ELSEVIER

Journal of Organometallic Chemistry 559 (1998) 81–89

Journal of Organometallic Chemistry

Triosmium clusters containing thiazolide ligand: crystal structures of $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-3,4-}\eta^2\text{-H}\overline{\mathrm{C{=}NC{=}CHS}})]$ and $[(\mu\text{-H})\mathrm{Os_3(CO)_9}(\mu\text{-3,4-}\eta^2\text{-H}\overline{\mathrm{C{=}NC{=}CHS}})(\mathrm{PPh_3})]$

Kazi A. Azam [a], Michael B. Hursthouse [b,*], Syed A. Hussain [a], Shariff E. Kabir [a], K.M. Abdul Malik [b], Md. Mukhlesur Rahman [a], Edward Rosenberg [c]

[a] *Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh*
[b] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Park Place, Cardiff CF1 3TB, UK*
[c] *Department of Chemistry, University of Montana, Missoula, MT 59812, USA*

Received 24 October 1997

Abstract

The reaction of $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$ with thiazole at ambient temperature affords two isomeric isolable compounds $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-2,3-}\eta^2\text{-}\overline{\mathrm{C{=}NCH{=}CHS}})]$ **2** and $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-3,4-}\eta^2\text{-H}\overline{\mathrm{C{=}NC{=}CHS}})]$ **3** in 20 and 60% yields, respectively. Compound **3** reacts with $\mathrm{PPh_3}$ at 110°C to give $[(\mu\text{-H})\mathrm{Os_3(CO)_9}(\mu\text{-3,4-}\eta^2\text{-H}\overline{\mathrm{C{=}NC{=}CHS}})(\mathrm{PPh_3})]$ **4**, which exists as two isomeric forms in solution. Reaction of **3** with trimethyl phosphite at 110°C gives the substitution product $[(\mu\text{-H})\mathrm{Os_3(CO)_9}(\mu\text{-3,4-}\eta^2\text{-}\overline{\mathrm{HC{=}NC{=}CHS}})\{\mathrm{P(OMe_3}\}]$ **5**, which is structurally analogous to **4** in solution. Similarly compound **2** reacts with $\mathrm{PPh_3}$ at 110°C to afford $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-2,3-}\eta^2\text{-}\overline{\mathrm{C{=}NCH{=}CHS}})(\mathrm{PPh_3})]$ **6**, which also exists as two isomers in solution. The compounds have been characterised by IR, ^{1}H-NMR and elemental analysis together with single crystal X-ray analysis for **3** and **4**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Carbonyl; Thiazolide; Crystal structure; Phosphine; Substitution

---

1. Introduction

The reactions of bimetallic clusters of osmium and ruthenium with heterocyclic ligands containing nitrogen [1–10] or sulphur [11–13] as heteroatoms have extensively been studied because of their relevance to modelling the industrially important hydrodenitrogenation (HDN) or hydrodesulphurisation (HDS) processes. There are few reports, however, concerning the reactivities of the lightly stabilised cluster $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$ with organic heterocycles containing N and S atoms [14,15].

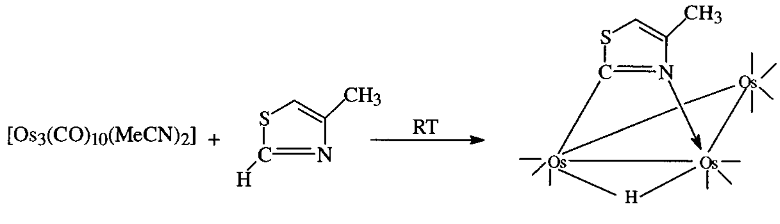
Recently we reported [16] the reaction of $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$ with 4-methylthiazole at room temperature (r.t.) leading to the formation of $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-2,3-}\eta^2\text{-}\overline{\mathrm{C{=}NCMe{=}CHS}})]$ **1** by activation of the C-2 H atom and coordination of the thiazolide ligand through the nitrogen and C-2 atoms (Scheme 1).

In this paper we report the reaction of $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$ with thiazole to give two isomeric compounds $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-2,3-}\eta^2\text{-}\overline{\mathrm{C{=}NCH{=}CHS}})]$ **2** and $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-3,4-}\eta^2\text{-H}\overline{\mathrm{C{=}NC{=}CHS}})]$ **3** by the activation of C-2 and C-4 H atoms, respectively. We also describe the reactions of **2** and **3** with phosphines and the crystal structures of **3** and its $\mathrm{PPh_3}$ substituted derivative **4**.

---

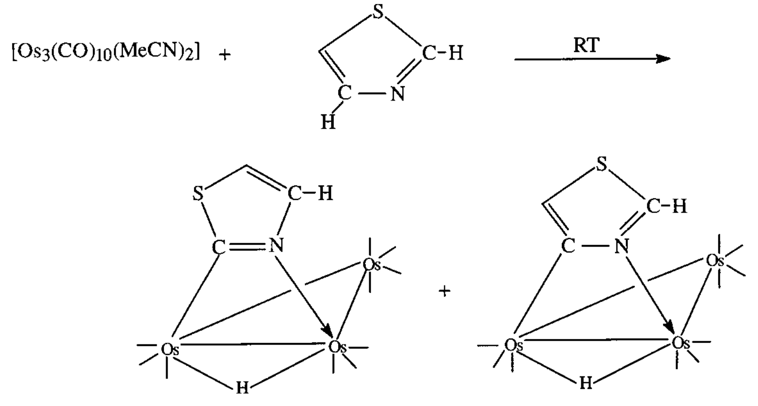
* Corresponding auhtor. Tel.: +44 1222 874068; fax: +44 1222 874029; e-mail: hursthouse@cardiff.ac.uk

PII S0022-328X(98)00416-1



1

Scheme 1. The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 4-methylthiazole at r.t. leading to the formation of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **1**.



2 **3**

Scheme 2. The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with thiazole at ambient temperature to give the isomeric compounds **2** and **3**.

2. Results and discussion

The lightly stabilised bis-acetonitrile cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with thiazole at ambient temperature to give the isomeric compounds $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})]$ **2** and $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}H\overline{C{=}NC{=}CHS})]$ **3** (Scheme 2) in 20 and 60% yields, respectively.

This is in sharp contrast to the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 4-methylthiazole which results solely in **1** [16]. Both compounds **2** and **3** have been characterised by IR, ^{1}H-NMR and elemental analysis together with a single crystal X-ray analysis study for **3**. In terms of electron counting, the clusters are electron precise.

The IR spectrum of **2** in the carbonyl stretching region is very similar to that of **1** in both the appearance and position of the bands [16], indicating that they have similar structures. The ^{1}H-NMR of **2** shows a singlet hydride resonance at δ −14.93 and two doublets at δ 7.40 and 7.01 ($J = 3.6$ Hz) for the C-4 and C-5 ring protons indicating that **2** is formed by the oxidative addition of C(2)–H bond. The structural assignments of **2** were based on a comparison of the ν(CO) stretching frequencies with those of **1** and the magnitude of H–H coupling of the thiazolide ring protons and their chemical shift.

