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Synthesis and reactivity of tetramethylthioureatriosmium clusters: crystal structures of $[(\mu\text{-H})Os_3(CO)_8(\mu_3\text{-S})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ and $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(PPh_3)]$

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Abstract

The reaction of $[Os_3(CO)_{12}]$ with tetramethylthiourea and water in the presence of a methanolic solution of Me_3NO at 80°C leads to the isolation of the known compound $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **4** in 55% yield and the new compound $[(\mu\text{-H})Os_3(CO)_8(\mu_3\text{-S})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **5** in 10% yield. Treatment of $[Os_3(CO)_{12}]$ with water in the presence of a methanolic solution of Me_3NO at 80°C yields the new compound $[Os_3(CO)_{10}(\mu\text{-OH})(\mu\text{-OMeCO})]$ **8** and the known compounds $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})]$ **6** and $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})]$ **7** in 40, 15 and 21% yields, respectively. The analogous reactions of the undecacarbonyl compounds $[Os_3(CO)_{11}(L)]$ with Me_3NO and H_2O afford $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(L)]$ {$L = SC(NMe_2)_2$, **4**, 60%; $L = PPh_3$, **9**, 55%; $L = P(OMe)_3$, **10**, 52%}. Compound **4** reacts with a series of two electron donor ligands L at ambient temperature to give $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(L)]$ ($L = PPh_3$, **9**, 91%; $L = P(OMe)_3$, **10**, 89%; $L = {}^t\text{BuNC}$, **11**, 85%; L = pyridine, **12**, 72%) by the displacement of the tetramethylthiourea ligand. Compound **5** also reacts with PPh_3 at r.t. to give $[(\mu\text{-H})Os_3(CO)_8(\mu_3\text{-S})(\mu\text{-OMeCO})(PPh_3)]$ **13**, which exists as two isomers in solution, in 93% yield. All the compounds are characterized by IR, ^{1}H-NMR and elemental analysis together with the X-ray structural determinations for **5** and **9**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Carbonyl; Tetramethylthiourea; Clusters; Crystal structures

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1. Introduction

The synthesis and reactivity of polynuclear ruthenium carbonyl complexes possessing thiourea ligands have widely been investigated in recent years [1–8]. These reactions are usually associated with the cleavage of C–S, C–N, N–H and/or C–H bonds of alkyl substituted thiourea ligands and markedly influenced by the nature of the thiourea substituents. In comparison with the extensive ruthenium carbonyl cluster chemistry of thiourea ligands, only a limited number of thiourea derived osmium clusters have been reported in the literature [9,10]. For example we [10] and others [9] have recently reported triosmium clusters containing edge and triply bridging thiourea ligands from the reactions of lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ with thioureas (Scheme 1).

In the course of our investigation on the reactivity of $[Os_3(CO)_{12}]$ with tetamethylthiourea in the presence of a methanolic solution of $Me_3NO \cdot 2H_2O$ as reaction promoter we obtained the 50 e^- cluster $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **4** as the minor

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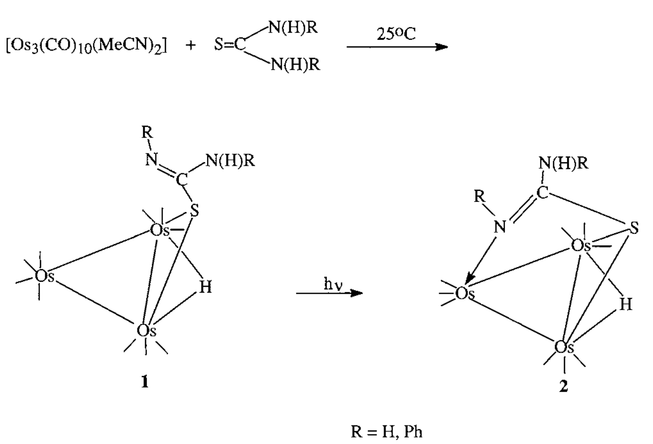
product (10% yield) in addition to the major product $[Os_3(CO)_{11})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **3** (56%) (Scheme 2). The crystal structures of both these compounds were also reported [10].

As a part of our continued studies of the reactions of thiourea ligands with triosmium clusters, we set out to examine the reactivity of $[Os_3(CO)_{11}(L)]$ $\{L = CO, PPh_3, SC(NMe_2)_2, P(OMe)_3\}$ with water and a methanolic solution of anhydrous Me_3NO and this led to an interesting group of compounds $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(L)]$ which have been fully characterized and their chemical properties investigated. We have also studied the reaction of **4** with a variety of donor ligand L which displaces the tetramethylthiourea ligand to afford $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(L)]$ $\{L = PPh_3, P(OMe)_3, {}^t\text{BuNC}, \text{pyridine}\}$. The synthetic and characterization details of these species as well as the crystal structures of two compounds are described herein.

2. Results and discussion

The reaction of $[Os_3(CO)_{12}]$ with tetramethylthiourea and water in the presence of a methanolic solution of Me_3NO at 80°C yields $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **4** and $[(\mu\text{-H})Os_3(CO)_8(\mu_3\text{-S})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **5** in 55 and 10% yields, respectively (Scheme 3). The present route to **4** is found to be more efficient than that described earlier [10].

