ELSEVIER

Journal of Organometallic Chemistry 494 (1995) 273-278

Journal of Organometallic Chemistry

Synthesis and characterization of triosmium clusters containing the 2-(benzylthio)benzoyl ligand

Siu-Ming Lee, Kung-Kai Cheung, Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Received 3 January 1995

Abstract

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with an equimolar proportion of 2-(benzylthio)-benzaldehyde (**1**) gives three new compounds: two yellow isomers of $[Os_3(CO)_{10}(\mu\text{-H})(C_{14}H_{11}OS)]$ (**2a** and **2b**) and an orange crystalline compound $[Os_3(CO)_9(\mu\text{-H})(C_{14}H_{11}OS)]$ (**3**). The molecular structures of **2b** and **3** are presented. Two different kinds of bonding mode of the ligand were observed, bidentate through S and C(O) in **2** and terdentate through S, C(O) and O in **3**.

Keywords: Osmium; Cluster; Carbonyl; Acyl; Crystal structure

1. Introduction

The chemistry of triosmium clusters is dominated by species containing soft donor atoms such as sulphur and phosphorus [1]. However, clusters containing hard oxygen atom ligands are of interest since they are important in the study of chemical activation of CO on cluster surfaces.

It has been shown that $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ react with aldehydes and ketones to give acyl clusters of the type $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-RCO})]$ via the cleavage of the C–H bond and coordination to the metal via the lone pair of oxygen [2]. However, examples of the clusters involving both sulphur and oxygen donor atoms in the same ligand are relatively rare [3]. We report here the synthesis of new triosmium clusters derived from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-(benzylthio)benzaldehyde (**1**). There are two possible reaction sites in this ligand: the CHO group and the sulphur atom. We decided to investigate the coordination modes involving the hard and soft donor atoms in triosmium clusters when both are present.

2. Results and discussion

The reaction of 2-(benzylthio)benzaldehyde (**1**) with an equimolar amount of $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing chloroform afforded a mixture of products (Scheme 1). Separation by preparative thin layer chromatography (TLC), gave $[Os_3(CO)_{12}]$ (3%; $R_f \approx 0.9$), two yellow isomers of $[Os_3(CO)_{10}(\mu\text{-H})(C_{14}H_{11}OS)]$ (**2a** (30%; $R_f \approx 0.5$), and **2b** (10%; $R_f \approx 0.1$)) an orange crystalline compound $[Os_3(CO)_9(\mu\text{-H})(C_{14}H_{11}OS)]$ (**3** (25%; $R_f \approx 0.4$)) and two other unidentified products (each less than 5%).

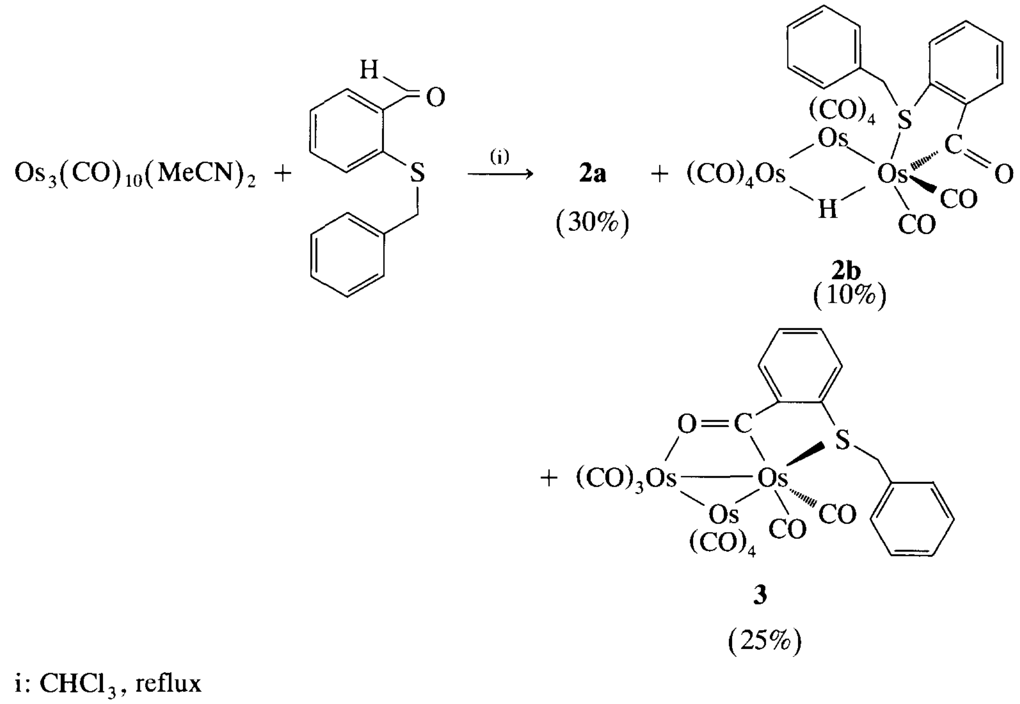
The complexes were characterized by the usual spectroscopic methods (Table 1). The IR spectra in the carbonyl region for all the complexes show signals due to terminal carbonyl ligands. The ^1H NMR spectra recorded at ambient temperature, show the phenyl protons as a multiplet centred at $\delta = 7.50$ ppm. The methylene protons of **2a** and **2b**, unlike that of **1** which gave a singlet at $\delta = 4.10$ ppm gave an AB quartet centred at $\delta = 4.50$ ppm, while those of **3** gave two doublets at $\delta = 4.15$ and 5.2 (J = 12 Hz) ppm due to *gem* coupling of the CH_2 group. The Os–H resonances of **2a**, **2b** and **3** appear at $\delta = -18.86$, -18.82 and -15.83 ppm respectively.

