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FULL PAPER

Synthesis, structural characterization and reactivities of hexaosmium carbonyl clusters with six-membered cyclic thioether and thioxane ligands

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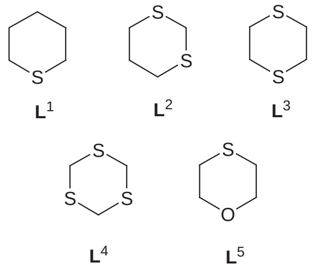
Cluster complexes $[Os_6(CO)_{15}\{S(CH_2)_4CH_2\}\{\mu\text{-}S(CH_2)_4CH_2\}]$ **1** and $[Os_5(CO)_{15}\{S(CH_2)_4CH_2\}]$ **2** were isolated from the reaction of $[Os_6(CO)_{16}(MeCN)_2]$ with $S(CH_2)_4CH_2$ (L^1) in 24 and 22% yields respectively. Cluster degradation from **1** to **2** can be achieved by addition of a stoichiometric quantity of L^1 in $CHCl_3$ under reflux. Monosubstituted cluster complex $[Os_6(CO)_{16}\{\mu\text{-}S(CH_2)_3SCH_2\}]$ **3** containing a $S(CH_2)_3SCH_2$ (L^2) ligand bridging across an Os–Os edge *via* one of the sulfur atoms was isolated in good yield from a similar reaction. However, similar reaction between $[Os_6(CO)_{16}(MeCN)_2]$ and $S(CH_2)_2SCH_2CH_2$ (L^3) gave $[Os_6(CO)_{16}\{S(CH_2)_2SCH_2CH_2\}_2]$ **4** as the major product instead. The two thio ligands are found to co-ordinate in terminal fashion to two different vertices of the Os_6 core. Interaction of tridentate sulfur donor ligand $SCH_2SCH_2SCH_2$ (L^4) with $[Os_6(CO)_{16}(MeCN)_2]$ afforded $[Os_6(CO)_{14}(\mu\text{-}CO)(SCH_2SCH_2SCH_2)]$ **5** in which the ligand L^4 was found to cap over a triangular face of the Os_6 skeleton. Treatment of mixed-donor ligand $S(CH_2)_2OCH_2CH_2$ (L^5) yielded a pair of isomeric complexes $[Os_6(CO)_{15}\{S(CH_2)_2OCH_2CH_2\}\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}]$ **6** and $[Os_6(CO)_{15}\{O(CH_2)_2SCH_2CH_2\}\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}]$ **7**. Carboxylation of **6** gave $[Os_6(CO)_{16}\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}]$ **8** and $[Os_6(CO)_{18}]$. Hydrogenation of **6** led to the formation of dihydrido cluster $[Os_6(CO)_{15}(\mu\text{-}H)_2\{S(CH_2)_2OCH_2CH_2\}\{\mu\text{-}S(CH_2)_2OCH_2CH_2\}]$ **9**. The metal skeleton of **9** can be described as two fused tetrahedra sharing a common edge. All new compounds were fully characterized by spectroscopic and analytical techniques. In addition the structures of **1**, **2**, **3**, **4**, **5**, **6**, **8** and **9** were established by X-ray crystallography.

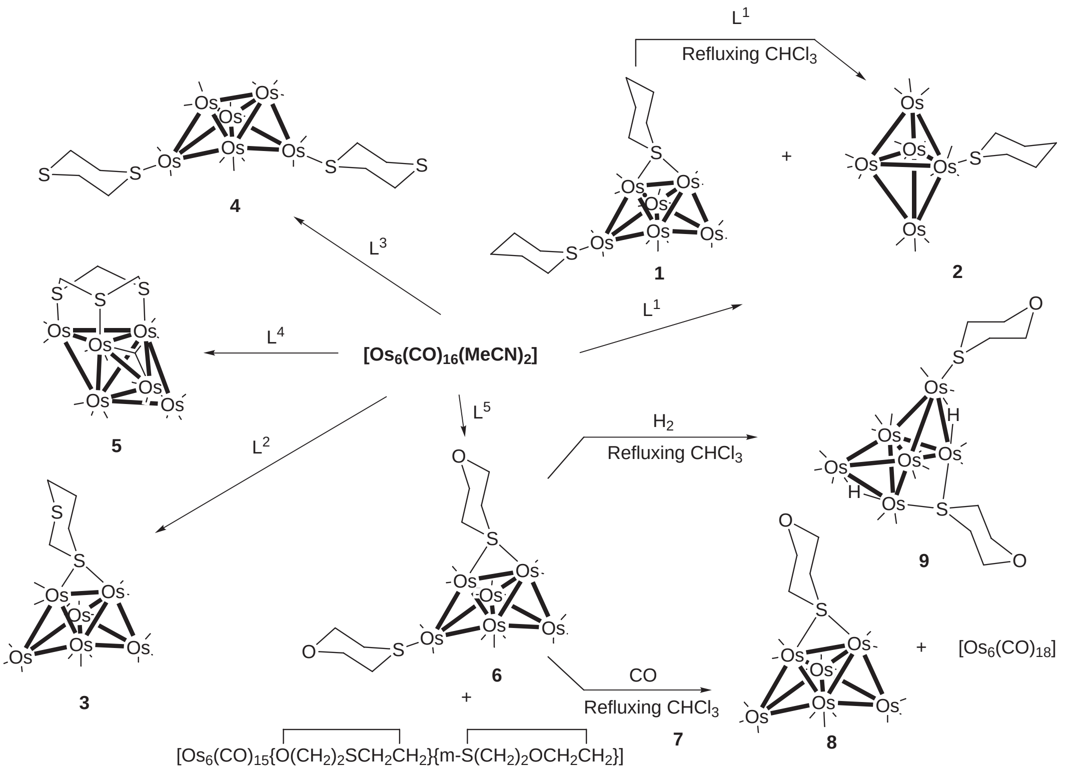
Introduction

Following the industrial applications of hydrodesulfurization in fossil fuel purification,[1] much interest has been shown in cluster compounds bearing sulfur heteroatoms. A new class of cluster derivatives containing sulfido ligands has been extensively studied and reported in tri-,[2] tetra-,[3] and penta-[4] osmium systems by Adams and co-workers over the past decades. These have been widely used in the systematic build-up of high nuclearity clusters[5] as exemplified by the thermally activated coupling of $[Os_4(CO)_{13}(\mu_3\text{-}S)_2]$ and $[Os_3(CO)_{10}(MeCN)_2]$ to yield the heptanuclear cluster compound $[Os_7(CO)_{20}(\mu_4\text{-}S)_2]$.[6] The ring-opening oligomerization of thiirane[7] and thietane[8] have been shown to be catalysed by $[Os_6(CO)_{16}(MeCN)_2]$ and $[Os_4(CO)_{11}(SCH_2CH_2CH_2)(\mu\text{-}H)_4]$ respectively. Recently we have also reported some triosmium alkylidyne clusters containing cyclic thioether ligands that undergo facile isomerization.[9] However, further explorations on these cyclic sulfur donor ligands in larger cluster systems are relatively rare. Herein we report the syntheses, spectroscopic studies and reactivities of a series of cyclic sulfur-containing hexaosmium carbonyl clusters.

