Journal of Organometallic Chemistry, 435 (1992) 157–167
Elsevier Sequoia S.A., Lausanne
JOM 22676

Triosmium clusters containing bridging sulphur, hydrido, and diphosphine ligands: a study of hydride site preferences and mobility

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(Received January 29, 1992)

Abstract

Reaction of dppm ($Ph_2PCH_2PPh_2$) with $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ in refluxing toluene leads to the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(dppm)]$ (**1**) (34% yield), the crystal structure of which has been determined. If the reaction is carried out at higher temperatures in refluxing octane, it gives the known cluster $[Os_3(CO)_8(\mu\text{-}dppm)_2]$ (11%) in addition to **1**. Cluster **1** is protonated to give $[Os_3(\mu\text{-}H)_3(\mu_3\text{-}S)(CO)_7(dppm)]^+$, isolated as its hexafluorophosphate salt. The bridging dppm compound $[Os_3(CO)_{10}(dppm)]$ reacts with RSH (R = Ph, or $4\text{-}MeC_6H_4$) in refluxing toluene to give the thiolato hydrido clusters $[Os_3(\mu\text{-}H)(\mu\text{-}SR)(CO)_8(dppm)]$, which on protonation with trifluoroacetic acid give the protonated species $[Os_3(\mu\text{-}H)_2(\mu\text{-}SR)(CO)_8(dppm)]^+$, isolated as their hexafluorophosphate salts. We have examined the hydride coordination sites with respect to the position of the μ-dppm ligand and the effect of the μ-dppm ligand on the mobility of hydrides in these complexes.

Introduction

Earlier we and others described the synthesis of the triosmium clusters $[Os_3(CO)_{10}(\mu\text{-diphosphine})]$ with the bridging diphosphine ligands, $Ph_2P(CH_2)_n\text{-}PPh_2$ where $n = 1\text{–}4$ [1,2]. Protonation of these clusters gave the cations $[Os_3(\mu\text{-}$

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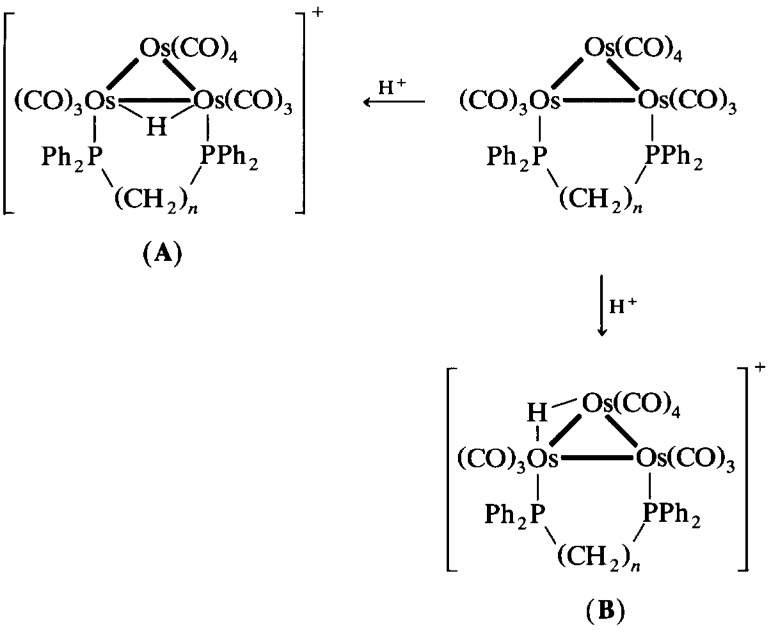


Scheme 1.

H)(CO)$_{10}$(μ-diphosphine)]$^+$ with hydride ligands in different sites depending upon the value of n (Scheme 1) [3]. For the dppe ($n = 2$), dppp ($n = 3$), and dppb ($n = 4$) complexes, the most stable isomer has the hydride positioned on the same Os–Os edge as the diphosphine bridge, although in some cases other isomers were formed initially and slowly converted into the stable form. The diphosphine-bridged edge is expected to be the most basic site in the cluster (structure **A**). The structure of [Os$_3$(μ-H)(CO)$_{10}$(dppe)][PF$_6$] was determined by X-ray crystallography confirming the conclusions from the NMR data [4]. However, [Os$_3$(CO)$_{10}$(μ-dppm)] ($n = 1$) is protonated on one of the other Os–Os edges to give structure **B** (Scheme 1). Protonation of M–M bonds is known to lead to a lengthening of the M–M bond and an opening up of the angles θ to the adjacent equatorial ligands (Fig. 1) (see ref. 4 for an example). This is because the hydride position rather than the metal–metal vector now defines the octahedral coordination axes of the metal

