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Reactivity of [(μ-H)$Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}$] with organic heterothiols; X-ray structures of [H(μ-H)$Os_3(CO)_8(\eta^2$-pyS)$\{Ph_2PCH_2P(Ph)C_6H_4\}$] and [$Os_3(CO)_8(\mu$-η^2-pyS)$\{Ph_2PCH_2P(Ph)C_6H_4\}$]

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Abstract

The reaction of [(μ-H)$Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}$] (**3**) with pyridine-2-thiol (pySH, C_5H_4NSH) at room temperature gave two novel clusters [(μ-H)$Os_3(CO)_8$(μ-pyS)(μ-dppm)] (**4**) and [H(μ-H)$Os_3(CO)_8(\eta^2$-pyS)$\{Ph_2PCH_2P(Ph)C_6H_4\}$] (**5**) in 55 and 15% yields, respectively. Compound **4** is formed by simple oxidative addition of pySH and demetallation of the phenyl ring of dppm ligand whereas the 50-electron cluster **5** results from oxidative addition of pySH and coordination of the thiolate moiety as a chelating ligand and cleavage of one of the metal–metal bonds. The analogous reaction of **3** with pySH at 80°C gave the new compound [$Os_3(CO)_8(\mu$-η^2-pyS)$\{Ph_2PCH_2P(Ph)C_6H_4\}$] (**6**) in 20% yield together with **4** and **5** in 40 and 7% yields, respectively. Compound **6** contains a chelating/bridging pyS ligand and an orthometallated dppm ligand. In contrast, the reaction of **3** with pyrimidine-2-thiol (pymSH, $C_4H_3N_2SH$) at room temperature and at 80°C affords only the simple oxidative addition product [(μ-H)$Os_3(CO)_8$(μ-pymS)(μ-dppm)] (**7**). Compound **6** reacts with molecular hydrogen to give **5** and **4** in 20 and 10% yields, respectively. Compound **5** was converted to **6** (30%) with the formation of **3** (10%) by refluxing in heptane at 98°C. The new complexes **4**, **5**, **6** and **7** have been characterized by spectroscopic data together with X-ray structure determinations for **5** and **6**.

Keywords: Triosmium; Pyridine-2-thiol; Pyrimidine-2-thiol, Carbonyl; Crystal structure

1. Introduction

The chemistry of transition metal clusters with heterocyclic organic molecules has attracted considerable attention in recent years [1–7]. The presence of heteroatoms such as sulfur [8–10] and nitrogen [11–13] introduces novel reactivities, and this frequently stabilizes the metal cluster framework with respect to degradational fragmentation when subjected to forcing reaction conditions. Thus the reactivity of organic heterocyclic molecules containing nitrogen and sulfur atoms such as thioamide [7], pyridine-2-thiol [14], and pyrimidine-2-thione [15] towards metal carbonyl clusters is an interesting area of research. Pyridine-2-thione and pyrimidine-2-thione give rise to an extensive chemistry with considerable structural diversity [16], since as neutral ligands they can in principle coordinate both in the

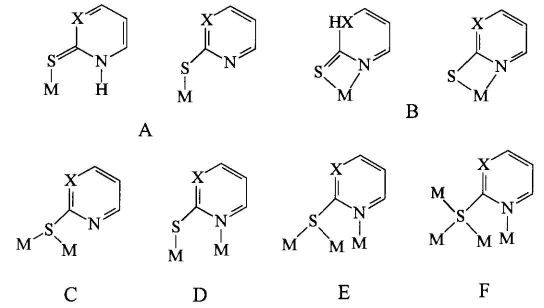

Fig. 1. Different co-ordination modes of pyridine-2-thione and pyrimidine-2-thione.

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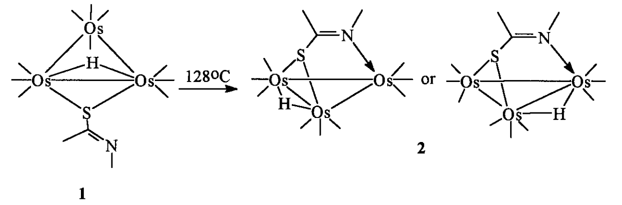
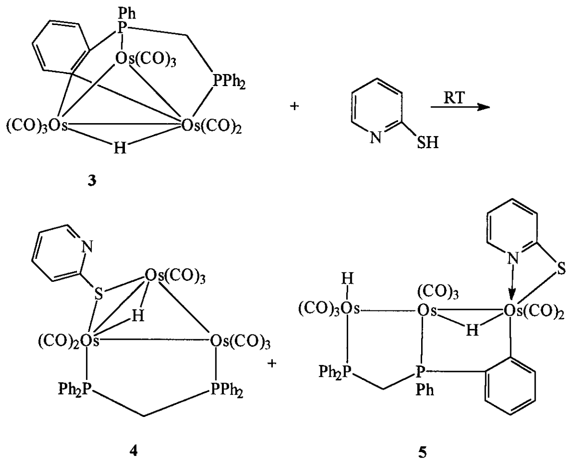


Scheme 1.