For **2b** and **3**, single-crystal X-ray diffraction studies were undertaken. Suitable crystals were obtained by slow evaporation of a CH_2Cl_2/n-hexane solution at

---

* Corresponding author.

SSDI 0022-328X(95)05430-8



Scheme 1. The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-(benzylthio)benzaldehyde (**1**).

room temperature for 2 days. Attempts to obtain suitable crystals of **2a** were unsuccessful since the complex decomposed slowly in the solution even at −20°C, as was evident from the IR spectra. However, the fast atom bombardment (FAB) mass spectra of **2a** and **2b**, both gave a molecular peak at $m/z = 1080$, indicating that they are isomers. The molecular structures of **2b** and **3** together with the atomic labelling schemes, are shown in Figs. 1 and 2 respectively. Selected bond lengths and angles are presented in Tables 2 and 3, and the atomic coordinates in Tables 4 and 5.

The structure of **2b** consists of a triosmium framework with the sulphur and the carbonyl carbon atom of the ligand bonded to the same osmium atom, Os(1), in axial and equatorial positions respectively to form a five-membered metallocycle. Similar bonding was observed in $[Os_3H(CO)_{10}(RC{=}CHCO)]$ (R = Me or Ph) and $[Os_3H(CO)_{10}(RC{=}CHCOMe)]$ (R = Me or Ph) [2d,2e]. It is of interest that **2b** contains a non-coordinated oxygen atom, in contrast with previous observations [2] of μ_2-η^2 bonding. The carbonyl C–O distance (1.24(1) Å) is significantly longer than that in the free ligand (1.205(3) Å) [4], probably owing to weakening of the π character in the C=O bond upon coordination of the carbon atom to the metal. This coordination mode is relatively rare in the coordination of acyl ligands to metal atoms in transition metal clusters.

The bridging hydride, which shows up in the ^{1}H

Table 1
Spectroscopic data for **2a**, **2b** and **3**

Compound	IR(ν_{CO}) [a] (cm^{-1})	IR(ν_{CO}) [b] (cm^{-1})	^{1}H NMR [c] δ (ppm)	FAB mass spec [d]
2a	2108m, 2068s, 2058s, 2015s		7.50 (m, 9H, Ar–H), 4.55 (dd, 2H, J = 12 Hz, CH_2), −18.82 (s, 1H, Os–H)	1080 (1080)
2b	2017s, 2090sh, 2071vs, 2043vs, 2024vs, 2008vs, 1988vs, 1942s	1602	7.70 (m, 9H, Ar–H), 4.50 (dd, 2H, J = 12 Hz, CH_2), −18.86 (s, 1H, Os–H)	1081 (1080)
3	2093m, 2053s, 2015s, 1994s, 1972m, 1948m	1463	7.50 (m, 9H, Ar–H), 5.20 (d, 1H, J = 12 Hz), 4.15 (d, 1H, J = 12 Hz), −15.83 (s, 1H, Os–H)	1050 (1050)

[a] Recorded in CH_2Cl_2.
[b] KBr disc.
[c] Recorded in CD_2Cl_2.
[d] Based on ^{192}Os (calculated values given in parentheses).