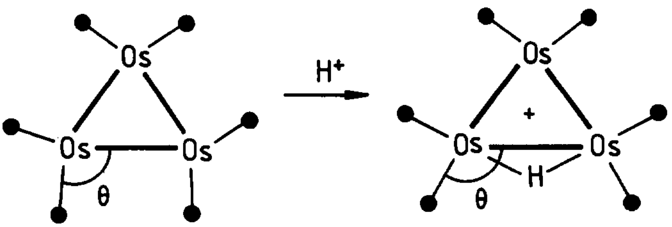


Fig. 1. Protonation of substituted derivatives of [Os$_3$(CO)$_{12}$] showing its effect on the positions of the equatorial ligands and the magnitude of the angle θ.

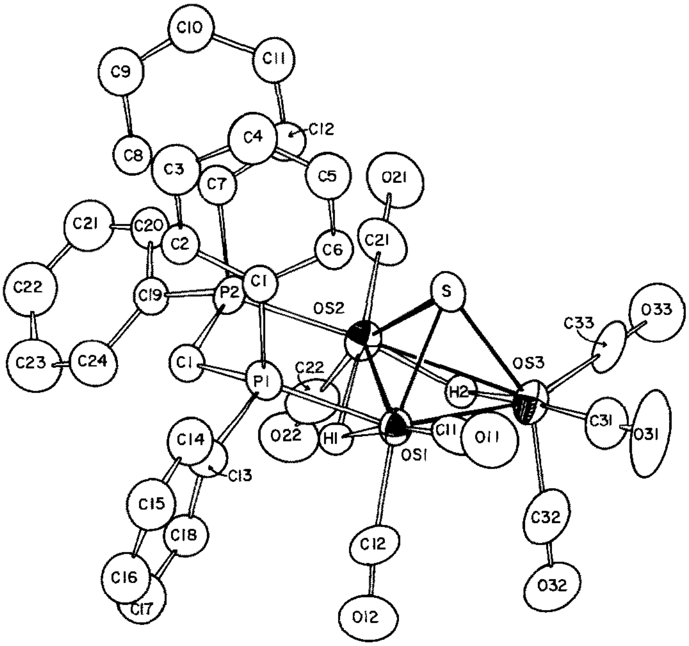


Fig. 2. Molecular structure of the compound [$Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)$]; the hydride positions are those determined using HYDEX [8].

atoms and the ligands *cis* and *trans* to the hydride are positioned with respect to the hydride site. For both reasons, a dppm-bridged edge cannot accommodate the bridging hydride if, as in these cases, the hydride is required to lie in the M_2P_2 plane. In this paper we describe some other dppm bridged clusters, their protonation reactions, and the effects of the dppm ligands on the hydride positioning and mobility.

Results and discussion

The cluster compounds are readily prepared. Reaction of H_2S with [$Os_3(CO)_{12}$] gives [$Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$] quantitatively [5] and this reacts with $Ph_2PCH_2PPh_2$ (dppm) to give [$Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)$] (**1**). Protonation of cluster **1** gives [$Os_3(\mu\text{-}H)_3(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)$]$^+$, which was isolated as the hexafluorophosphate salt. Another series of complexes was derived from [$Os_3(CO)_{10}(\mu\text{-}dppm)$] by reaction with PhSH or $4\text{-}MeC_6H_4SH$. The complexes [$Os_3(\mu\text{-}H)(\mu\text{-}SR)(CO)_8(\mu\text{-}dppm)$] ($R = C_6H_5$ or $4\text{-}MeC_6H_4$) obtained in this way could be protonated and the cations isolated as [$Os_3(\mu\text{-}H)_2(\mu\text{-}SR)(CO)_8(\mu\text{-}dppm)$]$PF_6$. The compound [$Os_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(dppm)$] was previously obtained by reaction of PhSH with [$Os_3(CO)_9(dppm)(MeCN)$] [6].

