

# Linked triosmium cluster complexes containing thiolato–carboxylato ligands: the crystal and molecular structures of $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-SC}_6\text{H}_4\text{CO}_2)]$ and $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2)]$

Eric W. Ainscough, Andrew M. Brodie\*, Richard K. Coll, Angelika J.A. Mair, Joyce M. Waters

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

Received 7 June 1995

## Abstract

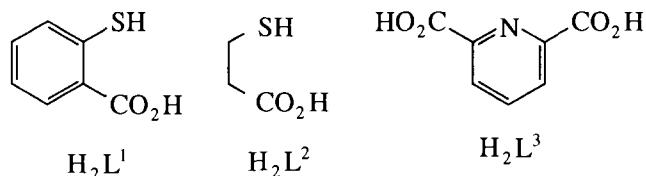
The triosmium cluster,  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ , reacts with the difunctional thiolato–carboxylate ligands, 2-mercaptobenzoic acid ( $\text{H}_2\text{L}^1$ ), 3-mercaptopropanoic acid ( $\text{H}_2\text{L}^2$ ) and 2,6-dicarboxypyridine ( $\text{H}_2\text{L}^3$ ), to form the linked clusters,  $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-L})]$  ( $\text{L} = \text{L}^1, \text{L}^2$  and  $\text{L}^3$ ). The clusters have been fully characterised by spectroscopic means and the structures of two of them,  $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-L})]$  ( $\text{L} = \text{L}^1$  and  $\text{L}^2$ ), established by single crystal X-ray analyses. In both cases the osmiums form two triangles, with the carboxylate bridging one edge of one triangle and the sulphur that of a second.

**Keywords:** Osmium cluster; Crystal structure; Bridging ligand; Thiolato; Carboxylato

## 1. Introduction

Triosmium clusters are known to undergo reaction with organosulphur compounds [1–10], but less is known about reactions with carboxylic acids or clusters formed with ligands containing several functional groups [3,4,11,12]. An important focus for current research in metal cluster compounds has been the synthesis of higher nuclearity clusters and one potential synthetic route may involve the linking of smaller clusters with bridging ligands containing several functional groups. Our work concerns the synthesis and characterisation of osmium clusters formed from the reactions of thiols and carboxylic acids and the formation of linked osmium triangular clusters using ligands which contain two functional groups. In this study we report that the ligands  $\text{H}_2\text{L}$  ( $\text{L} = \text{L}^1, \text{L}^2$  and  $\text{L}^3$ ) react readily with the lightly stabilised cluster,  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ , to form clusters formulated as  $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-L})]$ . The products have been characterised by means of infrared, hydrogen-1 NMR and mass spectroscopy as well as elemental analysis. Molecular structures for the products containing  $\text{L}^1$  (2-thiolatobenzoate dianion) and  $\text{L}^2$

(3-thiolatopropanoate dianion) have been determined by single-crystal X-ray diffraction.



## 2. Results and discussion

Analytical and spectroscopic data for the new clusters are given in Table 1. The reactions proceed under mild conditions requiring only stirring at room temperature in dichloromethane. IR spectroscopy in the metal carbonyl region shows sulphur bound triosmium clusters are formed first with the carboxylate group remaining initially uncoordinated. The reactions are rapid for the thiol moieties, being complete within 10 min; reactions with the carboxylate functions require more time (ca. 1 h) for completion. Reactions with a 1:1 molar ratio of  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  to ligand yield the

\* Corresponding author.

