Trinuclear Osmium Clusters containing Bidentate $Ph_2PCH_2PPh_2$ and $Me_2PCH_2PMe_2$ Ligands: *X*-Ray Crystal Structures of the Complexes $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ and $[Os_3H(OH)(CO)_8(Ph_2PCH_2PPh_2)]$†

Stephen R. Hodge, Brian F. G. Johnson, Jack Lewis,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The clusters $[Os_3(CO)_{10}(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) and $[Os_3(CO)_{10}(dmpm)]$ (dmpm = $Me_2PCH_2PMe_2$) react with trimethylamine *N*-oxide in acetonitrile solution to give $[Os_3(CO)_9(dppm)(MeCN)]$ (**1**) and $[Os_3(CO)_9(dmpm)(MeCN)]$ (**2**) respectively. The acetonitrile ligand of (**1**) and (**2**) is readily displaced by other two-electron donor ligands to give $[Os_3(CO)_9(dppm)L]$ [L = PPh_3, $P(OMe)_3$, or Bu^tNC] and $[Os_3(CO)_9(dmpm)L]$ [L = $P(OMe)_3$ or C_2H_4]. Thermolysis of $[Os_3(CO)_9(dmpm)(C_2H_4)]$ or $[Os_3(CO)_{10}(dmpm)]$ gives the cyclometallated product $[Os_3H(CO)_9(Me_2PCHPMe_2)]$. The acetonitrile complex (**1**) also reacts with HX (X = Cl or SR, R = alkyl) to give clusters of general formula $[Os_3H(X)(CO)_8(dppm)]$, whereas for X = OH or OMe the only product isolated is $[Os_3H(CO)_8\{Ph_2PCH_2PPh(C_6H_4)\}]$. The dmpm derivative (**2**) reacts similarly with HCl and RSH. The cluster $[Os_3H(OH)(CO)_8(dppm)]$, which can be prepared from $[Os_3H(OH)(CO)_{10}]$ and dppm, was found to have a different structure from $[Os_3H(Cl)(CO)_8(dppm)]$. All the products were characterised by i.r. and n.m.r. spectroscopy. The structures of $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ and $[Os_3H(OH)(CO)_8(dppm)]$ were confirmed by *X*-ray crystallography.

The use of the bridging phosphine ligands $Ph_2PCH_2PPh_2$ (dppm) and $Me_2PCH_2PMe_2$ (dmpm) in binuclear metal complexes is now well established.[1] These studies have been extended to polynuclear metal cluster systems, especially the trinuclear ruthenium species.[2] In the triosmium systems the preparation of $[Os_3(CO)_{10}(dppm)]$ and its conversion into the novel unsaturated species $[Os_3H(CO)_8\{Ph_2PCH_2PPh(C_6H_4)\}]$ has been reported.[3] We[4] and others[5] have shown that $[Os_3H(CO)_8\{Ph_2PCH_2PPh(C_6H_4)\}]$ has an extensive and interesting chemistry.

As an extension to this work we have investigated the chemistry of $[Os_3(CO)_{10}(dppm)]$ and $[Os_3(CO)_{10}(dmpm)]$, in particular the reactions of their acetonitrile derivatives $[Os_3(CO)_9(dppm)(MeCN)]$ and $[Os_3(CO)_9(dmpm)(MeCN)]$. This has led to the synthesis and characterisation of several new derivatives of general formula $[Os_3(CO)_9(L\text{–}L)L]$ and $[Os_3H(X)(CO)_8(L\text{–}L)]$ where L–L = dppm or dmpm, L = PR_3, $CNBu^t$, or C_2H_4, and X = Cl, SR, or OH. Several of these derivatives have been previously prepared from reactions of $[Os_3H(CO)_8\{Ph_2PCH_2PPh(C_6H_4)\}]$.[4]

We have also looked at the thermolysis of $[Os_3(CO)_{10}(dmpm)]$ in order to compare it with that of $[Os_3(CO)_{10}(dppm)]$[3] and with other monodentate phosphine-substituted triosmium clusters.[6]

Results and Discussion

In acetonitrile solution $[Os_3(CO)_{10}(dppm)]$ reacts with trimethylamine *N*-oxide (Me_3NO) to give $[Os_3(CO)_9(dppm)(MeCN)]$ (**1**). The dmpm derivative $[Os_3(CO)_9(dmpm)(MeCN)]$ (**2**) can be prepared in a similar way from $[Os_3(CO)_{10}(dmpm)]$. The i.r. spectra of these acetonitrile-substituted compounds, recorded immediately after preparation, indicate that their formation from $[Os_3(CO)_{10}(L\text{–}L)]$ is essentially quantitative. Attempts to purify (**1**) and (**2**) by t.l.c. led to extensive decomposition and so subsequent reactions were carried out on the initial solutions.