We have determined the crystal structure of [$Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)$] (**1**) by X-ray diffraction, and the molecular structure is shown in Fig. 2, with selected bond lengths and angles in Table 1. The structure is based on that of [$Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$] [7], which has a triply-bridging S atom capping an osmium

Table 1

Selected bond lengths (Å) and angles (°) for the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$

Os(1)–Os(2)	2.8981(4)	Os(3)–S	2.381(2)
Os(2)–Os(3)	2.9212(6)	Os(1)–P(1)	2.329(3)
Os(1)–Os(3)	2.7658(6)	Os(2)–P(2)	2.327(3)
Os(1)–S	2.381(2)	P(1)–C(1)	1.863(9)
Os(2)–S	2.405(2)	P(2)–C(1)	1.870(7)
Os(1)–S–Os(2)	74.53(6)	S–Os(1)–P(1)	99.06(7)
Os(2)–S–Os(3)	75.23(7)	S–Os(2)–P(2)	99.95(8)
Os(1)–S–Os(3)	71.00(5)	Os(1)–P(1)–C(1)	111.0(3)
Os(1)–Os(2)–P(2)	91.93(5)	Os(2)–P(2)–C(1)	111.9(3)
Os(2)–Os(1)–P(1)	92.34(4)		

triangle with the hydride ligands along Os–Os edges well below the Os_3 plane on the opposite side from the S atom. The Os–Os bond lengths are unaffected by the introduction of the dppm bridge. The dppm ligand bridges two Os atoms with the P atoms occupying what are approximately equatorial positions although they are significantly above the metal plane on the sulphur side. This is because the axial CO ligands are aligned roughly *trans* to the S capping atom and so are splayed out. To keep as close to octahedral angles at the metal atoms as possible, the P atoms are positioned as they are above the metal plane. Because neither hydride ligand has to lie in the five-membered ring formed by dppm, one hydride is easily accommodated on the same edge as the dppm ligand. The hydrides were not located from the diffraction data but their positions were calculated using HYDEX [8], an energy minimization program. Their positions may also be deduced by looking at the positions of the surrounding ligands.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of **1** at −50°C are consistent with this structure in solution. The ^1H NMR spectrum shows two hydride signals (δ −19.21 and −20.04) (Fig. 3). The double triplet pattern at δ −19.21 is assigned to the hydride between Os(1) and Os(2) and the double doublet at δ −20.04 to that between Os(1) and Os(3). Between −50 and 20°C, the signals broaden somewhat and a central component to the doublet pattern appears, increasing in height between 10 and 20°C. At 50°C, two broad signals are observed. These changes result from two separate processes, one rather faster than the other. Process A (Scheme 2) would lead to phosphorus exchange and to a change of the double doublet for H^x into a double triplet with the effective *J*-value for the triplet half that in the doublet as it averages its coupling between the two ^{31}P nuclei. This accounts for the appearance of the central component inside the doublet at 20°C. However, before the triplet structure is properly resolved a second rather slower process becomes apparent in the spectrum (process B). At 50°C the spectrum is just a little below the coalescence temperature for process B. We have not analysed the line shapes to obtain kinetic data but the clear observation of H^x–H^y exchange probably means that the isomeric form with the dppm ligand along the Os–Os edge that is not H-bridged can only be slightly higher in energy than the observed ground state form.

The protonated species $[Os_3(\mu\text{-}H)_3(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]^+$ (**2**) gives two ^1H NMR multiplets in intensity ratio 1:2, entirely consistent with a hydride ligand at