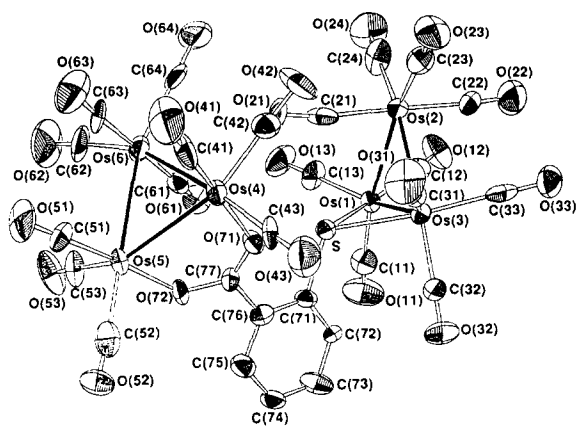


Fig. 1. ORTEP diagram of  $[\{Os_3H(CO)_{10}\}_2(\mu-L^1)]$  showing the labelling scheme used. Ellipsoids are drawn at the 20% probability level; hydrogen atoms have been omitted for clarity.

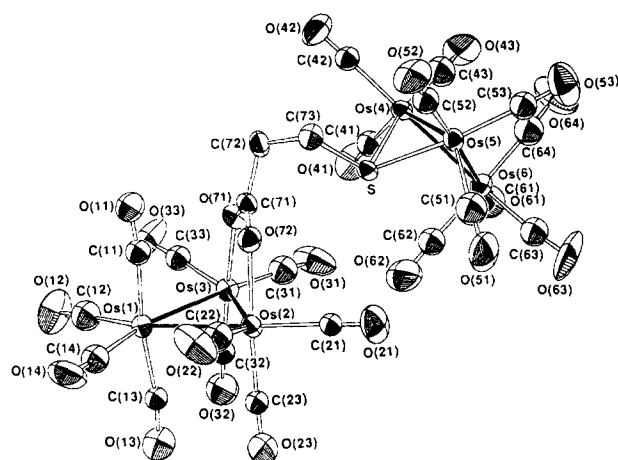


Fig. 2. ORTEP diagram of  $[\{Os_3H(CO)_{10}\}_2(\mu-L^2)]$  showing the labelling scheme used. Details as in Fig. 1.

bis(triosmium) clusters,  $[\{Os_3H(CO)_{10}\}_2(\mu-L)]$ , preferentially with unreacted ligand remaining.

As mentioned above, IR spectroscopy proved to be a useful probe for the reactions. In the metal carbonyl region ( $2200\text{--}1900\text{ cm}^{-1}$ ) of the spectra, similar patterns are seen for the osmium triangles with either thiolate or carboxylate bridges but band positions are not identical, thus giving an overall complex appearance. However, the highest energy band can be identified in each case [13] and is at  $2108\text{--}2109\text{ cm}^{-1}$  for the thiolate bridged triangles and at  $2113\text{--}2114\text{ cm}^{-1}$  for the carboxylate triangles. The hydrogen-1 NMR spectra afford ready identification of thiolate or carboxylate bridging. In addition to the expected resonances due to the ligand protons, all spectra contain resonances in the region expected for bridging hydrides [1,2,11,12]. For the thiolate bridged osmium triangles, the spectra exhibit a hydride resonance in the region near  $-17\text{ ppm}$ , whereas for carboxylates the hydride resonance appears about  $-10\text{ ppm}$ . The mass spectra of the clusters exhibit a characteristic isotope pattern due to the seven

osmium isotopes. In all instances experimental spectra closely matched simulated spectra.

In the preparation of the carboxylate clusters evidence was obtained from the proton NMR spectra for an intermediate which exhibited a resonance near  $-13\text{ ppm}$ . This resonance gradually disappeared as the reaction proceeded. These intermediates also exhibited shifts in the positions of the other resonances to higher frequencies by about  $0.2\text{ ppm}$ . We were unable to isolate any of these species, the solid products obtained always being those containing the carboxylate bridge. A more detailed study has been made of this phenomenon and the results will be reported elsewhere [14].

