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Reactivity of the unsaturated triosmium cluster $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ with dithiols; X-ray structures of $[Os_3(CO)_8(\mu\text{-}SCH_2CH_2CH_2S)(Ph_2PCH_2PPh_2)]\cdot 1/2CH_2Cl_2$ and $[(\mu\text{-H})Os_3(CO)_7(\mu_3\text{-}\eta^3\text{-}SCH_2CH_2CHS)(Ph_2PCH_2PPh_2)]\cdot 1/2H_2O$

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Abstract

Treatment of the unsaturated cluster $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**1**) with $HS(CH_2)_nSH$ ($n = 1$, 1,2-ethanedithiol; $n = 2$, 1,3-propanedithiol) lead to the novel compounds $[(\mu\text{-H})Os_3(CO)_8\{\mu\text{-}S(CH_2)_nS\}\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**9**, $n = 2$, 49%; **12**, $n = 3$, 56%) and $[Os_3(CO)_8\{\mu\text{-}S(CH_2)_nS\}(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**10**, $n = 2$, 20%; **13**, $n = 3$, 22%). The 52-electron compounds **9** and **12** contain a bridging hydride, a bridging dithiolato and an orthometallated dppm ligand while the 50-electron compounds **10** and **13** contain a doubly bridging dithiolato and a bridging dppm ligand. Compounds **9** and **12** are converted into **10** and **13** in 55 and 56% yields, respectively, by thermolysis at 110°C. Photolysis of **9** and **12** also gives **10** and **13** but in somewhat lower yields. Compounds **10** and **13** undergo decarbonylation and aliphatic C–H bond activation of the dithiolato moiety at 128°C to give $[(\mu\text{-H})Os_3(CO)_7(\mu_3\text{-}\eta^3\text{-}SCH_2CHS)(Ph_2PCH_2PPh_2]$ (**11**) and $[(\mu\text{-H})Os_3(CO)_7(\mu_3\text{-}\eta^3\text{-}SCH_2CH_2CHS)(Ph_2PCH_2PPh_2]$ (**14**) containing a bridging hydride, a triply bridging dithiolato and a bridging dppm ligand. Thermolysis of **9** and **12** at 128°C also gives **11** and **14** in 43 and 51% yields, respectively. Compounds **13** and **14** have been characterised by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Osmium; Dithiolate; Phosphine; Carbonyl; Crystal structures

1. Introduction

Thiolato bridged triosmium clusters of the type $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SR})]$ (R = Et or Ph) with the hydride and SR bridging the same Os–Os edge have been formed by simple oxidative addition reaction of thiols with $[Os_3(CO)_{12}]$ or better with $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_3(CO)_{10}(C_6H_8)]$ [1–3]. The dppm substituted compound $[Os_3(CO)_{10}(\mu\text{-dppm})]$ and its acetonitrile derivative $[Os_3(CO)_9(\mu\text{-dppm})(MeCN)]$ react with organic thiols to give $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-SR})(\mu\text{-dppm})]$ (R = Et or Ph) in which the hydride and thiolato ligand bridge one of the unbridged osmium–osmium edges [4,5]. We have previously reported the reactions of the unsaturated triosmium compound $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**1**) with thiols such as ethanethiol, propane-2-thiol and thiophenol, and observed a remarkable influence of the steric bulk of the thiols on the type of product obtained [6]. For example, thiophenol having the bulkiest substituent gives only the simple oxidative addition product $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-dppm})(\mu\text{-SPh})]$ while less bulky thiols such as ethanethiol and propane-2-thiol give the novel 50-electron compounds $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-}SC_2H_5)(\eta^1\text{-}$

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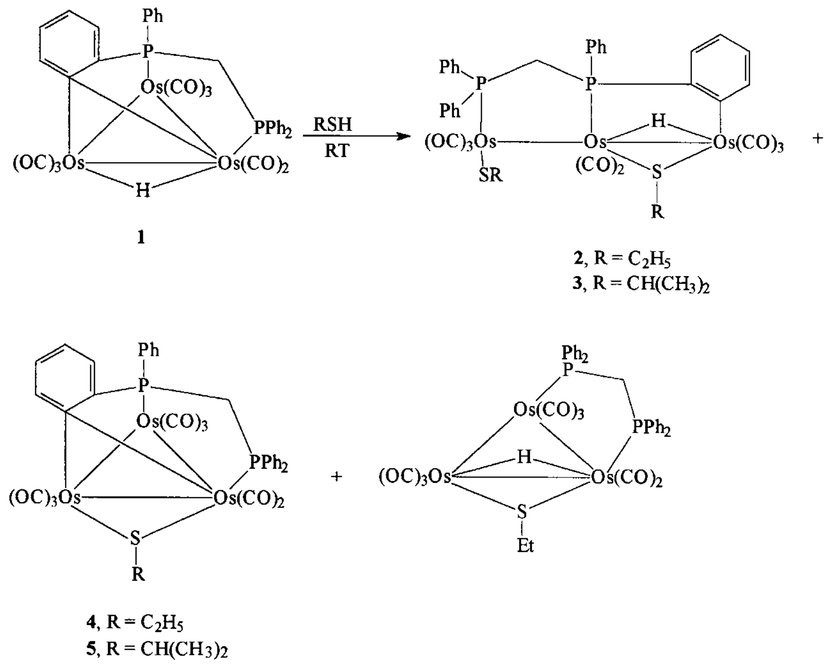
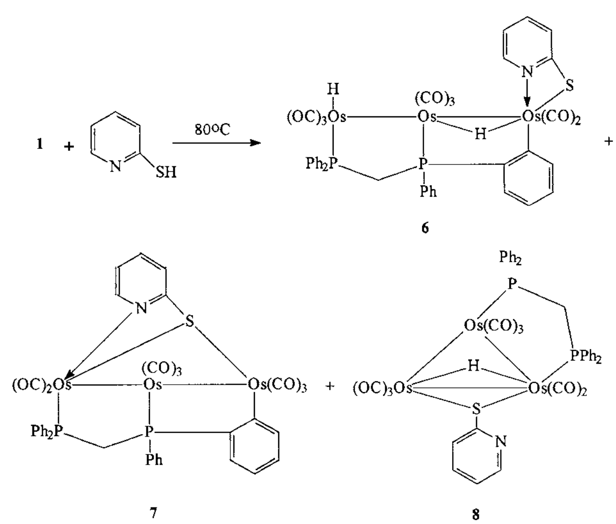


Scheme 1.