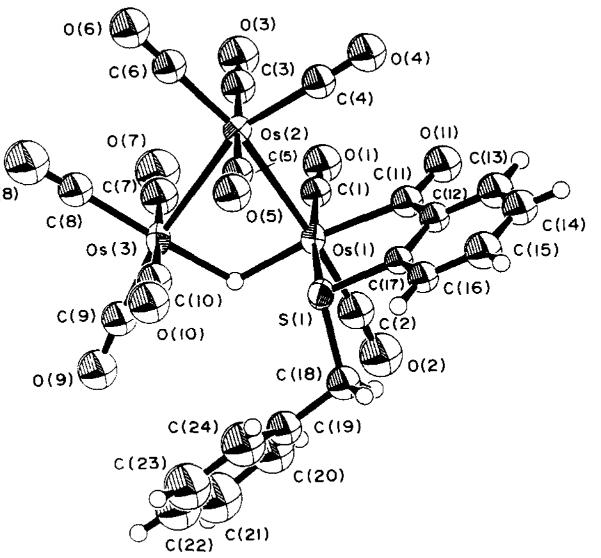


Fig. 1. The molecular structure of $[Os_3(CO)_{10}(\mu\text{-}H)(C_{14}H_{11}OS)]$ (**2b**).

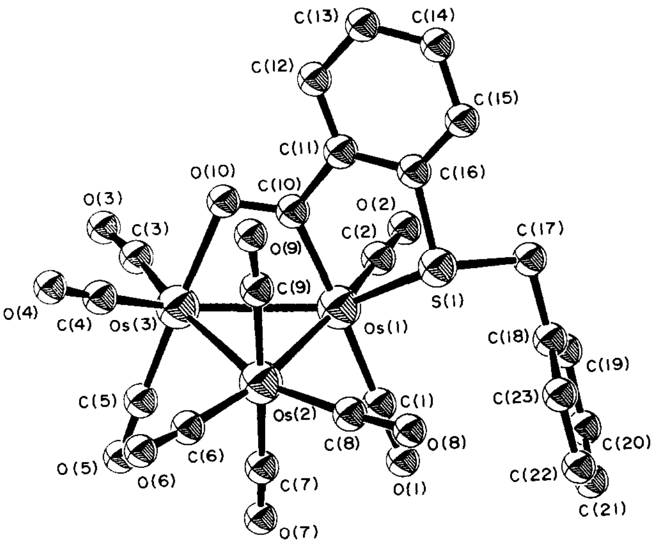


Fig. 2. The molecular structure of $[Os_3(CO)_9(\mu\text{-}H)(C_{14}H_{11}OS)]$ (**3**).

Table 2
Selected bond distances (Å) and bond angles (°) for $[Os_3(CO)_{10}(\mu\text{-}H)(C_{14}H_{11}OS)]$ (**2b**)

Bond distances			
Os(1)–Os(2)	2.906(1)	Os(1)–Os(3)	3.071(1)
Os(2)–Os(3)	2.924(1)	Os(1)–C(11)	2.06(2)
Os(1)–S(1)	2.416(6)	C(11)–O(11)	1.24(2)
C(11)–C(12)	1.50(3)	S(1)–C(17)	1.79(2)
S(1)–C(18)	1.81(2)		
Bond angles			
Os(1)–Os(2)–Os(3)	63.52(3)	Os(1)–S(1)–C(17)	100.2(7)
Os(1)–S(1)–C(18)	113.9(8)	Os(1)–C(11)–O(11)	126(1)
Os(1)–C(11)–C(12)	118(1)	S(1)–C(18)–C(19)	113(1)
S(1)–C(17)–C(12)	117(1)	C(11)–C(12)–C(17)	120(1)

Table 3
Selected bond distances (Å) and bond angles (°) for $[Os_3(CO)_9(\mu\text{-}H)(C_{14}H_{11}OS)]$ (**3**)

Os(1)–Os(2)	2.8906(6)	Os(1)–Os(3)	2.8970(6)
Os(2)–Os(3)	2.8460(7)	Os(1)–S(1)	2.364(3)
Os(1)–C(10)	2.03(1)	Os(3)–O(10)	2.149(8)
C(10)–O(10)	1.26(1)	C(10)–C(11)	1.47(2)
S(1)–C(16)	1.79(1)	S(1)–C(17)	1.84(1)
Os(1)–Os(2)–Os(3)	60.66(2)	Os(2)–Os(1)–Os(3)	58.91(2)
Os(1)–Os(3)–Os(2)	60.43(2)	Os(1)–S(1)–C(16)	100.6(4)
Os(1)–S(1)–C(17)	112.7(4)	Os(1)–C(10)–O(10)	121.5(8)
Os(1)–C(10)–C(11)	120.8(8)	Os(1)–Os(3)–C(3)	113.1(4)
Os(1)–Os(2)–C(8)	92.0(4)	Os(3)–O(10)–C(10)	104.7(6)
Os(3)–Os(1)–C(2)	113.7(4)	S(1)–C(16)–C(11)	115.2(8)
S(1)–C(17)–C(18)	107.7(9)	C(10)–C(11)–C(16)	117.0(10)