Results and discussion



The reaction (Scheme 1) of preformed labile cluster $[Os_6(CO)_{16}(MeCN)_2]$ with L^1 yielded the hexanuclear $[Os_6(CO)_{15}\{S(CH_2)_4CH_2\}\{\mu\text{-}S(CH_2)_4CH_2\}]$ **1** and pentanuclear $[Os_5(CO)_{15}\{S(CH_2)_4CH_2\}]$ **2** species together with small amount of the known cluster $[Os_3(CO)_{12}]$.[10] Facile replacement of the labile MeCN ligand to yield mono- and di-substituted cluster derivatives has previously been reported in the triosmium system.[11,12] Cluster **1** consists of an identical metal-core architecture to that in the parent cluster $[Os_6(CO)_{18}]$. A perspective drawing of cluster **1** with the atomic numbering scheme is shown in Fig. 1. Selected bond parameters are presented in Table 1. The metal–metal bond distances are comparable to the corresponding values in $[Os_6(CO)_{18}]$.[13] However, the Os(1)–Os(4) vector [2.931 Å] is significantly longer than Os(1)–Os(3) [2.823 Å], leading to a ‘distorted’ bicapped tetrahedron. The observed bond elongation may be attributed to steric influence between the bulky L^1 and equatorial CO on Os(4). The Os(2)–Os(5) bond distance is the shortest M–M bond length [2.679 Å] which might be due to the ‘clamping’ effect of the bridging ligand. Two ligands L^1 are co-ordinated to the Os_6 core in a terminal and a bridging mode respectively. According to the eighteen electron rule, the vertices Os(1) and Os(6) are electron deficient and hence susceptible to nucleophilic attack.[14,15] Similar edge bridging of heteroatoms across a central tetra-



Scheme 1

Table 1 Selected bond distances (Å) and angles (°) for cluster **1**

Os(1)–Os(2)	2.740(1)	Os(4)–Os(5)	2.795(1)
Os(1)–Os(3)	2.823(1)	Os(4)–Os(6)	2.848(1)
Os(1)–Os(4)	2.931(1)	Os(5)–Os(6)	2.714(1)
Os(2)–Os(3)	2.859(1)	Os(1)–S(1)	2.368(5)
Os(2)–Os(4)	2.753(1)	Os(2)–S(2)	2.269(4)
Os(2)–Os(5)	2.679(1)	Os(5)–S(2)	2.276(5)
Os(3)–Os(4)	2.766(1)		
Os(3)–Os(5)	2.845(1)	Os(2)–S(2)–Os(5)	72.2(1)
Os(3)–Os(6)	2.838(1)	Os(5)–Os(2)–S(2)	54.0(1)
		S(2)–Os(5)–Os(2)	53.8(1)

Table 2 Selected bond distances (Å) and angles (°) for cluster **2**

Os(1)–Os(2)	2.893(1)	Os(3)–Os(5)	2.773(1)
Os(1)–Os(3)	2.765(1)	Os(4)–Os(5)	2.813(1)
Os(1)–Os(4)	2.776(1)	Os(2)–S(1)	2.430(4)
Os(2)–Os(3)	2.832(1)	Os(4) · · · C(4)	2.49(1)
Os(2)–Os(4)	2.828(1)		
Os(2)–Os(5)	2.833(1)	Os(2)–C(4)–O(4)	158(1)
Os(3)–Os(4)	2.790(1)		

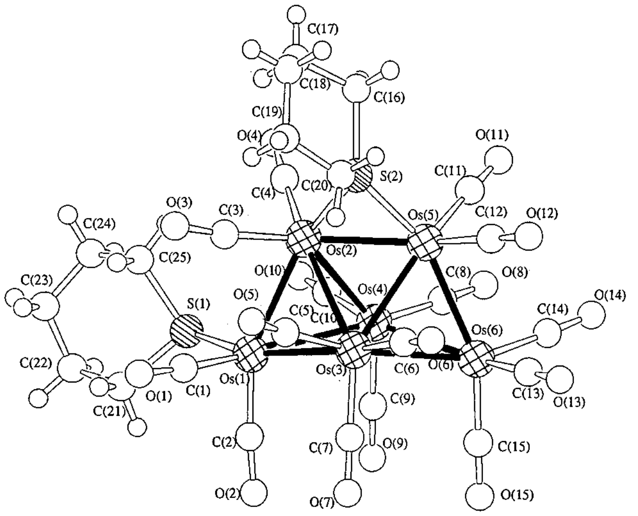


Fig. 1 Molecular structure of cluster **1** showing the atom-labelling scheme for non-hydrogen atoms.

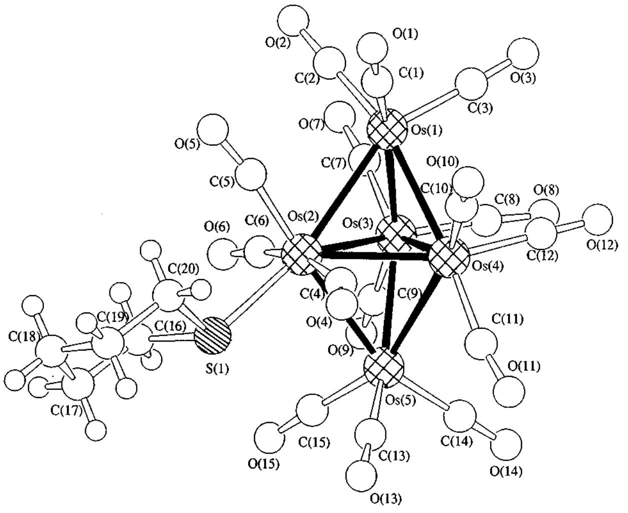


Fig. 2 Molecular structure of cluster **2**.

hedron is also observed in $[Os_6(CO)_{16}(\mu\text{-}H)(\mu\text{-}C_8H_{11})]$.[16] However, the Os(2)–S(2) and Os(5)–S(2) distances [2.269(4) and 2.276(5) Å, respectively] are considerably shorter than those found in other thietane and thiolate bridging analogues $[Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})]$[17] and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\overline{SCH_2CMe_2}CH_2Cl)]$,[18] respectively. Both ligands are in the stable chair conformation.

Cluster **2** was found to be a pentanuclear osmium compound having a trigonal bipyramidal metal core arrangement with fifteen terminally bonded carbonyl ligands (Fig. 2). Selected bond parameters are in Table. 2. The Os(2) atom, which has four terminally bonded ligands, is considerably electron-rich and all Os–Os vectors involving Os(2) are significantly longer than other metal–metal bonds in the structure. This phenomenon is

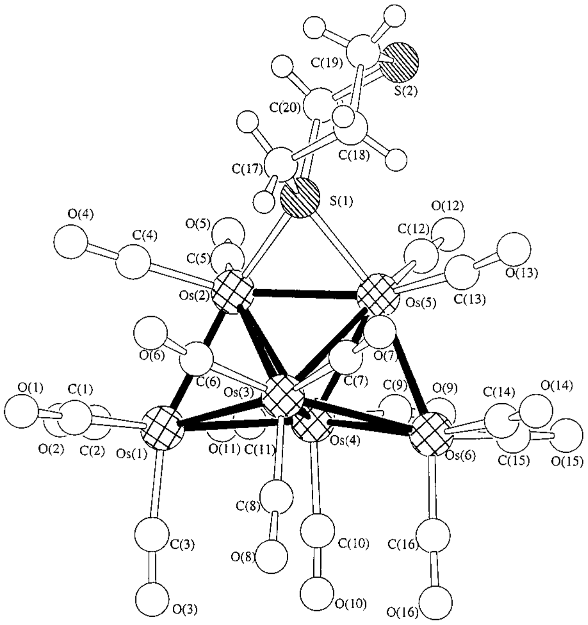


Fig. 3 Molecular structure of cluster **3**.