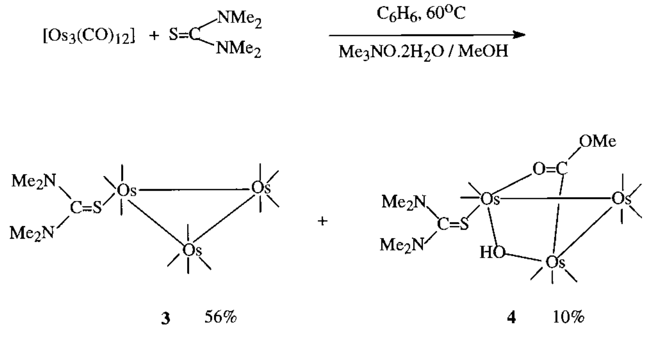
Compound **5** has been characterized by infrared, ^{1}H-NMR, elemental analysis and single crystal diffraction analysis. The X-ray structure of **5** is depicted in Fig. 1 and selected bond distances and angles are presented in Table 1. The molecule consists of a triangle of osmium atoms with metal–metal bonds along two edges [Os(1)–Os(2) = 2.9488(7) and Os(1)–Os(3) = 2.8440(8) Å] and a non-bonded separation of 3.7518(8) Å along the Os(2)–Os(3) edge, with eight terminal carbonyl ligands, a bridging hydride ligand, a μ_3-sulphido ligand, a terminally coordinated tetramethylthiourea ligand and a bridging OMeCO grouping. The most interesting ligand is the methoxycarbonyl (OMeCO) ligand that is believed to have been formed by deprotonation of a methanolic OH bond (by NMe_3) followed by attack of CH_3O^- at a coordinated CO ligand. This ligand bridges the Os(2) and Os(3) atoms through the acyl carbon atom C(9) to Os(3) and the oxygen atom O(9) to Os(2). The Os(3)–C(9) and Os(2)–O(9) distances of 2.079(12) and 2.104(8) Å are similar to those found in other acyl bridged osmium cluster complexes [11–14]. The hydride ligand bridges the Os(2)–Os(3) edge and causes significant lengthening of this bond [2.9488(7) Å] compared with the unbridged Os(1)–Os(2) bond [2.8440(8) Å]. The Os_3 framework is capped by the sulfur ligand which functions as a four electron donor and is envisaged as resulting from the cleavage of the C–S bond of a tetramethylthiourea ligand. The Os–S(1) bonds involving Os(2) and Os(3) [2.413(3) and 2.411(3) Å] are symmetrical and about 0.04 Å longer than that involving Os(1) [2.375(3) Å]. The tetramethylthiourea ligand is coordinated to Os(2) through the sulfur atom at an equatorial site; the observed Os(2)–S(2) distance 2.419(3) Å is close to the corresponding distances [2.431(4) Å] in **3** [10] and [2.375(5) Å] in $[Os_3(CO)_{11}(\eta^1\text{-SCH}_2\text{CH}_2\text{CH}_2)]$ [15] but is significantly shorter than that [2.496(4) Å] found in **4** [10]. In terms of electron counting, compound **5** is electorn preciese (50 e$^-$) if one considers only two metal–metal bonds. The ^{1}H-NMR spectrum of **5** contains three singlets at d 3.40, 3.29 and −18.19 with relative intensities 3:12:1 and is consistent with the X-ray structure.



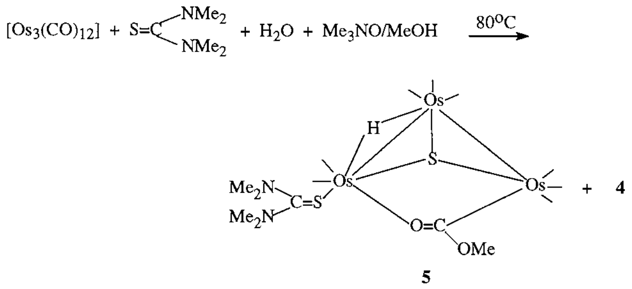
Scheme 1.

Treatment of $[Os_3(CO)_{12}]$ with H_2O in the presence of a methanolic solution of Me_3NO at 80°C resulted in the isolation of the two known compounds $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})]$ **6** [16] and $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})]$ **7** [17] along with the new compound $[Os_3(CO)_{10}(\mu\text{-OH})(\mu\text{-OMeCO})]$ **8** in 15, 21 and 40% yields respectively (Scheme 4).

Compound **8** has been characterized on the basis of elemental analysis and ^{1}H-NMR and infrared spec-



Scheme 2.



Scheme 3.

troscopy. The ^{1}H-NMR spectrum exhibits two singlets at δ 3.96 and −0.52 with relative intensities 3:1; no signals have been observed in the hydride region. The singlet at δ 3.96 is due to the methyl protons of the methoxycarbonyl ligand and that at δ −0.52 is assigned to the hydrogen of the bridging –OH group.

To establish the generality of this synthetic route for compounds of the type $[Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}OMeCO)(L)]$ we have examined the reactions of the undecacarbonyl compounds $[Os_3(CO)_{11}(L)]$ {L = SC(NMe$_2$)$_2$, PPh$_3$ or P(OMe)$_3$} with water in the presence of a methanolic solution of anhydrous trimethylamine-*N*-oxide. Accordingly when $[Os_3(CO)_{11}(L)]$ {L = SC(NMe$_2$)$_2$, PPh$_3$ or P(OMe)$_3$}are treated with H_2O and Me_3NO/CH_3OH at 80°C the 50 e$^-$ compounds $[Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}OMeCO)(L)]$ {L = SC(NMe$_2$)$_2$, **4**, 60%; L = PPh$_3$, **9**, 55%; L = P(OMe)$_3$, **10**, 52%} are obtained (Scheme 5.)

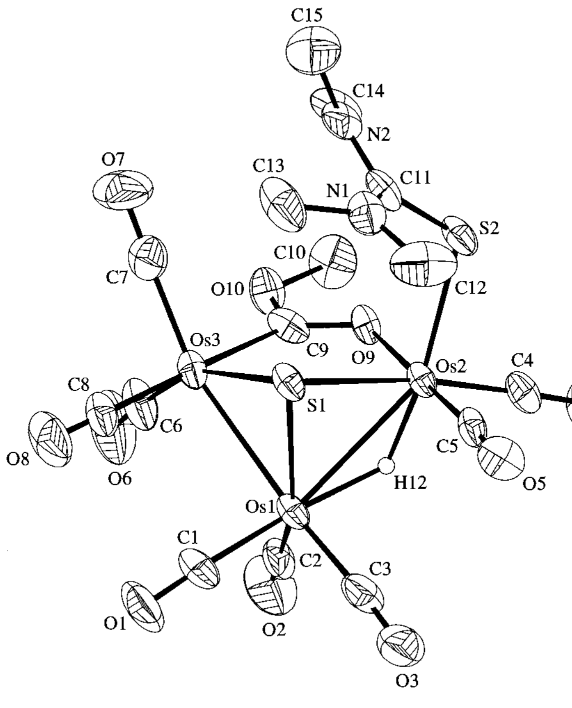


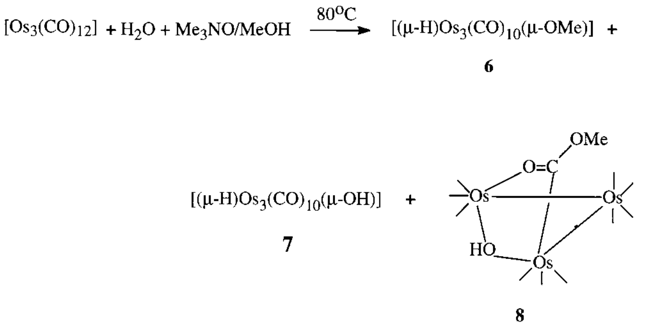
Fig. 1. Molecular structure of $[(\mu\text{-}H)Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}OMeCO)\{\eta^1\text{-}SC(NMe_2)_2\}]$ **5** showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level. The methyl hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for $[(\mu\text{-}H)Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}OMeCO)\{\eta^1\text{-}SC(NMe_2)_2\}]$ **5**