### 2.1. Crystal structures of $[\{Os_3H(CO)_{10}\}_2(\mu-L^1)]$ and $[\{Os_3H(CO)_{10}\}_2(\mu-L^2)]$

Crystals suitable for X-ray diffraction were obtained for both complexes by slow evaporation of chloroform solutions. The structures of the two clusters are similar

Table 1  
Analytical and spectroscopic data for the complexes

Complex	$m/z$ [ $M^+$ ( $^{192}Os$ )]	Analyses (%) <sup>b</sup>			$^1H$ NMR (ppm) <sup>c</sup>			$\nu(CO)(cm^{-1})$ <sup>d</sup>				
		C	H	N	Os–H	C–H						
$[\{Os_3H(CO)_{10}\}_2(\mu-L^1)]$	1866	17.68 (17.48)	0.36 (0.33)		–16.90 –10.10	7.88dd, 7.30t,	7.60t 7.10dd	2113w, 2069s, 1997ms,	2108w, 2024vs, 1988m,	2076ms, 2011s, 1985m		
$[\{Os_3H(CO)_{10}\}_2(\mu-L^2)]$	1819 <sup>a</sup>	15.40 (15.28)	0.35 (0.33)		–17.50 –10.50	2.47t,	2.34t	2113w, 2064s, 2021sh, 1980sh,	2109mw, 2059sh, 2009vs, 1970vw	2076vs, 2027vs, 1999m,	2067s, 2025sh, 1989ms,	
$[\{Os_3H(CO)_{10}\}_2(\mu-L^3)]$	1879	17.51 (17.36)	0.29 (0.27)	0.71 (0.75)	–9.98	7.30d,	7.20t	2114w, 2065sh, 2015s,	2104vw, 2051w, 2001m,	2076s, 2034sh, 1989m	2068s, 2027vs	

<sup>a</sup>  $MH^+$ . <sup>b</sup> Calculated values in parenthesis. <sup>c</sup> In  $CDCl_3$ . <sup>d</sup> In cyclohexane, except for the  $L^3$  complex, which is in  $CH_2Cl_2$ .

Table 2

Selected bond lengths (Å) and angles (°) for  $[(Os_3H(CO)_{10})_2(\mu-L^1)]$  with estimated standard deviations in parentheses

Os(1)–Os(2)	2.864(1)	Os(1)–S	2.429(3)
Os(1)–Os(3)	2.847(1)	Os(3)–S	2.407(3)
Os(2)–Os(3)	2.855(1)	S–C(71)	1.808(14)
Os(4)–Os(5)	2.930(1)	Os(5)–O(72)	2.108(8)
Os(4)–Os(6)	2.873(1)	O(71)–C(77)	1.250(14)
Os(5)–Os(6)	2.863(1)	O(72)–C(77)	1.292(15)
Os(4)–O(71)	2.146(7)	C(76)–C(77)	1.494(15)
Os(2)–Os(1)–Os(3)	60.0(0)	Os(2)–Os(3)–S	80.8(1)
Os(1)–Os(3)–Os(2)	60.3(0)	Os(1)–S–Os(3)	72.2(1)
Os(1)–Os(2)–Os(3)	59.7(0)	Os(3)–S–C(71)	111.2(4)
Os(1)–Os(3)–S	54.3(1)	Os(1)–S–C(71)	116.0(4)
Os(3)–Os(1)–S	53.6(1)	S–C(71)–C(76)	118.0(9)
Os(2)–Os(1)–S	80.2(1)		
Os(4)–Os(5)–Os(6)	59.5(0)	Os(4)–Os(5)–O(72)	80.4(2)
Os(5)–Os(4)–Os(6)	59.1(0)	Os(4)–O(71)–C(77)	126.0(7)
Os(5)–Os(6)–Os(4)	61.4(0)	Os(5)–O(72)–C(77)	127.8(7)
Os(6)–Os(4)–O(71)	92.8(3)	O(71)–C(77)–O(72)	124(1)
Os(6)–Os(5)–O(72)	94.5(3)	O(71)–C(77)–C(76)	120(1)
Os(5)–Os(4)–O(71)	81.0(2)	O(72)–C(77)–C(76)	116(1)