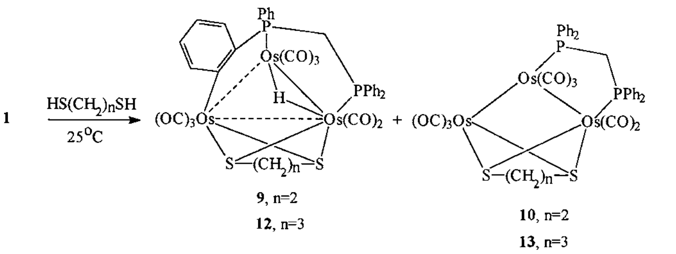
$SC_2H_5)\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**2**) and $[(\mu\text{-}H)Os_3(CO)_8\{\mu\text{-}SCH(CH_3)CH_3\}\{\eta^1\text{-}SCH(CH_3)CH_3\}\text{-}\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**3**) as the major products and the 48 electron species $[Os_3(CO)_8(\mu\text{-}SC_2H_5)\text{-}(Ph_2PCH_2P(Ph)C_6H_4\}]$ (**4**) and $[Os_3(CO)_8(\mu\text{-}SCH(CH_3)CH_3\}\{Ph_2PCH_2P(Ph)C_6H_4\}$ (**5**) as the minor products along with a small amount of $[(\mu\text{-}H)Os_3(CO)_8(\mu\text{-dppm})(\mu\text{-SEt})]$ in case of ethanethiol [6] (Scheme 1).

Recently we reported [7] the reactions of **1** with organic heterocyclic thiols such as pyridine-2-thiol and pyrimidine-2-thiol; the latter gives only simple oxidative addition product $[(\mu\text{-}H)Os_3(CO)_8(\mu\text{-}N_2SC_4H_3)(\mu\text{-dppm})]$ in high yield while the former affords the 52-electron compounds $[H(\mu\text{-}H)Os_3(CO)_8(\eta^2\text{-}NSC_5H_4)\{Ph_2PCH_2P\text{-}(Ph)C_4H_4\}]$ (**6**) and $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}NSC_5H_4)\text{-}\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**7**) and the simple oxidative addition product $[Os_3(CO)_8(\mu\text{-}NSC_5H_4)(\mu\text{-dppm})]$ (**8**) (Scheme 2).

The use of alkanedithiolates to stabilize transition metal cluster compounds by serving as chelating or bridging ligands preventing cluster fragmentation during the course of catalytic reactions has received increasing attention [8–18]. Adams et al. [19] reported the synthesis of dithiolato bridged di- and tri-metallic compounds *anti*-$[Ru_3(CO)_7(\mu\text{-}SCH_2CH_2S)_2]$, *syn*-$[Ru_3(CO)_7(\mu\text{-}SCH_2CH_2S)_2]$ and $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ from the ring opening reaction of 1,2,5,6-tetrathiacyclooctane with $[Ru_3(CO)_{12}]$ at 40°C. The dithiolato bridged di-iron compound $[Fe_2(CO)_6\text{-}(\mu\text{-}SCH_2CH_2S)]$ has been reported from the reaction of $[Fe_3(CO)_{12}]$ with 1,2-ethanedithiol [20] while the osmium compound $[Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ was obtained from the pyrolysis of $[\{(\mu\text{-}H)Os_3(CO)_{11}\text{-}(SCH_2CH_2SCH_2CH_2)]$ as well as from the direct reaction of $[Os_3(CO)_{12}]$ with 1,4-dithiacyclohexane [21]. Lewis et al. [22] reported $[\{(\mu\text{-}H)Os_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ from the reaction of the lightly ligated cluster $[Os_3(CO)_{10}(MeCN)_2]$ with 1,3-propanedithiol. In a recent study we found that $[Ru_3(CO)_{12}]$ reacts with 1,2-ethanedithiol at 68°C to afford the known compound $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ while the analogous reaction with 1,3-propanedithiol yields $[\{(\mu\text{-}H)Ru_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ and $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ [23]. The bidentate dithi-



Scheme 2.



Scheme 3.

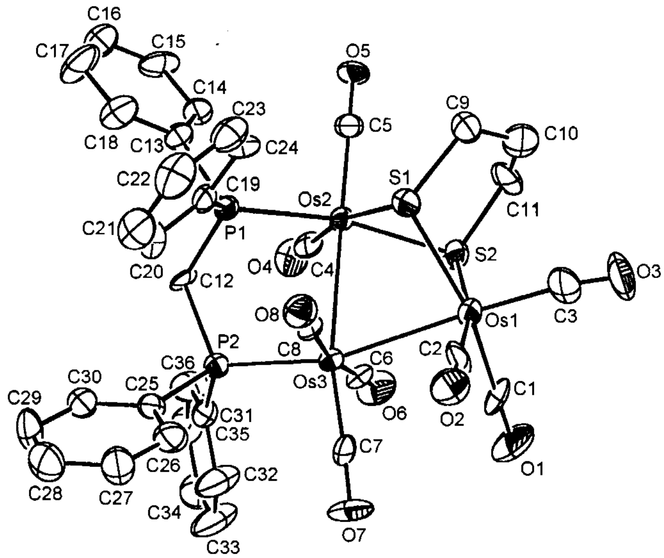


Fig. 1. X-ray structure of $[Os_3(CO)_8\{\mu\text{-}S(CH_2)_3S\}\ (\mu\text{-}Ph_2PCH_2PPh_2)]$ (**13**) showing the atom numbering scheme. Thermal ellipsoids are drawn at 40% probability level. The hydrogen atoms are omitted for clarity.