The close similarity of their ν(CO) stretching frequencies indicates that compounds **2** and **3** are a structurally analogous pair of isomers. The ^{1}H-NMR of **3** contains a singlet hydride resonance at δ −15.08 and two doublets at δ 8.65 and 6.70 ($J = 1.8$ Hz) for the ring protons with a relative integrated intensity of 1:1:1, respectively. The observation of the ring protons as two doublets, their chemical shifts and the magnitude of H–H coupling constants are consistent with the activation of C(4)–H proton of the ligand. Although the ^{1}H-NMR spectroscopic data indicate activation of the C(4)–H proton and subsequent coordination of the C(4) carbon to the metal, we could not be certain about which heteroatom was coordinated to the metal.

The structure determined by X-ray diffraction for **3** is consistent with that deduced from the spectroscopic data. In the crystals of **3**, there are two crystallographically-independent but chemically-equivalent molecules in an asymmetric unit. The respective bond lengths and angles in the two molecules show only minor (in most cases statistically insignificant) variations, but the molecules differ in their relative orientations in the unit cell, most probably for efficient packing. A general view of the structure of one molecule (**A**) is shown in Fig. 1. Selected bond distances and angles given in Table 1. The atom numbering scheme used is the same in the two molecules.

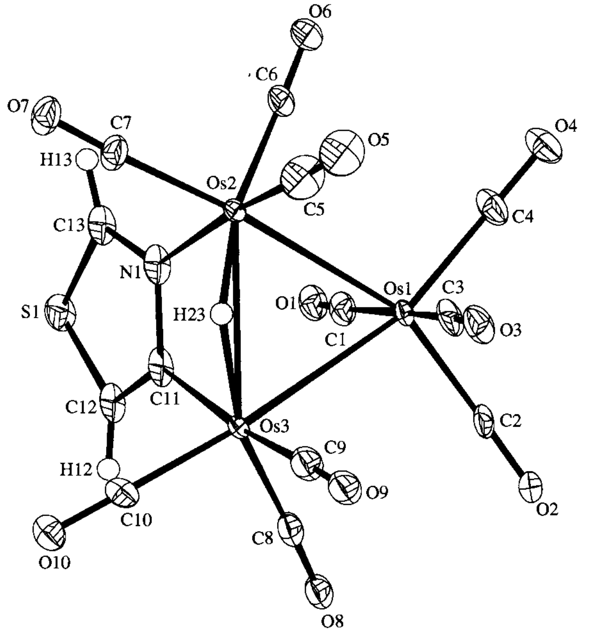


Fig. 1. Solid-state structure of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}\overline{HC{=}NC{=}CHS})]$ **3** showing the atom labelling scheme for one independent molecule (**A**). Thermal ellipsoids are drawn at 50% probability level.

The compound consists of an isosceles triangle of osmium atoms with ten terminal carbonyl ligands, and with the hydride and the thiazolide ligand bridging the same edge of the osmium triangle. The Os–Os bond spanned by the bridging ligands is significantly longer than the other two Os–Os bonds in both molecules (2.9536(9) vs. 2.8864(11), 2.8809(10) Å in **A**, 2.9630(9) vs. 2.8756(11), 2.8790(9) Å in **B**). These latter values are comparable with the average Os–Os distance of (2.877(3) Å) found in $[Os_3(CO)_{12}]$ [17]. It is to be noted that the lengthening of the doubly bridged Os–Os edge compared with the two unbridged edges is by no means unique and has been observed in the related 4-methylthiazolide complexes $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$, $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ and $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ [16]. Thus in these complexes, the Os–Os distances along the doubly bridged edges are 2.9340(8), 2.9674(9) and 2.9528(6) Å, respectively, compared with the average distances along the non-bridged edges 2.8720, 2.8699 and 2.8922 Å. As in the above three complexes, the thiazolide ligand in **3** is also η^2 coordinated through the Os(3)–C(11) σ bond and two electron donor bond from N(1) to Os(2). It is seen from Fig. 1 that the bridging thiazolide is nearly perpendicular to the plane of the osmium triangle. The dihedral angle between the Os_3 and thiazolide planes is 80.0(2) and 79.2(2)° for molecules **A** and **B**, respectively. Similarly the bridging hydride is also located far from the Os_3 plane, pre-