and are shown in Figs. 1 and 2. Selected bond lengths and angles are given in Tables 2 and 3. In both structures the osmiums form two triangles with the carboxylate bridging one edge of one triangle and the sulphur that of a second. The Os–Os distances [2.847(1)–2.930(1) Å] are similar to reported values [6–8,11,12,15–19] for  $\mu-O_2CR_2$  and  $\mu-S$  bridged clusters. The Os–O distances [2.075(17)–2.146(7) Å] and Os–S distances [2.402(5)–2.429(3) Å] are also similar to reported values as are the C–O distances in the carbonyls and the C–C distances within the ligands [6–8,11,12,15–23]. It is interesting to note that the Os–Os

bond lengths for the osmiums which are bridged by the sulphur atom are shorter compared with the others in the same triangle (2.847(1), 2.850(1) Å; cf. 2.851(1)–2.864(1) Å), whereas those for the carboxylate bridged osmiums are longer (2.918(1), 2.930(1) Å; cf. 2.863(1)–2.873(1) Å). This effect has been observed for carboxylate-bridged clusters in other structures but is sensitive to the presence of other ligands. There appears to be no consistent trend for thiolate-bridged clusters. The relative orientation of the triangles for the two structures has been found to differ. For the  $L^1$  complex the osmium triangles lie in a *cis* arrangement to one another whereas in the  $L^2$  complex they are *trans*. This difference may be due to packing considerations.

Table 4

Crystallographic data<sup>a</sup> for  $[(Os_3H(CO)_{10})_2(\mu-L^1)]$  and  $[(Os_3H(CO)_{10})_2(\mu-L^2)]$ 

Compound	$[(Os_3H(CO)_{10})_2(\mu-L^1)]$	$[(Os_3H(CO)_{10})_2(\mu-L^2)]$
Formula	$C_{27}H_6O_{22}Os_6S$	$C_{23}H_6O_{22}Os_6S$
<i>M</i>	1843.58	1807.55
Colour	yellow	yellow
Crystal size (mm)	0.20 × 0.18 × 0.15	0.35 × 0.20 × 0.12
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
<i>a</i> (Å)	12.885(2)	9.575(3)
<i>b</i> (Å)	16.955(3)	13.671(5)
<i>c</i> (Å)	9.209(2)	27.964(6)
$\alpha$ (°)	95.20(2)	90.00
$\beta$ (°)	106.33(1)	97.19(2)
$\gamma$ (°)	93.73(1)	90.00
<i>U</i> (Å <sup>3</sup> )	1914	3632
<i>Z</i>	2	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	3.219	3.306
$\mu$ (Mo <i>K</i> $\alpha$ ) (cm <sup>-1</sup> )	200.0	210.8
<i>F</i> (000)	1632	3167
Total data	7475	6995
Unique data	7428	5582
Data with $I_0 > 3.0\sigma(I_0)$	5430	4145
Scan range (in $\theta$ ) (°)	0.8 + 0.34 tan $\theta$	1.2 + 0.34 tan $\theta$
Aperture-horizontal (mm)	1.6 + 0.8 tan $\theta$	1.8 + 0.8 tan $\theta$
Aperture-vertical (mm)	4	4
$\theta$ range (°)	2–25	2–22.5
Parameters refined	505	371
<i>R</i> <sup>b</sup>	0.0377	0.0466
<i>R<sub>w</sub></i>	0.0440	0.0498
<i>k</i>	0.1646	2.0030
<i>g</i>	0.01499	0.001494

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

<sup>b</sup>  $R = [\sum(|F_o| - k|F_c|)/\sum|F_o|]$ ,  $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]$ .

