The reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with carboxylic acids: the crystal and molecular structures of $[Os_3H(CO)_{10}(C_6H_4(OH)CO_2)]$ and $[Os_3H(CO)_{10}(C_6H_5COS)]$

Eric W. Ainscough *, Andrew M. Brodie *, Richard K. Coll [1], Brett A. Coombridge,
Joyce M. Waters

Department of Chemistry, Massey University, Palmerston North, New Zealand

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Abstract

The triosmium cluster, $[Os_3(CO)_{10}(CH_3CN)_2]$, undergoes reaction with carboxylic acids to form clusters containing a chelating μ,η^2-carboxylate ligand and a hydride bridge across one edge of the triangle via an intermediate species postulated, from IR and NMR studies, to contain a coordinated μ,η^1-carboxylate ion. The structure of the cluster, $[Os_3H(CO)_{10}(C_6H_4(OH)CO_2)]$ (1), has been determined by single-crystal X-ray diffraction and contains the 2-hydroxobenzoate ligand bound via the carboxylate oxygens in the μ,η^2-mode. A thiocarboxylate analogue of the postulated intermediate, viz. $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2), has been obtained and its structure determined by single crystal X-ray diffraction. The $C_6H_5COS^-$ ion, which is bound in the μ,η^1-mode through the sulfur atom, bridges two of the osmium atoms of the triangle. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Osmium cluster; Crystal structure; Carboxylate; Thiocarboxylate

1. Introduction

The osmium cluster, $[Os_3(CO)_{10}(CH_3CN)_2]$, and similar substitutionally labile species, have been reported to undergo reaction with carboxylic acids (HL) under mild conditions to form $[Os_3H(CO)_{10}L]$ where L is the deprotonated form of the ligand [1–7]. Spectroscopic and X-ray studies have shown that the products contain a hydride and a chelated, three-atom, μ,η^2-carboxylate bridge across the same edge of the osmium triangle. Unidentate μ^1-carboxylate binding to triosmium triangles is rare, although it has been observed with the trifluoroacetate ion [5]. Osmium clusters in which one oxygen atom of a functional group forms a one-atom μ,η^1-bridge have been prepared by reaction of functionalised clusters with water or alcohols [1,5]. Thiols react

in a similar manner to alcohols forming clusters containing μ,η^1-thiolate and hydride bridges [1,2,8,9].

During the preparation of linked triosmium cluster complexes containing thiolato-carboxylato ligands we obtained evidence from proton NMR spectroscopy for intermediate species [2]. In this paper we have made a more detailed study of this phenomenon by investigating the reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with a range carboxylic acids. The formation of the unstable reaction intermediate has been detected by IR and ^{1}H-NMR spectroscopy and the reaction to the final μ,η^2-carboxylate product followed. We have determined the X-ray structure for the μ,η^2-(2-hydroxobenzoate) complex, $[Os_3H(CO)_{10}(C_6H_4(OH)CO_2)]$ (1), which was isolated during these studies. Attempts to isolate the intermediates were unsuccessful, but the reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with thiobenzoic acid produced the thiolate analogue of the postulated μ,η^1-reaction intermediate: i.e. $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2),

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* Corresponding authors.
[1] Present address: Department of Chemistry, The University of Waikato, Hamilton, New Zealand.

which has been characterised by single-crystal X-ray diffraction.

2. Results and discussion

At room temperature (r.t.), the time for completion of the reaction of carboxylic acids with $[Os_3(CO)_{10}(CH_3CN)_2]$, to produce new clusters containing a chelate μ,η^2-carboxylate bridge, can be several hours or even days and is dependent upon the particular carboxylic acid used. In contrast reactions with thiols are complete within minutes. Hence the progress of the carboxylic acid reactions is conveniently followed by spectroscopic means.

2.1. NMR spectroscopic studies

Preliminary proton NMR studies on the reactions of a range of carboxylic acids with $[Os_3(CO)_{10}(CH_3CN)_2]$ in deuteropropanone all showed the solutions to contain two species, viz. one with an osmium-hydride resonance near -10 ppm and one with a resonance around -13 ppm. (Details are: trichloroacetic acid -13.07, -9.91; trifluoroacetic acid -14.21, -9.90; propanoic acid -12.89, -10.30; benzoic acid -12.68. -10.05; p-chlorobenzoic acid -12.68, -10.07; p-nitrobenzoic acid -12.61, -10.03 ppm.) Although the initial intensity ratios observed varied, in all cases the ca. -10 ppm signal increased in intensity with time at the expense of the resonance at ca. -13 ppm. A typical reaction profile, that for propanoic acid, is shown in Fig. 1. The resonances at ca. -10 ppm observed for the final reaction products are characteristic of a bridging hydride adjacent to the expected chelate μ,η^2-carboxylate bridge [5]. The resonances at ca. -13 ppm mostly fall in the range (-12 to -13 ppm) exhibited by a bridging hydride opposite a one-atom oxygen bridge, such as seen in $[Os_3H(CO)_{10}(OR)]$ alkoxide complexes [5], and hence the intermediate species is also postulated to contain one oxygen atom from the carboxylate bridging two osmiums in a μ,η^1-fashion. Initially, in the propanoic acid reaction, another hydride signal is seen at -13.18 ppm (Fig. 1) but this disappears rapidly and is presumably indicative of a relatively short-lived species, possibly containing a monodentate μ^1-carboxylate ligand, e.g. $[Os_3H(CO)_{10}(MeCN)(CH_3CH_2CO_2)]$, although no evidence was found for this in the IR.