olato ligands in these complexes are generally robust and lend stability of these complexes. We also investigated the reaction of diphosphine substituted triruthenium compounds $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ and $[Ru_3(CO)_{10}(\mu\text{-dppe})]$ with dithiols and observed that the product formation depends on the length of the methylene chain of the diphosphine ligand [24]. For example, the reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ with 1,3-propanedithiol gives the dinuclear product $[Ru_2(CO)_4\{\mu\text{-}S(CH_2)_3S\}(\mu\text{-dppm})]$ while $[Ru_3(CO)_{10}(\mu\text{-dppe})]$ gives the trinuclear complexes $[(\mu\text{-}H)Ru_3(CO)_8\{\mu\text{-}S(CH_2)_3SH\}(\mu\text{-dppe})]$ and $[Ru_3(CO)_5\text{-}\{\mu\text{-}S(CH_2)_3S\}_2\ (\eta^2\text{-dppe})]$. In the present paper we describe the results of our studies on the reactions of **1** with dithiols, including an unprecedented C-H bond activation of the methylene group of the coordinated dithiolato ligand.

2. Results and discussion

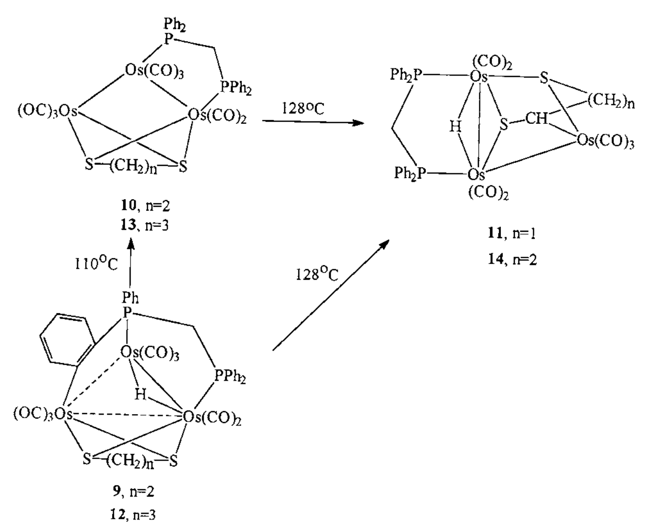
Treatment of **1** with two equivalents of $HS(CH_2)_nSH$ ($n = 2$, 1, 2-ethanedithiol; $n = 3$, 1,3-propanedithiol) at room temperature gave the novel compounds $[(\mu\text{-}H)Os_3(CO)_8\{\mu\text{-}S(CH_2)_nS)\}\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**9**, $n = 2$, 49%; **12**, $n = 3$, 56%) and $[Os_3(CO)_8\text{-}\{(\mu S(CH_2)_nS)(Ph_2PCH_2\ PPh_2)]$ (**10**, $n = 2$, 20%; **13**, $n = 3$, 22%) (Scheme 3), which were characterized by spectroscopic methods, together with a single crystal X-ray analysis for **13**·$1/2CH_2Cl_2$.

The infrared spectra of **9** and **12** are very similar and indicate that all the carbonyl ligands are terminal. The $^{13}C\{^1H\}$-NMR spectra indicate the presence of eight carbonyl groups. The aromatic regions show well separated multiplets characteristic of orthometallated dppm ligand, in addition to the usual resonances arising from the methylene protons of the ligands. The high field doublets of a doublet is assigned to the bridging hydride which is coupled to two nonequivalent ^{31}P nuclei. Futhermore, the appearance of the hydride resonances as a doublet of doublets is indicative of the hydride bridging the same Os–Os edge as the phosphorus atoms of the orthometallated dppm ligand. The $^{31}P\{^1H\}$-NMR spectra show two doublets indicating that the two phosphorus nuclei are nonequivalent. The mass spectra contain molecular ion peaks and fragment ions formed by the loss of up to eight CO ligands. Assuming that the dithiolato ligand serves as a six-electron donor and the orthometallated diphosphine ligand donates five electron, the molecule contains a total of 52 valence electrons and in the presence of one metal-metal bond each metal atom formally obeys the 18-electron rule. The dithiolato ligand bridges one of the open osmium-osmium edges with each sulfur atom bonded to both metal atoms. The coordination of the dithiolato ligands in these compounds is very similar to that observed in the compounds $[Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ and $[Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)]$ [21].

The X-ray structure of **13** is depicted in Fig. 1, and selected bond distances and angles are listed in Table 1. It is based on an Os_3 unit with two metal-metal bonds, Os(1)–Os(3) = 2.8790(12) and Os(2)–Os(3) = 2.9031(10) Å, and a non-bonded separation of 3.4252(11) Å between Os(1) and Os(2). The metal–metal bonded distances in this complex are close to the average value 2.877 Å in $[Os_3(CO)_{12}]$ [25] and the non-bonded distance is somewhat longer than those in the related doubly bridged complexes, 3.365(1) Å in $[Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)]$ [21] and 3.233(2) Å in $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ [26]. The structure contains eight terminal carbonyl groups, a bridging demetallated dppm ligand and a bridging dithiolato moiety. Os(1) and Os(3) are each associated with three and Os(2) is linked to two terminal carbonyl ligands. The 1,3-propanedithiolato ligand forms two bridges between the pair of non-bonded osmium atoms through the S atoms and serves as a six-electron donor. The dppm ligand bridges one of the metal–metal bonded edges and acts as a four-electron donor. It is observed that the dppm bridged Os–Os bond is considerably longer than the unbridged bond. The two Os–P bonds are different, with the Os(2)–P(1) distance of 2.346(4) Å being slightly longer than the Os(3)–P(2) distance of 2.322(4) Å. This is presumably a consequences of the extra electron density on Os(2) due to the thiolato bridge. The Os–S–Os bridges are nearly symmetrical with Os–S distances lying in the narrow range 2.435(4)–2.467(4) Å and these values are similar to those reported for the related osmium and ruthenium complexes [19,21]. The Os(1)–S(1)/S(2)–Os(2) angles [88.14(14)/89.25(14)°] are nearly identical. The molecule contains a total of 50 valence electrons and in the presence of two metal–metal bonds, each metal atom formally achieves an 18-electron configuration.