Table 3

Selected bond lengths (Å) and angles (°) for  $[(Os_3H(CO)_{10})_2(\mu-L^2)]$  with estimated standard deviations in parentheses

Os(1)–Os(2)	2.863(1)	Os(3)–O(71)	2.075(17)
Os(1)–Os(3)	2.872(1)	O(71)–C(71)	1.268(26)
Os(2)–Os(3)	2.918(1)	O(72)–C(71)	1.265(28)
Os(2)–O(72)	2.113(18)	C(71)–C(72)	1.511(36)
Os(4)–Os(5)	2.850(1)	Os(4)–S	2.410(6)
Os(4)–Os(6)	2.851(1)	Os(5)–S	2.402(5)
Os(5)–Os(6)	2.853(1)	S–C(73)	1.833(25)
Os(1)–Os(2)–Os(3)	59.6(0)	Os(3)–Os(2)–O(72)	79.4(4)
Os(1)–Os(3)–Os(2)	59.3(0)	Os(2)–O(72)–C(71)	129(1)
Os(2)–Os(1)–Os(3)	61.2(0)	Os(3)–O(71)–C(71)	129(1)
Os(1)–Os(2)–O(72)	91.4(4)	O(71)–C(71)–O(72)	121(2)
Os(1)–Os(3)–O(71)	94.5(5)	O(71)–C(71)–C(72)	119(2)
Os(2)–Os(3)–O(71)	80.9(4)	O(72)–C(71)–C(72)	120(2)
Os(4)–Os(5)–Os(6)	60.0(0)	Os(6)–Os(5)–S	81.2(1)
Os(5)–Os(4)–Os(6)	60.1(0)	Os(4)–S–Os(5)	72.6(2)
Os(5)–Os(6)–Os(4)	59.9(0)	Os(4)–S–C(73)	110.4(9)
Os(4)–Os(5)–S	53.8(1)	Os(5)–S–C(73)	109.0(8)
Os(5)–Os(4)–S	53.6(1)	S–C(73)–C(72)	107(1)
Os(6)–Os(4)–S	81.2(1)		

Table 5  
Atom coordinates ( $\times 10^4$ ) for  $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu - \text{L}^1)]$

Atom	x	y	z
Os(1)	7561.3(4)	2167.4(3)	5825.7(6)
Os(2)	8288.2(4)	3731.0(3)	7386.3(6)
Os(3)	8716.4(4)	3277.1(3)	4564.4(5)
Os(4)	3240.3(4)	3075.5(3)	8352.0(6)
Os(5)	4026.9(4)	1504.5(3)	8767.5(6)
Os(6)	3127.3(4)	2292.6(4)	10950.2(6)
S	9473(2)	2212(2)	5951(3)
O(11)	6589(11)	657(8)	3738(18)
O(12)	5316(9)	2604(7)	5793(16)
O(13)	7855(12)	1394(8)	8739(14)
O(21)	10253(8)	3020(7)	9394(11)
O(22)	6235(11)	4413(8)	5577(15)
O(23)	9678(9)	5349(6)	8162(15)
O(24)	7279(14)	3677(10)	9989(17)
O(31)	836(9)	4303(7)	5491(16)
O(32)	9036(10)	2625(7)	1548(13)
O(33)	7347(9)	4530(6)	3049(13)
O(41)	5197(10)	4149(7)	10182(17)
O(42)	1865(11)	4332(6)	9222(16)
O(43)	3486(11)	3815(7)	5537(15)
O(51)	6294(8)	1943(8)	10971(15)
O(52)	5132(8)	764(6)	6465(13)
O(53)	3744(10)	-11(7)	10146(18)
O(61)	955(9)	1379(6)	9122(13)
O(62)	3493(16)	1061(10)	13226(19)
O(63)	5335(11)	3191(9)	12711(16)
O(64)	1976(14)	3484(11)	12468(16)
O(71)	1851(7)	2354(5)	6868(10)
O(72)	2508(7)	1165(5)	7145(11)
C(11)	7014(11)	1204(9)	4516(19)
C(12)	6117(13)	2443(9)	5765(19)
C(13)	7768(13)	1699(10)	7643(18)
C(21)	9576(11)	3269(9)	8540(17)
C(22)	6978(13)	4146(9)	6192(15)
C(23)	9102(12)	4761(8)	7878(18)
C(24)	7691(11)	3711(11)	9069(21)
C(31)	10047(12)	3956(8)	5131(18)
C(32)	8909(11)	2869(7)	2647(15)
C(33)	7851(12)	4076(8)	3607(14)
C(41)	4462(10)	3709(8)	9487(21)
C(42)	2368(11)	3830(8)	8918(17)
C(43)	3322(13)	3498(9)	6572(17)
C(51)	5441(12)	1793(9)	10107(15)
C(52)	4694(12)	1026(9)	7228(20)
C(53)	3854(11)	545(9)	9648(20)
C(61)	1741(12)	1715(8)	9718(16)
C(62)	3352(14)	1539(12)	12395(19)
C(63)	4530(13)	2842(11)	12001(19)
C(64)	2420(14)	3073(12)	11850(17)
C(71)	-163(10)	1454(7)	4722(15)
C(72)	-865(10)	1104(7)	3367(13)
C(73)	-593(13)	522(8)	2462(20)
C(74)	422(11)	266(9)	2921(17)
C(75)	1205(14)	604(9)	4300(18)
C(76)	903(10)	1234(8)	5157(15)
C(77)	1791(10)	1620(7)	6502(14)