The acetonitrile groups in complexes (**1**) and (**2**) can be displaced by other two-electron donor ligands to give compounds of general formula $[Os_3(CO)_9(dppm)L]$ [L = PPh_3, $P(OMe)_3$, or Bu^tNC] and $[Os_3(CO)_9(dmpm)L]$ [L = $P(OMe)_3$ or C_2H_4] respectively. The position of substitution of the ligand L was determined from the spectroscopic properties of the complexes (Table 1).

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[Os_3(CO)_9(dppm)(PPh_3)]$ at 316 K shows a sharp singlet due to the phosphorus of the PPh_3 group and a featureless broad band due to the two phosphorus atoms of the dppm. On cooling, the signal due to dppm sharpens, to give at 256 K an AB pattern with $J(PP) = 54$ Hz. The signal due to PPh_3 remains sharp throughout and shows no observable coupling to the dppm phosphorus atoms. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at 233 K shows six signals of intensities 2:2:2:1:1:1 due to the carbonyls. This is consistent with the structure where the dppm bridges two equatorial sites and the PPh_3 ligand is in an equatorial site on the unique osmium atom (Figure 1). The fluxional process which results in the two phosphorus atoms of the dppm becoming equivalent can be rationalised in terms of the PPh_3 group moving between the two equivalent equatorial sites on the unique osmium atom.

The ^1H n.m.r. spectrum of $[Os_3(CO)_9(dppm)(Bu^tNC)]$ indicates that the Bu^tNC occupies an axial site on the osmium atom to which the dppm is not bonded (Figure 1). Comparison of i.r. spectra (Table 2) indicates that the MeCN ligand in $[Os_3(CO)_9(dppm)(MeCN)]$ also occupies an axial site, whereas the ethylene ligand in $[Os_3(CO)_9(dmpm)(C_2H_4)]$ is equatorial (Figure 1). A similar set of ligands has been shown by i.r. comparisons to occupy the same categories of co-ordination sites in complexes of the type $[Os_3(CO)_{11}L]$.[7]

In a non-co-ordinating solvent, such as chloroform or dichloromethane, $[Os_3(CO)_9(dppm)(MeCN)]$ loses the acetonitrile ligand with concomitant metallation of an aryl carbon–hydrogen bond to give $[Os_3H(CO)_9\{Ph_2PCH_2PPh(C_6H_4)\}]$.[4]

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† μ_3-[Bis(dimethylphosphino)methyl-*C*(Os^1)*P*(Os^2)*P′*(Os^3)]-2,3-μ-hydrido-*triangulo*-tris(tricarbonylosmium) and 1,2-μ-bis(diphenylphosphino)methane-1,1,2,2,3,3,3,3-octacarbonyl-1,2-μ-hydrido-1,2-μ-hydroxo-*triangulo*-triosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. N.m.r. spectral data for the complexes: ^1H in $CDCl_3$ (standard $SiMe_4$), ^{31}P-{^1H} in CH_2Cl_2 [standard $P(OMe)_3$], and ^{13}C-{^1H} in $CDCl_3$ (standard $SiMe_4$); *J* in Hz