Scheme 2.

'thione' and in the tautomeric 'thiol' form (–NH–C=S $\rightleftharpoons$ –N=C–SH) [17–23]. The coordination chemistry displayed by tautomeric ligands of this type is also very interesting. Pyridine-2-thione [22] and pyrimidine-2-thione [1] are known to act as monodentate ligands through the sulfur atom A [17,18,23,24], as chelating ligands through the sulfur and nitrogen atoms B [21,25], as bridging ligands through the sulfur atom C [15], and as bridging ligands through the nitrogen and sulfur atoms linking two D [26], three E [15,22,27] or four metal atoms F [14] (Fig. 1).

Pyridine-2-thione is a special case of thioamide which reacts with $[M_3(CO)_{12}]$ to give $[(\mu\text{-H})M_3(CO)_9(\mu\text{-pyS})]$ (M = Os, Ru) in which pyS acts as a five electron donor ligand. Interestingly, $[(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-pyS})]$ thermally decarbonylates to give $[(\mu\text{-H})Ru_3(CO)_7(\mu_3\text{-pyS})]_3$ which exists as a tricluster system held together substantially through the Ru_3S_3 ring [14]. Thioamido complexes of the type $[Ru_2(CO)_6(L)_2]$ and $[(\mu\text{-H})Ru_3(CO)_9(L)]$ are obtained [28] when $[Ru_3(CO)_{12}]$ reacts with the heterocyclic thioamide, benzothiazoline-2-thione (HL). In contrast, the reaction of HL with $[Fe_3(CO)_{12}]$ affords $[Fe_3(CO)_9S_2]$ by desulfurization of the thioamide ligand [29]. Lewis et al. [7] investigated the reactions of a series of heterocyclic thioamides with the lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ and obtained the decacarbonyl compounds $[(\mu\text{-H})Os_3(CO)_{10}L]$ in which the thioamido ligands are binding in the thiolate form as depicted in **1** rather than in the thione form found for the free thioamides. Decarbonylation of these complexes either thermally, or by the reaction with trimethylamineoxide, give $[(\mu\text{-H})Os_3(CO)_9L]$ (**2**) which exist as two isomers in solution as depicted in Scheme 1.

Recently we described [30] the reactions of the unsaturated triosmium cluster $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**3**) with mono thiols such as ethanethiol, propane-2-thiol and thiophenol, and observed a remarkable control of the steric bulk of the thiols on product formation. As part of on going studies of the reactivity of trimetallic clusters with thiols, we now report on the reactions of **3** with pyridine-2-thiol (pySH) and pyrimidine-2-thiol (pymSH).

2. Results and discussion

Treatment of $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**3**) with two equivalents of pySH in dichloromethane or benzene at room temperature gives the new clusters $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-pyS})(\mu\text{-dppm})]$ (**4**) (55%) and $[H(\mu\text{-H})Os_3(CO)_8(\eta^2\text{-pyS})\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**5**) (15%) (Scheme 2). Both these compounds have been characterized by elemental analysis, infrared, ^1H- and ^{31}P-NMR spectroscopic data together with a crystal structure analysis for **5**.

The infrared spectrum of **4** in the carbonyl region is very similar to that of $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-SEt})(\mu\text{-dppm})]$ [30] and $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-SPh})(\mu\text{-dppm})]$ [30] suggesting that they have similar structures. The ^1H-NMR spectrum of **4** shows a multiplet for the aromatic protons at δ 6.91–8.45 and two sets of multiplets at δ 5.40 and 4.77 for the methylene protons of the dppm ligand. The high field doublet at δ -15.90 ($J = 30.2$ Hz) is assigned to the bridging hydride which is coupled to only one phosphorus nucleus. The $^{31}P\{^1H\}$-NMR spectrum contains two doublets at δ -23.4 and -24.7 ($J = 41.8$ Hz) due to nonequivalent and mutually coupled ^{31}P nuclei. The mass spectrum of **4** shows molecular ion peak at m/z 1290, which fragmented by the loss of eight CO groups. Thus based on spectroscopic data and by analogy with the above related compounds, it is proposed that **4** has a structure with the pyS and the hydride ligands bridging one of the Os–Os edges not spanned by the dppm ligand.