Os(1)–C(1)	1.878(14)	Os(1)–C(2)	1.90(2)
Os(1)–C(3)	1.92(2)	Os(1)–S(1)	2.375(3)
Os(1)–Os(3)	2.8440(8)	Os(1)–Os(2)	2.9488(7)
Os(1)–H(12)	1.83[a]	Os(2)–C(5)	1.860(13)
Os(2)–C(4)	1.934(14)	Os(2)–O(9)	2.105(8)
Os(2)–S(1)	2.413(3)	Os(2)–S(2)	2.418(3)
Os(2)–H(12)	1.69[a]	Os(3)–C(7)	1.91(2)
Os(3)–C(6)	1.91(2)	Os(3)–C(8)	1.97(2)
Os(3)–C(9)	2.079(12)	Os(3)–S(1)	2.411(3)
S(2)–C(11)	1.715(13)	O(9)–C(9)	1.257(14)
O(10)–C(9)	1.352(13)		
C(1)–Os(1)–C(2)	91.5(6)	C(1)–Os(1)–C(3)	88.8(6)
C(2)–Os(1)–C(3)	102.7(6)	C(1)–Os(1)–S(1)	103.0(4)
C(2)–Os(1)–S(1)	142.5(4)	C(3)–Os(1)–S(1)	111.9(5)
C(1)–Os(1)–Os(3)	90.6(4)	C(2)–Os(1)–Os(3)	91.9(4)
C(3)–Os(1)–Os(3)	165.4(5)	S(1)–Os(1)–Os(3)	54.13(7)
C(1)–Os(1)–Os(2)	154.3(4)	C(2)–Os(1)–Os(2)	112.8(4)
C(3)–Os(1)–Os(2)	93.7(4)	S(1)–Os(1)–Os(2)	52.57(7)
Os(3)–Os(1)–Os(2)	80.71(2)	C(1)–Os(1)–H(12)	174[a]
C(2)–Os(1)–H(12)	83[a]	C(3)–Os(1)–H(12)	89[a]
S(1)–Os(1)–H(12)	83[a]	Os(3)–Os(1)–H(12)	93[a]
Os(2)–Os(1)–H(12)	32[a]	C(5)–Os(2)–C(4)	91.1(5)
C(5)–Os(2)–O(9)	179.3(4)	C(4)–Os(2)–O(9)	88.5(4)
C(5)–Os(2)–S(1)	90.2(3)	C(4)–Os(2)–S(1)	171.6(4)
O(9)–Os(2)–S(1)	90.2(2)	C(5)–Os(2)–S(2)	95.6(4)
C(4)–Os(2)–S(2)	90.1(4)	O(9)–Os(2)–S(2)	83.9(2)
S(1)–Os(2)–S(2)	98.02(10)	C(5)–Os(2)–Os(1)	92.0(4)
C(4)–Os(2)–Os(1)	120.3(4)	O(9)–Os(2)–Os(1)	88.6(2)
S(1)–Os(2)–Os(1)	51.41(7)	S(2)–Os(2)–Os(1)	148.58(8)
C(5)–Os(2)–H(12)	102[a]	C(4)–Os(2)–H(12)	87[a]
O(9)–Os(2)–H(12)	78[a]	S(1)–Os(2)–H(12)	85[a]
S(2)–Os(2)–H(12)	162[a]	Os(1)–Os(2)–H(12)	35[a]
C(7)–Os(3)–C(6)	98.5(7)	C(7)–Os(3)–C(8)	92.0(5)
C(6)–Os(3)–C(8)	94.0(6)	C(7)–Os(3)–C(9)	89.7(5)
C(6)–Os(3)–C(9)	85.8(5)	C(8)–Os(3)–C(9)	178.3(5)
C(7)–Os(3)–S(1)	105.8(5)	C(6)–Os(3)–S(1)	155.2(5)
C(8)–Os(3)–S(1)	89.8(4)	C(9)–Os(3)–S(1)	89.7(3)
C(7)–Os(3)–Os(1)	158.7(5)	C(6)–Os(3)–Os(1)	102.5(5)
C(8)–Os(3)–Os(1)	89.6(4)	C(9)–Os(3)–Os(1)	88.8(3)
S(1)–Os(3)–Os(1)	52.97(7)	Os(1)–S(1)–Os(3)	72.91(9)
Os(1)–S(1)–Os(2)	76.02(8)	Os(3)–S(1)–Os(2)	102.11(10)
C(11)–S(2)–Os(2)	110.0(4)	C(9)–O(9)–Os(2)	124.1(7)
O(9)–C(9)–O(10)	114.0(10)	O(9)–C(9)–Os(3)	129.0(8)
O(10)–C(9)–Os(3)	117.0(9)	Os(1)–H(12)–Os(2)	114[a]

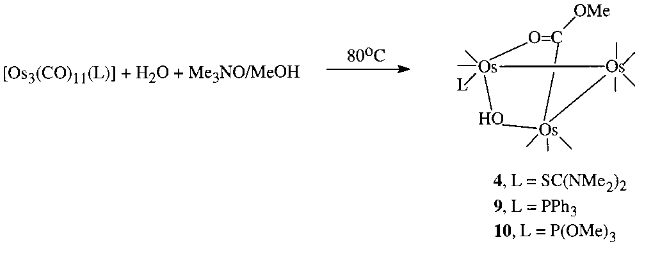
[a] The dimensions associated with the bridging hydride are only approximate.

The formation of **4** from the above reaction indicates that the previous formation of **4** as mentioned in Scheme 2 proceeds through the intermediacy of **3**. Both compounds **9** and **10** have been characterized by elemental analyses as well as infrared, ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy together with a single crystal-structure determination for **9**. The X-ray structure of **9** is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. The molecule consists of a triangular cluster of three osmium atoms with two almost identical metal–metal bonds [Os(1)–Os(3) = 2.8720(10) and Os(1)–Os(2) = 2.8763(14) Å] which are



Scheme 4.