$[Os_3(CO)_9(dppm)(PPh_3)]$	δ_H	7.3 (m, Ph), 4.96 [t, *J*(HP) 10.4, PCH_2P]
	$\delta_P{}^a$	−141.1 (s), −165.8 [d, *J*(PP) 54], −169.5 [d, *J*(PP) 54]
	$\delta_C{}^b$	197.2 (2 C, s), 196.5 (2 C, s), 194.9 (2 C, s), 184.2 (1 C, s), 182.7 (1 C, s), 178.2 (1 C, s)
$[Os_3(CO)_9(dppm)\{P(OMe)_3\}]$	δ_H	7.5—7.3 (20 H, m, Ph), 5.00 [2 H, t, *J*(HP) 10.5, PCH_2P], 3.63 [9 H, d, *J*(HP) 12.4, $POCH_3$]
$[Os_3(CO)_9(dmpm)\{P(OMe)_3\}]$	δ_H	3.77 [2 H, t, *J*(HP) 10.8, PCH_2P], 3.60 [9 H, d, *J*(HP) 12.4, $POCH_3$], 1.85 [12 H, m, $N^c = 8.8$, PCH_3]
$[Os_3(CO)_9(dppm)(Bu^tNC)]$	δ_H	7.3 (m, Ph), 5.14 [dt, *J*(HH) 15.0, *J*(HP) 9.3, PCHP], 4.96 [dt, *J*(HH) 15.0, *J*(HP) 10.4, PCHP], 1.47 (s, Bu^t)
$[Os_3(CO)_9(dmpm)(C_2H_4)]$	δ_H	3.9 [2 H, t, *J*(HP) 10.6, PCH_2P], 2.20 (4 H, s, C_2H_4), 1.89 (m, $N^c = 8.8$, PCH_3)
$[Os_3H(CO)_9(Me_2PCHPMe_2)]$	δ_H	2.93 [1 H, td, *J*(HP) 9.5, *J*(HH) 1.9, PCHP], 2.07 (6 H, m, $N^c = 8.0$, PCH_3), 1.47 (6 H, m, $N^c = 8.0$, PCH_3), −18.45 [1 H, td, *J*(HP) 10.3, *J*(HH) 1.9, OsHOs]
$[Os_3H(Cl)(CO)_8(dppm)]$	δ_H	7.8—7.1 (m, Ph), 5.97 [ddd, *J*(HH) 15.8, *J*(HP) 10.9, 8.6, PCHP], 4.46 [dt, *J*(HH) 15.8, *J*(HP) 12.0, PCHP], −12.85 [d, *J*(HP) 32.2, OsHOs]
$[Os_3H(SMe)(CO)_8(dppm)]$	δ_H	7.6—7.3 (m, Ph), 5.52 [dt, *J*(HH) 15.7, *J*(HP) 10.1, PCHP], 4.73 [dt, *J*(HH) 15.7, *J*(HP) 11.0, PCHP], 2.11 (s, SCH_3), −16.03 [d, *J*(HP) 29.1, OsHOs]
$[Os_3H(SEt)(CO)_8(dppm)]$	δ_H	7.7—7.1 (m, Ph), 5.41 [ddd, *J*(HH) 15.3, *J*(HP) 11.2, 9.0, PCHP], 4.85 [dt, *J*(HH) 15.3, *J*(HP) 10.3, PCHP], 2.11 (m, SCH_2CH_3), 0.94 [t, *J*(HH) 7.3, SCH_2CH_3], −16.19 [d, *J*(HP) 30.8, OsHOs]
	δ_P	−165.9 [d, *J*(PP) 39], −168.7 [d, *J*(PP) 39]
$[Os_3H(SMe)(CO)_8(dmpm)]$	δ_H	4.36 [1 H, dt, *J*(HH) 14.5, *J*(HP) 9.9, PCHP], 3.38 [1 H, dt, *J*(HH) 14.5, *J*(HP) 11.5, PCHP], 2.33 (3 H, s, SCH_3), 2.12 [3 H, d, *J*(HP) 9.6, PCH_3], 1.92 [3 H, d, *J*(HP) 7.9, PCH_3], 1.90 [3 H, d, *J*(HP) 8.5, PCH_3], 1.81 [3 H, d, *J*(HP) 8.9, PCH_3], −16.14 [1 H, d, *J*(HP) 26.2, OsHOs]
$[Os_3H(SEt)(CO)_8(dmpm)]$	δ_H	4.40 [dt, *J*(HH) 14.5, *J*(HP) 9.8, PCHP], 3.37 [dt, *J*(HH) 14.5, *J*(HP) 11.4, PCHP], 2.50 (dq, SCH_2CH_3), 2.2—2.1 (m, SCH_2CH_3, PCH_3), 2.0—1.7 (m, PCH_3), 1.20 [t, *J*(HH) 7.3, SCH_2CH_3], −16.26 [d, *J*(HP) 26.6, OsHOs]
	δ_P	−202.0 [d, *J*(PP) 35], −202.1 [d, *J*(PP) 35]
$[Os_3H(SPh)(CO)_8(dmpm)]$	δ_H	7.2—7.1 (m, Ph), 4.43 [dt, *J*(HH) 14.5, *J*(HP) 9.8, PCHP], 3.42 [dt, *J*(HH) 14.5, *J*(HP) 11.2, PCHP], 2.15 [d, *J*(HP) 9.5, PCH_3], 2.0—1.8 (m, PCH_3), −15.87 [d, *J*(HP) 26.7, OsHOs]
$[Os_3H(OH)(CO)_8(dppm)]$	δ_H	7.4—7.3 (m, Ph), 3.78 [dtd, *J*(HH) 13.4, 1.7, *J*(HP) 11.4, PCHP], 2.69 [dt, *J*(HH) 13.4, *J*(HP) 10.7, PCHP], 0.44 [td, *J*(HP) 4.3, *J*(HH) 1.5, μ-OH], −11.68 [t, *J*(HP) 11.9, OsHOs]
	δ_P	−152.8 (s)