Changes are also observed for resonances due to the ligand C–H protons as the reactions proceed (Table 1) and these parallel the Os–H signal changes. For example, in the case of the propanoic acid (**5**), the intermediate shows a quartet at 2.24 and a triplet at 0.90 ppm assignable to the CH_2 and CH_3 protons respectively. With time, these decrease in intensity moving to 2.16

and 0.99 ppm, the values for the final μ,η^2-carboxylate complex, $[Os_3H(CO)_{10}(CH_3CH_2CO_2)]$. Similar changes are seen for the OH and aromatic protons in the 2-hydroxobenzoic acid reaction (Table 1) and in this case the structure of the final product has been con-
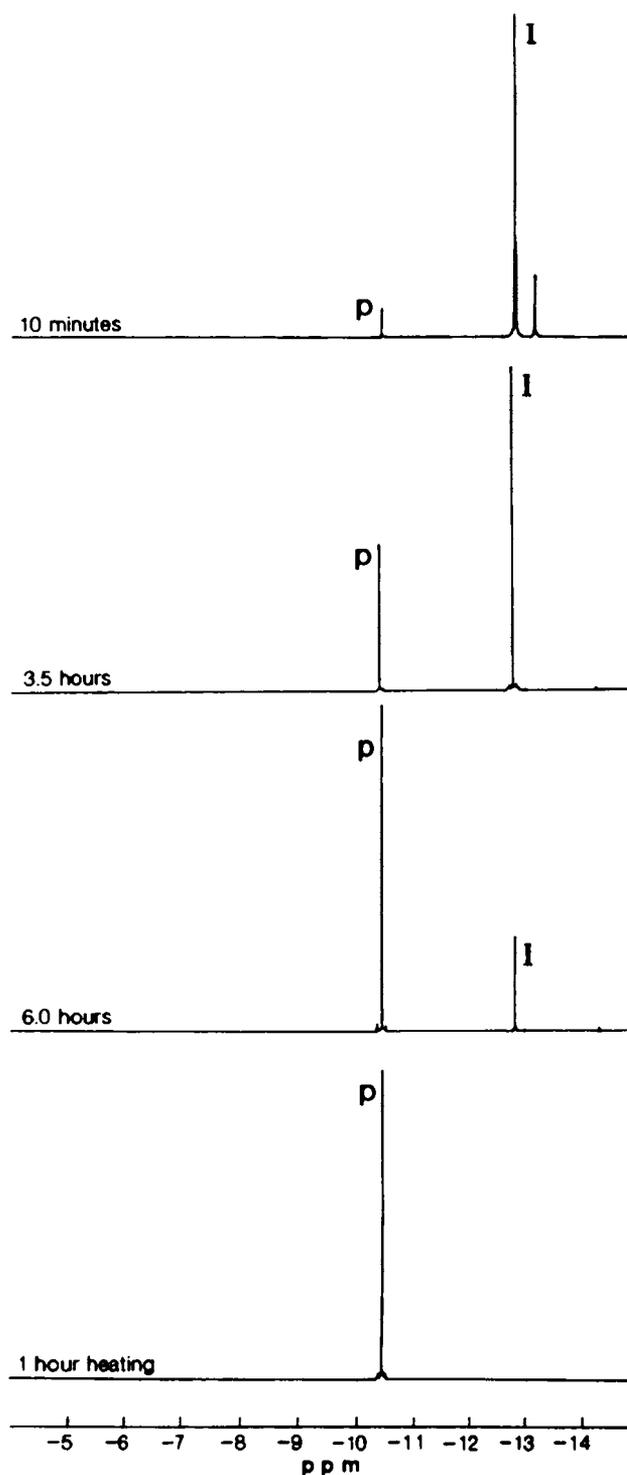

Fig. 1. Changes to the ^{1}H-NMR spectrum observed during the r.t. reaction of propanoic acid with $[Os_3(CO)_{10}(CH_3CN)_2]$. The final spectrum was recorded after heating at 60°C. **P**, final product; **I**, intermediate species.

Table 1
^{1}H-NMR data of intermediates[a] for the reaction of carboxylic acids with [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$]

Acid[b]	Os–H	H3	H4	H5	H6	Other
1	−12.59s(−10.03s)[c]	6.86dd(6.88dd)	6.66td(6.81td)	7.24td(7.36td)	7.51dd(7.61dd)	9.22s(9.22s)[d]
2	−12.70s(−10.10s) −17.10s(−16.90s)[e]	6.75dd(7.10dd)	6.95t(7.30t)	7.50t(7.60t)	7.70dd(7.88dd)	
3	−12.65s(−10.05s) −17.20s(−17.11s)[e]		7.50dd(7.85dd)	6.90dd(7.18dd)	8.30dd(8.53dd)	
4	−12.84s(−10.50s) −17.53s(−17.50s)[e]					2.30t(2.34t)[f], 2.41t(2.47t)[f]
5	−12.82s(−10.47s)[c]					2.16q(2.24q)[f], 0.99t(0.90t)[g]

[a] Values for final products are given in parentheses and are taken from refs. [2,8] except where otherwise stated.
[b] 1, 2-hydroxobenzoic; 2, 2-mercaptobenzoic; 3, 3-carboxy-2-mercaptopyridine; 4, 3-mercaptopropanoic; 5, propanoic.
[c] This work.
[d] OH proton.
[e] Hydride opposite the thiolate bridge.
[f] CH$_2$ protons.
[g] CH$_3$ protons.

firmed by the single crystal X-ray structure of the complex, [Os$_3$H(CO)$_{10}$(C$_6$H$_4$(OH)CO$_2$)] (Section 2.4).