An X-ray structure determination showed that compound **5** crystallizes as a dichloromethane solvate. A molecule of this cluster is depicted in Fig. 2 and selected bond distances and angles are given in Table 1. The basic structure consists of an array of three osmium atoms with two different metal–metal bonds [Os(1)–Os(2) = 2.9412(9) Å] and [Os(1)–Os(3) = 3.2151(10) Å]. The Os(2)···Os(3) distance [4.7521(12) Å] is too long for any significant metal–metal interaction. One terminal metal atom [Os(3)] is associated with two terminal CO ligands while the other terminal [Os(2)] and central [Os(1)] atoms are each linked to three terminal CO ligands. The $Ph_2PCH_2P(Ph)C_6H_4$ ligand forms one bridge between Os(1) and Os(2) through the two phosphorus atoms, and a second bridge between Os(1) and Os(3) involving one phosphorus and one *ortho*-phenyl carbon atoms. Of the two hydride ligands, one is bridging between the Os(1)–Os(3) edge whilst the other is terminally bonded with Os(2). The Os(1)–Os(2) edge, bridged by the orthometallated dppm ligand, is considerably longer than the average metal–metal bond [2.877(3) Å] in $[Os_3(CO)_{12}]$ [31] but close to the value of [2.957(3) Å] in $[(\mu\text{-}H)Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(P^iPr_3)]$ [32]. The doubly bridged Os(1)–Os(3) edge shows marked elongation compared with the other Os–Os bond, which is consistent with the fact that a bridging hydride on a metal cluster causes significant lengthening of the bridged metal–metal edge if another bridging ligand along the same edge does not have any bond shortening effect [33]. Similar long metal–metal bonds were also observed in $[(\mu\text{-}H)Os_3(CO)_9(\mu\text{-}Me_2PCHPMe_2)]$ [Os–Os = 3.104(1) Å] [34], $[H(\mu\text{-}H)Os_3(CO)_7(\mu\text{-}dppm)(\mu\text{-}PPh_2)]$ [Os–Os = 3.1486(8) Å] [35] and $[(\mu\text{-}H)Ru_3(CO)_7\{\mu_3\text{-}\eta^4\text{-}P(C_6H_5)CHP(C_6H_5)(C_6H_4)\}(\mu\text{-}dppm)]$ [Ru–Ru = 3.205(1) Å] [36]. It may be mentioned here that the bridging and terminal hydrides in **5** were obtained from difference map and are also consistent with spectroscopic data (see below).

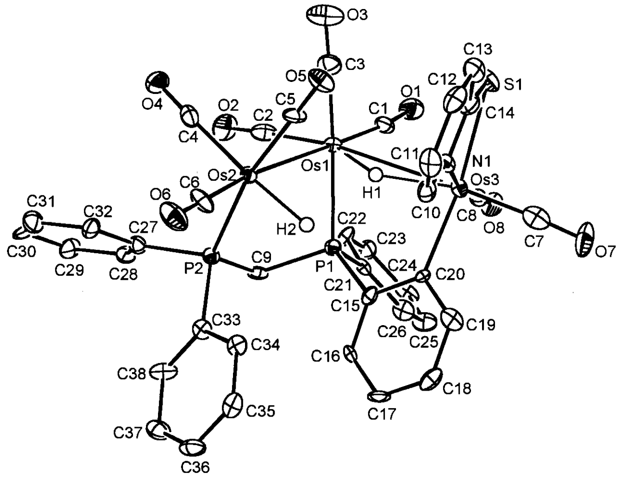


Fig. 2. Molecular structure of $[H(\mu\text{-}H)Os_3(CO)_8(\eta^2\text{-}pyS)\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**5**) showing the atom labeling. Thermal ellipsoids are drawn ad 50% probability level. The hydrogen atoms except those bonded to the osmium atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **5**