comparable with the corresponding distances [2.875(1) and 2.836(1) Å] in **4** [10]. The third edge of the triangle defined by Os(2) and Os(3) does not have any metal–metal bonding, and as observed in **4** it is doubly bridged by the methoxycarbonyl and the hydroxy ligands. The Os···Os non-bonded distance 3.3776(14) Å in the present compound is virtually identical with that [3.379(1) Å] in **4**. The disposition of the two bridging ligands and the nine terminal CO groups in the two compounds are also closely similar. The osmium–oxygen bond distances involving the hydroxy bridge, Os(3)–O(12) = 2.118(7) and Os(2)–O(12) = 2.138(7) Å, are comparable with the corresponding values 2.148(8) and 2.084(9) Å in **4** and other cluster complexes, e.g. 2.135(5) and 2.118(5) Å in $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-OH})(PMe_2Ph)]$ [18] and 2.137(8) and 2.157(8) Å in $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-OH})(\mu\text{-dppm})]$ [19]. However the Os(2)–C(10) bond length to the methoxycarbonyl bridge in **9** [2.028(2) Å] is slightly shorter than that [2.108(12) Å] in **4** but the Os(3)–O(10) bond length [2.140(7) Å] is similar to that [2.159(8) Å] in **4** [10]. The PPh_3 ligand is coordinated to Os(3) and occupies an equatorial site. The Os(3)–P(1) distance of 2.377(3) Å is similar to those in other phosphine substituted triosmium clusters, e.g. 2.354(2) Å in $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-C=NCH}_2CH_2CH_2)(PPh_3)]$ [20], 2.376(3) Å in $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-2,3-}\eta^2\text{-C=NCMe=CHS})(PPh_3)]$ [21] and 2.353(4) Å in $[(\mu\text{-H})Os_3(CO)_9\{\mu\text{-1,2-}\eta^2\text{-C}_9H_5(CH_3)N\}(PPh_3)]$ [22]. The overall structure of the molecule of **9** is very similar to that of **4**, with exception of the triphenylphosphine ligand coordinated to Os(2) instead of the *S*-coordinated tetramethylthiourea ligand in **4**.



Scheme 5.

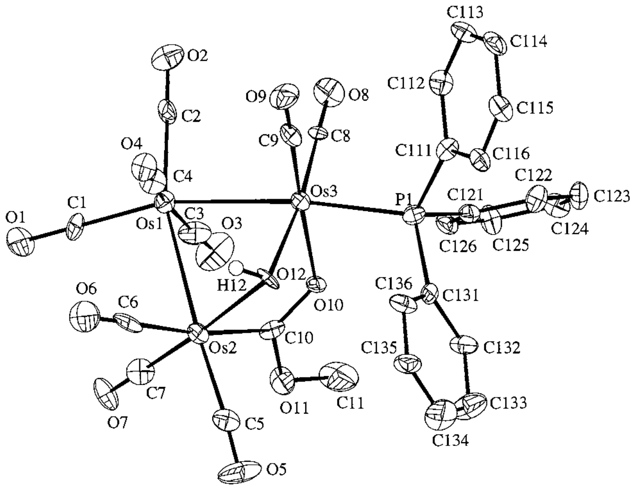


Fig. 2. Molecular structure of $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(PPh_3)]$ **9** showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level. The methyl and phenyl hydrogen atoms are omitted for clarity.

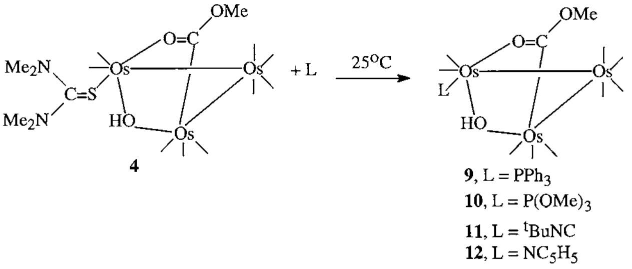
The ^{1}H- and ^{31}P-NMR spectra of **9** and **10** are consistent with their proposed formulations and the crystal structure of **9**. The infrared spectra of **9** and **10** show, in addition to absorptions of the terminal carbonyl ligands, bands characteristic of bridging hydroxy and methoxycarbonyl ligands. The ^{1}H-NMR spectra of each of **9** and **10** exhibit, in addition to proton resonances due to either phosphine or phosphite and methyl protons of the bridging acyl group, a high field doublet (δ −1.98, $J = 4.8$ Hz for **9** and δ −0.56, $J = 5.9$ Hz for **10**) and is assigned to the hydrogen of the hydroxyl group. The doublet of the bridging OH proton is due to coupling with the ^{31}P nucleus. The chemical shifts of the OH protons are in the range of values found for the OH protons of other structurally characterized hydroxy bridged triosmium clusters, e.g. $[(\mu\text{-H})Os_3(CO)_9(\mu\text{-OH})(PMe_2Ph)]$ (δ −1.60) [18], **4** (δ −1.08) [10], $[(\mu\text{-H})Os_3(\mu\text{-OH})(CO)_8\{\mu\text{-dppm}\}]$ (δ −0.44 [19]. The ^{31}P-NMR spectra of **9** and **10** consist of a single signal, and do not show any significant change on varying the recording temperature suggesting that **9** and **10** exist as single isomers.

We have already shown that the η^1-coordinated tetramethylthiourea ligand in **3** is labile and could be easily displaced with two electron donor ligands L ($L = PPh_3$, CH_3CN or NC_5H_5) [10]. Keeping this in mind we exploited the lability of the tetramethylthiourea ligand in **4** for the selective preparation of other monosubstituted clusters and observed that an easy reaction occurs when **4** reacts with an excess of L{L = PPh_3, $P(OMe)_3$, ^{t}BuNC or NC_5H_5} in CH_2Cl_2 at ambient temperature. The displacement of the tetramethylthiourea ligand from **4** affords $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(L)]$ in high yields {L = PPh_3, **9**, 91%; L = $P(OMe)_3$, **10**, 90%; L = ^{t}BuNC, **11**, 85: L = pyridine, **12**, 72%} (Scheme 6).

Table 2
Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_9(\mu\text{-OH}(\mu\text{-OMeCO})(PPh_3)]$ **9**