Table 1
Selected bond lengths (Å) and angles (°) for **3**

Molecule **A**		Molecule **B**	
Bond lengths (Å)			
Os(1)–Os(2)	2.8864(11)	Os(1′)–Os(2′)	2.8756(11)
Os(1)–Os(3)	2.8809(10)	Os(1′)–Os(3′)	2.8790(9)
Os(2)–Os(3)	2.9536(9)	Os(2′)–Os(3′)	2.9630(9)
Os(2)–N(1)	2.144(11)	Os(2′)–N(1′)	2.119(12)
Os(3)–C(11)	2.112(13)	Os(3′)–C(11′)	2.110(14)
Os(2)–H(23)	1.79[a]	Os(2′)–H(23′)	1.96[a]
Os(3)–H(23)	1.97[a]	Os(3′)–H(23′)	1.68[a]
Os–C(CO)[b]	1.92(2)	C–O[b]	1.15(2)
S(1)–C(12)	1.694(14)	S(1′)–C(12′)	1.711(13)
S(1)–C(13)	1.728(13)	S(1′)–C(13′)	1.71(2)
N(1)–C(13)	1.32(2)	N(1′)–C(13′)	1.33(2)
N(1)–C(11)	1.39(2)	N(1′)–C(11′)	1.39(2)
C(11)–C(12)	1.35(2)	C(11′)–C(12′)	1.35(2)
Bond angles (°)			
Os(3)–Os(1)–Os(2)	61.61(2)	Os(2′)–Os(1′)–Os(3′)	61.98(2)
C(2)–Os(1)–C(3)	93.5(6)	C(2′)–Os(1′)–C(3′)	92.9(6)
C(3)–Os(1)–C(4)	91.3(6)	C(3′)–Os(1′)–C(4′)	92.9(6)
C(2)–Os(1)–C(4)	99.4(6)	C(2′)–Os(1′)–C(4′)	97.1(6)
C(2)–Os(1)–C(1)	90.8(6)	C(2′)–Os(1′)–C(1′)	91.6(6)
C(3)–Os(1)–C(1)	172.9(6)	C(3′)–Os(1′)–C(1′)	173.0(6)
C(4)–Os(1)–C(1)	93.4(6)	C(4′)–Os(1′)–C(1′)	91.9(6)
C(3)–Os(1)–Os(3)	87.1(4)	C(3′)–Os(1′)–Os(3′)	86.4(4)
C(2)–Os(1)–Os(3)	96.9(4)	C(2′)–Os(1′)–Os(3′)	100.1(4)
C(4)–Os(1)–Os(3)	163.7(4)	C(4′)–Os(1′)–Os(3′)	162.8(4)
C(1)–Os(1)–Os(3)	86.8(4)	C(1′)–Os(1′)–Os(3′)	87.6(4)
C(3)–Os(1)–Os(2)	87.1(4)	C(3′)–Os(1′)–Os(2′)	86.7(4)
C(2)–Os(1)–Os(2)	158.5(4)	C(2′)–Os(1′)–Os(2′)	162.1(4)
C(4)–Os(1)–Os(2)	102.1(4)	C(4′)–Os(1′)–Os(2′)	100.8(4)
C(1)–Os(1)–Os(2)	86.8(4)	C(1′)–Os(1′)–Os(2′)	87.3(4)
Os(1)–Os(2)–Os(3)	59.10(3)	Os(1′)–Os(2′)–Os(3′)	59.07(2)
C(6)–Os(2)–C(5)	94.3(7)	C(6′)–Os(2′)–C(5′)	92.7(6)
C(6)–Os(2)–C(7)	96.5(6)	C(6′)–Os(2′)–C(7′)	97.8(6)
C(5)–Os(2)–C(7)	92.2(7)	C(5′)–Os(2′)–C(7′)	93.1(6)
C(5)–Os(2)–N(1)	173.3(6)	C(5′)–Os(2′)–N(1′)	175.7(5)
C(6)–Os(2)–N(1)	92.1(5)	C(6′)–Os(2′)–N(1′)	91.6(6)
C(7)–Os(2)–N(1)	88.9(5)	C(7′)–Os(2′)–N(1′)	87.1(6)
C(5)–Os(2)–Os(1)	91.2(5)	C(5′)–Os(2′)–Os(1′)	91.8(4)
C(6)–Os(2)–Os(1)	86.8(4)	C(6′)–Os(2′)–Os(1′)	85.7(4)
C(7)–Os(2)–Os(1)	175.0(4)	C(7′)–Os(2′)–Os(1′)	173.8(5)
N(1)–Os(2)–Os(1)	87.2(3)	N(1′)–Os(2′)–Os(1′)	87.7(3)
C(5)–Os(2)–Os(3)	105.3(5)	C(5′)–Os(2′)–Os(3′)	107.3(4)
C(6)–Os(2)–Os(3)	140.3(4)	C(6′)–Os(2′)–Os(3′)	139.1(4)
C(7)–Os(2)–Os(3)	116.4(5)	C(7′)–Os(2′)–Os(3′)	115.7(4)
N(1)–Os(2)–Os(3)	68.4(3)	N(1′)–Os(2′)–Os(3′)	68.8(3)
Os(1)–Os(3)–Os(2)	59.29(2)	Os(1′)–Os(3′)–Os(2′)	58.95(2)
C(8)–Os(3)–C(9)	95.3(6)	C(8′)–Os(3′)–C(9′)	91.6(7)
C(8)–Os(3)–C(10)	96.0(6)	C(8′)–Os(3′)–C(10′)	95.2(7)
C(10)–Os(3)–C(9)	93.6(6)	C(9′)–Os(3′)–C(10′)	93.4(6)
C(8)–Os(3)–C(11)	92.7(6)	C(8′)–Os(3′)–C(11′)	93.6(6)
C(9)–Os(3)–C(11)	171.6(6)	C(9′)–Os(3′)–C(11′)	174.4(6)
C(10)–Os(3)–C(11)	88.0(6)	C(10′)–Os(3′)–C(11′)	88.3(6)
C(8)–Os(3)–Os(1)	86.4(4)	C(8′)–Os(3′)–Os(1′)	86.0(5)
C(10)–Os(3)–Os(1)	174.6(4)	C(10′)–Os(3′)–Os(1′)	175.6(5)
C(9)–Os(3)–Os(1)	91.0(5)	C(9′)–Os(3′)–Os(1′)	90.8(4)
C(11)–Os(3)–Os(1)	87.1(4)	C(11′)–Os(3′)–Os(1′)	87.4(4)
C(8)–Os(3)–Os(2)	140.6(5)	C(8′)–Os(3′)–Os(2′)	139.6(4)
C(9)–Os(3)–Os(2)	103.5(4)	C(9′)–Os(3′)–Os(2′)	107.0(5)
C(10)–Os(3)–Os(2)	116.7(4)	C(10′)–Os(3′)–Os(2′)	118.3(4)
C(11)–Os(3)–Os(2)	68.5(4)	C(11′)–Os(3′)–Os(2′)	67.5(4)
Cs(2)-H(23)-Os(3)	102[a]	Os(2′)–H(23′)–Os(3′)	109[a]

Table 1 (*Continued*)

Molecule **A**		Molecule **B**	
C(12)–S(1)–C(13)	90.5(7)	C(13′)–S(1′)–C(12′)	89.4(7)
C(13)–N(1)–C(11)	114.4(11)	C(13′)–N(1′)–C(11′)	112.2(12)
C(13)–N(1)–Os(2)	134.9(10)	C(13′)–N(1′)–Os(2′)	137.6(10)
C(11)–N(1)–Os(2)	110.5(8)	C(11′)–N(1′)–Os(2′)	110.2(9)
C(12)–C(11)–N(1)	111.5(12)	C(12′)–C(11′)–N(1′)	112.1(12)
C(12)–C(11)–Os(3)	135.9(11)	C(12′)–C(11′)–Os(3′)	134.4(10)
N(1)–C(11)–Os(3)	112.6(9)	N(1′)–C(11′)–Os(3′)	113.5(10)
C(11)–C(12)–S(1)	112.4(11)	C(11′)–C(12′)–S(1′)	112.7(10)
N(1)–C(13)–S(1)	110.9(11)	N(1′)–C(13′)–S(1′)	113.5(10)

[a] The parameters involving the bridging hydride are only approximate.

[b] Average values for both molecules.

sumably on steric grounds due to the presence of a second bridging ligand along the same Os–Os edge. This is in contrast with triosmium clusters containing only one bridging hydride along a particular edge, where the hydride is placed very close to the Os_3 plane, e.g. $[(\mu\text{-H})Os_3(CO)_9(\text{4-methylquinoline})(PPh_3)]$ [18].