Table 1
Selected bond lengths (Å) and bond angles (°) for **13**

Bond lengths			
Os(1)–Os(3)	2.8790(12)	Os(2)–Os(3)	2.9031(10)
Os(1)–S(2)	2.441(4)	Os(1)–S(1)	2.457(4)
Os(2)–P(1)	2.346(4)	Os(2)–S(2)	2.435(4)
Os(2)–S(1)	2.467(4)	Os(3)–P(2)	2.322(4)
S(1)–C(9)	1.85(2)	S(2)–C(11)	1.79(2)
P(1)–C(12)	1.793(14)	P(1)–C(13)	1.845(8)
P(1)–C(19)	1.796(9)	P(2)–C(12)	1.848(14)
P(2)–C(25)	1.856(9)	P(2)–C(31)	1.832(10)
Bond angles			
Os(1)–Os(3)–Os(2)	72.65(3)	S(2)–Os(1)–S(1)	77.01(14)
S(2)–Os(2)–S(1)	76.92(14	P(1)–Os(2)–S(2)	168.14(14)
P(1)–Os(2)–S(1)	102.09(14)	C(9)–S(1)–Os(1)	107.3(6)
C(9)–S(1)–Os(2)	104.8(5)	Os(1)–S(1)–Os(2)	88.14(14)
C(11)–S(2)–Os(2)	106.8(6)	C(11)–S(2)–Os(1)	107.6(7)
Os(2)–S(2)–Os(1)	89.25(14)		



Scheme 4.

The spectroscopic data of **13** are consistent with its crystal structure. The infrared spectrum indicates the presence of eight terminal carbonyl ligands, and the ^{1}H-NMR spectrum contains four multiplets for the methylene protons, in addition to the usual resonances arising from the phenyl protons of the dppm ligand. No signals have been observed in the bridging hydride region. The ^{31}P{^{1}H}-NMR spectrum shows two doublets indicating that the two phosphorus atoms are nonequivalent. The ^{13}C{^{1}H}-NMR spectrum indicates the presence of eight carbonyl ligands. The IR, ^{1}H-, ^{31}P{^{1}H}- and ^{13}C{^{1}H}-NMR spectra of **10** are very similar to those of **13**, suggesting that the compounds are structurally similar.

It is known that trimetallic clusters with only one or two metal–metal bonds undergo decarbonylation by both thermal and photochemical methods. We therefore explored the thermal and photochemical reactivity of **9** and **12** to see if one or both of their Os–Os bonds could be reformed by removal of one or two carbonyl ligands respectively. Thermolysis of **9** and **12** in refluxing toluene followed by the usual chromatographic work up gave the demetallated compounds $[Os_3(CO)_8(\mu\text{-}SCH_2CH_2S)(Ph_2PCH_2PPh_2)]$ (**10**) and $[Os_3(CO)_8(\mu\text{-}SCH_2CH_2CH_2S)(Ph_2PCH_2PPh_2)]$ (**13**) resulting from the transfer of the bridging hydride to the orthometallated phenyl ring of the dppm ligand followed by reformation of one of the metal–metal bonds. Compounds **10** and **13** were also formed in the initial reactions of **1** with $HS(CH_2)_nSH$ at 25°C. It was also noted that the compounds **9** and **12** could be converted into **10** and **13** at 110°C but not at an appreciable rate under the conditions of the original preparation at 25°C. It thus appears that the products in the original reaction were formed by different routes.

The decarbonylation reactions of **10** and **13** were investigated to see if the open Os–Os edge in these compounds could be reformed by the removal of CO. It was found that the decarbonylation of **10** and **13** in refluxing octane at 128°C gave the methylene activated products **11** and **14**, which were characterized by spectroscopic methods together with a single crystal structure analysis for **14**·1/2H_2O (Scheme 4).

The solid state structure of **14** is shown in Fig. 2, and selected bond distances and angles are collected in Table 2. Only one of the two independent complex molecules is shown in this figure; the other independent molecule has the same structure with very similar geometry parameters. For the sake of brevity, the following discussion is based on the parameters of molecule 1 only. The structure of **14** consists of an Os_3 triangle with two metal–metal bonds [Os(1)–Os(3) = 2.863(2), Os(2)–Os(3) = 2.9724(13) Å] and a non bonded separa-

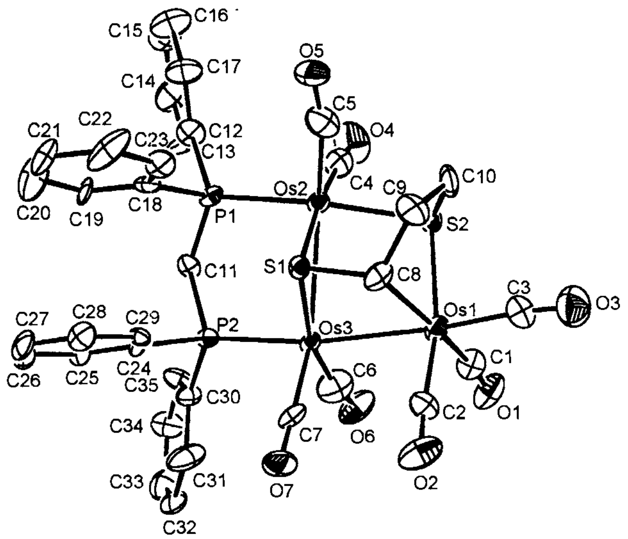


Fig. 2. X-ray structure of a single molecule of $[(\mu\text{-H})Os_3(CO)_7(\mu_3\text{-}\eta^3\text{-}SCH_2CH_2CHS)(Ph_2PCH_2PPh_2)]$ (**14**) showing the atom numbering scheme. Thermal ellipsoids are drawn at 40% probability level. The hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for **14**