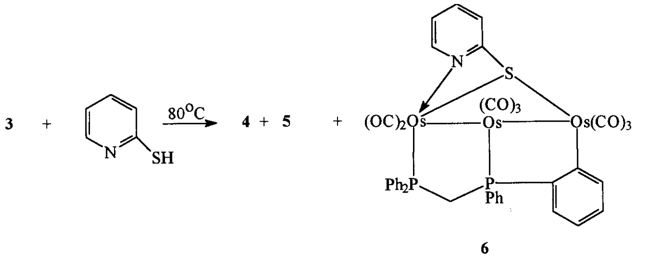
Bond lengths			
Os(1)–Os(2)	2.9412(9)	Os(1)–Os(3)	3.2151(10)
Os(1)–P(1)	2.379(2)	Os(2)–P(2)	2.378(2)
Os(3)–C(20)	2.122(8)	Os(3)–N(1)	2.145(8)
Os(3)–S(1)	2.518(3)	S(1)–C(14)	1.713(10)
N(1)–C(10)	1.336(11)	N(1)–C(14)	1.363(11)
Os(1)–H(1)	1.62 [a]	Os(3)–H(1)	1.88 [a]
Os(2)–H(2)	1.76 [a]	Os–C(CO)	1.904 [b]
P–C	1.831 [b]	O–C	1.147 [b]
Bond angles			
C(1)–Os(1)–C(3)	92.8(4)	C(1)–Os(1)–C(2)	94.9(4)
C(3)–Os(1)–C(2)	90.6(4)	C(1)–Os(1)–P(1)	96.2(3)
C(3)–Os(1)–P(1)	170.0(3)	C(2)–Os(1)–P(1)	92.9(3)
C(1)–Os(1)–Os(2)	179.1(3)	C(3)–Os(1)–Os(2)	86.3(3)
C(2)–Os(1)–Os(2)	85.2(3)	P(1)–Os(1)–Os(2)	84.70(6)
C(6)–Os(2)–C(5)	91.9(4)	C(6)–Os(2)–C(4)	97.3(4)
C(5)–Os(2)–C(4)	95.2(4)	C(6)–Os(2)–P(2)	91.7(3)
C(5)–Os(2)–P(2)	169.2(3)	C(4)–Os(2)–P(2)	94.5(3)
C(6)–Os(2)–Os(1)	171.0(3)	C(5)–Os(2)–Os(1)	84.4(3)
C(4)–Os(2)–Os(1)	91.2(3)	P(2)–Os(2)–Os(1)	90.56(6)
C(7)–Os(3)–C(8)	84.4(4)	C(7)–Os(3)–C(20)	90.0(4)
C(8)–Os(3)–C(20)	94.7(4)	C(7)–Os(3)–N(1)	92.7(3)
C(8)–Os(3)–N(1)	170.6(3)	C(20)–Os(3)–N(1)	94.2(3)
C(7)–Os(3)–S(1)	94.3(3)	C(8)–Os(3)–S(1)	105.3(3)
C(20)–Os(3)–S(1)	159.8(2)	N(1)–Os(3)–S(1)	65.9(2)
C(14)–S(1)–Os(3)	79.5(3)	C(19)–C(20)–C(15)	115.8(7)
C(19)–C(20)–Os(3)	119.6(6)	C(15)–C(20)–Os(3)	124.6(6)
Os–C–O	176.7 [b]		

[a] Approximate values.

[b] Average values.

The pyS ligand in **5** displays a N, S chelating mode of coordination to Os(3). This ligand donates three electrons to the cluster via a two electron donor bond involving the lone pair of electrons of N(1) and one electron donor bond from S(1) to the same metal atom Os(3). Such coordination modes of the heterocyclic ligand have been observed in mononuclear complexes [21], but to our knowledge compound **5** provides the first example of a cluster compound containing the pyS ligand in a purely chelating mode. The Os–N [2.147(8) Å] and Os–S [2.518(3) Å] bonds in the chelate in **5** are slightly longer than the corresponding (average) values [2.134 and 2.430 Å] in monomeric $[Os(CO)_2(pyS)_2]$ [37].

The spectroscopic data of **5** are in accord with the solid state structure. The infrared spectrum of **5** shows ν(CO) absorption bands in the region characteristic of terminal CO ligands. The ^{1}H-NMR spectrum shows a multiplet at δ 6.20–7.88 (23 H) for aromatic protons. Another two multiplets at δ 5.20 and 3.75 are attributed to the methylene protons of dppm. The two high field signals at δ -9.04 (dd) and -12.30 (d) are attributed to the terminal and bridging hydrides, respectively. The terminal hydride is coupled to two nonequivalent phosphorus atoms of the dppm ligand and appears as a doublet of a doublet, and the bridging hydride is coupled to only one phosphorus nucleus and appears as a doublet. The $^{31}P\{^1H\}$-NMR spectrum displays two doublets at δ -8.7 and -14.7 ($J = 64.4$ Hz) which indicates that the two phosphorus nuclei are nonequivalent.



Scheme 3.

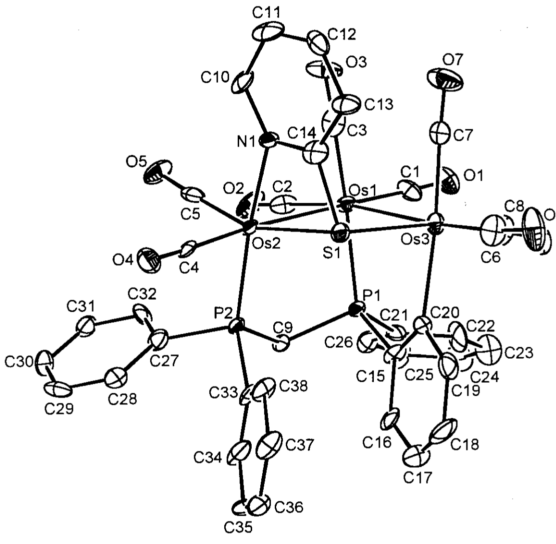


Fig. 3. Molecular structure of $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-pyS})\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**6**) showing the atom labeling. Thermal ellipsoids are drawn ad 50% probability level. The hydrogen atoms are omitted for clarity.

In contrast to the reaction at room temperature which afforded **4** and **5**, the reaction of **3** with pySH in benzene at 80°C gives the novel compound $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-pyS})\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**6**) in 20% yield in addition to **4** (40%) and **5** (7%) (Scheme 3).