For the mercapto-carboxylic acids, H$_2$L [H$_2$L = 2-mercaptobenzoic acid (2) 3-carboxy-2-mercaptopyridine (3) and 3-mercaptopropionic acid (4)], the reactions with [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] which give the linked triosmium cluster species, [{Os$_3$H(CO)$_{10}$}$_2$(μ-L)] [2,8], also proceed via similar intermediates but four resonances are seen in the osmium-hydride region (Table 1) in each case. Two of the signals (at ca. −13 and ca. −10 ppm) match those for the carboxylato complexes discussed above and are assigned in the same fashion. The two resonances at ca. −17 ppm are typical of a bridged osmium-hydride opposite a μ,η^1-sulfur bridge [2,8] and are assigned accordingly. The fact that these two peaks are close to each other, being only 0.3 ppm or less apart, is consistent with the major changes, as the reaction progresses, being associated with the carboxylate-osmium interaction and not the osmium-thiolato one.

2.2. IR spectroscopic studies

IR studies further support the assignment of the intermediate as a complex containing a one-atom, carboxylate bridge. The progress of the reactions of [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] with propanoic, p-nitrobenzoic

and p-chlorobenzoic acids in dichloromethane was monitored by IR spectroscopy. After a short time (ca. 10 min) there is no evidence for the presence of the starting materials: either cluster or free carboxylic acid ligand, and there are new absorbances in the metal-carbonyl region of the spectra. The new absorbances observed are identical to those reported [6] for the final reaction products: i.e. a cluster containing a chelate μ,η^2-carboxylate and hydride bridge. In addition to these changes, a new broad v_{asym}(CO$_2$) absorbance in the range 1605–1620 cm^{-1} [e.g. for 5 at 1605 cm^{-1}] observed at the early stage of the reaction, is consistent with the presence of μ,η^1-carboxylate [10] with the one oxygen atom bridging two osmium atoms. As the reaction proceeds this absorbance disappears and is replaced by a strong absorbance in the range 1540–1560 cm^{-1} [e.g. for (5) at 1550 cm^{-1}] assigned to the v_{asym}(CO$_2$) vibration for the symmetrical μ,η^2-carboxylate group. The IR spectra for the v(CO) stretches in the metal-carbonyl region show no changes during this phase of the reaction indicating that the symmetries of the 'Os(CO)$_3$' and 'Os(CO)$_4$' moieties are not altering significantly. Hence, it seems likely that the changes to the IR spectra in the v_{asym}(CO$_2$) region are due to changes in the interaction of the carboxylate group of the ligand with the triosmium cluster. Both the NMR and the IR data are consistent with the formation of a
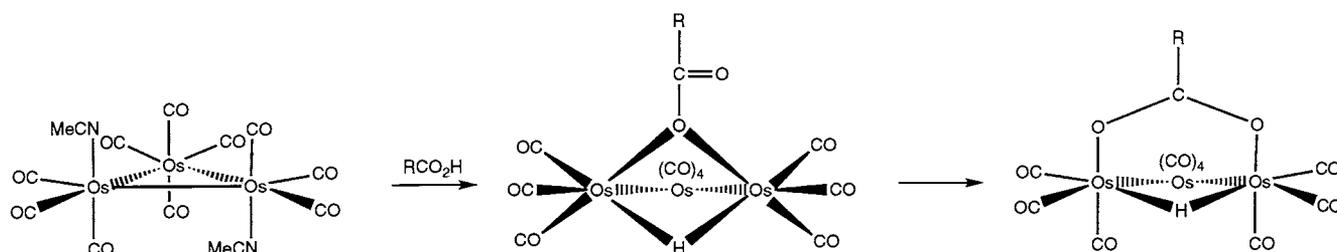
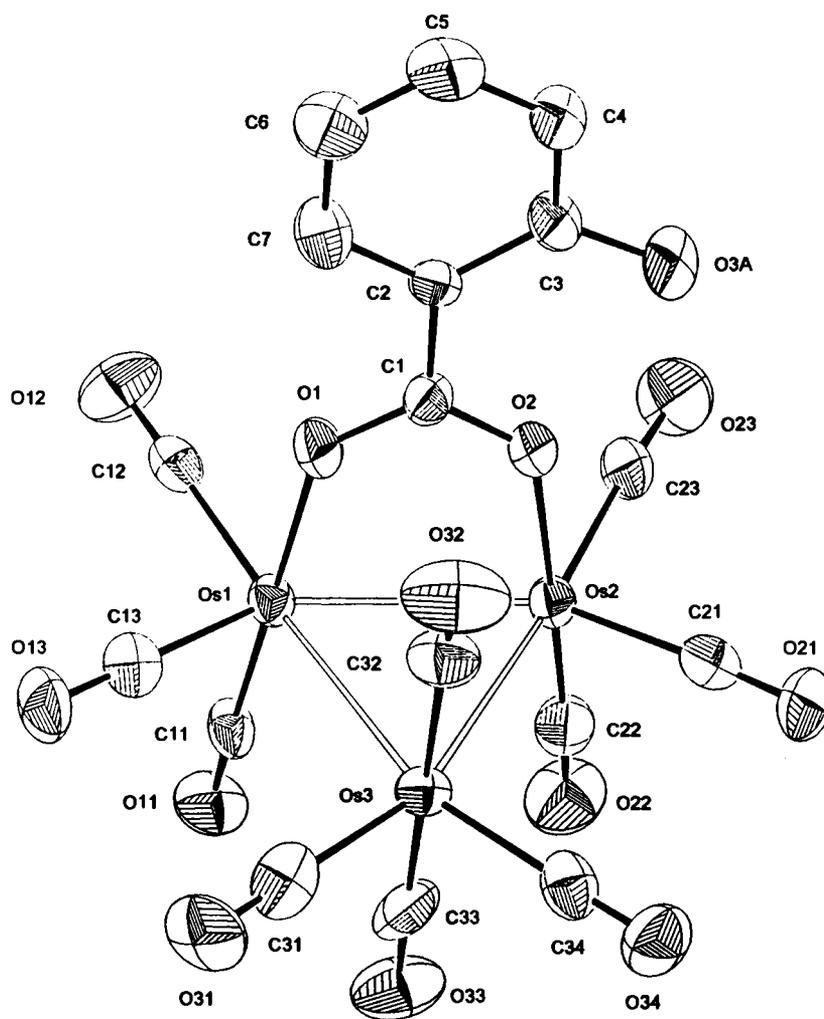Fig. 2. Proposed scheme for the reaction of [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] with carboxylic acids.