Mass spectra were recorded by the liquid secondary ion mass spectroscopy (LSIMS) technique using a Varian VG70-250S mass spectrometer from samples in a *m*-nitrobenzyl alcohol matrix. Hydrogen-1 NMR spectra were recorded on a JEOL GX270 spectrometer. Elemental analyses were determined at the Campbell Mi-

Table 6  
Atom coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\times 10^3$ ) for  $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu - \text{L}^2)]$

Atom	x	y	z	U
Os(1)	255.7(9)	3955.4(8)	1092.2(4)	
Os(2)	-2416.8(9)	3135.7(7)	1228.6(4)	
Os(3)	-625.7(9)	2174.1(8)	599.8(4)	
Os(4)	-2661.8(9)	-1849.9(7)	1515.5(4)	
Os(5)	-4792.1(9)	-1064.2(8)	2030.2(4)	
Os(6)	-5456.0(10)	-1609.3(8)	1043.0(4)	
S	-2995(5)	-151(4)	1700(2)	
O(11)	1602(19)	2686(16)	1914(7)	
O(12)	3088(19)	4216(22)	708(10)	
O(13)	-1264(19)	5221(17)	289(7)	
O(14)	347(28)	5791(16)	1753(10)	
O(21)	-5242(20)	2198(17)	1352(9)	
O(22)	-2301(25)	4535(17)	2079(7)	
O(23)	-3939(21)	4535(17)	507(10)	
O(31)	-1756(33)	343(19)	52(10)	
O(32)	-1308(25)	3294(18)	-340(9)	
O(33)	2460(21)	1856(27)	452(10)	
O(41)	-1443(23)	-1535(24)	556(7)	
O(42)	154(21)	-2015(18)	2124(10)	
O(43)	-2902(31)	-4019(18)	1274(14)	
O(51)	-6993(20)	562(19)	1873(11)	
O(52)	-3857(21)	-569(19)	3080(7)	
O(53)	-6749(23)	-2632(20)	2338(10)	
O(61)	-5192(29)	-2494(22)	71(9)	
O(62)	-4689(25)	405(20)	641(10)	
O(63)	-8548(20)	-1051(27)	971(12)	
O(64)	-6123(33)	-3684(20)	1391(10)	
O(71)	-183(15)	1299(12)	1206(6)	
O(72)	-1444(15)	2060(13)	1701(6)	
C(11)	1009(24)	3138(20)	1613(10)	39(6)
C(12)	2086(32)	4094(25)	849(12)	61(8)
C(13)	-752(22)	4681(19)	585(9)	34(5)
C(14)	321(25)	5127(22)	1475(10)	45(6)
C(21)	-4234(21)	2521(18)	1311(8)	30(5)
C(22)	-2351(26)	3999(22)	1768(11)	48(7)
C(23)	-3331(22)	4015(19)	789(9)	34(5)
C(31)	-1340(32)	1041(26)	290(13)	61(8)
C(32)	-1057(24)	2886(20)	41(10)	41(6)
C(33)	1270(26)	1959(21)	510(10)	47(7)
C(41)	-1865(27)	-1608(22)	923(11)	48(7)
C(42)	-884(25)	-1930(20)	1931(10)	40(6)
C(43)	-2831(32)	-3213(28)	1356(13)	69(9)
C(51)	-6162(31)	-54(26)	1923(12)	60(8)
C(52)	-4143(25)	-732(21)	2692(11)	43(6)
C(53)	-6040(26)	-2055(22)	2212(10)	47(7)
C(61)	-5296(27)	-2102(23)	397(12)	49(7)
C(62)	-4940(28)	-320(25)	804(11)	52(7)
C(63)	-7407(29)	-1225(24)	981(11)	54(8)
C(64)	-5920(30)	-2841(27)	1292(12)	65(9)
C(71)	-680(22)	1349(17)	1605(8)	
C(72)	-348(23)	537(19)	1968(10)	
C(73)	-1672(22)	247(20)	2193(9)	