Os(1)–Os(3)	2.8720(10)	Os(1)–Os(2)	2.8763(10)
Os(1)–C(1)	1.889(13)	Os(1)–C(4)	1.911(12)
Os(1)–C(2)	1.914(12)	Os(1)–C(3)	1.94(2)
Os(2)–C(7)	1.883(14)	Os(2)–C(5)	1.925(12)
Os(2)–C(6)	1.952(14)	Os(2)–C(10)	2.028(11)
Os(2)–O(12)	2.139(8)	Os(3)–C(9)	1.863(13)
Os(3)–C(8)	1.879(10)	Os(3)–O(12)	2.118(7)
Os(3)–O(10)	2.140(7)	Os(3)–P(1)	2.377(3)
O(10)–C(10)	1.283(14)	C(10)–O(11)	1.358(13)
C(1)–Os(1)–C(4)	93.9(5)	C(1)–Os(1)–C(2)	103.7(5)
C(4)–Os(1)–C(2)	95.9(6)	C(1)–Os(1)–C(3)	95.3(6)
C(4)–Os(1)–C(3)	166.9(6)	C(2)–Os(1)–C(3)	90.9(5)
C(1)–Os(1)–Os(3)	162.6(4)	C(4)–Os(1)–Os(3)	81.0(4)
C(2)–Os(1)–Os(3)	93.4(4)	C(3)–Os(1)–Os(3)	87.4(5)
C(1)–Os(1)–Os(2)	91.1(4)	C(4)–Os(1)–Os(2)	85.5(4)
C(2)–Os(1)–Os(2)	165.0(4)	C(3)–Os(1)–Os(2)	85.1(4)
Os(3)–Os(1)–Os(2)	71.97(2)	C(7)–Os(2)–C(5)	90.9(5)
C(7)–Os(2)–C(6)	92.7(5)	C(5)–Os(2)–C(6)	96.2(5)
C(7)–Os(2)–C(10)	91.3(5)	C(5)–Os(2)–C(10)	90.9(5)
C(6)–Os(2)–C(10)	171.8(5)	C(7)–Os(2)–O(12)	170.3(4)
C(5)–Os(2)–O(12)	95.9(4)	C(6)–Os(2)–O(12)	93.5(4)
C(10)–Os(2)–O(12)	81.6(4)	C(7)–Os(2)–Os(1)	90.9(4)
C(5)–Os(2)–Os(1)	176.3(4)	C(6)–Os(2)–Os(1)	87.0(4)
C(10)–Os(2)–Os(1)	85.7(3)	O(12)–Os(2)–Os(1)	82.0(2)
C(9)–Os(3)–C(8)	87.5(5)	C(9)–Os(3)–O(12)	94.5(4)
C(8)–Os(3)–O(12)	172.4(4)	C(9)–Os(3)–O(10)	173.1(4)
C(8)–Os(3)–O(10)	98.3(4)	O(12)–Os(3)–O(10)	80.3(3)
C(9)–Os(3)–P(1)	91.7(4)	C(8)–Os(3)–P(1)	92.4(4)
O(12)–Os(3)–P(1)	94.9(2)	O(10)–Os(3)–P(1)	84.3(2)
C(9)–Os(3)–Os(1)	95.8(4)	C(8)–Os(3)–Os(1)	90.0(3)
O(12)–Os(3)–Os(1)	82.4(2)	O(10)–Os(3)–Os(1)	88.0(2)
P(1)–Os(3)–Os(1)	172.17(8)	Os(2)–O(12)–Os(3)	105.0(3)
Os(3)–O(10)–C(10)	115.8(6)	Os(2)–C(10)–o(11)	121.3(8)
Os(2)–C(10)–O(10)	124.3(8)	O(10)–C(10)–O(11)	114.1(9)

Compounds **11** and **12** are both characterized by elemental analysis, infrared and ^{1}H-NMR spectroscopic data. The close similarity of the IR spectra of **11** and **12** in the carbonyl stretching region to those of **9** and **10** indicate that they are most probably isostructural. In addition to ν(CO) bands compound **11** also exhibits an absorption which corresponds to terminal *tert*-butyl isocyanide ligand (2177 cm^{-1}) [23]. In the ^{1}H-NMR spectra **11** and **12** give rise to the characteristic resonances of μ-OH (δ −0.87 for **11**; −1.54 for **12**) and μ-OMeCO (δ 3.95 for **11**; 3.92 for **12**) ligands as well as signals of a terminal *tert*-butyl isocyanide at δ 1.59 for **11** and *N*-coordinated pyridine at δ 8.57, 7.72 and 7.42 for **12**. The ^{1}H-NMR spectrum of **12** provided clear evidence for the η^1(N)-bonding mode and the signals are shifted downfield from the free pyridine [24].



Scheme 6.

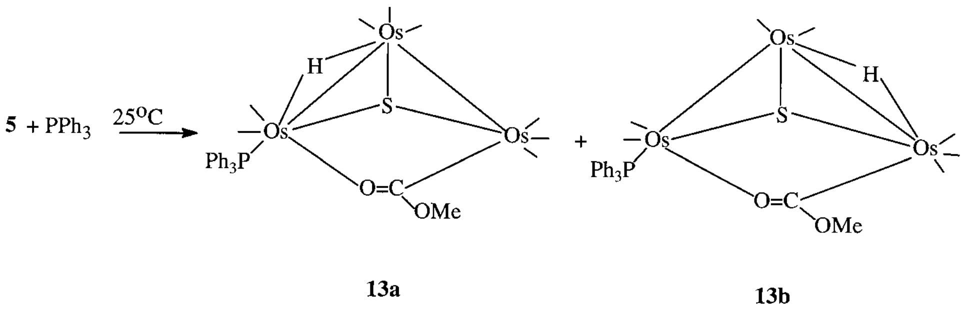
The analogous reaction of **5** with PPh$_3$ at r.t. afforded the corresponding substituted product $[(\mu\text{-H})Os_3(CO)_8(\mu_3\text{-S})(\mu\text{-OMeCO})(PPh_3)]$ **13** in 93% yield (Scheme 7).

The ^{1}H-NMR spectrum of **13** contains two singlets at δ 3.05 and 2.96 for the methyl protons of the methoxycarbonyl ligand and two hydride resonances at δ −14.68 and −14.92 with relative intensities 2:1 respectively. The ^{31}P{^{1}H}-NMR spectrum exhibits two singlets at δ 15.7 and 18.2 in a ratio of 2:1. Thus both ^{1}H- and ^{31}P-NMR spectra of **13** indicated the presence of two isomers in solution in a ratio 2:1. The major isomer, (**13a**) which shows a hydride doublet at δ −14.68 with phosphorus–hydrogen coupling constant of 7.8 Hz, has the same structure as the precursor, the tetramethylthiourea ligand being substituted by PPh$_3$. It is also noted that **13b** exhibits no coupling between the phosphorus and the hydride, which prompts us to believe that the phosphine ligand in **13b** occupies a position at the unbridged osmium atom. This type of isomerization has previously been reported in related phosphine substituted triosmium compounds [20,22,25].

Thus the reactions of [Os$_3$(CO)11(L)] with water and Me$_3$NO/CH$_3$OH represents a general and efficient method for the synthesis of complexes of the type $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(L)]$ resulting from the combined formation of bridging MeOCO and OH ligands accompanied by opening of metal–metal bond. Furthermore the reaction of **4** and **5** with two electron donor ligands such as PPh$_3$, P(OMe)$_3$, ^{t}BuNC and pyridine under mild conditions demonstrate that the tetramethylthiourea ligands in these complexes are relatively labile.