Fig. 3. ORTEP diagram of [Os$_3$H(CO)$_{10}$(C$_6$H$_4$(OH)CO$_2$)] (**1**) showing the labelling scheme used. Ellipsoids were drawn at the 50% probability level. Only the major site for atom O(3) is shown.

compound with the formulation [Os$_3$H(CO)$_{10}$(RCO$_2$)] with the carboxylate binding in a μ,η^1-fashion through one oxygen atom and then converting to the symmetrical chelating μ,η^2-mode. The proposed reaction scheme, which is given in Fig. 2, requires the bridging hydride to move from below the triosmium plane, where it is opposite the one-atom oxygen bridge, into the metal plane in the final product, in order to maintain an approximate octahedral geometry around the osmium atoms [11].

2.3. Reaction of [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] with thiobenzoic acid

Because we were unable to isolate clusters containing μ,η^1-carboxylate groups, the reaction of [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] with thiobenzoic acid was investigated. The reaction proceeds under mild conditions (stirring at r.t.) and progress can be readily followed

by spectroscopic means. The mass spectrum, IR and ^{1}H- and ^{13}C-NMR spectra (see Section 3, Experimental) indicated that the product of this reaction is a cluster complex containing a μ,η^1-thiolate and a hydride bridge across one edge of an osmium triangle, viz. [Os$_3$H(CO)$_{10}$(C$_6$H$_5$COS)]. For example, the osmium-hydride resonance at -17.67 ppm is characteristic of a μ^1-H atom lying along the same edge of the osmium triangle as a μ^1-S atom [2,8]. The structure of this cluster was subsequently confirmed by a single-crystal X-ray diffraction analysis (Section 2.4). The fact that in this cluster coordination occurs only through the sulphur atom adds some support for the structure of the proposed intermediate in the carboxylate cluster reaction. The propensity for sulphur to bridge across adjacent osmium atoms in triangular triosmium clusters [1,2,8,9] would explain why it is possible to isolate such a species from the thiobenzoic acid reaction.
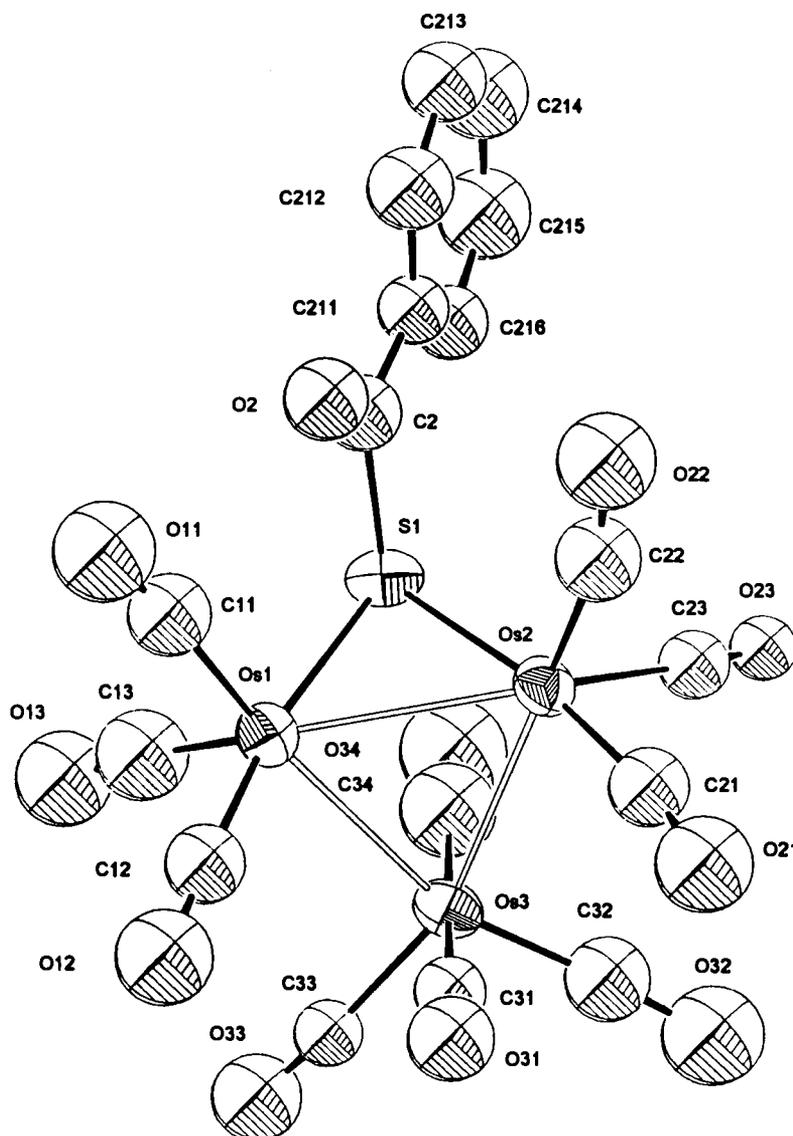
Fig. 4. ORTEP diagram for molecule 1 of $[Os_3H(CO)_{10}(C_6H_5COS)]$ (**2**) showing the labelling scheme used. Ellipsoids were drawn at the 50% probability level.