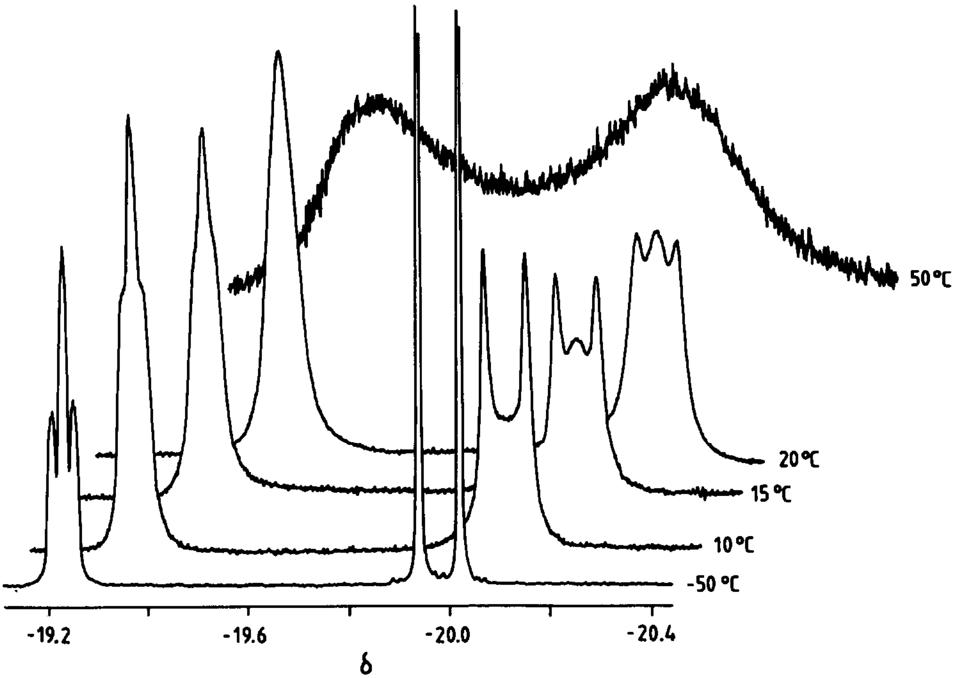
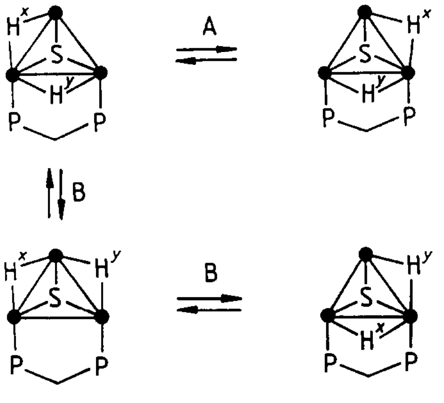


Fig. 3. ^1H NMR spectra for the compound $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$ in $CDCl_3$ in the hydride region.

each edge. The pattern of these multiplets is complex because of second-order (virtual) coupling effects (Fig. 4). The spin system can be analysed as an ABB′MXX′ system and coupling is observed between the two ^{31}P nuclei and the three hydride nuclei and also between the unique hydride ligand and one of the CH_2 protons. In the $^1H\{^{31}P\}$ NMR spectrum the multiplet at δ −19.70 has collapsed to a narrow doublet and that at δ −19.10 to a doublet of triplets. The spectra are consistent with a static structure in which there is no hydride mobility. This confirms the



Scheme 2.

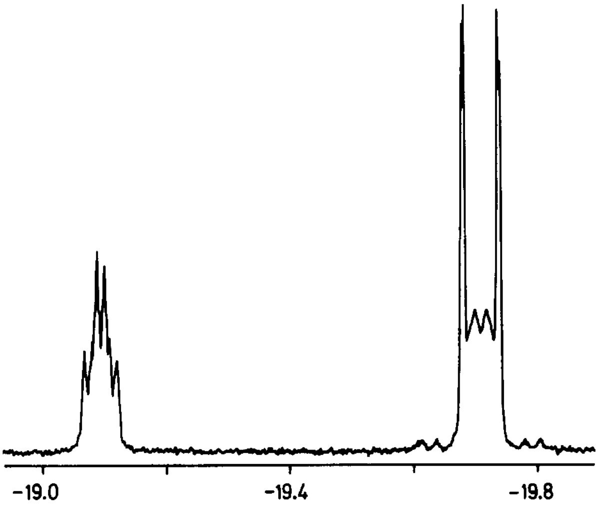
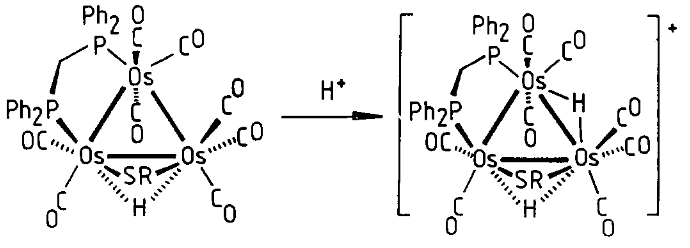


Fig. 4. ^1H NMR spectrum of the protonated compound $[Os_3(\mu\text{-}H)_3(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)][PF_6]$ in $CDCl_3$ in the hydride region at 27°C.

principle that hydrides migrate to vacant Os–Os edges as in Scheme 1. When all edges are occupied fluxionality is suppressed.