### 3. Experimental

Infrared spectra were recorded in solutions using 0.5 nm NaCl cells on a BIO-RAD FTS-40 spectrometer.

croanalytical Laboratory, University of Otago. All solvents were dried by distillation over calcium hydride and all reactions, but not work up, carried out under an atmosphere of dry dioxygen-free dinitrogen. The cluster,  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ , was prepared by the literature method [24] and the ligands were obtained commercially from Aldrich Chemical Co. and used without further purification. The reaction products were purified by TLC using plates coated with 2 mm of Merck Kieselgel 60 PF<sub>254</sub> and elution with hexane–dichloromethane mixtures.

### 3.1. Syntheses

$[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-L})]$  ( $\text{L} = \text{L}^1, \text{L}^2$  and  $\text{L}^3$ ). The cluster  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  (40 mg, 42.8  $\mu\text{mol}$ ) was stirred with 0.5 molar equivalent of the ligand in dichloromethane (20  $\text{cm}^3$ ) at room temperature for 1 h. The solvent was removed under reduced pressure and the products were purified by TLC to yield yellow microcrystals; yields were in the range 60–70%.

### 3.2. Molecular structure determination of $\{\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-L}^1)\}$ and $\{\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\mu\text{-L}^2)\}$

Crystals suitable for X-ray work were obtained by the slow evaporation of chloroform solutions. The crystal data, data collection and structure solution details are given in Table 4. The unit cell parameters were determined by the least-squares refinement of 25 accurately centred reflections in the shell  $15 < \theta < 18^\circ$  for the  $\text{L}^1$  cluster and  $15 < \theta < 20^\circ$  for the  $\text{L}^2$  cluster.

### 3.3. Data collection and processing

The data were collected at room temperature using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K  $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) in the  $\omega/2\theta$  mode with  $2 < \theta < 25^\circ$  for the  $\text{L}^1$  cluster and  $2 < \theta < 22.5^\circ$  for the  $\text{L}^2$  cluster. Reflection intensities were corrected for the effects of Lorentz and polarisation effects and the crystal stability was monitored two-hourly by observation of three standard reflections (decay of 4.3% and 11.4% for the  $\text{L}^1$  and  $\text{L}^2$  clusters respectively). Empirical absorption corrections were made based on azimuthal scans (R merging 0.04, 0.039; minimum, maximum transmission 0.12, 0.45 and 0.14, 0.66 for the  $\text{L}^1$  and  $\text{L}^2$  clusters respectively).

### 3.4. Structure solution and refinement

The structures were solved by the heavy atom method after location of the osmium atoms from the Patterson map. Refinement of the structures was carried out by

the full-matrix least-squares technique. All atoms were refined assuming anisotropic thermal motion for the  $\text{L}^1$  cluster and all Os, S, O and the three non-phenyl ligand C atoms for the  $\text{L}^2$  cluster. The remaining atoms were assigned isotropic thermal parameters. For the  $\text{L}^1$  cluster hydrogen atoms for the ligand were added in calculated positions ( $\text{C-H} = 0.96 \text{ \AA}$ ) and refined riding on their corresponding carbons; a single fixed thermal parameter (0.1) was used. Atomic coordinates are given in Tables 5 and 6. Programs and computers used, and sources of scattering factor data are given in Ref. [13].