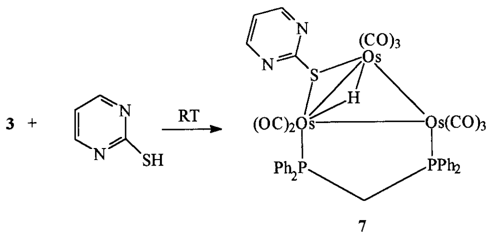
Compound **6** has been characterized by elemental analysis, infrared, ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy and X-ray crystallography. The structure of **6** is shown in Fig. 3 and selected bond distances and angles are given in Table 2. As in **5**, the molecule of **6** consists of a triangular array of osmium atoms with two metal–metal bonds, but in this case the open edge is bridged by the sulfur atom of the pyS ligand to give a nearly planar Os_3S framework. The coordination of the orthometallated dppm ligand to the three osmium atoms is very similar in both compounds, but the bonding mode of pyS is different. In **5**, it forms only a chelate ring with a terminal osmium atom, whereas in **6**, in addition to a similar chelate, it also forms a bridge between the terminal metal atoms. The eight CO groups in the molecule are distributed as shown in Fig. 3.

The two metal–metal bonds in **6** have nearly the same values, Os(1)–Os(2) = 2.9660(10) and Os(1)–Os(3) = 2.9541(11) Å, and are comparable with the Os(1)–Os(2) bond (bridged by the orthometallated dppm ligand) in **5** and that in $[(\mu\text{-}H)Os_3(CO)_8\{Ph_2PCH_2P(Ph)\text{-}C_6H_4\}(P^iPr_3)]$ [32]. The presence of a sulfur bridge along the non-bonding Os(1)···Os(3) edge in **6** reduces this distance to 3.972 (2) Å from the corresponding value 4.7521(12) Å in **5**. Both the pyS and the orthometallated dppm ligands in **6** act as five-electron donor, which results in a total of 50 valence electrons and is consistent with the presence of only two formal Os–Os bonds in the trinuclear cluster. The Os–S–Os bridge is asymmetric with Os(1)–S(1) and Os(3)–S(1) distances of 2.480(5) and 2.439(4) Å, respectively and Os(1)–S(1)–Os(3) angle of 107.7(2)°. The Os–S distances in this complex are smaller than the Os–S bond in **5**, and close to those in other sulfur bridged triosmium and triruthenium clusters [1,38,39]. The geometry parameters in the pyS ligand in both **5** and **6** are

Table 2
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths			
Os(1)–Os(2)	2.9660(10)	Os(1)–Os(3)	2.9541(11)
Os(1)–P(1)	2.350(4)	Os(2)–P(2)	2.332(5)
Os(2)–N(1)	2.126(15)	Os(2)–S(1)	2.480(5)
Os(3)–S(1)	2.439(4)	Os(3)–C(20)	2.19(2)
S(1)–C(14)	1.76(2)	N(1)–C(10)	1.35(2)
N(1)–C(14)	1.30(3)	Os–C(CO)	1.908 [a]
P–C	1.846 [a]	O–C	1.155 [a]
Bond angles			
C(3)–Os(1)–C(1)	96.0(8)	C(3)–Os(1)–C(2)	93.0(8)
C(1)–Os(1)–C(2)	97.5(8)	C(3)–Os(1)–P(1)	170.4(5)
C(1)–Os(1)–P(1)	92.0(6)	C(2)–Os(1)–P(1)	91.1(5)
C(3)–Os(1)–Os(3)	92.8(6)	C(1)–Os(1)–Os(3)	91.6(6)
C(2)–Os(1)–Os(3)	168.6(6)	P(1)–Os(1)–Os(3)	81.81(12)
C(3)–Os(1)–Os(2)	83.8(5)	C(1)–Os(1)–Os(2)	175.9(6)
C(2)–Os(1)–Os(2)	86.6(6)	P(1)–Os(1)–Os(2)	87.83(11)
Os(3)–Os(1)–Os(2)	84.27(3)	C(5)–Os(2)–C(4)	94.5(8)
C(5)–Os(2)–N(1)	95.2(7)	C(4)–Os(2)–N(1)	92.0(6)
C(5)–Os(2)–P(2)	91.6(5)	C(4)–Os(2)–P(2)	87.3(5)
N(1)–Os(2)–P(2)	173.2(4)	C(5)–Os(2)–S(1)	159.6(5)
C(4)–Os(2)–S(1)	94.6(5)	N(1)–Os(2)–S(1)	66.3(4)
P(2)–Os(2)–S(1)	107.0(2)	C(5)–Os(2)–Os(1)	88.7(6)
C(4)–Os(2)–Os(1)	175.6(5)	N(1)–Os(2)–Os(1)	90.8(4)
P(2)–Os(2)–Os(1)	89.53(11)	S(1)–Os(2)–Os(1)	83.39(10)
C(6)–Os(3)–C(8)	92.3(9)	C(6)–Os(3)–C(7)	90.1(9)
C(8)–Os(3)–C(7)	94.6(8)	C(6)–Os(3)–C(20)	91.6(8)
C(8)–Os(3)–C(20)	89.7(8)	C(7)–Os(3)–C(20)	175.3(7)
C(6)–Os(3)–S(1)	93.5(7)	C(8)–Os(3)–S(1)	169.0(7)
C(7)–Os(3)–S(1)	94.7(5)	C(20)–Os(3)–S(1)	80.8(5)
C(6)–Os(3)–Os(1)	175.1(7)	C(8)–Os(3)–Os(1)	90.5(6)
C(7)–Os(3)–Os(1)	85.7(7)	C(20)–Os(3)–Os(1)	92.3(5)
S(1)–Os(3)–Os(1)	84.35(11)	C(14)–S(1)–Os(3)	103.6(6)
C(14)–S(1)–Os(2)	78.8(8)	Os(3)–S(1)–Os(2)	107.7(2)
C(15)–C(20)–C(19)	114(2)	C(15)–C(20)–Os(3)	125.1(13)
C(19)–C(20)–Os(3)	120.6(14)	Os–C–O	175.3 [a]