We also examined the protonation of the known dppm complex $[Os_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(dppm)]$ (**3**), which was previously synthesised by reaction of $[Os_3(CO)_9(dppm)(MeCN)]$ with PhSH [6]. We synthesised it and the $4\text{-}MeC_6H_4SH$ analogue (**4**) by reaction of $[Os_3(CO)_{10}(dppm)]$ with PhSH or $4\text{-}MeC_6H_4SH$ in refluxing toluene. The crystal structures of the complexes $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_8(\mu\text{-}dppm)]$ [6] and $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}dppm)]$ [9] show that the three bridging ligands link the same pair of osmium atoms so that the hydride ^1H NMR resonances are triplets. In contrast, the complexes $[Os_3(\mu\text{-}H)(\mu\text{-}SAr)(CO)_8(\mu\text{-}dppm)]$ give hydride resonances as doublets supporting a structure like the ruthenium compound with the dppm and the SAr ligands on different edges [10].

Scheme 3 shows the structure of these SAr complexes. The hydride is coupled to one ^{31}P nucleus ($J = 31.0$ Hz for Ar = phenyl and $J = 29.5$ Hz for Ar = tolyl) in each case and the J-values are consistent with the hydride and the P atom being mutually *trans*. The other ^{31}P atom is presumed to be coordinated as shown and as found for the crystal structure of the ruthenium compound. It is not obvious why



Scheme 3.

different structures are obtained for $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_8(dppm)]$ where X = H, OH, or SAr, but we believe that the thermodynamically stable geometry is formed in each case. Certainly when X = SAr the same isomer is found whether SAr or dppm is introduced first.

Protonation might be expected to give a product with the incoming hydride ligand coming in to bridge the most substituted Os atoms, that is entering at the most basic site. The ^1H NMR spectra of the protonated compounds $[Os_3(\mu\text{-}H)_2(\mu\text{-}SR)(CO)_8(\mu\text{-}dppm)]^+$, both isolated as their PF_6^- salts (**5**) (R = Ph) and (**6**) ($R = 4\text{-}MeC_6H_4$), can be quite clearly interpreted in terms of the hydride bridging the Os–Os edge not bridged by the dppm ligand. Both hydride signals appear as doublets, and the structure shown in Scheme 3 is the most likely. We can then ask why the hydride does not occupy the most basic edge as in the protonation of $[Os_3H_2(\mu_3\text{-}S)(CO)_7(dppm)]$. The key probably lies in the strictly equatorial substitution of the P atom at the $Os(CO)_3$ group; the required increase in the Os–Os–P angle at this atom on protonation on the dppm-bridged edge is not possible. The only possible remaining site for protonation is that observed. As in the case of the protonation of $[Os_3(CO)_{10}(dppm)]$, the site that is apparently the most basic is not protonated for steric reasons. It is not a consequence of the hydride being big but of the need to shift the other ligands to maintain favourable angles on protonation. The protonated compound, $[Os_3H_2(\mu\text{-}SAr)(CO)_8(dppm)]^+$, is non-fluxional because there are no available sites to which to move the hydride ligands.

Experimental

The clusters $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ [4] and $[Os_3(CO)_{10}(dppm)]$ [1] were prepared by published methods. IR spectra of CH_2Cl_2 solutions were recorded on a Perkin–Elmer 580B spectrometer and NMR spectra on a Bruker WH300 or a Varian VXR400 spectrometer. $^{31}P\{^1H\}$ NMR shifts are referenced to 85% H_3PO_4.