2.4. Crystal structures for $[Os_3H(CO)_{10}(C_6H_4(OH)-CO_2)_2]$ (1) and $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2)

A view of the structures of **1** and **2** is shown in Figs. 3 and 4. Selected bond lengths and angles are given in Tables 2 and 3, and atom coordinates in Tables 4 and 5. For **2**, there are two independent molecules in the asymmetric unit. The osmium atoms for both clusters form a triangle with the carboxylate forming a three-atom μ^2-bridge along an edge of the triangle for **1**, and the sulphur a μ^1-bridge for **2**. The Os–Os bond length for osmiums which are bridged by the carboxylate in **1** is longer compared with the others in the same triangle [2.894(1) Å, cf. 2.866(1), 2.875(1) Å]. Lengthening of the Os–Os bond has been observed in other similar clusters containing a chelate carboxylate bridge, but this effect is sensitive to the presence of other donor

atoms coordinated to the osmiums [12–15]. In contrast, the Os–Os bond lengths of the osmium atoms bridged by the sulfur atoms lie within the range (albeit at the upper end) for those found between the other osmiums [2.854(2) and 2.857(2) Å cf. 2.839(1)–2.858(2) Å]. The Os–O bond distances [2.136(10) and 2.157(10) Å] for **1**, Os–S bond distances [2.399(9)–2.438(9) Å] for **2**, and metal carbonyl distances for both clusters are similar to reported values [2,8,12–22]. In the 2-hydroxobenzoate complex, the hydroxo group does not interact with an osmium atom but it does make a close approach (< 2.8 Å) to a neighbouring carboxylate oxygen [O(3a)...O(2) 2.606 Å and O(3b)...O(1) 2.631 Å], indicating a strong intra-molecular hydrogen bond [23]. Also for **1**, the O(1)–C(2)–O(2) μ^2-carboxylate bond angle at 121.2(1)° is close to the ideal trigonal angle of 120° and the C–O bond lengths [1.255(16) and 1.295(13) Å]

Table 2
Selected bond distances (Å) and angles (°) for [Os$_3$H(CO)$_{10}$C$_6$H$_4$(OH)(CO$_2$)] (1) with estimated standard deviations in parentheses

Os(2)–Os(1)	2.894(1)	Os(2)–O(2)	2.136(10)
Os(3)–Os(1)	2.866(1)	C(1)–O(1)	1.255(16)
Os(2)–Os(3)	2.875(1)	C(1)–O(2)	1.295(13)
Os(1)–O(1)	2.157(10)		
O(2)–Os(2)–Os(1)	80.8(2)	Os(1)–O(1)–C(1)	127.9(9)
O(1)–Os(1)–Os(2)	81.1(2)	Os(2)–O(2)–C(1)	128.5(9)
O(1)–C(1)–O(2)	121.2(1)		

indicate partial double bond character for both these bonds (expected C–O single and C=O double bond lengths are 1.36 and 1.23 Å, respectively [24]). On the other hand, for 2, where the ligand carbonyl oxygen is not coordinated to an osmium atom the mean CO bond length is shorter (1.178 Å) and is best regarded as double bond whereas the mean carbon–sulfur distance (1.876 Å) points to a single bond (expected value ~1.8 Å [25]).

3. Experimental

3.1. General methods

Instrumentation, general procedures, and sources of starting materials are given in Ref. [2]. The atom labelling scheme used for the ^{13}C-NMR studies is given in Fig. 5 and assignments were made based on those reported for similar clusters [26].

Table 3
Selected bond lengths (Å) and angles (°) for [Os$_3$H(CO)$_{10}$(C$_6$H$_5$COS)] (2) with estimated standard deviations in parentheses

Molecule 1		Molecule 2	
Os(2)–Os(1)	2.854(2)	Os(5)–Os(4)	2.857(2)
Os(3)–Os(2)	2.839(1)	Os(4)–Os(6)	2.858(2)
Os(3)–Os(1)	2.852(2)	Os(5)–Os(6)	2.847(2)
Os(2)–S(1)	2.438(9)	Os(4)–S(2)	2.399(9)
Os(1)–S(1)	2.405(8)	Os(5)–S(2)	2.423(8)
S(1)–C(2)	1.910(38)	S(2)–C(1)	1.831(37)
O(2)–C(2)	1.156(38)	O(1)–C(1)	1.199(34)
Os(2)–S(1)–Os(1)	72.2(2)	Os(5)–S(2)–Os(4)	72.7(2)
C(2)–S(1)–Os(1)	109.0(11)	C(1)–S(2)–Os(4)	110.7(11)
C(2)–S(1)–Os(2)	104.9(12)	C(1)–S(2)–Os(5)	101.4(11)
O(2)–C(2)–S(1)	121.8(30)	O(1)–C(1)–S(2)	121.4(29)
C(211)–C(2)–S(1)	110.8(23)	C(111)–C(1)–S(2)	116.4(20)
C(211)–C(2)–O(2)	127.0(34)	C(111)–C(1)–O(1)	122.2 (33)