3. Experimental

All reactions unless otherwise noted were carried out by using standard Schlenk techniques under an atmosphere of prepurified nitrogen. The solvents were dried over appropriate drying agents and distilled under nitrogen prior to use. Infrared spectra were recorded on a Bruker IFS25 spectrophotometer. ^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker AC200 spectrometer. Chemical shifts are referenced to internal TMS {^{1}H} and to external 85% H$_3$PO$_4$ {^{31}P}. Elemental analysis were performed at the microanalytical Laboratory of the Institut für Anorganische und Analytische Chemie, Universität Freiburg, Germany. The clusters [Os$_3$(CO)$_{11}$(PPh$_3$)] and [Os$_3$(CO)$_{11}$ {P(OMe)$_3$}] were prepared according to liter-



Scheme 7.

ature methods [26]. $Me_3NO\cdot 2H_2O$ was dehydrated by following published procedures [21].

3.1. Reaction of $[Os_3(CO)_{12}]$ with tetramethylthiourea and water in the presence of $Me_3NO/MeOH$

A methanolic solution (5 cm^3) of Me_3NO (0.021 g, 0.283 mmol) was added dropwise to a benzene solution (100 cm^3) of $[Os_3(CO)_{12}]$ (0.205 g, 0.226 mmol), tetramethylthiourea (0.060 g, 0.452 mmol) and 4–5 drops of water at 80°C. The reaction mixture was heated to reflux for 3 h. The volatiles were removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (3:1) gave two bands. The faster moving minor band gave $[(\mu\text{-H})Os_3(CO)_8(\mu_3\text{-S})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **5** as pale yellow crystals (0.024 g, 10%) after recrystallization from hexane/CH_2Cl_2 at −20°C (Found: C, 17.58; H, 1.47; N, 2.66. $C_{15}H_{16}N_2O_{10}Os_3S_2$ requires: C, 17.68; H, 1.58; N, 2.75%). IR (νCO, CH_2Cl_2): 2076s, 2038vs, 2023s, 1994s, 1975s, 1960s cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.40 (s, 3H), 3.29 (s, 12H), −18.19 (s,^{1}H). The slower moving major band afforded the previously reported [10] compound $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})\{\eta^1\text{-SC(NMe}_2)_2\}]$ **4** as yellow crystals (0.128 g, 55%).

3.2. Reaction of $[Os_3(CO)_{11}\{\eta^1\text{-SC(NMe}_2)_2\}]$ 3 with water in the presence of Me_3NO/CH_3OH

To a refluxing benzene solution (100 cm^3) of **3** (0.075 g, 0.074 mmol) and water (4–5 drops) was added dropwise a methanolic solution (5 cm^3) of Me_3NO (0.011 g, 0.148 mmol) over 30 min. The reaction mixture was refluxed for 1 h during which time analytical TLC showed complete consumption of **3**. The solvent was removed in vacuo and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave one major band which afforded **4** (0.046 g, 60%) as yellow crystals.

3.3. Reaction of $[Os_3(CO)11(PPh_3)]$ with water in the presence of Me_3NO/CH_3OH

A similar reaction to that above of $[Os_3(CO)_{11}(PPh_3)]$ (0.136 g, 0.119 mmol), water (4–5 drops) and a methanolic solution (5 cm^3) of Me_3NO (0.014 g, 0.184 mmol) at 80°C in benzene (60 cm^3) for 1 h followed by similar chromatographic separation eluting with hexane/CH_2Cl_2 (10:3, v/v) gave two bands. The faster moving band afforded unconsumed starting material (0.010 g) while the second band yielded $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})(PPh_3))]$ **9** as yellow crystals (0.042 g, 55%) after recrystallization from hexane/CH_2Cl_2 at −20°C (Found: C, 30.25; H, 1.42. $C_{29}H_{19}O_{12}Os_3P$ requires: C, 30.00; H, 1.65%). IR (νCO, CH_2Cl_2): 2086s, 2049vs, 2003vs, 1991s, 1979s, 1960sh, 1931w cm^{-1}, KBr, ν(OH) 3432m, br, methoxycarbonyl, 1477m cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.42–7.56 (m, 15H), 3.58 (s, 3H), −1.98(d, 1H, $J = 4.8$ Hz); $^{31}P\{^1H\}$-NMR: δ 19.4 (s).

3.4. Reaction of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ with water in the presence of Me_3NO/CH_3OH

An identical reaction of a methanolic solution (5 cm^3) of Me_3NO (0.014 g, 0.186 mmol), $[Os_3(CO)_{11}\{P(OMe)_3\}]$ (0.108 g, 0.108 mmol) and water (4–5 drops) in benzene (60 cm^3) followed by similar chromatographic separation as above yielded $[Os_3(CO)_9(\mu\text{-OH})(\mu\text{-OMeCO})\{P(OMe)_3\}]$ **10** as yellow crystals (0.057 g, 52%) after recrystallization from hexane/CH_2Cl_2 at −20°C (Found: C, 16.54; H, 1.22. $C_{14}H_{13}O_{15}Os_3P$ requires: C, 16.44; H, 1.28%). IR (νCO, CH_2Cl_2): 2088m, 2049vs, 2007vs, 1988sh, 1978s, 1960w, 1935w cm^{-1}; KBr ν(OH): 3434m, br, cm^{-1}; methoxycarbonyl: 1489 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.90(s, 3H), 3.75(d, 9H, $J = 11.8$ Hz), −0.56(d, 1H, $J = 5.9$ Hz); $^{31}P\{^1H\}$-NMR: δ 14.5 (s).

Table 3
Crystal data and details of data collection and structure refinement for [(μ-H)$Os_3(CO)_8${μ_3-S)(μ-OMeCO){η^1-SC($NMe_2)_2$}] **5** and [$Os_3(CO)_9${μ-OH)(μ-OMeCO)(PPh_3)] **9**[a]

	5	**9**
Empirical formula	$C_{15}H_{16}N_2O_{10}Os_3S_2$	$C_{29}H_{19}O_{12}Os_3P$
Formula weight	1019.02	1161.01
Unit cell dimensions		
a (Å)	9.7628(8)	10.166(3)
b (Å)	16.786(2)	9.557(3)
c (Å)	16.095(2)	33.137(5)
β (°)	106.650(11)	93.32(2)
V (Å^3)	2527.1(5)	3214(2)
D_{calc}(Mg m^{-3})	2.678	2.399
Absorption coefficient (mm^{-1})	15.261	11.941
F(000)	1840	2128
Crystal size (mm)	0.22 × 0.16 × 0.15	0.25 × 0.20 × 0.16
θ range for data collection (°)	2.20 to 24.99	2.22 to 25.00
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	−11, 11; −18, 18; −14, 19	−10, 9; −11, 11; −37, 31
Reflections collected	10 840	8401
Independent reflections	3854	4409
R_{int}	0.0870	0.0862
Absorption correction factors	0.837–1.019	0.732–0.998
Data/restraints/parameters	3854/0/294	4409/19/410
Goodness-of-fit on F^2	1.042	1.086
R_1/wR_2 (all unique data)	0.0556/0.1072	0.0579/0.1346
R_1/wR_2 [data with $I > 2\sigma(I)$][b]	0.0464/0.1055	0.0509/0.1327
Largest diff. peak and hole (e Å^{-3})	4.150 and −1.976	4.067 and −1.851