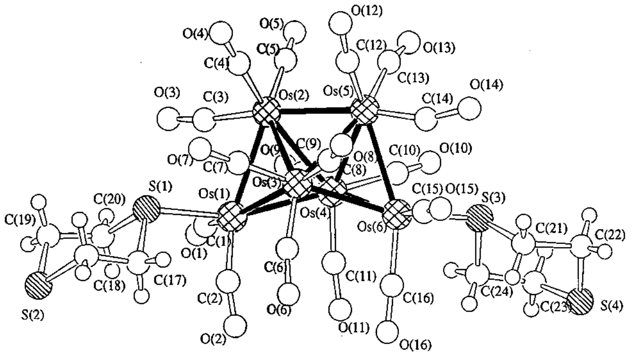


Fig. 4 Molecular structure of cluster **4**.

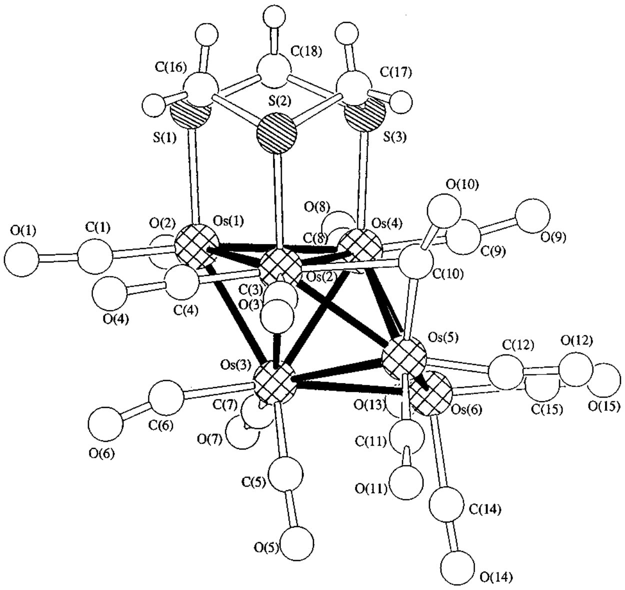


Fig. 5 Molecular structure of cluster **5**.

generally in line with those observed in other $Os_5(CO)_{15}(L)$ [L = CO,[19] PMe_3[20] or $P(OMe)_3$[21]] analogues. Besides, this kind of electronic imbalance within a metal core leads to the formation of 'semibridging' carbonyl ligands. Cotton[22] has suggested that this type of interaction could alleviate the polar nature of donor–acceptor metal–metal bonds. Cluster **2** also manifests this effect in C(4)–O(4) [Os(2)–C(4)–O(4) 158°; Os(4)···C(4) 2.49 Å]. On the electronic grounds, as in the rationalization of site preference in cluster **1**, nucleophilic attack would be expected on the apical atoms which are relatively electron deficient. However, the solid state structure of compound **2** revealed the co-ordination of L^1 in the equatorial plane of the metal core. This observation can be attributed to the better σ-donating ability of L^1, together with three carbonyl ligands, stabilizing the dative metal–metal bonds originated from electron rich Os(2).[23]

Using an excess of ligand in the reaction leads to higher yields of compounds **1** and **2** and also the disappearance of the known cluster $[Os_3(CO)_{12}]$. However, a number of additional products in relatively low yields are also observed and are proposed to be multi-substituted hexaosmium species based on the spectroscopic and elemental analyses. Treatment of **1** with a stoichiometric quantity of L^1 in refluxing $CHCl_3$ leads to the formation of **2**. Therefore, we believe **1** is likely to be an intermediate for the formation of **2**. Unfortunately, we are not able to isolate and characterize the mononuclear osmium fragment formed in this conversion.

Under similar reaction conditions, both 1,3-dithiane (L^2) and 1,4-dithiane (L^3) reacted with $[Os_6(CO)_{16}(MeCN)_2]$. However, the major products isolated from these reactions are rather different from that with L^1. Clusters **3** and **4** were isolated in moderate yields. Positive FAB MS of **3** revealed an intense molecular envelope centre at *m*/*z* 1709 (Table 3), which along with the ^1H NMR spectroscopy suggested that it consists of a monosubstituted ligand in a Os_6 core. Its molecular structure was ascertained by a single crystal X-ray analysis. A perspective drawing of it with atomic numbering scheme is shown in Fig. 3 and important bond parameters are summarized in Table 4. Its metal core arrangement is similar to that of **1**, comprising six osmium atoms in a bicapped tetrahedral mode. The Os–Os bond lengths in the structure span a range [2.713 to 2.867 Å] which is commonly observed for Os–Os single bonds except for the one bridged by the thio ligand [Os(2)–Os(5) 2.662 Å].

The ^1H NMR spectra can be interpreted with reference to the solid state structure of compound **4**. The spectrum of **4** exhibits four groups of well defined multiplets in close proximity due to two individual ligands in the same magnetic environment. The molecular structure of cluster **4** established by X-ray analysis is depicted in Fig. 4 and some important bond parameters are given in Table 5. The Os_6 metal skeleton contains a more symmetrical ligand deposition with a non-crystallographic twofold axis passing through the midpoints of Os(3)–Os(4) and Os(2)–Os(5). Two ligands are terminally bonded to the two vertices of the polyhedron. Both S(2) and S(4) are unco-ordinated and might be able to act as donor groups for further cluster buildup. However, cluster **4** does not react with labile clusters such as $[Os_6(CO)_{16}(MeCN)_2]$ and $[Os_3(CO)_{10}(MeCN)_2]$[24] to give linked clusters. Attempts to generate a pentanuclear species as in compound **1** using an excess of ligand at elevated reaction temperature only led to cluster decomposition. It is also noteworthy that no C–S bond cleavages were observed under forcing thermolytic conditions which contrasts to those findings in triosmium analogues.[25]

Treatment of ligand L^4 with an equivalent of $[Os_6(CO)_{16}(MeCN)_2]$ gave a moderate yield of cluster **5** as the major product isolated upon TLC purification. The molecular structure of **5** is shown in Fig. 5 and selected bond lengths and angles are summarized in Table 6. The tridentate ligand asymmetrically caps the triangular face defined by Os(1)–Os(2)–Os(4) forming a cage and slightly tilted towards Os(1)–Os(2) edge as is evident from the non-orthogonal bond angles S(1)–Os(1)–Os(4), S(2)–Os(2)–Os(4) and S(3)–Os(4)–C(9). Facial cappings by this type of ligand have also been observed in $[Ru_3(CO)_9(\overline{SCH_2SCH_2SCH_2})]$,[26] $[Rh_4(CO)_9(\overline{SCH_2SCH_2SCH_2})]$[27] and $[Ir_4(CO)_9(\overline{SCH_2SCH_2SCH_2})]$.[28] The