The thiazolide ligands in both molecules are planar within experimental error. The S–C distances (1.694(14)–1.728(13), average 1.711 Å) are shorter than that expected for a S–C single bond (1.81 Å) [19]. Similarly, the N(1)–C(11) bond lengths (1.39(2) Å in both molecules) are somewhat shorter than that expected of a C–N single bond (1.47 Å) [19], whilst the N(1)–C(13) bonds (1.32(2) and 1.33(2) Å) are somewhat longer than that expected for a C=N double bond (1.25 Å) [19]. These values of the bond lengths in the heterocyclic ligand indicates that the 5-membered is involved in some degree of delocalisation. Similar values for the C–N distances were observed in other related triosmium carbonyl clusters containing amine derived [4] and heterocyclic [16,18] ligands. The average Os(3)–C(11) and Os(2)–N(1) distances for the two molecules in **3**, 2.111(14) and 2.132(12) Å, respectively, are comparable with those found in the related 4-methylthiazolide cluster **1** (2.105 (12) and 2.166(11) Å, respectively) [16]. The Os–C(CO) distances (1.88(2)–1.98(2), average 1.92 Å) and the Os–C–O angles (173.5(12)–179.2(13), average 177.7°) are as expected for this type of osmium carbonyl complexes. The basic structure of **3** is similar to that adopted by **1** except that in the latter it is the C(2)–H bond which was activated but in the present case, the C(3)–H bond is activated followed by subsequent coordination. It is also worth noting that compound **3** is formed in far greater yield than **2** (60 and 20%, respectively). This is probably due to the more favorable steric arrangement in **3** where the sulphur atom of the thiazolide ring is pointed well away from the osmium triangle.

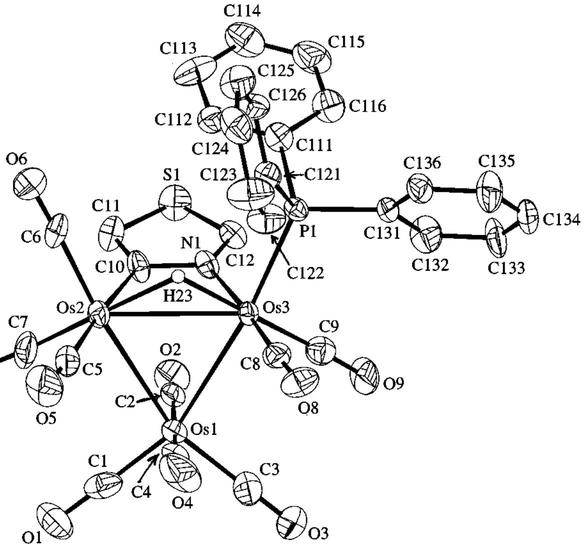
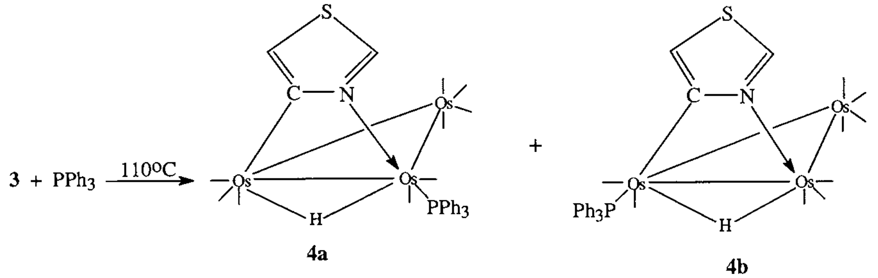


Fig. 2. Solid-state structure of $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-}\overline{HC{=}NC{=}CHS})(PPh_3)]$ **4** showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level. The ring H atoms are omitted for clarity.

In contrast to **1**, which reacts with PPh_3 to give the mono- and bis-substituted products, compound **3** reacts with PPh_3 at 112°C to give only the monophosphine-substituted derivative $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-}\overline{HC{=}NC{=}CHS})(PPh_3)]$ **4** in 60% yield (Scheme 3).

Compound **4** has been characterised by IR, ^{1}H-NMR and elemental analysis together with a single crystal X-ray diffraction study. The ν(CO) stretching frequencies of **4** are similar in position and intensities to those



Scheme 3. Reaction of compound **3** with PPh_3 at 112°C to give two isomers of the monophosphine-substituted derivative $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-}\overline{HC{=}NC{=}CHS})(PPh_3)]$ **4a** and **4b**.

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths (Å)			
Os(1)–Os(3)	2.8770(9)	Os(1)–Os(2)	2.8782(8)
Os(2)–Os(3)	2.9789(8)	Os(3)–P(1)	2.386(3)
Os(2)–C(10)	2.108(12)	Os(3)–N(1)	2.152(10)
Os(2)–H(23)	1.87[a]	Os(3)–H(23)	1.70[a]
Os–C(CO)[b]	1.91(2)	C–O[b]	1.15(2)[b]
S(1)–C(12)	1.684(13)	S(1)–C(11)	1.75(2)
N(1)–C(12)	1.30(2)	N(1)–C(10)	1.36(2)
C(10)–C(11)	1.35(2)		
Bond angles (°)			
C(1)–Os(1)–C(3)	101.3(7)	C(1)–Os(1)–C(2)	91.1(6)
C(3)–Os(1)–C(2)	91.3(6)	C(1)–Os(1)–C(4)	93.6(6)
C(3)–Os(1)–C(4)	94.1(7)	C(2)–Os(1)–C(4)	172.0(6)
C(1)–Os(1)–Os(3)	159.5(5)	C(3)–Os(1)–Os(3)	99.1(5)
C(2)–Os(1)–Os(3)	89.0(4)	C(4)–Os(1)–Os(3)	84.4(4)
C(1)–Os(1)–Os(2)	97.2(5)	C(3)–Os(1)–Os(2)	161.5(5)
C(2)–Os(1)–Os(2)	88.1(4)	C(4)–Os(1)–Os(2)	85.0(4)
Os(3)–Os(1)–Os(2)	62.34(2)	C(7)–Os(2)–C(6)	97.0(6)
C(7)–Os(2)–C(5)	91.8(7)	C(6)–Os(2)–C(5)	93.8(6)
C(7)–Os(2)–C(10)	91.0(6)	C(6)–OS(2)–C(10)	88.7(6)
C(5)–Os(2)–C(10)	176.1(5)	C(7)–Os(2)–Os(1)	86.8(5)
C(6)–Os(2)–Os(1)	173.3(4)	C(5)–Os(2)–Os(1)	91.6(4)
C(10)–Os(2)–Os(1)	85.7(4)	C(7)–Os(2)–Os(3)	139.6(5)
C(6)–Os(2)–Os(3)	115.5(4)	C(5)–Os(2)–Os(3)	108.3(4)
C(10)–Os(2)–Os(3)	67.8(3)	Os(1)–Os(2)–Os(3)	58.81(2)
C(8)–Os(3)–C(9)	90.8(6)	C(8)–Os(3)–N(1)	175.2(5)
C(9)–Os(3)–N(1)	93.7(5)	C(8)–Os(3)–P(1)	90.4(5)
C(9)–Os(3)–P(1)	100.4(5)	N(1)–Os(3)–P(1)	90.4(3)
C(8)–Os(3)–Os(1)	92.7(5)	C(9)–Os(3)–Os(1)	86.1(5)
N(1)–OS(3)–OS(1)	85.9(3)	P(1)–Os(3)–Os(1)	172.76(9)
C(8)–Os(3)–Os(2)	107.8(4)	C(9)–OS(3)–OS(2)	140.2(5)
N(1)–Os(3)–Os(2)	67.6(3)	P(1)–Os(3)–Os(2)	113.96(9)
Os(1)–Os(3)–Os(2)	58.85(2)	Os(2)–H(23)–Os(3)	113.0[a]
C(12)–S(1)–C(11)	89.5(7)	C(12)–N(1)–C(10)	115.2(11)
C(12)–N(1)–Os(3)	133.9(9)	C(10)–N(1)–Os(3)	110.9(8)
C(11)–C(10)–N(1)	112.0(12)	C(11)–C(10)–Os(2)	134.1(10)
N(1)–C(10)–OS(2)	113.8(8)	C(10)–C(11)–S(1)	110.1(11)
N(1)–C(12)–S(1)	113.1(11)		

[a] The parameters involving the bridging hydride are only approximate.