Table 4
Atom coordinates ($\times 10^4$) for [Os$_3$H(CO)$_{10}$(C$_6$H$_4$(OH)CO$_2$)] (1) with estimated standard deviations in parentheses

Atom	x	y	z
Os(1)	1715.2(0.2)	2276.0(0.6)	5783.3(0.4)
Os(2)	1321.5(0.2)	2406.9(0.6)	7404.2(0.4)
Os(3)	1489.4(0.2)	−91.9(0.6)	6637.8(0.4)
O(1)	968(4)	2560(11)	5220(7)
O(2)	674(5)	2676(11)	6472(7)
O(3a)	−213(5)	3419(18)	6434(10)
O(3b)	391(14)	2959(53)	3705(26)
O(11)	2757(5)	2022(14)	6617(9)
O(12)	1928(6)	4886(13)	4922(9)
O(13)	1890(5)	473(13)	4289(7)
O(21)	802(6)	845(15)	8665(9)
O(22)	2260(6)	2284(17)	8660(10)
O(23)	1158(7)	5081(14)	8145(9)
O(31)	1733(6)	−2140(15)	5315(10)
O(32)	457(6)	−24(15)	5608(12)
O(33)	2514(5)	−181(14)	7708(10)
O(34)	1133(6)	−1930(15)	7957(9)
C(1)	622(7)	2765(16)	5619(9)
C(2)	154(6)	3119(15)	5104(9)
C(3)	−242(6)	3423(17)	5526(9)
C(4)	−670(6)	3710(19)	5026(10)
C(5)	−720(6)	3758(20)	4117(12)
C(6)	−347(7)	3491(21)	3707(12)
C(7)	90(7)	3167(20)	4188(12)
C(11)	2369(6)	2096(17)	6290(9)
C(12)	1840(7)	3931(16)	5234(11)
C(13)	1802(6)	1122(19)	4849(11)
C(21)	988(7)	1453(19)	8181(12)
C(22)	896(8)	2289(17)	8205(12)
C(23)	1213(7)	4128(18)	7849(10)
C(31)	1647(7)	−1385(20)	5795(12)
C(32)	822(8)	35(18)	5966(13)
C(33)	2135(8)	−86(19)	7303(12)
C(34)	1268(7)	−1248(20)	7463(11)

3.2. Reaction studies

The final μ,η^2-carboxylate products were characterised on the basis of previously reported ^{1}H-NMR and IR spectral data [2,6]. For the preliminary ^{1}H-NMR studies, the cluster, [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$], (8 mg) and the stoichiometric quantity of the appropriate carboxylic acid were dissolved in deuterated propanone (1.5 cm^3) and the reaction carried out in an NMR tube. The solution was heated in a water bath (at ca. 60°C) at the latter stages of the reaction to ensure completion. For the studies listed in Table 1, data were recorded in deuterochloroform. Solution IR studies were carried out using 10 mg of the cluster, [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$], and the stoichiometric quantity of the appropriate carboxylic acid dissolved in dichloromethane (20 cm^3). The solution was sampled at regular intervals in the metal-carbonyl region with the solvent volume being reduced by evaporation using a stream of dry dinitrogen gas before measuring the values of the less intense

$v_{asym}(CO_2)$ bands. At the final stages of the reaction the solution was heated under reflux to ensure completion.

3.2.1. $[Os_3H(CO)_{10}(C_6H_4(OH) CO_2)]$ (1)

The complex, $[Os_3(CO)_{10}(CH_3CN)_2]$ (70 mg, 75.1 µmol) in dichloromethane (10 ml) was stirred with 2-hydroxybenzoic acid (10.4 mg, 75.1 µmol), initially at r.t. and then under reflux for 1.5 h. The solvent was removed under reduced pressure and the product purified by TLC (eluent 1:1 hexane:dichlormethane) to yield the yellow product; yield 40 mg, 54%. (Found: C, 20.65; H, 0.61; $C_{17}H_6O_{13}Os_3$ requires: C, 20.65; H, 0.62%). IR (cyclohexane): $v(CO)$ 2114w, 2075s, 2064s, 2028s, 2011s, 1985w. ^{1}H-NMR: see Table 1. ^{13}C-NMR: δ (CDCl$_3$): 184.06, C7; 181.94, 181.12, A,B; 175.34, 174.16, 174.05, 173.56, C,D,E,F; 159.16, C1; 135.92, C6; 131.25, C5; 119.42, C3; 117.26, C4; 115.50, C2. M^+(^{192}Os) 994.

3.2.2. $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2)

The cluster $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2) was prepared in a similar manner to 1 by the reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ (40 mg, 42.9 µmol) with thiobenzoic acid (6.0 mg, 42.9 µmol), except that the reaction was stirred at r.t. for 12 h and not heated. The product was obtained as yellow microcrystals; yield 30.9 mg, 68%. (Found: C, 20.83; H, 0.76; S, 3.09; $C_{17}H_6O_{11}Os_3S$ requires: C, 20.65; H, 0.61; S, 3.24%). IR (cyclohexane): $v(CO)$ 2109w, 2071s, 2062s, 2023s, 2015s, 2005m, 1990w, 1987w. ^{1}H-NMR δ (CDCl$_3$): -17.67, H, s, H$-$Os; 8.25, 2H, d, H2, H6; 7.73, 1H, t, H4; 7.53, 2H, t, H3, H5. ^{13}C-NMR δ (CD$_3$COCD$_3$): 195.37, C7; 181.06, 179.93, A,B; 176.32, 170.49, D,E; 173.60, C; 168.89, F; 135.05, C4; 132.94, C1; 130.38, C2. C6; 129.18, C3, C5. M^+(^{192}Os) 994.