Table 3 Spectroscopic data for clusters **1** to **9**

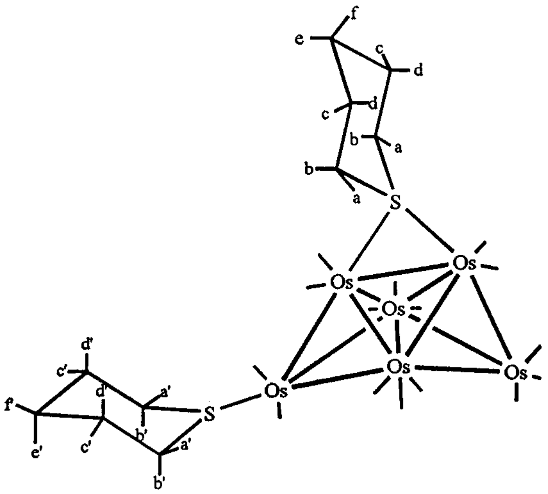
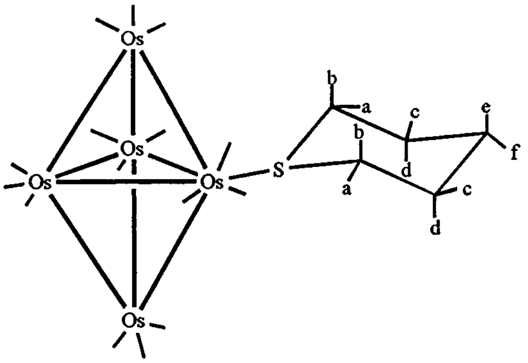
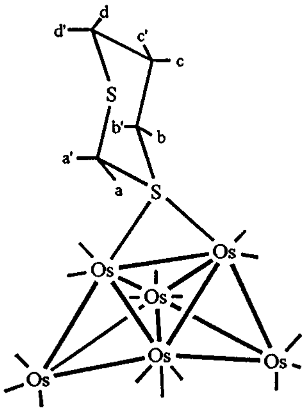
Complex	IR, $\tilde{\nu}$(CO)[a]/cm^{-1}	^{1}H NMR, δ(*J*/Hz)[b]	Mass, *m*/*z*[c]
 **1**	2073s, 2018s, 2005s, 1983m	3.07–3.12 (m, 4 H, H_a, H_b) 2.76–2.83 (m, 4 H, $H_{a'}$ or $H_{b'}$) 1.41 (m, 1 H, $H_{e'}$ or $H_{f'}$) 1.35 (m, 1 H, H_e or H_f) 1.11 (m, 2 H, $H_{c'}$ or $H_{d'}$) 0.96 (m, 2 H, H_c or H_d) 0.87 (m, 2 H, H_c or $H_{d'}$) 0.77 (m, 2 H, H_c or H_d) 0.57 (m, 1 H, $H_{e'}$ or $H_{f'}$) 0.35 (m, 1 H, H_e or H_f)	1765 (1765)
 **2**	2089w, 2068m, 2055s, 2032vs, 2010m, 1979w	2.86 (m, 2 H, H_a or H_b) 2.47 (m, 2 H, H_a or H_b) 1.35 (m, 1 H, H_e or H_f) 0.96 (m, 2 H, H_c or H_d) 0.77 (m, 2 H, H_c or H_d) 0.35 (m, 1 H, H_e or H_f)	1473 (1473)
 **3**	2080w, 2068w, 2024 (br)	4.34 (m, 2 H, H_a, $H_{a'}$) 3.57 (m, 2 H, H_b, $H_{b'}$) 2.05 (m, 2 H, H_d, $H_{d'}$) 1.96 (m, 2 H, H_c, $H_{c'}$)	1709 (1709)

Table 3 (*Contd.*)

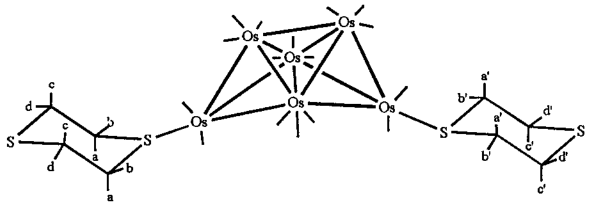
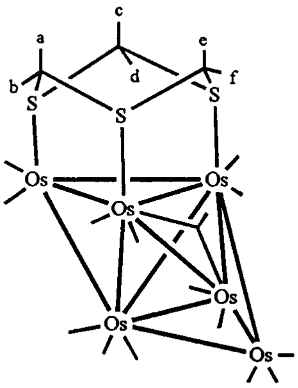
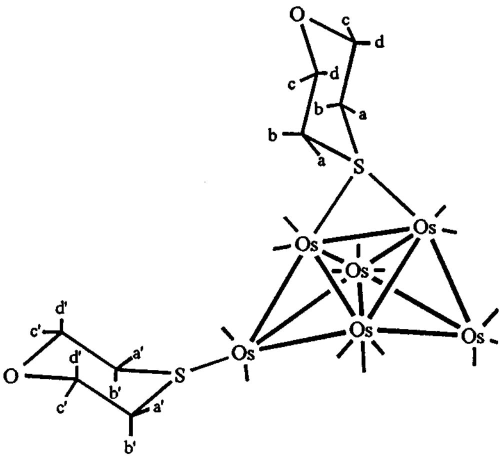
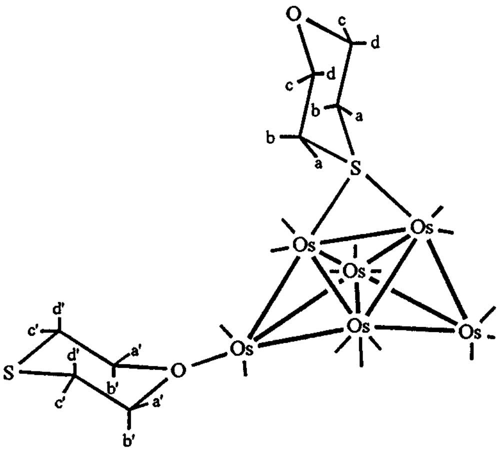
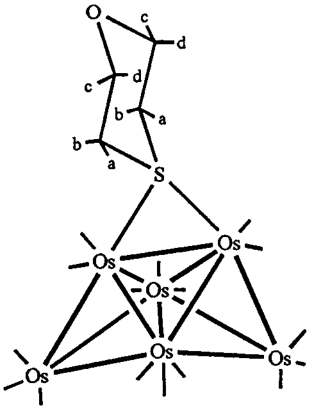
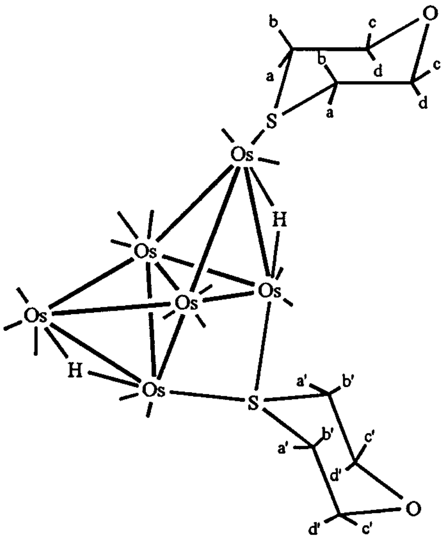
Complex	IR, $\tilde{\nu}$(CO)^a/cm^{-1}	^{1}H NMR, δ(*J*/Hz)^b	Mass, *m*/*z*^{c}
 **4**	2093w, 2080w, 2064s, 2032s, 2024vs, 2001s, 1941w	3.78–3.80 (m, 4 H, H_a, $H_{a'}$ or H_b, $H_{b'}$) 2.86–2.92 (m, 4 H, H_b, $H_{b'}$ or H_a, $H_{a'}$), 1.92–2.02 (m, 4 H, H_c, H_d or $H_{c'}$, $H_{d'}$) 1.67–1.71 (m, 4 H, $H_{c'}$, $H_{d'}$ or H_c, H_d)	1829 (1829)
 **5**	2084s, 2039s, 2020vs, 1999m, 1968w	2.86–2.92 (m, 2 H, H_a, H_b) 1.92–2.02 (m, 2 H, H_e, H_f) 1.67–1.71 (m, 2 H, H_c, H_d)	1699 (1699)
 **6**	2078s, 2020vs, 2006vs, 1985 (br)	3.34–3.43 (m, 4 H, H_a, H_b, $H_{a'}$, $H_{b'}$) 2.45–2.51 (m, 4 H, H_c, H_d, $H_{c'}$, $H_{d'}$)	1769 (1769)
 **7**	2081s, 2019vs, 2005vs, 1983 (br)	4.67–4.78 (m, 2 H, $H_{a'}$ or $H_{b'}$) 4.41–4.44 (m, 2 H, $H_{c'}$ or $H_{d'}$) 3.38–3.41 (m, 2 H, H_a or H_b) 2.62–2.78 (m, 2 H, H_c or H_d)	1769 (1769)