Reaction of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ with dppm

(a) In toluene. A toluene solution (70 cm^3) of the triosmium cluster (0.2258 g) and dppm (0.303 g, 3 mol/mol of Os_3) was heated under reflux under nitrogen for 16 h. The solvent was removed under reduced pressure and TLC (SiO_2; eluant, light petroleum (b.p. 30–40°C)/dichloromethane, 2:1, v/v) gave two bands. The fastest gave an uncharged starting cluster (0.103 g) and the next gave $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(dppm)]$ (**1**) as pale yellow crystals from a hexane/dichloromethane mixture (0.106 g, 34% yield, 57% conversion). Anal. Found: C, 32.55; H, 1.9; P, 5.35%. $C_{32}H_{24}O_7Os_3P_2S$ calc.: 32.45; H, 2.05; P, 5.25%. $\nu(CO)$ (CH_2Cl_2): 2057s, 2032s, 1989s, 1976s, 1956sh, 1927w cm^{-1}. ^1H NMR ($CDCl_3$, 27°C): δ 7.33 (m, Ph); 4.66 (dtt, CH_2); 3.56 (dt, CH_2); −19.21 (dt, OsH, $J = 1.4$, 8.8 Hz); −20.04 (dd, OsH, $J = 1.4$, 32.5 Hz).

(b) In octane. A similar reaction of the triosmium cluster (0.150 g) and dppm (0.202 g, 3 mol/mol of Os_3) in refluxing octane for 4 h followed by a similar work-up gave starting cluster (0.075 g), cluster **1** (0.031 g, 15%), and $[Os_3(CO)_8(dppm)_2]$ [11] (0.030 g, 11%) in order of elution.

Protonation of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(dppm)]$ *(1)*

The ^1H NMR spectrum of a CD_2Cl_2 solution containing cluster **1** (0.030 g) and trifluoroacetic acid (0.020 cm^3, 10 mol/mol of Os_3) indicated that complete protonation had occurred. The solvent was removed under reduced pressure and the residue dissolved in methanol (4 cm^3). To the solution was added a methanolic solution of NH_4PF_6 (0.012 g) followed by a few drops of water to give a pale yellow precipitate. The solvent was decanted from this precipitate which was then dried and extracted with dichloromethane. Addition of diethyl ether to the CH_2Cl_2 solution gave pale yellow crystals of $[Os_3(\mu\text{-}H)_3(\mu_3\text{-}S)(CO)_7(dppm)]PF_6$ (**2**) (0.027 g, 80%). ν(CO) (CH_2Cl_2): 2118s, 2057vs, 2045s, 2001s, 1975m cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.1–7.7 (m, Ph); 5.37 (dtt, CH_2); 3.76 (dt, CH_2); −19.04 (m, OsH); −19.67 (m, OsH_2) (B and AA′ parts of an AA′BMXX′ spectrum, respectively).

Reactions of $[Os_3(CO)_{10}(\mu\text{-}dppm)]$ *with thiols*

(a) With thiophenol. A solution of the dppm cluster (0.169 g) and thiophenol (0.045 g, 3 mol/mol of Os_3) in toluene (30 cm^3) was refluxed under nitrogen for 3 h while the colour changed slowly from yellow to orange. The solvent was removed under reduced pressure and TLC of the residue (SiO_2; eluant, light petroleum (b.p. 30–40°C)/dichloromethane, 10:3, v/v) gave one main band from which the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(dppm)]$ (**3**) was isolated as orange crystals (0.086 g, 49%) from hexane/dichloromethane mixtures. Anal. Found: C, 36.5; H, 2.0; P, 4.7. $C_{39}H_{28}O_8Os_3P_2S$ calc.: C, 36.35; H, 2.2; P, 4.8%. ν(CO) (CH_2Cl_2): 2065vs, 2024m, 1989sh, 1934s, 1921w cm^{-1}. ^1H NMR ($CDCl_3$, 27°C): δ 7.51 (m, Ph); 5.75 (m, CH_2); 4.61 (m, CH_2); −15.75 (d, OsH, $J = 31.0$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −28.42 (s); −29.02 (s).