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

### Acknowledgements

The authors acknowledge the New Zealand Lottery Grants Board for the provision of funding towards equipment and chemicals and to Massey University for the award of Post-Doctoral Fellowships (to R.K.C and A.J.A.M). We thank Mr J. Allen, Horticultural and Food Research Institute of New Zealand Ltd., for the measurement of mass spectra.

### References

- [1] K. Burgess, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, 233 (1982) C55.
- [2] A.M. Brodie, H.D. Holden, J. Lewis and M.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1986) 633.
- [3] D.F. Shriver, H.D. Kaesz and R.D. Adams (eds.), *The Chemistry of Metal Cluster Complexes*, VCH Publishers Ltd, New York, 1990.
- [4] K. Burgess, *Polyhedron*, 3 (1984) 1175.
- [5] R.D. Adams, D.F. Foust and B.E. Segmüller, *Organometallics*, 2 (1983) 308.
- [6] R.D. Adams, N.M. Golembeski and J.P. Selegue, *J. Am. Chem. Soc.*, 103 (1981) 546.
- [7] R.D. Adams, Z. Dawoodi, D.F. Foust and B.E. Segmüller, *Organometallics*, 2 (1983) 315.
- [8] H.D. Holden, B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Uden, *Acta Crystallogr. Sect.C*, 39 (1983) 1197.
- [9] R.D. Adams, I.T. Horváth and Hoon-Sik Kim, *Organometallics*, 3 (1984) 548.
- [10] A.J. Arce, J. Manzur, M. Marquez, Y. De Sanctis and A.J. Deeming, *J. Organomet. Chem.*, 412 (1991) 177.
- [11] J.R. Shapley, G.M. St. George, M.R. Churchill and F.J. Hollander, *Inorg. Chem.*, 21 (1982) 3295.
- [12] B.F.G. Johnson, J. Lewis, P.R. Raithby, V.P. Saharan and W.T. Wong, *J. Chem. Soc., Chem. Commun.* (1991) 365.
- [13] E.W. Ainscough, A.M. Brodie, R.K. Coll, T.G. Kotch, A.J. Lees, A.J.A. Mair and J.M. Waters, *J. Organomet. Chem.*, submitted for publication.
- [14] E.W. Ainscough, A.M. Brodie, B.A. Coombridge and J.M. Waters, unpublished results.
- [15] E.W. Ainscough, A.M. Brodie, S.L. Ingham, T.G. Kotch, A.J.

- Lees, J. Lewis and J.M. Waters, *J. Chem. Soc., Dalton Trans.*, (1994) 1.
- [16] R.D. Adams, D.A. Katahira and L.W. Yang, *Organometallics*, *1* (1982) 235.
- [17] V.F. Allen, R. Mason, and P.B. Hitchcock *J. Organomet. Chem.*, *140* (1977) 297.
- [18] H.D. Holden, B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Uden, *Acta Crystallogr. Sect. C*, *39* (1983) 1200, 1203.
- [19] R.D. Adams and Z. Dawoodi, *J. Am. Chem. Soc.*, *103* (1981) 6510.
- [20] M.R. Churchill and B.G. DeBoer, *Inorg. Chem.*, *16* (1977) 878.
- [21] M.R. Churchill and H.J. Wasserman, *Inorg. Chem.*, *19* (1980) 2391.
- [22] K. Burgess, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Chem. Soc. Dalton Trans.* (1982) 2085.
- [23] C.H. MacGillivray and G.D. Rieck (eds.), *International Tables for X-ray Crystallography*, Vol. 3, Kynock Press, Birmingham, 1962.
- [24] S.R. Drake and R. Khattar, *Organometallic Synthesis*, *4* (1988) 234.