Table 4
Final atomic coordinates and isotropic displacement coefficients B_{eq} for $[Os_3(CO)_{10}(\mu\text{-}H)(C_{14}H_{11}OS)]$ (**2b**)

Atom	x	y	z	B_{eq} (Å^2)
Os(1)	0.59038(5)	0.11175(3)	0.62018(7)	2.60(2)
Os(2)	0.64084(5)	0.21982(3)	0.62086(6)	2.59(2)
Os(3)	0.76059(5)	0.14461(3)	0.69697(6)	2.74(2)
S(1)	0.6421(3)	0.1028(2)	0.4468(4)	3.1(1)
O(1)	0.5035(10)	0.1239(6)	0.824(1)	4.8(4)
O(2)	0.546(1)	−0.0024(7)	0.639(1)	6.0(4)
O(3)	0.563(1)	0.2314(7)	0.833(1)	5.5(4)
O(4)	0.4767(10)	0.2564(6)	0.534(1)	4.8(4)
O(5)	0.7217(10)	0.2173(6)	0.407(1)	4.7(4)
O(6)	0.725(1)	0.3235(7)	0.662(1)	5.2(4)
O(7)	0.685(1)	0.1516(7)	0.914(2)	6.5(5)
O(8)	0.876(1)	0.2323(7)	0.760(2)	6.6(5)
O(9)	0.8684(10)	0.0521(6)	0.754(1)	5.0(4)
O(10)	0.845(1)	0.1434(7)	0.484(1)	5.4(4)
O(11)	0.4134(10)	0.1351(6)	0.588(1)	4.6(4)
C(1)	0.540(1)	0.1197(8)	0.748(2)	3.0(4)
C(2)	0.563(1)	0.0417(10)	0.627(2)	4.4(5)
C(3)	0.593(1)	0.2247(9)	0.756(2)	3.8(5)
C(4)	0.539(1)	0.2433(9)	0.562(2)	3.6(5)
C(5)	0.689(1)	0.2152(8)	0.485(2)	3.1(4)
C(6)	0.695(1)	0.2850(9)	0.645(2)	3.7(5)
C(7)	0.712(1)	0.1491(10)	0.830(2)	4.5(5)
C(8)	0.833(1)	0.2010(9)	0.736(2)	3.9(5)
C(9)	0.828(1)	0.0875(9)	0.739(2)	3.9(5)
C(10)	0.813(1)	0.1427(9)	0.560(2)	3.9(5)
C(11)	0.480(1)	0.1258(8)	0.547(2)	3.3(4)
C(12)	0.480(1)	0.1291(8)	0.431(2)	2.9(4)
C(13)	0.410(1)	0.1424(9)	0.374(2)	4.2(5)
C(14)	0.411(1)	0.1438(9)	0.268(2)	4.1(5)
C(15)	0.483(1)	0.1325(9)	0.220(2)	4.5(5)
C(16)	0.554(1)	0.1212(8)	0.268(2)	3.1(4)
C(17)	0.552(1)	0.1194(7)	0.375(1)	2.6(4)
C(18)	0.656(1)	0.0363(9)	0.406(2)	3.7(5)
C(19)	0.736(1)	0.0135(9)	0.438(2)	3.9(5)
C(20)	0.740(2)	−0.019(1)	0.522(2)	6.2(7)
C(21)	0.819(2)	−0.042(1)	0.546(3)	8.4(9)
C(22)	0.882(2)	−0.026(1)	0.492(3)	6.9(7)
C(23)	0.882(2)	0.004(1)	0.411(3)	7.1(8)
C(24)	0.806(2)	0.026(1)	0.380(2)	6.5(7)

$B_{eq} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 5
Final atomic coordinates and isotropic displacement coefficients B_{eq} for $[Os_3(CO)_9(\mu\text{-}H)(C_{14}H_{11}OS)]$ (**3**)