	Molecule 1	Molecule 2
Bond lengths		
Os(1)–Os(3)	2.863(2)	2.8692(14)
Os(2)–Os(3)	2.9724(13)	2.986(2)
Os(1)–C(8)	2.21(2)	2.07(2)
Os(1)–S(2)	2.441(6)	2.425(6)
Os(2)–P(1)	2.358(6)	2.360(6)
Os(2)–S(2)	2.420(6)	2.424(6)
Os(2)–S(1)	2.424(5)	2.435(5)
Os(3)–P(2)	2.337(6)	2.360(6)
Os(3)–S(1)	2.406(6)	2.388(6)
S(1)–C(8)	1.81(2)	1.85(2)
S(2)–C(10)	1.74(2)	1.77(2)
Bond angles		
C(2)–Os(1)–Os(3)	88.2(8)	89.2(7)
C(1)–Os(1)–Os(3)	90.3(8)	88.6(8)
S(2)–Os(1)–Os(3)	86.13(14)	87.58(14)
P(1)–Os(2)–S(2)	173.4(2)	174.3(2)
P(1)–Os(2)–S(1)	94.3(2)	94.1(2)
S(2)–Os(2)–S(1)	86.0(2)	85.3(2)
C(4)–Os(2)–Os(3)	121.3(8)	118.6(8)
P(2)–Os(3)–S(1)	98.6(2)	98.0(2)
C(6)–Os(3)–Os(1)	97.1(9)	94.4(8)
P(2)–Os(3)–Os(1)	171.19(14)	171.3(2)
S(1)–Os(3)–Os(1)	73.50(14)	74.08(13)
C(6)–Os(3)–Os(2)	117.2(9)	116.9(8)
Os(1)–Os(3)–Os(2)	81.81(4)	81.15(4)
C(8)–S(1)–Os(3)	100.9(7)	95.8(8)
C(8)–S(1)–Os(2)	106.1(8)	104.8(7)
Os(3)–S(1)–Os(2)	76.0(2)	76.5(2)
C(10)–S(2)–Os(2)	105.4(8)	106.5(8)
C(10)–S(2)–Os(1)	94.8(8)	96.7(7)
Os(2)–S(2)–Os(1)	103.7(2)	103.5(2)

tion of 3.822(2) Å along Os(1)···Os(2). The molecule contains seven terminal carbonyl ligands, a bridging hydride ligand, a bridging dppm ligand, and a triply bridging $\mu_3\text{-}\eta^3\text{-}SCH_2CH_2CHS$ grouping formed by the activation of methylene C–H bond of the coordinated $\mu\text{-}SCH_2CH_2CH_2S$ ligand. Due to poor crystal quality, we were unable to locate the bridging hydride from difference map, but its presence along the Os(2)–Os(3) edge was indicated by spectroscopic data [27,28]. This conclusion is further supported by carbonyl ligand distribution. Thus the much wider Os(3)–Os(2)–C(4) and Os(2)–Os(3)–C(6) angles, 121.3(8) and 117.2(9)°, respectively, compared with Os(3)–Os(1)–C(1)/C(2) and Os(1)–Os(3)–C(6)/C(7) angles 90.3(8)/88.2(8) and 97.1(9)/93.0(7)°, respectively, are consistent with the presence of a bridging hydride along the Os(2)–Os(3) edge on the opposite side of the S(1) bridge. In **14**, the bridged Os(2)–Os(3) bond 2.9724(13) Å is significantly longer than the corresponding bond 2.9031(10) in **13**, and the unbridged Os(1)–Os(3) bond 2.863(2) Å is slightly shorter than the corresponding bond 2.8790(12) Å in **13**. The binding of the SCH_2CH_2CHS ligand in the cluster is particularly interesting. The S(2) atom of the $-CH_2S$ group forms a bridge between the pair of non–bonded Os atoms along Os(1)···Os(2) whilst the S(1) of the –CHS group links the dppm and hydride bridged Os(2)–Os(3) bond which is thus triply bridged. The C(8) atom of the –CHS moiety is also bonded to Os(1). This type of bonding of the dithiolato ligand ($\mu_3\text{-}\eta^3$-mode) is quite remarkable, and constitutes a very interesting aspect of the structure of **14**. The two Os–P bond distances in **14** [Os(2)–P(1) = 2.358(6), Os(3)–P(2) = 2.337(6) Å] show only minor differences and are comparable with the values found in **13** [2.346(4), 2.322(4) Å] and $[Os_3(CO)_{10}(\mu\text{-dppm})]$ [2.331(3), 2.308(3) Å} [29]

The $\mu_3\text{-}\eta^3\text{-}SCH_2CH_2CHS$ ligand serves as a seven electron donor and bridging dppm acts as a four electron donor; the molecule contains a total of 50 valence electrons and in the presence of two metal–metal bonds, each metal atom formally achieves an 18-electron configuration. The osmium–methyne carbon bond distance, Os(1)–C(8) = 2.21(2) Å, is comparable to those in the related compounds, e.g. 2.23(2) Å in $[Os_3(CO)_{11}\{\mu\text{-}SC(H)PhCH_2CHPh\}]$ [30], 2.19(2) Å in $[(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC{=}NCH_2CH_2CH_3)]$ [31], 2.229(11) Å in $[(\mu\text{-H})_2Os_3(CO)_7(CNPr)\{Ph_2PCHP(Ph)C_6H_4\}]$ [32] and 2.229(7) Å in $[(\mu\text{-H})Ru_3(CO)_7\{\mu_3\text{-}\eta^4\text{-}PhPCHP(Ph)C_6H_4\}(dppm)]$ [33]. Another notable feature of the structure is the severe compression of the metal chain from a linear arrangement; thus the Os(1)–Os(3)–Os(2) angle narrows down to only 81.81(4)°, and this is undoubtedly due to the bridging ligands between non-bonded pair of osmium atoms. Similar distortions in the Os–Os–Os angles from linearity have been reported for other triosmium clusters containing two metal–metal bonds, one of which is bridged by an organic ligand. Examples of such compounds include $[Os_3(CO)_{11}\{\mu\text{-SC(H)PhCH}_2\text{CHPh}\}]$ [84.06(5)°] [30] and $[H(\mu\text{-H})Os_3(CO)_7(\mu\text{-dppm})(\mu\text{-PPh}_2)_2]$ [82.99(2)°] [34]. The Os-S bond distances [Os(2)-S(1) = 2.424(5), Os(3)-S(1) = 2.406(5), Os(1)-S(2) = 2.441(5) and Os(2)–S(2) = 2.420(6) Å] in **14** are similar to those reported for $[Os_3(CO)_{11}\{\mu\text{-SC(H)PhCH}_2\text{CHPh}\}]$ [30], $[Os_3(CO)_{10}(\mu\text{-SCH}_2\text{CH}_2\text{S})]$ [21] and $[Ru_3(CO)_7\{\mu\text{-S(CH}_2)_3\text{S}\}_2]$ [19].