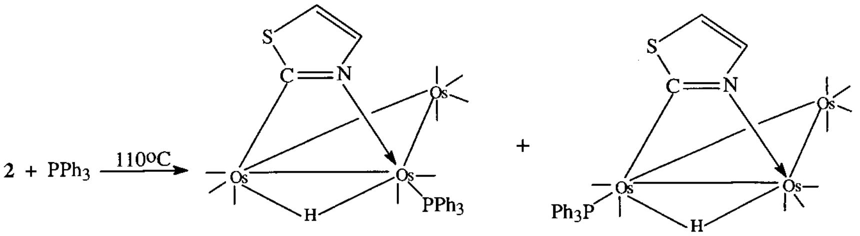
[b] Average values for both molecules.

Table 3
Crystal data and details of data collection and structure refinement for **3** and **4**[a]

	3	**4**
Empirical formula	$C_{13}H_3NO_{10}Os_3S$	$C_{30}H_{18}NO_9Os_3PS$
Formula weight	935.82	1170.08
a (Å)	18.647(4)	15.079(3)
b (Å)	9.248(3)	10.0162(8)
c (Å)	21.887(5)	21.211(3)
β (°)	96.57(2)	94.04(2)
V (Å^3)	3750(2)	2728.2(7)
Z	8	4
$D_{calc.}$ (g cm^{-3})	3.316	2.432
Absorption coefficient (mm^{-1})	20.446	11.622
$F(000)$	3296	2144
Crystal size (mm)	0.30 × 0.10 × 0.06	0.22 × 0.15 × 0.12
θ range for data collection (°)	1.87–25.04	1.92–25.04
Index ranges	$-20 \leq h \leq 18$, $-10 \leq k \leq 8$, $-20 \leq l \leq 24$	$-16 \leq h \leq 15$, $-8 \leq k \leq 11$, $-23 \leq l \leq 22$
Reflections collected	12033	12489
Independent reflections	5489	4883
R_{int}	0.0650	0.0943
Absorption correct. factors	0.789–1.135	0.799–1.091
Data/parameters	5489/505	4883/370
Goodness-of-fit on F^2	1.009	1.079
R_1/wR_2 (all data)	0.0497/0.0912	0.0688/0.1310
R_1/wR_2 [data with $I > 2\sigma(I)$]	0.0389/0.0895	0.0563/0.1290
Largest difference peak and hole (e Å^{-3})	3.147 and −2.326	2.182 and −2.675

[a] Details in common: Delft Instruments area detector diffractometer, Mo–K$_\alpha$ radiation, $\lambda = 0.71069$ Å, $T = 150(2)$ K, cell dimensions from 250 reflections, monoclinic, space group $P2_1/n$, full-matrix least-squares on F^2; R_1 and wR_2 as defined in ref. [17]. Weighting scheme, $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = [\max(F_o^2) + 2(F_c^2)]/3$ and $a = 0.0497$ and 0.0631 for **3** and **4**, respectively.

of [(μ-H)Os$_3$(CO)$_9$(μ-2,3-η^2-C=NCMe=CHS)(PPh$_3$)], showing only the terminal ν(CO) absorption bands [16]. The ^{1}H-NMR spectrum of **4** contains two hydride doublets at δ −14.32 ($J_{P-H} = 10.3$ Hz) and −14.11 ($J_{P-H} = 9.8$ Hz) with relative intensities of 15:1, respectively, indicating the presence of two isomers in solution. The ring proton resonance for one of the protons appears as a singlet at δ 6.48 while the resonance for the other is overlapped with the resonances of the



6a

6b

Scheme 4. Reaction of **2** with PPh$_3$ at 110°C resulting in two isomers of the monophosphine-substituted derivative [(μ-H)Os$_3$(CO)$_9$(μ-2,3-η^2-C=NCH=CHS)(PPh$_3$)] **6a** and **b**.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**

	x	y	z	U_{eq}
Molecule **A**				
Os(1)	6090.0(3)	1091.1(5)	690.3(3)	12.4(2)
Os(2)	6474.6(3)	3932.2(5)	1166.2(2)	11.4(2)
Os(3)	6347.3(3)	1464.9(5)	2003.9(2)	11.8(2)
S(1)	4251(2)	4198(4)	1937(2)	21(1)
N(1)	5462(6)	3950(12)	1541(6)	18(2)
C(1)	5101(8)	1615(14)	759(7)	18(2)
O(1)	4487(5)	1887(9)	743(4)	21(2)
C(2)	5848(8)	−916(15)	698(7)	19(2)
O(2)	5692(5)	−2129(9)	711(4)	19(2)
C(3)	7100(8)	726(15)	708(7)	21(2)
C(4)	5997(9)	1410(15)	−184(7)	24(3)
O(4)	5954(6)	1595(10)	−697(5)	27(2)
O(3)	7727(6)	451(10)	734(4)	23(2)
C(5)	7421(9)	3769(16)	909(9)	34(3)
O(5)	7978(6)	3736(11)	739(6)	36(3)
C(6)	6048(8)	4665(15)	399(7)	20(2)
O(6)	5774(6)	5117(10)	−51(5)	22(2)
C(7)	6696(9)	5786(15)	1549(7)	23(3)
O(7)	6833(6)	6879(10)	1750(5)	26(2)
C(8)	5808(9)	−260(15)	2063(7)	23(3)
O(8)	5476(6)	−1279(10)	2113(5)	24(2)
C(9)	7269(9)	515(15)	2026(7)	23(2)
O(9)	7801(6)	−57(10)	2059(5)	25(2)
C(10)	6466(8)	1874(14)	2857(7)	18(2)
O(10)	6531(5)	2135(10)	3383(4)	22(2)
C(11)	5412(7)	2772(14)	1928(6)	17(2)
C(12)	4777(7)	2760(14)	2168(7)	17(2)
C(13)	4916(7)	4861(15)	1524(7)	19(2)
Molecule **B**				
Os(1′)	8210.7(3)	5582.2(5)	−1243.7(3)	12.5(2)
Os(2′)	8037.0(3)	8563.7(5)	−917.9(3)	11.8(2)
Os(3′)	9280.4(3)	7621.5(5)	−1549.5(3)	13.1(2)
S(1′)	10071(2)	8256(4)	529(2)	20(1)
N(1′)	8982(6)	8344(11)	−289(5)	16(2)
C(1′)	8793(9)	5340(14)	−437(7)	19(2)
O(1′)	9102(6)	5182(9)	21(4)	20(2)
C(2′)	8595(8)	3826(15)	−1552(6)	19(2)
O(2′)	8817(5)	2771(9)	−1734(4)	18(2)
C(3′)	7681(9)	6064(15)	−2038(8)	26(3)
O(3′)	7344(6)	6318(10)	−2496(5)	26(2)
C(4′)	7373(8)	4733(14)	−942(7)	21(2)
O(4′)	6887(6)	4241(9)	−756(5)	24(2)
C(5′)	7227(8)	8788(15)	−1536(7)	22(3)
O(5′)	6747(6)	8978(10)	−1894(5)	26(2)
C(6′)	7450(8)	7853(14)	−331(7)	23(3)
O(6′)	7104(6)	7418(9)	39(5)	26(2)
C(7′)	8032(8)	10537(15)	−691(7)	20(2)
O(7′)	8025(5)	11729(9)	−546(5)	22(2)
C(8′)	9890(9)	6014(16)	−1585(7)	29(3)
O(8′)	10258(6)	4986(11)	−1581(5)	30(2)
C(9′)	8944(9)	7451(15)	−2400(7)	27(3)
O(9′)	8736(6)	7413(10)	−2923(5)	29(2)
C(10′)	10005(9)	9034(16)	−1689(7)	24(3)
O(10′)	10437(6)	9814(11)	−1766(5)	27(2)
C(11′)	9560(8)	7921(13)	−596(6)	15(2)
C(12′)	10184(8)	7864(13)	−218(6)	15(2)
C(13′)	9173(8)	8518(13)	312(7)	17(2)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