Atom	x	y	z	B_{eq} (Å^2)
Os(1)	0.86033(5)	0.33366(4)	0.25337(4)	2.39(1)
Os(2)	0.67640(6)	0.12001(4)	0.31232(4)	3.28(1)
Os(3)	1.01837(6)	0.21542(4)	0.37640(4)	2.77(1)
S(1)	0.6784(4)	0.2783(3)	0.0818(2)	3.05(7)
O(1)	0.716(1)	0.4788(8)	0.3970(8)	4.6(2)
O(2)	1.086(1)	0.5563(9)	0.2093(8)	5.3(2)
O(3)	1.385(1)	0.339(1)	0.4396(9)	6.7(3)
O(4)	0.999(1)	−0.033(1)	0.3825(10)	7.3(3)
O(5)	1.004(1)	0.2781(8)	0.6114(8)	4.5(2)
O(6)	0.572(2)	−0.093(1)	0.411(1)	8.9(3)
O(7)	0.695(1)	0.2947(9)	0.5238(8)	5.3(2)
O(8)	0.362(1)	0.128(1)	0.1981(10)	7.0(3)
O(9)	0.701(1)	−0.0432(10)	0.1091(9)	6.3(2)
O(10)	1.0269(9)	0.1760(7)	0.2083(6)	3.1(2)
C(1)	0.768(1)	0.423(1)	0.3442(9)	2.8(2)
C(2)	1.001(1)	0.470(1)	0.2274(10)	3.1(2)
C(3)	1.246(2)	0.295(1)	0.415(1)	4.5(3)
C(4)	1.011(2)	0.065(1)	0.383(1)	4.8(3)
C(5)	1.008(1)	0.253(1)	0.523(1)	3.3(2)
C(6)	0.612(2)	−0.009(1)	0.375(1)	5.6(3)
C(7)	0.689(1)	0.232(1)	0.444(1)	3.4(2)
C(8)	0.478(2)	0.122(1)	0.244(1)	4.8(3)
C(9)	0.692(2)	0.021(1)	0.183(1)	4.2(3)
C(10)	0.947(1)	0.2271(9)	0.1641(9)	2.3(2)
C(11)	0.914(1)	0.204(1)	0.0446(9)	3.0(2)
C(12)	0.994(1)	0.156(1)	−0.020(1)	3.5(2)
C(13)	0.958(2)	0.139(1)	−0.132(1)	4.7(3)
C(14)	0.839(2)	0.168(1)	−0.180(1)	4.0(3)
C(15)	0.751(2)	0.212(1)	−0.118(1)	3.9(3)
C(16)	0.789(1)	0.2308(10)	−0.0063(9)	2.7(2)
C(17)	0.668(2)	0.409(1)	0.037(1)	4.1(3)
C(18)	0.600(2)	0.475(1)	0.116(1)	3.8(3)
C(19)	0.688(2)	0.596(1)	0.167(1)	4.4(3)
C(20)	0.622(2)	0.652(1)	0.242(1)	5.2(3)
C(21)	0.477(2)	0.592(1)	0.258(1)	5.4(3)
C(22)	0.391(2)	0.473(1)	0.202(1)	5.6(3)
C(23)	0.447(2)	0.413(1)	0.129(1)	4.4(3)

$B_{eq} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

NMR spectrum, could not be located by X-ray diffraction. However, potential energy calculations [5] suggest that it bridges Os(1)–Os(3). The presence of μ_2-hydride elongates the Os(2)–Os(3) bond to 3.071(1) Å. For the other two edges, Os(1)–Os(2) (2.906(1) Å) and Os(2)–Os(3) (2.924(1) Å) are significantly longer than the average Os–Os distance (2.877 Å) in $[Os_3(CO)_{12}]$ [6]. The Os–H–Os in **2b** can be described as a three-centre two-electron bond, which is common in the bimetallic transition metal complexes (see for example [7]), but there are not many examples in triosmium clusters [3b,8]. The cluster valence electrons in **2b** is 48 in accord with the EAN rule.