(b) With p*-thiocresol.* A similar reaction using the dppm cluster (0.150 g) and $4\text{-}MeC_6H_4SH$ (0.045 g, 3 mol/mol of Os_3) in refluxing toluene for 4 h followed by work-up as above gave a yellow band yielding $[Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4Me\text{-}4)(CO)_8(dppm)]$ (**4**) as orange crystals (0.091 g, 57%) from a hexane/dichloromethane mixture. Anal. Found: C, 37.45; H, 2.5; P, 4.7. $C_{40}H_{30}O_8Os_3P_2S$ calc.: C, 37.0; H, 2.3; P, 4.65%. ν(CO) (CH_2Cl_2): 2065 vs, 2023m, 1993vs, 1969sh, 1954w, 1920w cm^{-1}. ^1H NMR ($CDCl_3$, 27°C): δ 7.42 (m, Ph); 4.81 (m, CH_2); 3.53 (m, CH_2); 2.35 (s, Me); −15.76 (d, OsH, $J = 29.5$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −28.66 (s); −28.85 (s).

Protonation of the thiolato complexes $[Os_3(\mu\text{-}H)(\mu\text{-}SR)(CO)_8(dppm)]$ *(3) and (4)*

Cluster 3. Addition of trifluoroacetic acid (0.018 cm^3, 10 mol/mol of Os_3) to a bright yellow solution of $[Os_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8(dppm)]$ (**3**) (0.030 g) in $CDCl_3$ (0.5 cm^3) gave a pale yellow solution and the ^1H NMR spectrum showed that complete protonation had occurred. Replacement of the solvent by methanol and addition of NH_4PF_6 (0.012 g) in methanol gave a solution that deposited a pale yellow precipitate on addition of water. Extraction with dichloromethane and precipitation with diethyl ether gave yellow crystals (0.017 g, 52%) of $[Os_3(\mu\text{-}H)_2(\mu\text{-}SPh)(CO)_8(dppm)]PF_6$ (**5**). Anal. Found: C, 32.3; H, 2.3; P, 6.75. $C_{39}H_{29}F_6O_8Os_3P_3S$ calc.: C, 32.6; H, 2.0; P, 6.45%. ν(CO) (CH_2Cl_2): 2130w, 2097m, 2063vs, 2059sh, 2015m, 2004s, 1995m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42 (m, Ph); 5.30 (m, Ph); −15.48 (d, OsH, $J = 22$ Hz); −18.52 (d, OsH, $J = 11$ Hz).

Cluster 4. Very similar treatment of cluster **4** (0.035 g) with trifluoroacetic acid (0.21 cm^3) and similar work-up gave $[Os_3(\mu\text{-}H)_2(\mu\text{-}SC_6H_4Me\text{-}4)(CO)_8(dppm)]PF_6$ (**6**) as yellow crystals from a dichloromethane/diethyl ether mixture (0.023 g,

Table 2

Fractional atomic coordinates for the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)]$

Atom	*x*	*y*	*z*
Os1	0.30439(1)	0.14791(2)	0.29186(1)
Os2	0.40221(1)	0.28974(3)	0.38825(1)
Os3	0.40292(1)	0.17326(3)	0.28611(1)
S	0.41104(8)	0.1093(2)	0.38331(9)
P1	0.26547(8)	0.1436(2)	0.3552(1)
P2	0.36738(8)	0.2975(2)	0.45556(9)
O11	0.2638(3)	−0.0626(4)	0.2307(3)
O12	0.1938(3)	0.2395(6)	0.1578(3)
O21	0.5371(3)	0.3089(6)	0.5162(3)
O22	0.3828(3)	0.5150(5)	0.3594(3)
O31	0.3683(3)	−0.0239(6)	0.2092(3)
O32	0.3332(3)	0.2903(6)	0.1509(3)
O33	0.5355(2)	0.1868(7)	0.3310(3)
C1	0.2826(3)	0.2642(6)	0.4039(4)
C11	0.2791(3)	0.0165(7)	0.2545(4)
C12	0.2343(4)	0.2054(7)	0.2085(4)
C21	0.4879(3)	0.3049(7)	0.4680(4)
C22	0.3879(3)	0.4321(7)	0.3695(4)
C31	0.3817(4)	0.0512(7)	0.2379(4)
C32	0.3600(3)	0.2459(8)	0.2026(4)
C33	0.4867(3)	0.1831(7)	0.3152(4)
C41	0.2931(3)	0.0450(6)	0.4215(3)
C42	0.3204(3)	−0.0408(6)	0.4189(4)
C43	0.3399(4)	−0.1161(8)	0.4681(4)
C44	0.3314(4)	−0.1061(7)	0.5191(4)
C45	0.3032(4)	−0.0208(7)	0.5200(4)
C46	0.2831(3)	0.0557(7)	0.4708(3)
C51	0.1797(3)	0.1371(6)	0.3045(4)
C52	0.1445(3)	0.2161(7)	0.2580(4)
C53	0.0796(4)	0.2106(8)	0.2170(4)
C54	0.0514(4)	0.1255(9)	0.2243(4)
C55	0.0866(4)	0.0495(9)	0.2689(5)
C56	0.1520(3)	0.0538(8)	0.3113(4)
C61	0.4038(3)	0.2217(6)	0.5340(4)
C62	0.4423(3)	0.1378(6)	0.5442(4)
C63	0.4662(4)	0.0751(7)	0.6025(4)
C64	0.4514(4)	0.0938(7)	0.6477(4)
C65	0.4150(4)	0.1762(7)	0.6375(4)
C66	0.3904(3)	0.2398(7)	0.5795(3)
C71	0.3708(3)	0.4231(6)	0.4884(3)
C72	0.4314(4)	0.4537(7)	0.5510(4)
C73	0.4357(4)	0.5475(8)	0.5781(4)
C74	0.3858(4)	0.6127(8)	0.5463(5)
C75	0.3264(4)	0.5856(8)	0.4832(5)
C76	0.3213(3)	0.4905(7)	0.4553(4)
H1	0.318	0.285	0.314
H2	0.422	0.300	0.327