Table 3 (*Contd.*)

Complex	IR, $\tilde{\nu}$(CO)[a]/cm^{-1}	^{1}H NMR, δ(J/Hz)[b]	Mass, m/z[c]
 **8**	2064s, 2037m, 2024s	3.91–3.94 (m, 2 H, H_a or H_b) 2.67–2.69 (m, 2 H, H_c or H_d)	1693 (1693)
 **9**	2084m, 2033m, 2020s, 2006vs, 1979w	3.68–3.75 (m, 4 H, H_a, H_b, $H_{a'}$, $H_{b'}$) 2.76–2.85 (m, 4 H, H_c, H_d, $H_{c'}$, $H_{d'}$) −11.98 (s, 1 H, OsH) −15.98 (s, 1 H, OsH)	1770 (1770)

[a] In CH_2Cl_2. [b] In C_6D_6. [c] Simulated values given in parentheses.

Table 4 Selected bond distances (Å) and angles (°) for cluster **3**

Os(1)–Os(2)	2.713(2)	Os(4)–Os(5)	2.759(2)
Os(1)–Os(3)	2.861(2)	Os(4)–Os(6)	2.867(2)
Os(1)–Os(4)	2.836(2)	Os(5)–Os(6)	2.714(2)
Os(2)–Os(3)	2.865(2)	Os(2)–S(1)	2.27(1)
Os(2)–Os(4)	2.771(3)	Os(5)–S(1)	2.26(1)
Os(2)–Os(5)	2.662(2)		
Os(3)–Os(4)	2.755(2)	Os(2)–S(1)–Os(5)	71.9(3)
Os(3)–Os(5)	2.852(2)	Os(5)–Os(2)–S(1)	53.9(3)
Os(3)–Os(6)	2.849(2)	S(1)–Os(5)–Os(2)	54.3(3)

Table 5 Selected bond distances (Å) for cluster **4**

Os(1)–Os(2)	2.869(2)	Os(3)–Os(6)	2.797(2)
Os(1)–Os(3)	2.829(2)	Os(4)–Os(5)	2.799(2)
Os(1)–Os(4)	2.808(2)	Os(4)–Os(6)	2.828(2)
Os(2)–Os(3)	2.794(2)	Os(5)–Os(6)	2.876(2)
Os(2)–Os(4)	2.779(2)		
Os(2)–Os(5)	2.756(2)	Os(1)–S(1)	2.36(1)
Os(3)–Os(4)	2.787(2)	Os(6)–S(3)	2.39(1)
Os(3)–Os(5)	2.786(2)		

metal–metal bond lengths in the triangle lie in the range of 2.793 to 2.836 Å which are comparable to the corresponding Os–Os vectors in $[Os_6(CO)_{18}]$.[13] All the carbonyl ligands are terminally bonded except the one bridging the polyhedral edge Os(2)–Os(5) which leads to the shortest metal–metal bond distance in the structure. Cluster **5** is rather stable and does not react with molecular hydrogen or carbon monoxide even under forcing conditions (in refluxing $CHCl_3$ for 24 h). The strong and rigid ligand chelation of ligand L^4 may account for the relative inertness of the complex towards hydrogenation and carboxylation.

Compounds **6** and **7** were isolated as a pair of isomers from the reactions with 1,4-thioxane (L^5) containing hetero-donor atoms S and O. The molecular structure of **6** is illustrated in Fig. 6 and pertinent bond parameters are given in Table 7. The bonding architecture of cluster **6** is similar to that of **1** with all their bonding parameters comparable. All attempts to obtain suitable single crystals of **7** were not successful owing to its instability in solution, however it is thought to be of similar structure to **6** according to FAB MS and ^{1}H NMR spectroscopies. In fact, the high resemblances between the IR patterns of **6** and **7**, along with their identical molecular ion envelopes exhibited in mass spectra, imply that both structures have similar carbonyl ligand depositions with disubstituted ligand L^5.

Table 6 Selected bond distances (Å) and angles (°) for cluster **5**

Os(1)–Os(2)	2.793(3)	Os(5)–Os(6)	2.704(3)
Os(1)–Os(3)	2.740(2)	Os(1)–S(1)	2.38(1)
Os(1)–Os(4)	2.836(2)	Os(2)–S(2)	2.42(1)
Os(2)–Os(3)	2.845(3)	Os(4)–S(3)	2.43(1)
Os(2)–Os(4)	2.824(3)		
Os(2)–Os(5)	2.663(3)	S(1)–Os(1)–Os(4)	94.6(3)
Os(3)–Os(4)	2.733(3)	S(1)–Os(1)–Os(2)	95.0(3)
Os(3)–Os(5)	2.791(3)	S(2)–Os(2)–Os(1)	92.3(3)
Os(3)–Os(6)	2.863(3)	S(2)–Os(2)–Os(4)	95.9(3)
Os(4)–Os(5)	2.835(3)	S(3)–Os(4)–Os(2)	89.7(3)
Os(4)–Os(6)	2.812(3)	S(3)–Os(4)–Os(1)	90.1(3)