Complex **3** also has a triosmium framework, but with nine terminally bonded carbonyl ligands. In contrast with **2b**, the lone pair of oxygen atoms bonded to Os(2) forms a μ_2-η^2 acyl bridge on the Os(1)–Os(2) edge. The C–O separation is longer than that in **2b**, indicating that there is a further weakening of the π bonding. This is also reflected in the decrease in ν(C=O) of aldehyde from 1694 cm^{-1} in **1** to 1602 cm^{-1} in **2b** and further to 1463 cm^{-1} in **3** (Table 1); a similar bonding picture has been observed for $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}RCO)]$ (R = Me, Ph or CH_2 Ph) [2a]. A five-membered metallocycle, like that in **2b**, is again formed by coordination of sulphur and carbonyl carbon to Os(1). The bond distance Os(2)–Os(3) is 2.8460(7) Å, which is shorter than the mean Os–Os distance in the parent binary compound $[Os_3(CO)_{12}]$ [6] and than the other two Os–Os bonds, but the bond lengths of Os(1)–Os(2) and Os(1)–Os(3) are very similar (2.8906(6) Å and 2.8970(6) Å respectively) and so the location of the hydride can be deduced by considering the angle between equatorial substituents among the triosmium cluster. By comparing the *cis*-Os–Os–CO angle, the average angle of the Os(1)–Os(3)–C(3) and Os(3)–Os(1)–C(2) angles is 113.4(4)° while the Os(1)–Os(2)–C(8) angle is 92.0(4)°. Since the Os(1)–Os(2)–C(3) angle is larger than the *cis*-Os–Os–CO angle in $[Os_3(CO)_{12}]$ (average, 98.2°) [6], indicating that the equatorial CO of the Os(1)–Os(3) edge is pushed back, we conclude that the hydride resides on the Os(1)–Os(3) edge.

The differences between the chemical shifts of the methylene proton in **2b** and **3** in ^{1}H NMR spectra may be related to the difference between the Os–S separation and S–CH_2 distance. In **3**, the Os–S and S–CH_2 distances are shorter than those in **2b** (see Tables 2 and 3), so that the electron-withdrawing effect is more pronounced in **3** and a lower field signal is observed. It is note worthy that in **3** the sulphur atom lies on an equatorial position of Os(1) and *trans* to an Os–Os bond while in **2b** the sulphur atom lies on an axial position which is *trans* to a CO ligand; the *trans* influence on the sulphur donor is higher in **2b** than in **3** and so a longer Os–S separation is observed. The Os–S distance in **3** is comparable with that in $[Os_3(CO)_{11}\text{-}\{S(CH_2)_3\}]$ in which the sulphur atom is again bonded in an equatorial position of Os (Os–S, 2.375(5) Å) [9].

The dihedral angle between the two phenyl rings in **1** is 101.7(1)° [4]. In **3**, the corresponding angle is 102.3(1)°, which is not significantly different. However, the dihedral angle between the two phenyl rings in **2b** is only 35.1(1)°. The dihedral angle between the osmium triangle and the five-membered metallocycle will be close to 90° since S and C occupy axial and equatorial positions respectively. In **2b**, the dihedral angle is 89.6(1)° but in **3** it is larger (dihedral angle, 95.9(1)°). The deviation may be due to coordination of oxygen to Os(3), leading to distortion of the planes.

3. Experimental details

3.1. Materials and general procedures

Unless otherwise stated, chemicals were obtained commercially and used as received. Solvents were purified before use and dried over appropriate reagents. Standard Schlenk-type techniques were used and all reactions were carried out under dinitrogen. Product separation by the TLC were carried out in air on silica (Merck Kieselgel 60 GF_{254}), prepared as aqueous slurry spread on glass plates and dried at 100°C. IR spectra were recorded either with a BIO-RAD FTS-7 IR spectrometer or a Shimazu IR-470 IR spectrometer. The ^1H NMR spectra were recorded with either a JEOL GSX 270 FT NMR (270 MHz) or a JEOL FX-90Q (90 MHz) spectrometer. Chemical shifts are relative to the internal reference $SiMe_4$ ($\delta = 0$). Mass spectra were recorded with a Finnigan MAT 95 instrument by the FAB technique.

The complex $[Os_3(CO)_{10}(MeCN)_2]$ was prepared by a published procedure [10]. 2-(Benzylthio)benzyl alcohol [11] and 2-(benzylthio)benzaldehyde [12] were prepared by previously reported methods with some modification as follows.

3.2. 2-(Benzylthio)benzyl alcohol

A solution of 2-mercaptobenzyl alcohol [13] (2 g, 14.3 mmol) in 5 ml of ethanol was added dropwise to the solution of NaOH (0.6 g, 15 mmol) in 25 ml of 95% ethanol, and the mixture was stirred at room temperature for 45 min. Ice-cooled benzyl bromide (1.7 ml, 14.3 mmol) in 10 ml of ethanol was added to the ice-cooled solution, and the mixture was heated under reflux for 8 h until an orange solution and white precipitate were formed. The solution was filtered, the ethanol was removed, and the orange residue was extracted with diethyl ether. The extract was washed with water and then with 10% aqueous NaOH and finally dried over $MgSO_4$. Removal of the ether gave an orange–brown solid, which was recrystallized from ethanol–petroleum ether (boiling point, 40–60°C) gave a yield of 2.8 g (85.1%) (melting point (m.p.), 48–49°C [11]).