phenyl protons of the PPh_3 ligand. The appearance of the hydride resonances as doublets and their nearly equal and relatively large P–H coupling constants indicates that PPh_3 ligand occupies stereochemically similar positions relative to the hydride in both the isomers. Based on our previous work with 4-methylthiazolide analogue [16] and the related μ-imidoyl complexes [7,20] we are inclined to believe that the two isomers probably differ by substitution at the N-bound osmium (**4a**) versus C-bound osmium atom (**4b**). We also believe that **4a** is the major isomer in solution. In view of the ambiguity in the ^{1}H-NMR data regarding the site of phosphine substitution, an X-ray structure determination was carried out on **4**.

Indeed, the solid state structure of **4** revealed it to have the structure proposed for **4a**. The molecular structure of **4** is shown in Fig. 2, selected bond distances and angles are presented in Table 2.

The molecule consists of an isosceles triangle of osmium atoms with a longer M–M bond along the edge bridged by the hydride and μ-η^2-thiazolide ligand. As proposed from the ^{1}H-NMR data the phosphine is *cisoid* to the hydride and substituted on the same metal atom as that bound to the N of the thiazolide ligand. The overall geometry of **4** closely resembles that of **3** with only slight elongation of the Os(2)–Os(3) bond (2.9789(8) Å in **4** and 2.958(1) Å (average) in **3**), presumably due the phosphine substitution at Os(3). The phosphine substitution at the N-bound osmium in this compound also causes lengthening of the C=N bond (1.39(2) compared with 1.32(2) Å in **3**), while the Os–C and Os–N bond lengths (2.108(12) and 2.152(10) Å, respectively) are very similar to those of **3**. The heterocyclic ring, bridging the same Os–Os edge as the hydride, is again nearly perpendicular to the Os_3 plane making a dihedral angle of 80.8(2)°. The Os–P distance 2.386(3) Å in **4** is comparable with those observed in other Os_3 clusters containing terminally-bound phosphine ligands, e.g. 2.376(3) Å in $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{\text{C=NCMe=CHS}})(PPh_3)]$ [16] and 2.364(3) and 2.395(3) Å in $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{\text{C=NCMe=CHS}})(PPh_3)]$ [16]. The dimensions of the PPh_3 ligand are as expected, with the Os–P–C and C–P–C angles (114.1(3)–117.0(3) and 101.9(4)–104.7(4)°), respectively, greater and smaller than the ideal tetrahedral value (109.45°). Other structural parameters are also as expected.

We have recently reported that the structures and isomers distribution of the mono and bis-phosphine substituted derivatives of μ-imidoyl [7,20] and quinoline [18] triosmium clusters depend on the structure of the heterocyclic ligand and the steric bulk of the phosphine ligand. In order to verify these observations, we have studied the reaction of **3** with $P(OMe)_3$ and obtained $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-H}\overline{\text{C=NC=CHS}})\{P(OMe_3\}]$ **5**. The ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopic data of this

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4**

	x	y	z	U_{eq}
Os(1)	72.1(4)	3301.8(6)	1290.1(3)	37(1)
Os(2)	1118.4(3)	997.6(5)	1669.3(3)	32(1)
Os(3)	23.2(3)	2408.9(5)	2576.4(2)	27(1)
S(1)	−1525(3)	−1344(4)	1840(2)	53(1)
P(1)	91(2)	1433(3)	3605(2)	30(1)
O(1)	543(10)	3376(13)	−88(6)	86(4)
O(2)	−1495(8)	1447(11)	891(6)	62(3)
O(3)	−1232(10)	5637(13)	1315(7)	87(4)
O(4)	1664(10)	5024(12)	1796(7)	87(4)
O(5)	2893(8)	2470(12)	1551(7)	74(4)
O(6)	2046(8)	−1509(11)	2141(6)	66(3)
O(7)	1049(9)	196(12)	291(6)	75(4)
O(8)	1017(7)	4843(10)	3107(6)	56(3)
O(9)	−1669(7)	4019(12)	2589(6)	72(4)
N(1)	−622(7)	650(11)	2184(5)	32(3)
C(1)	379(10)	3373(14)	478(9)	56(5)
C(2)	−905(11)	2101(15)	1054(7)	41(4)
C(3)	−721(12)	4779(17)	1313(8)	57(4)
C(4)	1106(10)	4321(14)	1614(7)	41(4)
C(5)	2228(11)	1993(14)	1610(7)	46(4)
C(6)	1708(10)	−585(15)	1987(8)	43(4)
C(7)	1078(11)	536(16)	800(9)	56(4)
C(8)	671(10)	3879(15)	2892(8)	44(4)
C(9)	−1040(10)	3378(14)	2589(7)	45(4)
C(10)	−108(9)	38(13)	1768(7)	36(3)
C(11)	−484(9)	−1103(13)	1536(7)	43(4)
C(12)	−1377(9)	73(13)	2261(6)	34(3)
C(111)	−388(6)	−258(7)	3627(5)	40(3)
C(112)	−1(6)	−1241(9)	3274(4)	46(4)
C(113)	−387(7)	−2500(8)	3217(5)	71(6)
C(114)	−1160(7)	−2775(8)	3512(6)	65(5)
C(115)	−1548(6)	−1792(11)	3864(5)	68(5)
C(116)	−1162(6)	−534(9)	3922(5)	51(4)
C(121)	1216(5)	1174(9)	4006(4)	38(3)
C(122)	1820(7)	2223(8)	4017(5)	56(5)
C(123)	2640(6)	2100(9)	4355(6)	76(6)
C(124)	2856(5)	927(10)	4681(5)	59(5)
C(125)	2251(6)	−122(8)	4670(5)	60(5)
C(126)	1431(5)	2(8)	4332(5)	44(4)
C(131)	−485(6)	2385(9)	4198(4)	35(3)
C(132)	−1355(6)	2785(10)	4041(4)	56(4)
C(133)	−1809(5)	3534(11)	4467(5)	62(5)
C(134)	−1393(7)	3883(10)	5049(4)	62(5)
C(135)	−523(7)	3482(10)	5206(4)	65(5)
C(136)	−69(5)	2733(10)	4780(4)	44(4)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