[a] At 256 K. [b] At 233 K. [c] $N = |^2J(HP) + {}^4J(HP)|$/Hz.

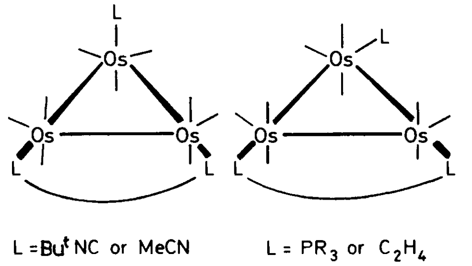


Figure 1. Isomeric structures of $[Os_3(CO)_9(L\text{–}L)L]$ (L–L = dppm or dmpm)

The complex $[Os_3(CO)_9(dmpm)(MeCN)]$ does not give a cyclometallated species on standing in dichloromethane but instead gives $[Os_3(CO)_{10}(dmpm)]$ and uncharacterised decomposition products. On heating $[Os_3(CO)_9(dmpm)(C_2H_4)]$ in octane, however, the metallated species $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ (**3**) is obtained. A more convenient preparation of (**3**) is to reflux $[Os_3(CO)_{10}(dmpm)]$ in xylene. Complex (**3**) was characterised on the basis of its ^1H n.m.r. spectrum and *X*-ray crystal structure.

The molecular structure of (**3**) is shown in Figure 2 and the bond parameters are given in Table 3. One of the methylene C–H bonds of the dmpm has been broken and the $Me_2PCHPMe_2$ ligand occupies the three axial sites on one side of the Os_3 triangle. The hydride was directly located and bridges the Os(1)–Os(2) edge, lying just out of the Os_3 plane. This long edge [3.104(1) Å] is consistent with the presence of the bridging hydride and the two *cis* carbonyls in the equatorial plane are bent away from the hydride, as expected.[8]

The ^1H n.m.r. spectrum of complex (**3**) in $CDCl_3$ solution (Table 1) is consistent with the same structure as in the solid state. The metal hydride signal shows coupling to the two phosphorus atoms and the magnitude of the coupling constant is typical for a *cis* HOsP arrangement.

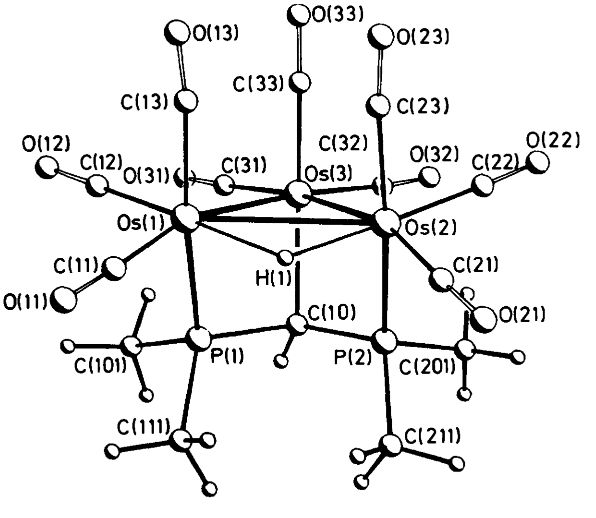


Figure 2. The molecular structure of $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ (**3**) showing the atom numbering scheme adopted

The complexes $[Os_3(CO)_9(L\text{–}L)(MeCN)]$ in cyclohexane react with hydrogen chloride to give $[Os_3H(Cl)(CO)_8(L\text{–}L)]$. The complex $[Os_3H(Cl)(CO)_8(dppm)]$ can also be prepared by heating $[Os_3H(Cl)(CO)_{10}]$ with the diphosphine (Scheme). The compounds were characterised by i.r., n.m.r., and mass (for the dmpm derivative) spectroscopy and analytical data.