3.3. 2-(Benzylthio)benzaldehyde

To the solution of 2-(benzylthio)benzyl alcohol (2 g, 8.70 mmol) in 50 ml of dichloromethane under nitrogen was added a fivefold excess of $BaMnO_4$. The mixture was stirred at room temperature for 15 h, and the dark-purple precipitate was then removed by filtration through Celite. Volatiles were removed in vacuo to give a pale-yellow oil. Crystallization of **1** from ethanol–diethylether mixture gave colourless needles (yield, 1.85 g (92%); (m.p. 78–79°C [12]).

3.4. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 1

To the solid mixture of $[Os_3(CO)_{10}(MeCN)_2]$ (50 mg, 0.0536 mmol) and 2-(benzylthio)benzaldehyde (12.5 mg, 0.055 mmol) were added 50 ml of chloroform. The mixture was heated under reflux with stirring for 15 h, during which the colour of the solution changed from yellow to orange. The solution was concentrated and subjected to preparative TLC, with *n*-hexane–CH_2Cl_2 (75:25 v/v) as eluent to give **2a** (17 mg, (30%)) ($R_f \approx 0.5$), **3** (14 mg (25%)) ($R_f \approx 0.4$), **2b** (6 mg (10%)) ($R_f \approx 0.1$) with a light-brown baseline. Spectroscopic data for **2a**, **2b** and **3** are given in Table 1. Crystals of **2b** and **3** were grown from the CH_2Cl_2/*n*-hexane mixture at room temperature for 2 days.

Table 6
Crystal data and details of data collection [a] for **2b** and **3**

Compound	**2b**	**3**
Formula	$C_{24}H_{12}O_{11}SOs_3$	$C_{23}H_{12}O_{10}SOs_3$
Formula weight	1079.01	1051.00
Colour, habit	Yellow, prisms	Orange, blocks
Crystal dimensions (mm)	0.22×0.24×0.32	0.20×0.34×0.44
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a (Å)	16.308(2)	9.182(1)
b (Å)	25.785(2)	12.308(1)
c (Å)	12.988(2)	12.897(1)
α (°)	90	101.00(2)
β (°)	90	99.17(2)
γ (°)	90	110.85(2)
V (Å^3)	5461(1)	1295.4
Z	8	2
D_{calc} (g cm^{-3})	2.623	2.694
F(000)	3904	948
Diffractometer	AFC7R	Nonius CAD4
μ(Mo Kα)(cm^{-1})	140.49	148.02
Scan rate in ω (° min^{-1})	16 (up to 4 scans)	1.06–16.48
Scan range (°)	$0.68 + 0.35 \tan \theta$	$0.55 + 0.35 \tan \theta$
2θ range (°)	4–45	2–45
Number of reflections collected	4017	3628
Number of unique reflections	4017	3374 (R_{int}: 0.024)
Number of observed reflections	2613 $[I_o > 3\sigma(I_o)]$	2760 $[I_o > 3\sigma(I_o)]$
Weighting scheme	$w = 4F_o^2/\sigma^2F_o^2$	$w = 4F_o^2/[\sigma^2(F_o^2) + 0.04(F_o^2)]^2$
R	0.038	0.032
R_w	0.056	0.040
Goodness of fit *s*	2.241	1.581
Largest $\Delta\sigma$	0.07	0.03
Number of parameters	177	169
Residual electron density (close to Os) (electrons Å^{-3})	0.88 to −1.40	1.30 to −0.85

[a] Details in common: temperature, 293 K; radiation, Mo Kα (λ = 0.71073 Å); background mesurement, each for 25% at both ends; absorption correction by Ψ scan method; ω–2θ scan mode; refined by full-matrix least-squares method.

3.5. X-ray analyses of compound **2b** and **3**

Intensity data were collected on a Rigaku AFC7R diffractometer (for **2b**) and an Enraf–Nonius CAD4 diffractometer (for **3**) using Mo Kα radiation (λ = 0.71073 Å). The intensity data were corrected for Lorentz and polarization effects and for absorption by the Ψ scan method [14]. The crystal data and data collection parameters for both compounds are summarized in Table 6. Both structures were solved by a combination of direct methods (SIR88) [15] and Fourier difference techniques and refined on F by full-matrix least-squares analysis with only Os and S atoms anisotropic until convergence was reached. The hydrogen atoms of the organic moieties were fixed in calculated positions (C–H, 0.96 Å). All calculations were carried out with a Silicon-Graphics computer using the program package TeXsan (from MSC) [16]. Tables of hydrogen atom coordinates and thermal parameters, and complete lists of bond distances and angles, have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We acknowledge financial support from the University of Hong Kong and the Hong Kong Research Grants Council. S.M. Lee acknowledges the receipt of a postgraduate studentship administrated by the University of Hong Kong.