[a] Details in common: Crystal system monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$, Mo–K$_\alpha$ radiation, $\lambda = 0.71069$ Å, $T = 150(2)$ K, cell dimensions from 250 reflections, full-matrix least-squares on F^2; R_1 and wR_2 as defined in Ref. [30]; weighting scheme, $w = 1/[\sigma^2(F_o^2) + (a \times P)^2]$, where $P = [\max(F_o^2) + 2 \times F_c^2)]/3$ and $a = 0.0541$ for **5** and 0.0901 for **9**.

[b] Data with $I > 2\sigma(I)] = 3175$ for **5** and 3931 for **9**.

3.5. Reaction of [$Os_3(CO)_{12}$] with water in the presence of Me_3NO/MeOH

A methanolic solution (5 cm^3) of Me_3NO (0.017 g, 0.226 mmol), was added dropwise to a refluxing benzene solution (40 cm^3) of [$Os_3(CO)_{12}$] (0.100 g, 0.110 mmol) containing 4 drops of water over 30 min. The resulting solution was heated to reflux 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 (3:1, v/v) developed three bands which yielded in order of elution: [(μ-H)$Os_3(CO)_{10}$(μ-OMe)] **6** (0.015 g, 15%), [(μ-H)$Os_3(CO)_{10}$(μ-OH)] **7** (0.020 g, 21%) and [$Os_3(CO)_{10}$(μ-OH)(μ-OMeCO) **8** (0.041 g, 40%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −20°C (Found: C, 15.66; H, 0.64. $C_{12}H_4O_{13}Os_3$ requires: C, 15.55; H, 0.44%). IR (νCO, hexane): 2107m, 2074vs, 2053s, 2022vs, 2002vs, 1995s, 1981w cm^{-1}, ^{1}H-NMR ($CDCl_3$): δ 3.96 (s, 3H), −0.52 (s, br, ^{1}H).

3.6. Reactions of [$Os_3(CO)_9$(μ-OH)(μ-OMeCO){η^1-SC-($NMe_2)_2$}] **4** with L (L = PPh_3, $P(OMe)_3$, ^{t}BuNC or pyridine)

The reactions **4** with PPh_3, $P(OMe)_3$, ^{t}BuNC or pyridine were performed by reacting **4** with 5 equiv. of the respective ligand, both dissolved in CH_2Cl_2. A typical reaction of **4** was carried out as follows: To a CH_2Cl_2 solution (25 cm^3) of **4** (0.050 g, 0.048 mmol) was added PPh_3 (0.064 g, 0.244 mmol). The reaction mixture was stirred at r.t. for 4 h during which time analytical TLC indicated complete consumption of **4**. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel.

Table 4
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for [(μ-H)$Os_3(CO)_8$(μ^3-S)(μ-OMeCO){η^1-SC($NMe_2)_2$}] **5**

	x	y	z	U_{eq}^{a}
Os(1)	3207.4(5)	1094.7(3)	4018.0(3)	37(1)
Os(2)	4875.1(5)	460.4(2)	2900.8(3)	32(1)
Os(3)	1009.9(5)	1030.1(2)	2416.7(3)	40(1)
S(1)	3347(3)	1618(2)	2674(2)	38(1)
S(2)	5327(4)	441(2)	1501(2)	48(1)
O(1)	1622(14)	2377(8)	4703(7)	93(4)
O(2)	1784(12)	−220(7)	4779(7)	87(4)
O(3)	5795(11)	1478(8)	5543(7)	83(3)
O(4)	6661(10)	−1043(5)	3442(6)	55(2)
O(5)	7378(10)	1487(6)	3785(6)	61(3)
O(6)	−1238(12)	13(8)	2915(9)	102(4)
O(7)	−431(16)	1230(7)	476(8)	108(5)
O(8)	−167(13)	2634(7)	2843(7)	92(4)
O(9)	3112(8)	−259(4)	2282(5)	38(2)
O(10)	875(9)	−631(5)	1799(6)	54(2)
N(1)	4847(12)	1984(6)	1069(7)	54(3)
N(2)	3450(11)	1084(7)	118(7)	49(3)
C(1)	2209(15)	1891(9)	4423(8)	55(4)
C(2)	2326(13)	282(9)	4505(8)	49(3)
C(3)	4878(16)	1349(9)	4953(10)	60(4)
C(4)	5997(13)	−499(8)	3227(8)	45(3)
C(5)	6445(13)	1090(7)	3441(8)	39(3)
C(6)	−432(16)	416(9)	2706(10)	62(4)
C(7)	93(16)	1161(8)	1207(10)	63(4)
C(8)	266(14)	2055(9)	2694(9)	54(3)
C(9)	1830(14)	−56(7)	2162(7)	40(3)
C(10)	1420(17)	−1396(8)	1630(10)	81(5)
C(11)	4484(13)	1230(7)	886(8)	41(3)
C(12)	6199(20)	2200(11)	1669(10)	97(6)
C(13)	3808(20)	2646(9)	827(10)	83(5)
C(14)	2667(17)	325(9)	3(9)	70(4)
C(15)	3202(20)	1563(10)	−650(10)	87(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Os_3(CO)_9(\mu\text{-}OH(\mu\text{-}OMeCO)(PPh_3)]$ **9**