[a] Average values.



Scheme 4.

similar with only minor differences. It is noted, however, that the C–S [1.76(2) Å] and N–C(S) [1.30(3) Å] distances in **6** are, respectively, slightly longer and shorter than the corresponding values [1.713(10) and 1.363(11) Å] in **5**. These differences are small and statistically insignificant, but appear to be real in view of the observed trend. It is suggested that they reflect a slight increase and a decrease, respectively, in the C–S and N–C(S) bond orders in **6** compared with **5**, and this is caused by the change in coordination modes of pyS in the two compounds. The lengths of both these bonds indicate appreciable double bond character [40].

Attachment of the $Ph_2PCH_2P(C_6H_4)Ph$ ligand in **6** is similar to that in **5**, although the Os(1)–P(1) and Os(2)–P(2) bond lengths of 2.350(4) and 2.332(5) Å are somewhat shorter than the corresponding distances [2.379(2) and 2.378(2) Å] in **5**. It is also observed that compression of the non-bonded Os···Os axis in **6**, compared with **5**, causes small angular variations in the ligand. The narrowing down of the C(15)–C(20)–C(24) angle in the metallated phenyl ring [115.8(7)° in **5** and 114(2)° in **6** from the expected value 120.0°] is manifested clearly in both the compounds.

The spectroscopic properties of **6** are in accordance with the X-ray structure. The infrared spectrum of **6** in the carbonyl-stretching region indicates that all the CO groups are terminally located. The ^1H-NMR spectrum shows a multiplet for aromatic protons at δ 6.10–8.47 and two multiplets at δ 5.87 and 4.11 due to the methylene protons of the orthometallated dppm ligand. The signals due to the heterocyclic ring protons are overlapped with phenyl protons of the orthometallated dppm ligand. The $^{31}P\{^1H\}$-NMR spectrum displays two doublets at δ -5.86 and -15.78 indicating that the phosphorus nuclei are nonequivalent.

In view of the fact that the structure of **6** differs from that of **5** in the displacement of two hydride ligands, we believe that **5** may be a precursor of **6**. This was verified by thermolysis of **5** in heptane at 98°C for 5 h, which gave **6** in 15% yield. The parent compound **3** formed by the displacement of the heterocyclic ligand was also obtained in 25% yield. From this observation we can conclude that the formation of **6** in the thermal reaction of **3** with pyridine-2-thiol takes place via the intermediate formation of **5**. Furthermore, compound **5** could not be converted into **4** even in refluxing heptane, suggesting that **4** does form through the intermediacy of **5**. Compound **6** reacts with molecular hydrogen at one atmosphere and 110°C to give **4** and **5** in 10 and 20% yields, respectively. Compound **5** is formed by the simple oxidative addition of one molecule of hydrogen whereas **4** results from the demetallation of phenyl ring of the orthometallated dppm ligand. Interestingly treatment of $[(\mu\text{-}H)Os_3(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$ **3** with pymSH at room temperature does not give the metal–metal cleavage products analogous to **5** or **6**; instead it gives the oxidative addition product $[(\mu\text{-}H)Os_3(CO)_8(\mu\text{-}pymS)(\mu\text{-}dppm)]$ (**7**) in 75% yield (Scheme 4).