The spectroscopic data of **14** are in accord with its X-ray structure. The ^{1}H-NMR spectrum shows seven equal intensity multiplets for seven different protons of thiolato and dppm ligands and one multiplet due to the phenyl protons of the dppm ligand. The hydride region contains a triplet implying that intra-molecular activation of a C–H bond had occurred in the cluster. The hydride resonance appears as a triplet because it is coupled equally to the two phosphorus atoms. The spectroscopic data of **11** are very similar to that **14** indicating that they are structurally similar. The ^{31}P{^{1}H}-NMR spectrum of **14** shows two doublets corresponding to two nonequivalent phosphorus atoms. The mass spectrum of **14** shows the molecular ion peak and the fragmentation pattern consistent with the loss of seven CO groups. Compounds **11** and **14** have also been synthesized by direct decarbonylation of **10** and **12** at 128°C. It is thus observed that formation of **11** and **14** takes place via the intermediate formation of **10** and **13**.

In summary, the reactivity of **1** with dithiols is smooth and remarkable, and provides access to two types of novel open triosmium compounds; (a) the 52 electrons compounds $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-SCH}_2\text{CH}_2\text{S})\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**9**) and $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**12**), containing a bridging dithiolato, a bridging hydride and an orthometallated dppm ligand, and (b) the 50-electron compounds $[Os_3(CO)_8(\mu\text{-SCH}_2\text{CH}_2\text{S})(Ph_2PCH_2PPh_2)]$ (**10**) and $[Os_3(CO)_8(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})(Ph_2PCH_2PPh_2)]$ (**13**) containing a bridging dppm and a bridging dithiolato ligand. Compounds **9** and **12** can be converted into **10** and **13** at 110°C or by photolysis but not under the conditions of the original preparation, at 25°C. However, the reaction conditions for the transformation of **9** and **11** to **10** and **13** are considerably more forcing than those used in the original reactions. When heated to 128°C, **9** and **10** undergo decarbonylation to yield the unprecedented complexes $[(\mu\text{-H})Os_3(CO)_7\{\mu_3\text{-}\eta^3\text{-SCH}_2\text{CHS}\}\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**11**) and $[(\mu\text{-H})Os_3(CO)_7\{\mu_3\text{ - }\eta^3\text{ - SCH}_2\text{CH}_2\text{CHS}\}\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**14**). Compounds **11** and **14** are formed by converting the doubly bridging dithiolato ligand into a hydride and a triply bridging $S(CH_2)_nCHS$ ligand by the cleavage of methylene C–H bond. Our studies show that **10** and **13** can be converted into **11** and **14** in moderate yields. This indicates that the formation **11** and **14** from the thermolysis of **9** and **12** takes place via the intermediate formation of **10** and **13**. It thus appears that in the original reactions, the compounds **10** and **13** are formed by two competing reactions involving two different processes.

3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over appropriate drying agents, distilled under nitrogen and degassed prior to use. Infrared spectra were recorded on a Shimadzu FTIR-8101 spectrophotometer. NMR spectra were recorded on a Varian Unity Plus 400 MHz and ARX 250 MHz spectrometers. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, New York. 1,2-Ethanedithol and 1,3-propanedithiol were purchased from Aldrich and used as received. The cluster $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P\text{-}(Ph)C_6H_4\}]$ was prepared according to the published procedure [35].

3.1. Reaction of $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P\text{-}(Ph)C_6H_4\}]$ (1) with 1,3-propanedithiol

To a CH_2Cl_2 solution (50 cm^3) of **1** (0.140 g, 0.119 mmol) was added 1,3-propanedithiol (0.026 g, 0.238 mmol) and the reaction mixture was stirred at room temperature for 18 h during which time the color changed from green to yellow. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (1:1, v/v) developed two bands. The faster moving band yielded $[Os_3(CO)_8(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})(Ph_2PCH_2PPh_2)]$ (**13**) 1/2CH_2Cl_2 (0.033 g, 22%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −20°C (Anal. Calc. for $C_{36}H_{28}O_8Os_3P_2S_2$, 1/2$CH_2Cl_2$: C, 33.02; H, 2.20. Found: C, 33.15; H, 2.32%). IR (νCO, CH_2Cl_2): 2064 vs, 2012 m, 1987 vs, 1958 w, 1944 m, 1919 w cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 20H), 4.87 (m, 1H), 4.17 (m, 1H), 3.09 (m, 4H), 2.42 (m, 2H); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 13.0 (d), −2.6 (d), $J = 78.2$ Hz; ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 188.7 (dd, $J = 7.4$, 3.8 Hz 1C), 186.8 (dd, $J = 7.5$, 4.0 Hz, 1C), 185.8 (d, $J = 5.3$ Hz, 1C), 183.6 (s, 1C), 181.4 (s, 1C), 180.9 (s, 1C), 174.7 (d, $J = 5.4$ Hz, 1C), 169.8 (dd, $J = 7.2$, 3.4 Hz, 1C); mass spectrum (m/z): 1284 [M]$^+$ The second band gave $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})\ \{Ph_2PCH_2P\text{-}(Ph)C_6H_4\}]$ (**12**) (0.086 g, 56%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −20°C (Anal. Calc. for $C_{36}H_{28}O_8Os_3P_2S_2$: C, 33.64; H, 2.20. Found:

C, 33.58; H, 2.15%). IR(νCO, CH_2Cl_2): 2107 s, 2029 v, 2008 m, 1994 w,1990 w,1967 m, 1940 w cm^{-1} ^{1}H-NMR(400 MHz, $CDCl_3$): δ 6.69, (m, 2H), 6.89 (m, 2H), 7.08 (m, 1H), 7.41 (m, 11H), 7.65 (m, 2H), 8.13 (m, 1H), 2.94 (m, 2H), 2.77 (m, 4H), 2.45 (m, 1H), 2.30 (m, 1H), −14.72 (dd, 1H, $J=9.2$ and 4.4 Hz); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ −2.7 (d), −16.0 (d), $J=$ 61.5 Hz; ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 186.2 (s, 1C), 183.0 (m, 2C), 178.6 (m, 2C), 172.0 (m, 2C), 165.8 (d, $J=1.8$ Hz, 1C); mass spectrum (*m*/*z*): 1284 [M]$^+$.

3.2. Thermolysis of [(μ-H)$Os_3(CO)_8$-(μ-$SCH_2CH_2CH_2S$){$Ph_2PCH_2P(Ph)C_6H_4$}] (**12**)

3.2.1. At 110°C

A toluene solution (20 cm^3) of **13** (0.070 g, 0.054 mmol) was refluxed at 110°C for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (3:2, v/v) gave a single band which afforded [$Os_3(CO)_8$(μ-$SCH_2CH_2CH_2S$)($Ph_2PCH_2PPh_2$)] (**13**) 1/2CH_2Cl_2 (0.039 g, 56%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −20°C.

3.2.2. At 128°C

A similar thermolysis of **12** (0.075 g, 0.058 mmol) in octane (20 cm^3) at 128°C for 4 h followed by similar chromatographic separation gave two bands. The faster moving band gave too small an amount for complete characterization. The second band gave [(μ-H)$Os_3(CO)_7$(μ_3-η^3-SCH_2CH_2CHS)($Ph_2PCH_2PPh_2$)] (**14**) 1/2H_2O (0.037, 51%) as yellow crystals after recrystallization from CH_2Cl_2/hexane at −20°C (Anal. Calc. for $C_{35}H_{28}O_7Os_3P_2S_2\cdot1/2H_2O$; C, 33.19; H, 2.31. Found: C, 33.32; H, 2.48%). IR (νCO, CH_2Cl_2): 2049 vs, 2033 s, 1987 m, 1973 vs, 1943 m, 1869 w cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.21, (m, 20H), 4.22 (m, 1H), 3.73 (m, 1H), 3.27 (m, 1H), 3.07 (m, 1H), 2.63 (m, 1H), 2.41 (m, 1H), 2.17 (m, 1H), −15.91 (t, 1H, $J=6.7$ Hz); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 14.1 (d), 2.6 (d), $J=102.6$, Hz; mass spectrum (*m*/*z*): 1256 [M]$^+$.

3.3. Thermolysis of [$Os_3(CO)_8$(μ-$SCH_2CH_2CH_2S$)($Ph_2PCH_2PPh_2$)] (**13**)

An octane solution (20 cm^3) of **13** (0.100 g, 0.078 mmol) was heated to reflux at 128°C for 3.5 h. A similar chromatographic separation to that above developed two bands. The faster moving band gave too small an amount for complete characterization while the second band yielded **14** (0.052 g, 53%).

3.4. Reaction of **1** with 1,2-ethanedithiol

A similar reaction to that above of **1** (0.150 g, 0.127 mmol) and 1,2-ethanedithiol (0.024 g, 0.254 mmol) in CH_2Cl_2 (50 cm^3) for 19 h followed by similar chromatographic separation gave [$Os_3(CO)_8$(μ-SCH_2CH_2S)($Ph_2PCH_2PPh_2$)] (**10**) (0.032 g, 20%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −20°C (Anal. Calc. for $C_{35}H_{26}O_8Os_3P_2S_2$: C, 33.06; H, 2.07. Found: C, 33.19; H, 2.17%); IR (νCO, CH_2Cl_2): 2066 vs, 2011 m, 1988 vs, 1963 w, 1940 m, 1921 w cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 20H), 4.93 (m, 1H), 4.0 (m, 1H), 3.43 (m, 4H); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 12.9 (d), −2.2 (d), $J=78.0$ Hz; mass spectrum (*m*/*z*): 1270 [M]$^+$ and [(μ-H)$Os_3(CO)_8$(μ-SCH_2CH_2S){$Ph_2PCH_2P(Ph)C_6H_4$}] (**9**) (0.080 g, 49%) as yellow crystals from hexane/CH_2Cl_2 at −20°C (Anal. Calc. for $C_{35}H_{26}O_8Os_3P_2S_2$: C, 33.06; H, 2.07. Found: C, 33.25; H, 2.22%). IR (νCO,CH_2Cl_2): 2106 s, 2032 vs, 2009 m, 1995 w, 1970 m, 1942 m, 1915 w cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.54 (m, 2H), 6.80 (m, 2H), 7.02 (m, 1H), 7.29 (m, 10H), 7.49 (m, 1H), 7.78 (m, 2H), 8.16 (m, 1H), 3.04 (m, 2H), 2.92 (m, 2H), 2.43 (m, 1H), 2.37 (m, 1H), −14.75 (dd, 1H, $J=9.2$, 4.4 Hz); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 1.9 (d), −13.5 (d), $J=66.7$, Hz; ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 186.0 (s, 1C), 182.6 (m, 2C), 178.8 (m, 2C), 172.0 (m, 2C), 165.7 (d, $J=1.5$ Hz, 1C); mass spectrum (*m*/*z*): 1270 [M]$^+$.