	x	y	z	U_{eq}^a
Os(1)	1362.3(5)	2147.9(5)	1807.0(2)	19(1)
Os(2)	145.4(5)	−561.8(5)	1846.6(1)	19(1)
Os(3)	−564.1(4)	1919.0(4)	1141.3(1)	16(1)
P(1)	−2349(3)	1592(3)	655(1)	18(1)
O(1)	3279(10)	1419(10)	2514(3)	34(2)
O(2)	2066(8)	5160(9)	1607(3)	32(2)
O(3)	−922(10)	3133(10)	2313(4)	46(3)
O(4)	3129(9)	835(9)	1188(3)	31(2)
O(5)	−1282(11)	−3360(10)	1887(3)	47(3)
O(6)	2946(10)	−1794(9)	1797(4)	42(3)
O(7)	391(10)	−470(10)	2761(3)	37(2)
O(8)	−956(9)	5028(9)	1147(3)	33(2)
O(9)	1340(9)	2317(9)	495(3)	33(2)
O(10)	−1977(7)	1370(8)	1568(2)	16(2)
O(11)	−2490(8)	216(9)	2118(3)	30(2)
O(12)	−142(8)	−241(8)	1209(2)	18(2)
C(1)	2541(12)	1708(13)	2251(4)	22(3)
C(2)	1788(12)	4044(12)	1683(4)	25(3)
C(3)	−50(15)	2765(13)	2132(5)	32(3)
C(4)	2442(12)	1317(12)	1419(4)	22(3)
C(5)	−771(13)	−2324(12)	1856(4)	23(3)
C(6)	1903(14)	−1352(13)	1807(4)	26(3)
C(7)	308(13)	−526(12)	2415(4)	26(3)
C(8)	−804(10)	3869(11)	1147(3)	11(2)
C(9)	614(13)	2194(12)	738(4)	22(3)
C(10)	−1584(11)	496(11)	1843(4)	16(3)
C(11)	−3736(15)	947(17)	2078(6)	50(4)
C(111)	−1966(11)	2075(11)	137(4)	18(3)
C(112)	−1526(12)	3462(13)	79(4)	24(3)
C(113)	−1222(12)	3900(13)	−291(4)	31(3)
C(114)	−1346(13)	3006(13)	−622(4)	26(3)
C(115)	−1779(12)	1658(13)	−560(4)	27(3)
C(116)	−2119(12)	1207(12)	−200(4)	24(3)
C(121)	−3803(11)	2616(12)	735(4)	21(3)
C(122)	−4731(12)	2882(12)	415(4)	25(3)
C(123)	−5824(12)	3703(13)	473(4)	28(3)
C(124)	−6020(13)	4273(12)	834(4)	25(3)
C(125)	−5140(12)	4047(13)	1160(4)	28(3)
C(126)	−4026(12)	3209(11)	1110(4)	21(3)
C(131)	−2889(12)	−233(11)	632(4)	22(3)
C(132)	−4091(12)	−637(11)	766(4)	25(3)
C(133)	−4395(14)	−2076(13)	772(5)	41(4)
C(134)	−3514(15)	−3044(13)	650(6)	43(4)
C(135)	−2337(13)	−2618(12)	518(4)	27(3)
C(136)	−2035(13)	−1251(11)	498(4)	25(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Elution with hexane/CH_2Cl_2 gave a single band which afforded $[Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}OMeCO)(PPh_3)]$ **9** as yellow crystals (0.051 g, (91%) after recrystallization from hexane/CH_2Cl_2 at −20°C.

$[Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}OMeCO)\{P(OMe)_3\}]$ **10**: Recrystallized from hexane/CH_2Cl_2 at −20°C; yield 0.049 g, 89%.

$[Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}OMeCO)(^tBuNC)]$ **11**: Pale yellow crystals, recrystallized from hexane/CH_2Cl_2 at 0°C; yield, 0.041g, 85% (Found: C, 19.85; H, 1.81; N, 1.62. $C_{16}H_{13}NO_{12}Os_3$ requires:C, 19.57; H, 1.33 N, 1.43%). IR (νCO, CH_2Cl_2): 2087s, 2049vs, 2006vs, 1988sh, 1978s,1960sh, 1946sh cm^{-1}, νCN: 2177 br cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.95(s, 3H), 1.59(s, 9H), −0.87 (s, 1H).

$[Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}OMeCO)(\eta^1\text{-}NC_5H_5)]$ **12**: Yellow crystals, recrystallized from hexane/CH_2Cl_2 at 0°C, yield, 0.034 g, 72% (Found: C, 19.42; H, 0.83; N, 1.35. $C_{16}H_9NO_{12}Os_3$ requires:C, 19.65; H, 0.93, N, 1.43%). IR (νCO, CH_2Cl_2): 2089m, 2050vs, 2005s, 1994s, 1979s, 1962m cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.57 (m, 2H), 7.92 (m, 1H), 7.42 (m, 2H), 3.92 (s, 3H), −1.54 (s, br, 1H).

3.7. Reaction of $[(\mu\text{-}H)Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}OMeCO)\{\eta^1\text{-}SC(NMe_2)_2\}]$ **5** with PPh_3

To a CH_2Cl_2 solution (20 cm^3) of **5** (0.020 g, 0.020 mmol) was added PPh_3 (0.028 g, 0.106 mmol). The reaction mixture was stirred at r.t. for 5 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (5:1, v/v) gave a single band which afforded $[(\mu\text{-}H)Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}OMeCO)(PPh_3)]$ **13** (0.021 g, 91%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 0°C (Found: C, 29.45; H, 1.82. $C_{28}H_{19}O_{10}Os_3PS$ requires:C, 29.26; H, 1.67%). IR (νCO, CH_2Cl_2): 2078s, 2042vs, 2023s, 1998s, 1980s, 1956sh cm^{-1}; ^{1}H-NMR ($CDCl_3$): (mixture of two isomers in 2:1 ratio), major isomer, δ 7.28–7.81 (m, 15H), 3.05 (s, 3H), −14.68 (d, 1H, $J = 7.8$ Hz), minor isomer, δ 7.28–7.81 (m, 15H), 2.96 (s, 3H), −14.92 (d, 1H); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 15.7 (s, major isomer), 18.2 (s, minor isomer). The phenyl resonances of the isomers are overlapped.

3.8. X-ray crystallography

Crystals of the complexes **5** and **9** were obtained as described above. X-ray measurements were made using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode (Mo) generator, in a manner described previously [27]. In both cases the data were corrected for absorption using DIFABS [28]. The crystallographic data, and the data collection and refinement details for **5** and **9** are presented in Table 3.

The structures were solved by direct methods (SHELXS-86) [29], developed via difference syntheses, and refined on F^2 by full-matrix least-squares (SHELXL-93) [30] using all unique data with intensities > 0. In both cases, the non-hydrogen atoms were anisotropic, and the methyl and phenyl hydrogen atoms were included in calculated positions (riding model).

The bridging hydride [H(12)] in **5** was located from difference maps but not refined. The OH hydrogen in **9** was also located from difference map and refined with a DFIX parameter = 1.08 Å for the O–H distance. In this structure the C(8), C(112) and O(7) atoms were also refined with the restraint ISOR = 0.005 to keep the displacement coefficients of these atoms 'approximately isotropic'. Final *R*-values are given in Table 3. Sources of scattering factors are as in ref. [30]. The molecular diagrams were drawn using SNOOPI [31]. Fractional co-ordinates are given in Tables 4 and 5.

Full crystallographic details including thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation.

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