electron donor, the formal electron count for the cluster **5** is 90 electrons, which by the Effective Atomic Number Rule is consistent with the presence of the observed nine Ru–Ru bonds in the structure.

These experiments indicate that it is possible to coordinate twelve-membered thioether macrocyclic rings to cluster carbonyls, and both the macrocyclic ring and the cluster core show considerable flexibility in configuration in order to facilitate this coordination. However, from the structural studies, it is apparent that the ([12]aneS_3) ligand does not have an appropriate "bite" to coordinate over a cluster face and stabilise the metal-metal bonding. Further investigations are in progress using thioethers with different ring sizes in order to "tailor" the ligand bite and macrocyclic configuration.

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