3.5. Thermolysis of [(μ-H)$Os_3(CO)_8$(μ-SCH_2CH_2S)-{$Ph_2PCH_2P(Ph)C_6H_4$}] (**9**)

3.5.1. At 110°C

A toluene solution (20 cm^3) of **9** (0.070 g, 0.054 mmol) was refluxed at 110°C for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (3:2, v/v) gave a single band which afforded [$Os_3(CO)_8$(μ-SCH_2CH_2S)($Ph_2PCH_2PPh_2$)] (**10**) (0.039 g, 55%).

3.5.2. At 128°C

A similar thermolysis of **9** (0.100g, 0.079 mmol) in refluxing octane (20 cm^3) at 128°C for 3 h followed by similar chromatographic work separation a single band which afforded [(μ-H)$Os_3(CO)_7$(μ^3-η^3-SCH_2CHS)-($Ph_2PCH_2PPh_2$)] (**11**) (0.042 g, 43%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −20°C (Anal. Calc. for $C_{34}H_{26}O_7Os_3P_2S_2$: C, 32.84; H, 2.11. Found: C, 32.62; H, 2.02%). IR (νCO,CH_2Cl_2): 2048 vs, 2032 vs, 1987 m, 1971 s, 1944 m, 1867 w, cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.20 (m, 20H), 4.28 (m, 1H), 3.71 (m, 1H), 3.04 (m, 1H), 2.65 (m, 1H), 2.45 (m, 1H), −15.88 (t, 1H, $J=6.8$ Hz); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 12.9 (d), 2.2 (d), $J=98.2$ Hz; mass spectrum (*m*/*z*): 1242 [M]$^+$.

3.6. Thermolysis of $[Os_3(CO)_8(\mu\text{-}SCH_2CH_2S)(Ph_2PCH_2PPh_2)]$ (**10**)

An octane solution (20 cm^3) of **10** (0.100 g, 0.078 mmol) was refluxed at 128°C for 3.5 h. A similar chromatographic separation to that above gave **11** (0.049 g, 50%).

3.7. Photolysis of $[(\mu\text{-}H)Os_3(CO)_8\text{-}(\mu\text{-}SCH_2CH_2CH_2S)\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**9**)

A benzene solution (90 cm^3) of **9** (0.100 g, 0.079 mmol) was photolyzed by a 250 W medium pressure mercury lamp for 1.5 h. The solvent was removed in vacuo and the residue was chromatographed by TCL on silica gel. Elution with hexane/CH_2Cl_2 (3:2, v/v) gave three bands. The faster moving band gave **10** (0.035 g, 35%). The second band gave small quantity of an uncharacterized compound while the third band afforded unconsumed **9** (0.015 g).

3.8. Photolysis of $[(\mu\text{-}H)Os_3(CO)_8\text{-}(\mu\text{-}SCH_2CH_2CH_2S)\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**12**)

A similar photolysis of **12** (0.100 g, 0.078 mmol) followed by similar chromatographic separation to that above gave **13** (0.040 g, 40%) and **12** (0.013 g).

Table 3
Crystal data and refinement results for **13** and **14**

Compound	**13**	**14**
Empirical formula	$C_{36}H_{28}O_8Os_3P_2S$, $\frac{1}{2}(CH_2Cl_2)$	$C_{35}H_{28}O_7Os_3P_2S_2$, $\frac{1}{2}H_2O$
Formula weight	1327.71	1266.24
Crystal system	Triclinic	Triclinic
Unit cell dimensions		
a (Å)	10.072(2)	12.956(3)
b (Å)	11.306(2)	16.332(4)
c (Å)	20.606(3)	20.754(4)
α (°)	81.621(13)	73.76(2)
β (°)	77.26(2)	74.96(2)
γ (°)	67.079(14)	68.03(3)
V (Å^3)	2103.3(6)	3851(2)
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	4
μ (Mo–K_α) (mm^{-1})	8.986	10.113
Crystal size (mm)	$0.20 \times 0.10 \times 0.05$	$0.26 \times 0.16 \times 0.10$
Crystal colour/shape	Yellow/plate	Yellow/prism
θ Range for data collection (°)	1.96–25.04	1.78–25.08
Reflections collected	8803	11590
Unique reflections (R_{int})	5720 (0.0565)	9282 (0.0889)
Data/restraints/parameters	5720/27/448	9282/328/798
Goodness-of-fit on F^2	0.933	0.908
Final R_1/wR_2 indices (all data)	$R_1 = 0.0619/0.1142$	$R_1 = 0.0727/0.1421$
R_1/wR_2 indices [$I > 2\sigma(I)$]	$R_1 = 0.0426/0.1110$	$R_1 = 0.0515/0.1364$

3.9. X-ray crystallography

Crystallographic measurements for compounds **13**·1/2CH_2Cl_2 and **14**·1/2H_2O were made at 150 using a FAST area detector diffractometer by following previously described procedures [36]. Both data sets were corrected for absorption using the program DIFABS [37]. The structures were solved by direct methods (SHELX-S) [38] and refined by full-matrix least squares on F^2 using all unique data with intensities > 0 (SHELXL-96) [39]. Crystals of **14** contained two identical cluster and one H_2O molecules per asymmetric unit. In **13**, a half-occupied CH_2Cl_2 solvate was present, which was refined with C–Cl lengths constrained to 1.75 Å and an ISOR = 0.01 restraint being used for the carbon and three partially occupied chlorine atoms. The quality of the crystals for **14** were rather poor, but the data enabled us to solve and refine the structure without any ambiguity. For this structure, group values were refined for the Os–C and C–O bonds (involving the carbonyl ligands) and ISOR = 0.01 restraints were used for a number of carbon and oxygen atoms. The bridging hydride in **14** could not be experimentally located, but its presence along the dppm bridged Os(2)–Os(3) edge was suggested from spectroscopic data and also consistent with carbonyl ligand distribution on the metal atoms.. The hydrogen atoms of the H_2O and CH_2Cl_2 solvates in the two structures were ignored. All other hydrogen atoms were included in calculated positions (riding model). The phenyl rings were refined as idealised hexagons (C–C 1.390 Å, C–C–C = 120.0°). Pertinent crystallographic data for the two complexes are presented in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146216 for compound **13** and CCDC no. 146217 for compound **14**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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