Table 7 Selected bond distances (Å) and angles (°) for cluster **6**

Os(1)–Os(2)	2.733(1)	Os(4)–Os(5)	2.795(1)
Os(1)–Os(3)	2.843(1)	Os(4)–Os(6)	2.837(1)
Os(1)–Os(4)	2.924(1)	Os(5)–Os(6)	2.731(1)
Os(2)–Os(3)	2.850(1)	Os(1)–S(1)	2.385(4)
Os(2)–Os(4)	2.764(1)	Os(2)–S(2)	2.272(4)
Os(2)–Os(5)	2.679(1)	Os(5)–S(2)	2.284(4)
Os(3)–Os(4)	2.754(1)		
Os(3)–Os(5)	2.855(1)	Os(2)–S(2)–Os(5)	72.0(1)
Os(3)–Os(6)	2.848(1)	Os(5)–Os(2)–S(2)	54.2(1)
		S(2)–Os(5)–Os(2)	53.8(1)

Table 8 Selected bond distances (Å) and angles (°) for cluster **8**

Os(1)–Os(2)	2.708(1)	Os(4)–Os(5)	2.878(1)
Os(1)–Os(3)	2.880(1)	Os(4)–Os(6)	2.841(1)
Os(1)–Os(4)	2.857(1)	Os(5)–Os(6)	2.726(1)
Os(2)–Os(3)	2.788(1)	Os(2)–S(1)	2.281(5)
Os(2)–Os(4)	2.865(1)	Os(5)–S(1)	2.263(5)
Os(2)–Os(5)	2.666(1)		
Os(3)–Os(4)	2.769(1)	Os(2)–S(1)–Os(5)	71.8(2)
Os(3)–Os(5)	2.757(1)	Os(5)–Os(2)–S(1)	53.8(1)
Os(3)–Os(6)	2.884(1)	S(1)–Os(5)–Os(2)	54.4(1)

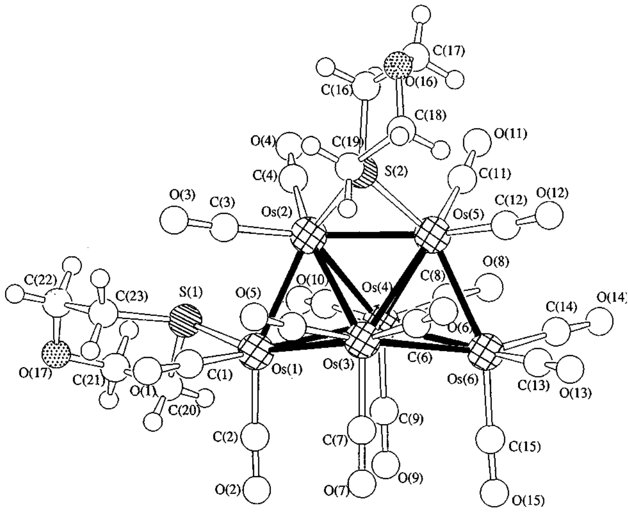


Fig. 6 Molecular structure of cluster **6**.

Table 9 Selected bond distances (Å) and angles (°) for cluster **9**

Os(1)–Os(2)	2.896(1)	Os(4)–Os(6)	2.778(2)
Os(1)–Os(3)	2.808(1)	Os(5)–Os(6)	2.857(2)
Os(1)–Os(4)	2.869(2)	Os(1)–S(1)	2.380(7)
Os(2)–Os(3)	2.888(1)	Os(2)–S(2)	2.321(7)
Os(2)–Os(4)	2.841(2)	Os(5)–S(2)	2.278(6)
Os(3)–Os(4)	2.771(2)		
Os(3)–Os(5)	2.879(2)	Os(2)–S(2)–Os(5)	99.1(2)
Os(3)–Os(6)	2.872(2)	S(2)–Os(5)–Os(3)	88.8(2)
Os(4)–Os(5)	2.826(1)	Os(5)–Os(3)–Os(2)	74.7(4)
		Os(3)–Os(2)–S(2)	87.7(2)

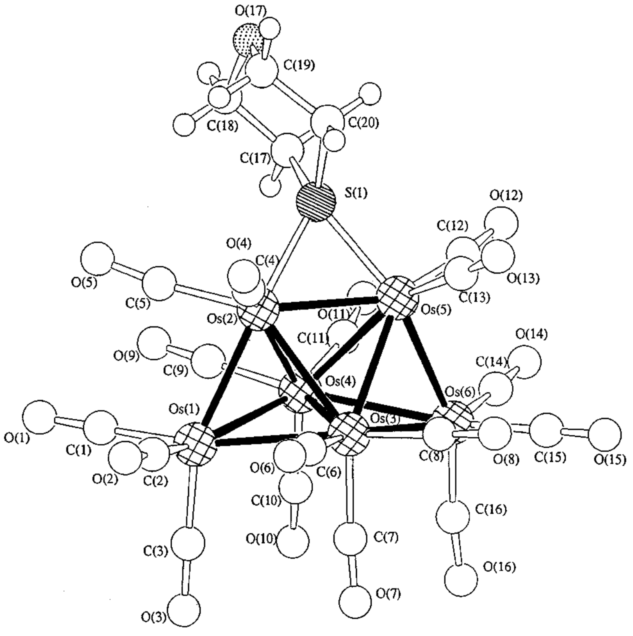


Fig. 7 Molecular structure of cluster **8**.

The only difference lies in their ^{1}H NMR spectra, with a considerably downfield shift shown by two groups of multiplets. With reference to the ^{1}H NMR spectrum of cluster **6**, this is unambiguously assigned to the terminally bonded ligand L^5. We believe the co-ordination of Os(1) *via* O atom in L^5 results in such changes in chemical shift. In the literature, the occurrence of terminally co-ordinated O-donors is not uncommon and there are many alkoxytriosmium clusters such as [Os$_3$(CO)$_{10}$(μ-H)(μ-OR)], R = H,[29] Me[30] or ^{n}Bu.[31] However, the difference in chemical reactivities between **1** and **6** towards neutral molecules such as CO and H$_2$ can be attributed to the presence of the reactive oxygen atom in L^5, which conferred higher reactivities to **6**. Facile displacement of a terminally bonded atom S(1) by a CO ligand from the metal framework afforded compound **8**. Complete conversion into the parent cluster, [Os$_6$(CO)$_{18}$], could be achieved upon further refluxing of compound **6** in CHCl$_3$ under a stream of CO for 48 h. Indeed, the metal–ligand architecture of **8** can be obtained in a similar reaction with L^2, as discussed previously. A perspective view of **8** is illustrated in Fig. 7 with selected bond parameters in Table 8. As in **3**, all sixteen carbonyl ligands are terminally bonded in cluster **8** with a thioxane ligand L^5 bridging the edge Os(2)–Os(5) of the central tetrahedron. The bonding parameters of both structures are in good agreement, except for the Os(3)–Os(6) vector in cluster **8** which is slightly elongated, leading to a distorted bicapped tetrahedron.