compound (see Section 3) indicate that it also exist as two isomers in solution which appear to be structurally similar with **4a** and **4b**.

The reaction of **2** with PPh_3 at 110°C affords the monophosphine-substituted derivative $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})(PPh_3)]$ **6** (Scheme 4) in 65% yield.

The compound has been characterised on the basis of IR, ^1H- and $^{31}P\{^1H\}$-NMR spectroscopic data and elemental analysis. The $\nu(CO)$ stretching frequencies are very similar to those of the corresponding 4-methylthiazolide analogue $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ [16]. In the ^1H-NMR spectrum the hydride resonances appear as two doublets at δ -14.60 ($J = 10.9$ Hz) and -14.50 ($J = 10.8$ Hz) with relative intensities 20:1 indicating the presence of two isomers in solution. The $^{31}P\{^1H\}$-NMR spectrum of **6** shows two singlets at δ -11.8 and -12.2 and this is again consistent with the presence of two isomers in solution. On the basis of these spectroscopic data, the two isomers of **6** are assigned structures **6a** and **b**, with the PPh_3 ligand bonded to the N-bound osmium and the C-bound osmium atom, respectively. This type of isomerisation has been previously observed in related triosmium [7,16,20] and triruthenium [21] clusters.

3. Experimental

All manipulations were carried out under an atmosphere of pre-purified N_2 by using conventional Schlenk techniques. Solvents were purified by distillation from an appropriate drying agent. Infrared spectra were recorded by using a Perkin-Elmer 1720 spectrophotometer. ^1H and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC 200 or Varian Unity Plus 400 spectrometer and calibrated against internal TMS $\{^1H\}$ or external H_3PO_4 (^{31}P). Elemental analyses were conducted by the Schwarzkopf Microanalytical Laboratory, New York. The cluster $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to the published procedure [22]. Thiazole was purchased from Aldrich and used as received.

3.1. *Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with thiazole*

Thiazole (162 μl, 2.28 mmol) was added to a dichloromethane solution (50 ml) of $[Os_3(CO)_{10}(MeCN)_2]$ (0.425 g, 0.456 mmol). After being stirred for 24 h at r.t., the volatiles were removed in vacuo and the residue was redissolved in dichloromethane and chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (10:1, v/v) resolved two yellow bands. The faster-moving band afforded $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})]$ **2** (0.085 g, 20%) as yellow crystals after recrystallisation from hexane/CH_2Cl_2 at −20°C. Anal. Calc. for $C_{13}H_3NO_{10}Os_3S$: C 16.68, H 0.32, N 1.50. Found: C, 16.82, H 0.38, N 1.52%. IR [hexane, $\nu(CO)$]: 2107w, 2067s, 2057s, 2025s, 2014s, 2006w, 1998s, 1990w, 1981w cm^{-1}. ^1H-NMR ($CDCl_3$): δ 7.40 (d, $J = 3.6$ Hz), 7.01 (d, $J = 3.6$ Hz), -14.93 (s, 1H). The second band yielded $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}H\overline{C{=}NC{=}CHS})]$ **3** (0.256 g, 60%) as yellow crystals after recrystallisation from hexane/CH_2Cl_2 at −20°C. Anal. Calc. for $C_{13}H_3NO_{10}Os_3S$: C 16.68, H 0.32, N 1.50. Found: C 16.89, H 0.50, N 1.61%. IR [hexane, $\nu(CO)$]: 2105w, 2066s, 2055s, 2023s, 2010s, 2004m, 1997m, 1994m, 1978w cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.65 (d, $J = 1.8$ Hz, 1H), 6.70 (d, $J = 1.8$ Hz, 1H), -15.08 (s, 1H).

3.2. Reaction of **3** with PPh_3

Compound **3** (0.125 g, 0.134 mmol), PPh_3 (0.070 g, 0.267 mmol) and toluene (50 ml) were combined in a flame dried Schlenk flask and the reaction mixture was refluxed for 8 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (10:3, v/v) gave two bands. The faster-moving band gave unconsumed **3** (0.005 g) and the second band afforded $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-H}\overline{C{=}NC{=}CHS})(PPh_3)]$ **4** (0.093 g, 60%) as orange crystals from hexane/CH_2Cl_2 at -20°C. Anal. Calc. for $C_{30}H_{18}NO_9Os_3PS$: C 30.79, H 1.55, N 1.20. Found: C, 30.87; H, 1.48; N, 1.15%. IR [CH_2Cl_2, ν(CO)]: 2089m, 2049s, 2010s, 1997m, 1978sh, 1938w cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.39–7.22 (m, 16H), 6.48 (s, 1H), -14.32 (d, $J = 10.3$ Hz, 1H), -14.11 (d, $J = 9.8$ Hz, 1H).

3.3. Reaction of **3** with $P(OMe)_3$

In a similar reaction to that described in Section 3.2, a sample of **3** (0.095 g, 0.102 mmol) was reacted with $P(OMe)_3$ (19 µl, 0.161 mmol) at 110°C for 8 h in toluene (40 ml), followed by similar chromatographic separation, resulted in unconsumed **3** (0.007 g) and $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-H}\overline{C{=}NC{=}CHS})\{P(OMe_3\}]$ **5** (0.058 g, 55%) as orange crystals after recrystallisation from hexane/CH_2Cl_2 at -20°C. Anal. Calc. for $C_{15}H_{12}NO_{12}Os_3PS$: C 17.46, H 1.17, N 1.36. Found: C, 17.65; H, 1.29; N, 1.38%. IR [CH_2Cl_2, ν(CO)]: 2087s, 2046vs, 2017s, 2002s, 1996sh, 1972m, 1962m cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.57 (d, $J = 1.6$ Hz, 1H), 6.60 (d, $J = 1.6$ Hz, 1H), 3.58 (d, $J = 11.8$ Hz, 9H), -15.07 (d, $J = 9.5$ Hz, 1H), -15.33 (d, $J = 10.0$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 111.9s, 115.7s.