References

[1] G.R. Frauenhiff, *Coord. Chem. Rev.*, *121* (1992) 131.
[2] (a) B.F.G. Johnson, J. Lewis, T.I. Odiaka and P.R. Raithby, *J. Organomet. Chem.*, *216* (1981) C56.
(b) K.A. Azam, A.J. Deeming and I.P. Rothwell, *J. Chem. Soc., Dalton Trans.*, (1981) 91.
(c) K. Burgess, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, *233* (1982) C55.
(d) A.J. Deeming, P.J. Manning, I.P. Rothwell, M.B. Hursthouse and N.P.C. Walker, *J. Chem. Soc., Dalton Trans.*, (1984) 2039.
(e) A.J. Arce, Y.D. Sanctis and A.J. Deeming, *J. Organomet. Chem.*, *295* (1985) 365.
(f) B.F.G. Johnson, J. Lewis and T.I. Odiaka, *J. Organomet. Chem.*, *307* (1986) 61.
(g) A.J. Arce, Y.D. Sanctis and A.J. Deeming, *J. Organomet. Chem.*, *311* (1986) 371.
(h) A.J. Arce, Y.D. Sanctis and A.J. Deeming, *Polyhedron*, *7* (1988) 979.
(i) A.J. Arce, P.A. Bates, S.P. Best. R.J.H. Clark, A.J. Deeming, M.B. Hursthouse, R.C.S. McQueen and N.I. Powell, *J. Chem. Soc., Chem. Commun.*, (1988) 478.
(j) M.W. Day, K.I. Hardcastle, A.J. Deeming, A.J. Arce and Y.D. Sanctis, *Organometallics*, *9* (1990) 6.
(k) A.J. Deeming, D. Nuel, N.I. Powell and C. Whittaker, *J. Chem. Soc., Dalton Trans.*, (1992) 757.
[3] (a) D.L. Keiter, D.S. Strickland, S.R. Wilson and J.R. Shapley, *J. Am. Chem. Soc.*, *108* (1986) 3846.
(b) G.D. Jarvinen and R.R. Ryan, *Organometallics*, *3* (1984) 1434.
(c) C.J. Adams, M.I. Bruce, D.A. Duckworth, P.A. Humphrey, O. Kühl, R.T. Tiekink, W.R. Cullen, P. Braunstein, S.C. Cea, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *467* (1994) 251.
[4] S.M. Lee and W.T. Wong, *Acta Crystallogr.*, submitted for publication.
[5] A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1980) 2509.
[6] M.R. Churchill and B.G. DeBoer, *Inorg. Chem.*, *16* (1977) 878.
[7] (a) K.S. Wong, W.R. Scheidt and J.A. Labinger, *Inorg. Chem.*, *18* (1979) 136.
(b) B. Balbash, S. Beral, H. Biersack, W.A. Herrmann, J.A. Labinger, W.R. Scheidt, F.J. Timmers and M.L. Ziegler, *Organometallics*, *7* (1988) 325.
(c) J.P. Olsen, T.F. Koetzle, S.W. Kirtley, M. Andrews, D.L. Tipton and R. Bau, *J. Am. Chem. Soc.*, *96* (1974) 6621.
[8] (a) A.J. Schultz, J.M. Williams, R.B. Calvert, J.R. Shapley and G.D. Stucky, *Inorg. Chem.*, *18* (1979) 319.
(b) M.R. Churchill and F. Hollander, *Inorg. Chem.*, *17* (1978) 3546.
(c) R.D. Adams and N.M. Golembestki, *Inorg. Chem.*, *18* (1979) 1909.
[9] R.D. Adams and M.P. Pompeo, *Organometallics*, *9* (1990) 1718.
[10] J.N. Nicholls and M.D. Vargas, *Inorg. Synth.*, *26* (1989) 289.
[11] G.W. Stacy, F.W. Villaescusa and T.E. Wollner, *J. Org. Chem.*, *30* (1965) 4074.
[12] D.A. Nation, M.R. Taylor and K.P. Wainwright, *J. Chem. Soc., Dalton Trans.*, (1992) 1557.
[13] A. Arnoldi and M. Carughi, *Synthesis*, (1988) 155.
[14] A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr., A 24* (1968) 351.
[15] M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, *22* (1989) 389.
[16] *TeXsan: Crystal Structure Analysis Package*, Molecular Structure Corporation, 1985, 1992.