60%). Anal. Found: C, 33.3; H, 2.5; P, 6.65. $C_{40}H_{31}F_6O_8Os_3P_3S$ calc.: C, 33.1; H, 2.1; P, 6.4%. ν(CO) (CH_2Cl_2): 2131w, 2099m, 2065vs, 2059sh, 2018m, 2006s, 1994s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.31 (m, Ph); 5.27 (m, CH_2); 2.35 (s, Me); -15.40 (d, OsH, $J = 21$ Hz); -18.50 (d, OsH, $J = 11$ Hz).

Crystal structure determination for $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-dppm})(CO)_7]$ *(1)*

A pale yellow crystal of 1, $C_{32}H_{24}O_7Os_3P_2S$, $M = 1185.16$, size $0.40 \times 0.30 \times 0.20$ mm^3, formed by cooling a hexane solution of the compound to −20°C, was fixed to a glass fibre mounted on a goniometer head on an Enraf–Nonius CAD4 diffractometer operating with Mo-K_α radiation ($\lambda = 0.71073$ Å). Auto-indexing and least-squares refinement of 25 reflections ($16 < 2\theta < 26°$) gave a monoclinic cell with $a = 26.982(2)$, $b = 13.202(1)$, $c = 24.208(2)$ Å, $\beta = 127.59(2)$, $U = 6833(3)$ $Å^3$, $Z = 8$, $D_c = 2.30$ g cm^{-3}. A total of 3372 unique, averaged reflections were collected at 25 ± 1°C by the ω–2θ method with 2θ up to 40°. Lorentz, polarization and empirical absorption (psi-scan method) corrections were made; μ(Mo-K_α) = 113.4 cm^{-1}, relative transmission coefficients from 1.000 to 0.548.

The structure solution by the Patterson method in the space group $C2/c$ using SHELXS-86 [12] revealed the positions of the osmium atoms; the remaining non-H atoms were located in successive difference Fourier syntheses and least-squares refinements. 2885 reflections with $F_o > 2\sigma(F_o)$ and 406 variable parameters were employed in the final refinements. The hydride ligands were positioned using the program HYDEX [8]. The largest peak in the final difference Fourier had a height of 0.29 e $Å^{-3}$; the maximum shift/e.s.d. was 0.00; the GOF and final R and R_w were 0.94, 0.0246 and 0.0314, respectively, where $R_w = [\Sigma w(|F_o| - |F_c|^2)/\Sigma w |F_o|^2]^{1/2}$ and $w = 4F_o^2/[\sigma(F_o)^2]^2$.

Calculations were carried out using a Microvax II computer running SDP/VAX [13]. Atomic coordinates are given in Table 2 and additional material has been deposited at the Cambridge Crystallographic Data Centre (thermal parameters and the remaining bond lengths and angles).

Acknowledgements

We thank the NSF for a grant towards the diffractometer and NATO for support for this collaboration between A.J.D. and K.I.H.

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