Compound **7** was characterized by elemental analysis, infrared, mass, ^1H- and ^{31}P-NMR spectroscopic data. A strong similarity of the infrared spectrum of **7** to that of **4** indicates that both structures are similar with the pymS ligand being coordinated to one of the unbridged Os–Os edges. The ^1H-NMR spectrum contains signals at δ 7.08–7.84 (m, 23H), 5.95 (m, 1H) and 4.42 (m, 1H). The multiplets at δ 5.95 and 4.42 are assigned to the methylene protons of the dppm ligand while the multiplet at δ 7.08–7.84 is due to the phenyl protons of the dppm ligand and as well as the ring protons of the heterocyclic ligand. Strong evidence for the activation of S–H bond and simultaneous bridging of the hydride and the pymS ligands to one of the Os–Os edges not bridged by the dppm ligand is provided by the ^1H-NMR spectrum. The spectrum shows, in addition to the resonances due to the phenyl, CH_2 and heterocyclic ring protons, a doublet at δ -12.87 ($J = 32.0$ Hz) for the bridging hydride owing to its coupling with only one phosphorus atom. The mass spectrum of **7** confirms the stoichiometry with a molecular ion peak at m/z 1290 and ions formed by stepwise loss of eight CO groups.

In summary, the most novel aspect of the present work is the isolation and characterization of **5** from the reaction of **3** with pySH at ambient temperature and its subsequent conversion to another novel compound **6** by thermal reaction at 80°C. Both compounds **5** and **6** are 50 electron clusters with two metal–metal bonds with the pyS moiety acting as a chelating ligand through the sulfur atom in **5** and as a μ-η^2-ligand in **6**. Another novel aspect of this work is the difference in reactivity of pymSH towards **3**, which afforded only the simple oxidative addition product **7** in high yield. This difference in reactivity may, at least in part, be due to electronic effects and further study is needed to confirm this.

3. Experimental

Unless stated otherwise, all reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents before use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker ARX-250 spectrometer. Mass spectra were recorded on a Varian MAT 312 mass spectrometer. Elemental analyses were performed by the microanalytical laboratories, Institut für Anorganische und Analytische Chemie, Freiburg Universitat, Germany. Pyridine-2-thiol and pyrimidine-2-thiol were purchased from Aldrich and used as received. The compound $[(\mu\text{-H})Os_3(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$ (**3**) was prepared according to the published procedure [41].

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

3.1.1. At room temperature

To a CH_2Cl_2 solution (20 cm^3) of **3** (0.050g, 0.042 mmol) was added pySH (0.009g, 0.084 mmol) and the reaction mixture was stirred at room temperature (r.t.) for 72 h. The solvent was removed under reduced pressure and the residue was subjected to TLC on silica gel. Elution with hexane–CH_2Cl_2 (7:3, v/v) developed two bands. The faster moving band gave unreacted **3** (0.012 g). The second band, after recrystallization from hexane–CH_2Cl_2 at -20°C, afforded $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-pyS})(\mu\text{-dppm})]$ (**4**) (0.030g, 55%) as orange crystals (Anal. Calc. for $C_{38}H_{27}NO_8Os_3P_2S$: C, 35.37; H, 2.11; N, 1.08. Found: C, 35.25; H, 2.08; N, 1.03%); IR (νCO, CH_2Cl_2): 2070vs, 2024s, 1995vs, 1953w, 1942m, 1938w cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$):δ 6.90–8.45 (m, 24H), 5.49 (m, 1H), 4.77 (m, 1H), -15.90 (d, $J=30.2$ Hz, 1H); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -23.4 (d, $J=41.8$ Hz), -24.7 (d, $J=41.8$ Hz); MS (m/z): 1290, and $[H(\mu\text{-H})Os_3(CO)_8(\eta^2\text{-pyS})\{Ph_2PCH_2P(Ph)C_6H_4\}]\cdot CH_2Cl_2$ (**5**) (0.009 g, 15%) as pale yellow crystals (Anal. Calc. for $C_{39}H_{29}Cl_2NO_8Os_3P_2S$: C, 34.05; H, 2.13; N, 1.02. Found: C, 34.22; H, 2.26; N, 1.12%). IR (νCO, CH_2Cl_2): 2081vs, 2049s, 2020vs 2000w, 1979m, 1943w; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 6.20–7.88 (m, 23H), 5.32(s, 2H), 5.20 (m, 1H), 3.75 (m, 1H) -9.04 (dd, $J=4.0$, 23.8 Hz, 1H), -12.30 (d, $J=14.7$ Hz, 1H); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -8.7 (d, $J=64.4$ Hz), -14.7 (d, $J=64.4$ Hz). The reaction of **3** with pySH in benzene at r.t. also gave the above products in similar yields.

3.1.2. At 80°C

To a benzene solution (20 cm^3) of **3** (0.145 g, 0.122 mmol) was added pySH (0.027 g, 0.243 mmol) and the reaction mixture was heated to reflux for 3 h. A similar chromatographic separation to that above gave $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-pyS})\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**6**) (0.032 g, 20%) as orange crystals after recrystallization from CH_2Cl_2–hexane at -20°C (Anal. Calc. for $C_{38}H_{25}NO_8Os_3P_2S$: C, 35.42; H, 1.96; N, 1.08. Found: C, 35.67; H, 2.15; N, 1.26%); IR (νCO, CH_2Cl_2): 2051s, 2008vs, 1987m, 1977w, 1939m, 1914w; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 6.10–8.47 (m, 23H), 5.87 (m, 1H), 4.11 (m, 1H); $^{31}P\{^1H\}$-NMR ($CDCl_3$), δ -5.8 (d, $J=67.7$ Hz) -15.7(d, $J=67.7$ Hz); **4** (0.063 g, 40%) and **5** (0.011 g, 7%).