Hydrogenation of compound **6** induced bond cleavage along the Os(2)–Os(5) edge and gave a new cluster **9**. Its molecular structure is presented in Fig. 8. Important bond parameters are summarized in Table 9. The metal core consists of six osmium atoms that are arranged in the form of two fused tetrahedra sharing a common edge. This kind of metal skeleton arrangement is rather rare in hexaosmium systems and a similar core is reported for [Os$_6$(CO)$_{12}$(μ-CNMe$_2$)$_2$(μ$_3$-SMe)$_2$(μ-H)$_2$].[32] The cleavage of the Os(2)–Os(5) bond not only gives a relatively long non-bonding Os · · · Os distance [3.50 *vs.* 2.679 Å in **6**] but also results in longer average Os–S distances [2.300 *vs.* 2.273 in **1** and 2.278 Å in **6** respectively]. Both ^{1}H NMR and a potential-energy calculation[33] suggested the presence of a pair of bridging hydrides across the Os(1)–Os(5) and Os(5)–Os(6) edges so as to complete the co-ordination sphere by 86 CVE which the edge-fused bi-tetrahedron should attain.[34]

Experimental

All reactions and manipulations were carried out in an

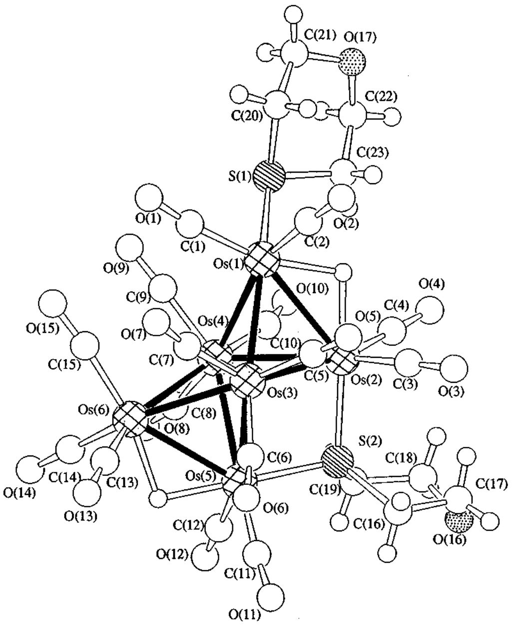


Fig. 8 Molecular structure of cluster **9**.

atmosphere of dry argon using standard Schlenk techniques. All solvents were purified and dried by standard methods prior to use.[35] Chemicals were purchased from Aldrich chemicals and used as received. The compound $[Os_6(CO)_{18}]$[36] was obtained from vacuum pyrolysis of $[Os_3(CO)_{12}]$ and the activated cluster $[Os_6(CO)_{16}(MeCN)_2]$ was prepared by the literature method.[37] Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer, using 0.5 mm thick calcium fluoride solution cells, proton NMR spectra on a Bruker DPX 300 spectrometer using C_6D_6 with reference to $SiMe_4$ ($\delta = 0$) and mass spectra on a Finnigan MAT 95 instrument by the fast atom bombardment technique, using *m*-nitrobenzyl alcohol or *a*-thioglycerol as the matrix solvent. Elemental analyses were conducted by Butterworth Laboratories, UK. Routine separation of products in air was performed by thin-layer chromatography (TLC) on plates coated with Merck Kieselgel 60 GF_{254}.

Syntheses

$[Os_6(CO)_{15}\{\overline{S(CH_2)_4C}H_2\}\{\mu\text{-}\overline{S(CH_2)_4C}H_2\}]$ 1 and $[Os_5(CO)_{15}\{\overline{S(CH_2)_4C}H_2\}]$ 2. The complex $[Os_6(CO)_{16}(MeCN)_2]$ (112 mg, 0.067 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and stirred with dropwise addition of one equivalent of L^1 (0.70 cm^3 diluted in 10 cm^3 CH_2Cl_2) under ambient conditions. After the reaction had proceeded for 4 h, the mixture gradually changed from blackish brown to turbid brown. It was then filtered and the volume reduced to 5 cm^3 *in vacuo*. The residue was subsequently purified by TLC using hexane–CH_2Cl_2 (20 : 10 v/v) as eluent. The first yellow band was found to be $[Os_3(CO)_{12}]$ (< 5%, as confirmed by IR spectroscopy). Two major bands of brown cluster **1** (R_f 0.70, 28 mg, 0.016 mmol, 24%) and red cluster **2** (R_f 0.65, 22 mg, 0.015 mmol, 22%) were then eluted consecutively (Found for **1**: C, 16.9; H, 1.0; S, 3.6. Calc. for $C_{25}H_{20}O_{15}Os_6S_2$ C, 17.0; H, 1.1; S, 3.6. Found for **2**: C, 14.4; H, 0.7; S, 2.1. Calc. for $C_{20}H_{10}O_{15}Os_5S$: C, 14.5; H, 0.7; S, 2.2%).

Conversion of compound 1 into 2. A deep brown solution of compound **1** (40 mg, 0.02 mmol) in refluxing $CHCl_3$ was added to an equivalent of L^1 (0.23 cm^3 diluted in 5 cm^3 CH_2Cl_2). Two bands were eluted [hexane–CH_2Cl_2 (10 : 10 v/v)] which were identified by solution IR as **2** (R_f 0.60, 18 mg, 0.012 mmol, 54%) and unchanged **1** (R_f 0.45, 10 mg, 0.006 mmol, 24%).

$[Os_6(CO)_{16}\{\mu\text{-}\overline{S(CH_2)_3SC}H_2\}]$ 3. Treatment of equimolar L^2 (7.2 mg, 0.06 mmol) with $[Os_6(CO)_{16}(MeCN)_2]$ (100 mg, 0.06 mmol) in CH_2Cl_2 (35 cm^3) under ambient conditions over a period of 24 h afforded a deep brown reaction mixture. Purification by TLC using hexane–CH_2Cl_2 (10 : 10 v/v) gave the brown cluster **3** (R_f 0.45, 30 mg, 0.018 mmol, 29%) together with several uncharacterized, low-yield products (Found: C, 14.1; H, 0.5; S, 1.8. Calc. for $C_{10}H_4O_8Os_3S$: C, 14.3; H, 0.5; S, 1.9%).

$[Os_6(CO)_{16}\{\overline{S(CH_2)_2SCH_2C}H_2\}_2]$ 4. To a solution of $[Os_6(CO)_{16}(MeCN)_2]$ (92 mg, 0.055 mmol) in CH_2Cl_2 (30 cm^3) was added L^3 (13 mg, 0.108 mmol). The reaction mixture was stirred at room temperature for 6 h during which time it darkened. Excess of solvent was then removed under reduced pressure, yielding a deep brown residue. This was then dissolved in CH_2Cl_2 (5 cm^3) and subjected to preparative TLC on silica using hexane–CH_2Cl_2 (10 : 30, v/v) as eluent. The brown cluster **4** was isolated as the major product (R_f 0.78, 32 mg, 0.017 mmol, 32%) (Found: C, 15.9; H, 0.9; S, 6.9. Calc. for $C_{12}H_8O_8Os_3S_2$: C, 15.7; H, 0.9; S, 7.0%).

$[Os_6(CO)_{14}(\mu\text{-}CO)(\overline{SCH_2SCH_2SC}H_2)]$ 5. A solution of $[Os_6(CO)_{16}(MeCN)_2]$ (75 mg, 0.045 mmol) was stirred with L^4 (5.4 mg, 0.045 mmol) in CH_2Cl_2 (30 cm^3) at ambient temperature for 3 h. After reduction in solvent volume, the filtrate was separated by preparative TLC on silica, with an eluent of hexane–CH_2Cl_2 (10 : 30 v/v). Compound **5** was isolated as the major product (R_f 0.35, 24 mg, 0.014 mmol, 31%) (Found: C, 12.5; H, 0.3; S, 5.5. Calc. for $C_6H_2O_5Os_2S$: C, 12.7; H, 0.4; S, 5.7%).