3.3. Molecular structure determination of $[Os_3H(CO)_{10}(C_6H_4(OH) CO_2)]$ (1) and $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2)

Crystals suitable for X-ray analysis were obtained by the slow evaporation of a chloroform solution for 1 and vapour diffusion (ethylacetate-methanol) for 2. The crystal data, data collection and structure solution details are given in Table 6. The unit cell parameters for both clusters were determined by the least squares refinement of 25 accurately centred reflections in the shell $13 < \theta < 16$, and the data were collected at r.t. using a Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) in the $\omega - 2\theta$ mode with $\pm h$, $+ k$, $+ l$ for 1 and $+ h$, $+ k$, $\pm l$ for 2. Reflection intensities were corrected for the effects of Lorentz and polarisation effects and the crystal stability monitored two-hourly by observation of three standard reflections. Crystal decay was linear (3.3%, 7.6% for 1 and 2, respectively) and the data were scaled accordingly. Empirical ab-

Table 5
Atom coordinates ($\times 10^4$) for $[Os_3H(CO)_{10}(C_6H_5COS)]$ (2) with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}
Os(1)	4082.1(1.2)	6103.9(0.5)	409.2(0.8)	
Os(2)	2201.3(1.2)	6590.5(0.4)	10921(0.8)	
Os(3)	3219.5(1.2)	6834.2(0.5)	− 573.0(0.8)	
Os(4)	−2598.9(1.2)	6523.9(0.4)	−3843.7(0.8)	
Os(5)	−813.6(1.2)	6101.8(0.5)	−4787.0(0.9)	
Os(6)	−1893.4(1.3)	6840.2(0.5)	−5589.8(0.9)	
S(1)	1702(8)	5988(3)	99(5)	
S(2)	−3160(8)	5954(3)	−4903(5)	
O(1)	−2839(26)	5517(10)	−3244(19)	80(8)
O(2)	2179(26)	5515(9)	1742(18)	76(7)
O(11)	5019(34)	5400(12)	1739(24)	115(11)
O(12)	6936(32)	6397(11)	809(22)	105(10)
O(13)	4246(32)	5718(11)	−1582(22)	102(10)
O(21)	3300(32)	7355(12)	2161(23)	105(10)
O(22)	1673(31)	6280(12)	3058(23)	111(11)
O(23)	−517(31)	6927(10)	207(21)	47(7)
O(31)	5585(27)	7183(9)	1024(19)	82(8)
O(32)	1811(34)	7654(12)	−1015(24)	113(11)
O(33)	4678(29)	6809(10)	−2261(20)	90(9)
O(34)	807(38)	6451(12)	−1927(26)	126(12)
O(41)	−2935(27)	6180(10)	−1829(19)	87(8)
O(42)	−1493(35)	7253(13)	−2681(25)	123(12)
O(43)	−5329(31)	6884(10)	−4551(21)	45(7)
O(51)	322(36)	5363(13)	−3732(25)	123(12)
O(52)	1945(29)	6454(10)	−4498(20)	94(9)
O(53)	−826(36)	5771(12)	−6855(27)	127(13)
O(61)	541(27)	7194(9)	−4076(19)	82(8)
O(62)	−3417(36)	7621(13)	−5869(25)	119(12)
O(63)	−616(28)	6874(9)	−7363(20)	83(8)
O(64)	−4430(33)	6425(11)	−6838(23)	110(11)
C(1)	−3030(32)	5504(12)	−4145(22)	55(8)
C(2)	1375(35)	5598(13)	1023(25)	63(9)
C(11)	4612(41)	5663(15)	1259(29)	78(12)
C(12)	5800(38)	6269(13)	691(25)	70(10)
C(13)	4165(44)	5857(17)	−767(33)	93(14)
C(21)	2789(38)	7053(14)	1758(26)	69(10)
C(22)	1852(41)	6445(15)	2305(29)	83(12)
C(23)	408(34)	6833(12)	530(23)	55(8)
C(31)	4676(34)	7050(12)	398(23)	56(8)
C(32)	2346(41)	7323(15)	−817(28)	75(11)
C(33)	4193(32)	6835(11)	−1608(22)	50(8)
C(34)	1750(50)	6591(17)	−1380(35)	101(15)
C(41)	−2862(37)	6295(13)	−2656(26)	70(10)
C(42)	−1940(45)	6937(16)	−3141(32)	90(13)
C(43)	−4379(36)	6753(13)	−4256(24)	66(10)
C(51)	−116(54)	5662(20)	−4116(39)	116(17)
C(52)	848(36)	6320(13)	−4592(24)	66(10)
C(53)	−849(61)	5859(22)	−6119(46)	146(24)
C(61)	−365(36)	7040(12)	−4647(24)	61(9)
C(63)	−1024(38)	6872(13)	−6654(26)	69(10)
C(62)	−2836(46)	7323(16)	−5751(31)	84(13)
C(64)	−3513(46)	6579(15)	−6371(31)	85(12)
C(111)	−3184(22)	5134(6)	−4691(15)	49(8)
C(112)	−3043(22)	4778(6)	−4162(15)	77(11)
C(113)	−3252(22)	4421(6)	−4684(15)	77(11)
C(114)	−3602(22)	4419(6)	−5736(15)	102(15)
C(115)	−3743(22)	4775(6)	−6265(15)	70(10)
C(116)	−3535(22)	5132(6)	−5743(15)	61(9)
C(211)	−26(18)	5465(7)	746(16)	55(8)
C(212)	−344(18)	5209(7)	1455(16)	83(12)
C(213)	−1609(18)	5032(7)	1269(16)	75(11)
C(214)	−2558(18)	5112(7)	375(16)	99(15)
C(215)	−2240(18)	5369(7)	−334(16)	96(14)
C(216)	−974(18)	5546(7)	−148(16)	61(9)
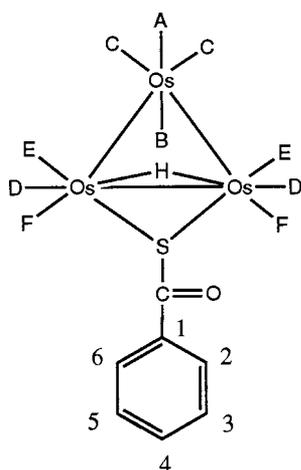
Fig. 5. Labelling scheme used for the ^{13}C-NMR assignments for $[Os_3H(CO)_{10}(C_6H_5COS)]$ (**2**). Similar schemes are used for the other complexes.