*3.2. Reaction of **3** with pymSH*

3.2.1. At room temperature

To a CH_2Cl_2 solution (25 cm^3) of **3** (0.075g, 0.063 mmol) was added pymSH (0.014g, 0.127 mmol) and the reaction mixture was stirred at r.t. for 72 h. The color of the reaction mixture was 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 (7:3, v/v) gave two bands which yielded, in order of elution, unreacted **3** ~ (0.005 g) and $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-pymS})(\mu\text{-dppm})]$ (**7**) (0.061 g, 75%) after recrystallization from hexane–CH_2Cl_2 at r.t. (Anal. Calc. for $C_{37}H_{26}N_2O_8Os_3P_2S$: C, 34.41; H, 2.03; N, 2.16. Found: C, 34.67; H, 2.18; N, 2.29%). IR (νCO, CH_2Cl_2): 2071vs, 2025s, 1996vs, 1943w, 1919w; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.08–7.84 (m, 23H), 5.95 (m, 1H), 4.42 (m, 1H), -12.87 (d, $J=32.0$ Hz, 1H); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -23.9 (d, $J=44.2$ Hz), -25.7 (d, $J=44.2$ Hz); MS (m/z) 1291.

3.2.2. At 80°C

To a benzene solution (15 cm^3) of **3** (0.100 g, 0.085 mmol) was added pymSH (0.019 g, 0.170 mmol) and the mixture refluxed 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 (7:3, v/v) gave two bands. The faster moving band gave $[Os_3(CO)_{10}(dppm)]$ (0.031 g, 30%). The second band gave $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-pymS})(\mu\text{-dppm})]$ (**7**) (0.049 g, 45%) after recrystallization from hexane–CH_2Cl_2 at -20°C.

*3.3. Reaction of **6** with molecular hydrogen*

Hydrogen gas was bubbled through a refluxing toluene solution (20 cm^3) of **6** (0.040 g, 0.031 mmol) at 110°C for 2 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (7:3, v/v) gave **4** (0.004 g, 10%) and **5** (0.008 g, 20%).

*3.4. Thermolysis of **5***

A heptane solution (25 cm^3) of **5** (0.050 g, 0.038 mmol) was refluxed at 98°C for 5 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (7:3, v/v) gave **3** (0.011 g, 25%), **6** (0.007 g, 15%) and **5** (0.010 g).

3.5. X-ray crystallography

Intensity data for **5** and **6** were recorded, respectively, on a FAST area detector and a CAD4 diffractometer using monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å). Both data sets were corrected for absorption effects using DIFABS [42]. The structures were solved by direct methods (SHELXS-96) [43] and refined on F^2 using all unique data (SHELXL-96) [44]. The non-hydrogen atoms were all anisotropic. The terminal and bridging hydrides in **5** were located from difference map, but these atoms were not refined. Other hydrogen atoms in both structures were included in calculated positions (riding model). The C_6H_5 rings were treated as idealized hexagons [C–C = 1.390 Å and C–C–C = 120.0°]. A summary of pertinent crystallographic and experimental data for the complexes is given in Table 3.

Table 3
Crystal data and refinement results for **5** and **6**

Compound	**5**	**6**
Empirical formula	$C_{38}H_{27}NO_8Os_3P_2S \cdot CH_2Cl_2$	$C_{38}H_{25}NO_8Os_3P_2S$
Formula weight	1375.13	1288.19
Temperature (K)	150	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.364(3)	10.389(3)
b (Å)	21.083(4)	31.765(5)
c (Å)	18.846(4)	11.989(2)
β (°)	91.92(3)	113.98(2)
V (Å^3)	4116(2)	3615.2(14)
Z	4	4
μ(Mo–K_α) (mm^{-1})	9.549	10.720
Crystal size (mm)	$0.08 \times 0.06 \times 0.06$	$0.40 \times 0.28 \times 0.22$
Crystal color/shape	yellow/prism	red/prism
θ range for data collection (°)	1.93–25.10	2.19–25.10
Reflections collected	16587	7028
Unique reflections (R_{int})	6126 (0.0728)	6403 (0.0452)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6126/18/469	6403/72/442
Goodness-of-fit on F^2	1.030	0.992
Final R_1/wR_2 indices (all data)	$R_1 = 0.0604/0.0627$	$R_1 = 0.1118/0.2283$
R_1/wR_2 indices [$I > 2\sigma(I)$]	$R_1 = 0.0366/0.0587$	$R_1 = 0.0548/0.1589$

4. Supplementary material

Crystallographic data for both compounds have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 145 566 (**5**) and 145 567 (**6**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-3360333) or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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