$[Os_6(CO)_{15}\{\overline{S(CH_2)_2OCH_2C}H_2\}\{\mu\text{-}\overline{S(CH_2)_2OCH_2C}H_2\}]$ 6 and $[Os_6(CO)_{15}\{\overline{O(CH_2)_2SCH_2C}H_2\}\{\mu\text{-}\overline{S(CH_2)_2OCH_2C}H_2\}]$ 7. To a CH_2Cl_2 solution (40 cm^3) of $[Os_6(CO)_{16}(MeCN)_2]$ (100 mg, 0.060 mmol), a dilute solution of an equivalent of L^5 (0.56 cm^3 diluted in 10 cm^3 CH_2Cl_2) was added dropwise with stirring for 24 h under ambient conditions. After reduction of solvent to *ca.* 5 cm^3, the residue was subjected to preparative TLC for purification using hexane–CH_2Cl_2 as eluent (10 : 10 v/v). Two consecutive bands of nearly equal abundance were then eluted: compound **6** (R_f 0.65, 20 mg, 0.011 mmol, 19%) and **7** (R_f 0.55, 18 mg, 0.010 mmol, 17%) (Found for **6**: C, 15.8; H, 0.8; S, 3.7. Calc. for $C_{23}H_{16}O_{17}Os_6S_2$: C, 15.6; H, 0.9; S, 3.6%).

Carboxylation of compound 6. Compound **6** (30 mg, 0.017 mmol) was dissolved in $CHCl_3$ (10 cm^3) to give a pale brown solution. It was purged by a stream of carbon monoxide at 1 atm continuously for 3 h and the reaction monitored by spot TLC and IR spectroscopy. Following evaporation of most of the solvent, the residue was purified by preparative TLC using hexane–CH_2Cl_2 (10 : 10 v/v) as eluent. Two brown bands were eluted, namely $[Os_6(CO)_{18}]$ (R_f 0.85, 6 mg, 0.004 mmol, 22%) and cluster **8** (R_f 0.55, 8 mg, 0.005 mmol, 28%) (Found for **8**: C, 14.5; H, 0.4; S, 1.9. Calc. for $C_{20}H_8O_{17}Os_6S$: C, 14.2; H, 0.5; S, 1.9%).

Hydrogenation of compound 6. The procedure described above was followed but using hydrogen instead of carbon monoxide. Compound **9** (R_f 0.40, 8 mg, 0.005 mmol, 27%) was isolated as the only major product along with traces of unchanged **6** (Found for **9**: C, 15.8; H, 0.9; S, 3.7. Calc. for $C_{23}H_{18}O_{17}Os_6S_2$: C, 15.6; H, 1.0; S, 3.6%).

Crystallography

Single crystals suitable for X-ray crystallographic analyses for clusters **1**–**6**, **8** and **9** were mounted on a glass fibre (except for **4** and **5**) or a Lindermann glass capillary (**4** and **5**) using epoxy resin. All samples except for **5** were obtained by slow evaporation of a saturated toluene–$CHCl_3$ solution at room temperature for several days. Brown crystals of cluster **5** were obtained

Table 10 Summary of crystal data and data collection parameters for clusters **1**–**6**, **8** and **9**

	1	**2**	**3**	**4**·0.5C_7H_8	**5**·0.5C_7H_8	**6**	**8**	**9**
Empirical formula	$C_{25}H_{20}O_{15}Os_6S_2$	$C_{20}H_{10}O_{15}Os_5S$	$C_{20}H_8O_{16}Os_6S_2$	$C_{27.5}H_{20}O_{16}Os_6S_4$	$C_{21.5}H_{10}O_{15}Os_6S_3$	$C_{23}H_{16}O_{17}Os_6S_2$	$C_{20}H_8O_{17}Os_6S$	$C_{23}H_{18}O_{17}Os_6S_2$
M	1765.74	1473.35	1709.59	1875.89	1745.69	1769.69	1693.53	1769.69
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	20.998(1)	9.062(1)	11.976(3)	9.181(1)	10.120(1)	10.314(1)	15.251(1)	8.992(1)
b/Å	15.341(2)	16.484(2)	13.059(4)	28.787(1)	11.170(1)	12.160(2)	12.358(2)	10.348(2)
c/Å	21.779(2)	18.892(2)	9.823(2)	16.533(1)	29.792(3)	14.420(2)	16.422(2)	18.637(2)
α/°	—	—	90.43(2)	—	—	108.01(2)	—	99.00(2)
β/°	—	94.76(1)	90.44(2)	102.38(1)	—	92.80(1)	102.29(1)	94.67(1)
γ/°	—	—	87.36(2)	—	—	102.84(2)	—	104.25(1)
U/Å^3	7015.7(9)	2812.3(5)	1534.6(6)	4268.0(6)	3367.7(5)	1663.4(5)	3024.1(5)	1647.0(5)
Z	8	4	2	4	4	2	4	2
μ(Mo-Kα)/cm^{-1}	218.18	226.37	249.32	180.38	227.84	230.10	252.38	232.39
No. reflections collected	59908	23912	4245	17557	21402	14561	20502	10408
No. unique reflections	7090	5330	4013	6612	2904	5736	5863	5630
R	0.050	0.045	0.067	0.065	0.062	0.048	0.053	0.061
R′	0.051	0.053	0.067	0.070	0.050	0.062	0.063	0.065
T of data collection/°C	25	25	25	25	25	25	25	25
R(int)	0.134	0.079	0.064	0.115	0.100	0.077	0.089	0.080

as a solvate of stoichiometry $\mathbf{5}\cdot0.5C_6H_5Me$ at -10 °C for 2 d. Diffraction data were collected at room temperature on a Rigaku AFC7R diffractometer (for cluster **3**) using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scan technique. Unit-cell parameters were determined from 25 accurately centred reflections. The stability of the crystal was monitored at regular intervals using three standard reflections and no significant decay was observed. For clusters **1**, **2**, **4**–**6**, **8** and **9**, data were collected on a MAR research image plate scanner using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and the ω scan technique. A summary of the crystallographic data and structure refinement is listed in Table 10. All diffracted intensities were corrected for Lorentz-polarization effects. Absorption correction by the ψ-scan method was applied for structure **3.** An approximate absorption correction by interimage scaling was applied for **1**, **2**, **4**–**6**, **8** and **9**. Space groups of all the crystals were determined from a combination of Laue symmetry check, and their systematic absences were confirmed by successful refinement of the structures. The structures were solved by a combination of direct methods: SIR 88[38] for **9**, SIR 92[39] for **1**–**6** and **8** along with Fourier-difference techniques. Structure refinements were made on F by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were generated in their idealized positions whereas all metal hydrides were estimated by potential-energy calculations.[33] All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[40]

CCDC reference number 186/1449.

See http://www.rsc.org/suppdata/dt/1999/2077/ for crystallographic files in .cif format.

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