sorption corrections were based on azimuthal scans (minimum, maximum transmission 0.2797, 0.0997 and 0.0981, 0.9988 for **1** and **2**, respectively). A total of 3791 and 8008 unique data were collected for **1** and **2**, respectively.

The structures were solved by the heavy atom method after the location of the osmium atoms from the Patterson map. Refinement of the structures was carried out by a full-matrix least squares technique; the programs and computers used and sources of atomic scattering factors areas are described in ref. [8]. Systematic absences for **2** indicated that it belonged to the space group $P2_1/c$ with two molecules in the asymmetric unit. Noticeable was the fact that for **2** the data for which $h + l = 2n$ were usually strong whereas those for $h + l = 2n + 1$, were very much weaker, but nevertheless had significant intensities. For **1** the absences were consistent with two space groups, Cc and $C2/c$. The centrosymmetric space group $C2/c$ ($Z = 8$ assuming one molecule in the asymmetric unit) was chosen: subsequent refinement of the structure confirmed the correctness of the choice. In **2** the atoms of the phenyl rings were refined as a rigid groups. All non-hydrogen atoms were refined using anisotropic thermal parameters for **1** and the osmium and sulphur atoms for **2**. The remaining non-hydrogen atoms for **2** were refined using isotropic thermal parameters. Hydrogen atoms for the phenyl rings were inserted in calculated positions for **1** and **2** [C–H = 0.96 Å]. In **1** a possible site for the bridging hydride [H(12)] was identified and this was included in the computations but not refined. The oxygen atom of the phenolic OH is disordered across the *ortho* positions, and was refined with a variable site occupancy (0.7:0.3 for sites 2 and 6).

Tables of H-atom coordinates and thermal parameters and a full list of bond lengths and angles have been deposited with the Cambridge Crystallographic Centre.

Table 6
Crystallographic data[a] for $[Os_3H(CO)_{10}(C_6H_4(OH)CO_2)]$ (**1**) and $[Os_3H(CO)_{10}(C_6H_5COS)]$ (**2**)

Compound	**1**	**2**
Formula	$C_{17}H_6O_{13}Os_3$	$C_{17}H_6O_{11}Os_3S$
M	988.82	988.88
Colour	Yellow	Yellow
Crystal size (mm^3)	$0.26 \times 0.20 \times 0.06$	Fragment $0.55 \times 0.35 \times 0.05$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	28.201(7)	10.242(2)
b (Å)	10.176(2)	33.87(1)
c (Å)	15.354(3)	13.654(2)
α (°)	90	90
β (°)	99.85(2)	103.71(2)
γ (°)	90	90
U (Å^3)	4339(6)	4602(2)
Z	8	4
$D_{calc.}$ (g cm^{-3})	3.025	2.856
μ (Mo–K$_\alpha$)(cm^{-1})	175.9	166.7
$F(000)$	3512	3520
Unique data	3791	8008
Data with $I_o > 3.0\sigma(I_o)$	2656	4363
Scan range (°)	$1.10 + 0.34 \tan \theta$	$1.10 + 0.34 \tan \theta$
Aperture-horizontal (mm)	$1.80 + 0.80 \tan \theta$	$1.90 + 1.0 \tan \theta$
Aperture-vertical (mm)	4	4
θ max (°)	25	25
Parameters refined	308	275
R^{b}	0.0501	0.0691
R_w	0.0517	0.0709
k	0.6622	7.255
g	0.010718	0.0033

[a] Details in common: scan type $\omega - 2\theta$ maximum scan time per reflection 60 s; pre-scan speed 20° min^{-1}; pre-scan acceptance criterion $\sigma(I)/I < 0.66$; required $\sigma(I)/I < 0.02$; function minimised $\Sigma w(|F_o| - |F_c|)^2$ where $w = k/[\sigma^2(F) + gF^2]$.
[b] $R = [\Sigma(|(|F_o| - k|F_c|)|/\Sigma|F_o|], R_w = [\Sigma_w(|(|F_o| - k|F_c|)|)^2/\Sigma w|F_o|^2]$.

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