3.4. Reaction of **2** with PPh_3

A toluene solution (30 ml) of **2** (0.055g, 0.059 mmol) and PPh_3 (0.031 g, 0.118 mmol) was refluxed for 8 h. The solvent was removed by rotary evaporation and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 gave one major band from which the cluster $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})(PPh_3)]$ **6** (0.045 g, 65%) was isolated as orange crystals after recrystallisation from hexane/CH_2Cl_2 at -20°C. Anal. Calc. for $C_{30}H_{18}NO_9Os_3PS$: C 30.79, H 1.55, N 1.20. Found: C, 30.68; H, 1.54; N, 1.24%. IR [CH_2Cl_2, ν(CO)]: 2086m, 2045s, 2008s, 1995s, 1970w, 1960w, 1939w cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.49–7.26 (m, 16H), 6.53 (d, $J = 2.6$ Hz, 1H), -14.60 (d, $J = 10.9$ Hz, 1H), -14.50 (d, $J = 10.8$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 11.8s, 12.2s.

3.5. X-ray crystallography

Crystals of complexes **3** and **4** were obtained as described above. All measurements were made at 150 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of rotating anode generator, with Mo–K$_\alpha$ radiation (graphite monochromator, $\lambda = 0.71069$ Å) in a manner described previously [23]. In both cases the unit cell parameters were obtained by least squares refinement of the diffractometer angles for 250 reflections. The crystal data, and the data collection and refinement details for the compounds are presented in Table 3.

All data sets were corrected for absorption using DIFFABS [24]. The structures were solved by direct methods (SHELXS86) [25], developed via difference syntheses, and refined on F^2 by full-matrix least-squares (SHELXL93) [26] using all unique data with intensities greater than zero. In both cases, the non-H atoms were anisotropic and the ring H atoms included in calculated positions (riding model). The bridging hydrides were located from difference maps but not refined.

Final R values are given in Table 3. The residual electron densities in the final difference maps did not indicate any feature of stereochemical significance. Fractional atom co-ordinates for the two compounds are given in Tables 4 and 5. Anisotropic displacement coefficients, H atom parameters and full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. The calculations were performed on a Pentium 200 MHz personal computer. Sources of scattering factors are as in ref. [26]. The molecular diagrams were drawn using SNOOPI [27].

Acknowledgements

We gratefully acknowledge the Islamic-Educational, Scientific and Cultural Organisation (ISESCO) Morocco for support for the purchase of $[Os_3(CO)_{12}]$ (K.A. Azam and S.E. Kabir). We also acknowledge the National Science Foundation (ER CHE 9319062) for support of this research and for matching funds for the purchase of a 400 MHz NMR (CHE 9302468). M.B. Hursthouse and K.M.A. Malik acknowledge the EPSRC support of the crystallography service at Cardiff.

References

[1] A. Eisenstadt, C.M. Giandomenico, M.F. Frederick, R.M. Laine, Organometallics 4 (1985) 2033.

[2] R.H. Fish, T. Kim, J.L. Stewart, J.H. Bushweller, R.K. Rosen, J.W Dupon, Organometallics 5 (1986) 2193.

[3] E. Rosenberg, S.E. Kabir, K.I. Hardcastle, M. Day, E. Wolf, Organometallics 9 (1990) 2214 and references therein.

[4] S.E. Kabir, M. Day, M. Irving, T. McPhillips, H. Minassian, E. Rosenberg, K.I. Hardcastle, Organometallics 10 (1991) 3997.

[5] M. Day, S. Hajela, S.E. Kabir, et al., Organometallics 10 (1991) 2743.

[6] M.P. Cifuentes, M.G. Humphrey, B.W. Skelton, A.H. White, J. Organomet. Chem. 458 (1993) 211.

[7] S.E. Kabir, E. Rosenberg, M. Day, K.I. Hardcastle, M. Irving, J. Clust. Sci. 5 (1994) 481.

[8] (a) J.A. Cabeza, L. Landazuri, L.A. Oro, A. Tiripicchio, M. Tiripicchio, J. Organomet. Chem. 322 (1987) C11. (b) J.A. Cabeza, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem Soc. Dalton. Trans. (1988) 1437.

[9] (a) G. Süss-Fink, T. Jenke, H. Heitz, M.A. Pellighellia, A. Tiripicchio, J. Organomet. Chem. 379 (1989) 311. (b) G.A. Foulds, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 294 (1985) 123.

[10] (a) S. Aime, R. Gobetto, F. Padovan, M. Botta, E. Rosenberg, R. Gellert, Organometallics 6 (1987) 2074. (b) M.W. Day, S. Hajela, R. Gobetto, L. Milone, D. Osella, R. Gellert, Organometallics 9 (1990) 913.

[11] A.J. Arce, A.J. Deeming, Y. De. Sanctis, R. Machado, J. Manzur, C. Rivas, J. Chem. Soc. Chem. Commun. (1990) 1568 and references therein.

[12] R.D. Adams, M.P. Pompeo, W. Wu, J.H. Yamamato, J. Am. Chem. Soc. 115 (1993) 8207.

[13] R.D. Adams, J.A. Belinski, J.H. Yamamato, Organometallics 11 (1992) 3422 and reference therein.

[14] A.M. Brodie, H.D. Holden, J. Lewis, M.J. Taylor, J. Chem. Soc. Dalton Trans. (1986) 633.

[15] Y.K. Au, K.K. Cheung, W.T. Wong, J. Chem. Soc. Dalton. Trans. (1995) 1047 and references therein.

[16] K.A. Azam, R. Dilshad, S.E. Kabir, et al., J. Chem. Soc. Dalton. Trans. (1996) 1731.

[17] M.R. Churchill, B.G. BeBoer, Inorg. Chem. 16 (1977) 828.

[18] S.E. Kabir, M. Tesmer, H. Vahrenkamp, M.B. Hursthouse, K.M.A. Malik, J. Organomet. Chem., in press.

[19] R.J. Gillespie, I. Hargittai, The VSEPR Model of Molecular Chemistry, Allyn and Bacon, Boston, 1991, pp. 18–19.

[20] M.W. Day, D. Espitia, K.I. Hardcastle, et al., Organometallics 10 (1991) 3550.

[21] M.A. Pellinghelli, A. Tiripiechio, J.A. Cabeza, L.A. Oro, J. Chem. Soc. Dalton. Trans. (1990) 1509.

[22] B.F.G. Johnson, J. Lewis, D.A. Pippard, J. Chem. Soc. Dalton Trans. (1981) 407.

[23] J.A. Darr, S.R. Drake, M.B. Hursthouse, K.M.A. Malik, Inorg. Chem. 32 (1993) 5704.

[24] N.P.C. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158, adapted for FAST geometry by A.I. Karaulov, University of Wales, 1991.

[25] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[26] G.M. Sheldrick, SHELXL93 program for crystal structure refinement, University of Gottingen, 1993.

[27] K. Davies, SNOOPI program for crystal structure drawing, University of Oxford, 1983.