Complexes (**1**) and (**2**) also react with thiols, RSH (R = H, Me, Et, Bu^t, or Ph), in refluxing dichloromethane to give $[Os_3H(SR)(CO)_8(L\text{–}L)]$ (Scheme). The i.r. spectra of these

Table 2. I.r. data (cm^{-1}) for the complexes (carbonyl region) recorded in cyclohexane unless specified otherwise

Compound	
$[Os_3(CO)_9(dppm)(MeCN)]$[a]	2 058m, 2 010(sh), 1 996s, 1 971vs, 1 946m, 1 924(sh)
$[Os_3(CO)_9(dmpm)(MeCN)]$[a]	2 054w, 2 000(sh), 1 990s, 1 964vs, 1 937m, 1 919(sh)
$[Os_3(CO)_9(dppm)(PPh_3)]$	2 066w, 2 011m, 2 001m, 1 983s, 1 966w, 1 939w
$[Os_3(CO)_9(dppm)\{P(OMe)_3\}]$	2 070w, 2 005s, 1 987vs, 1 967(sh), 1 942m
$[Os_3(CO)_9(dmpm)\{P(OMe)_3\}]$	2 069w, 2 000s, 1 985vs, 1 968(sh), 1 941m
$[Os_3(CO)_9(dppm)(Bu^tNC)]$	2 067(sh), 2 055m, 2 015m, 2 003s, 1 987s, 1 970(sh), 1 956m, 1 938m; ν(N–C) 2 172
$[Os_3(CO)_9(dmpm)(C_2H_4)]$[b]	2 071w, 2 004s, 1 980vs, 1 939m
$[Os_3H(CO)_9(Me_2PCHPMe_2)]$	2 083m, 2 050s, 2 023vs, 2 007m, 1 990m, 1 980s, 1 970w, 1 960w, 1 938w
$[Os_3H(Cl)(CO)_8(dppm)]$	2 079m, 2 033w, 2 007s, 1 997m, 1 988m, 1 968w, 1 956m, 1 933w
$[Os_3H(SMe)(CO)_8(dppm)]$	2 071m, 2 027w, 1 996s, 1 989(sh), 1 973m, 1 964w, 1 960(sh), 1 953w, 1 944w, 1 936w, 1 929w
$[Os_3H(SEt)(CO)_8(dppm)]$	2 070m, 2 026w, 1 996s, 1 988(sh), 1 972m, 1 963w, 1 959w, 1 953w, 1 944w, 1 936w, 1 928w
$[Os_3H(SBu^t)(CO)_8(dppm)]$	2 069s, 2 025m, 1 996vs, 1 989(sh), 1 966m, 1 960(sh), 1 954(sh), 1 946w, 1 933w, 1 929w
$[Os_3H(SPh)(CO)_8(dppm)]$[b]	2 069m, 2 024w, 1 994s, 1 972(sh), 1 956w, 1 946(sh), 1 927w
$[Os_3H(SMe)(CO)_8(dmpm)]$	2 070m, 2 020m, 1 994s, 1 987m, 1 972w, 1 958w, 1 947m, 1 927w
$[Os_3H(SEt)(CO)_8(dmpm)]$	2 070m, 2 020m, 1 993s, 1 987m, 1 971w, 1 958w, 1 947m, 1 925w
$[Os_3H(SPh)(CO)_8(dmpm)]$	2 071m, 2 021m, 1 995s, 1 989(sh), 1 975w, 1 959w, 1 948m, 1 929w
$[Os_3H(OH)(CO)_8(dppm)]$	2 069m, 2 006vs, 1 999(sh), 1 964s, 1 940w; ν(OH) 3 625

[a] In MeCN. [b] In CH_2Cl_2.

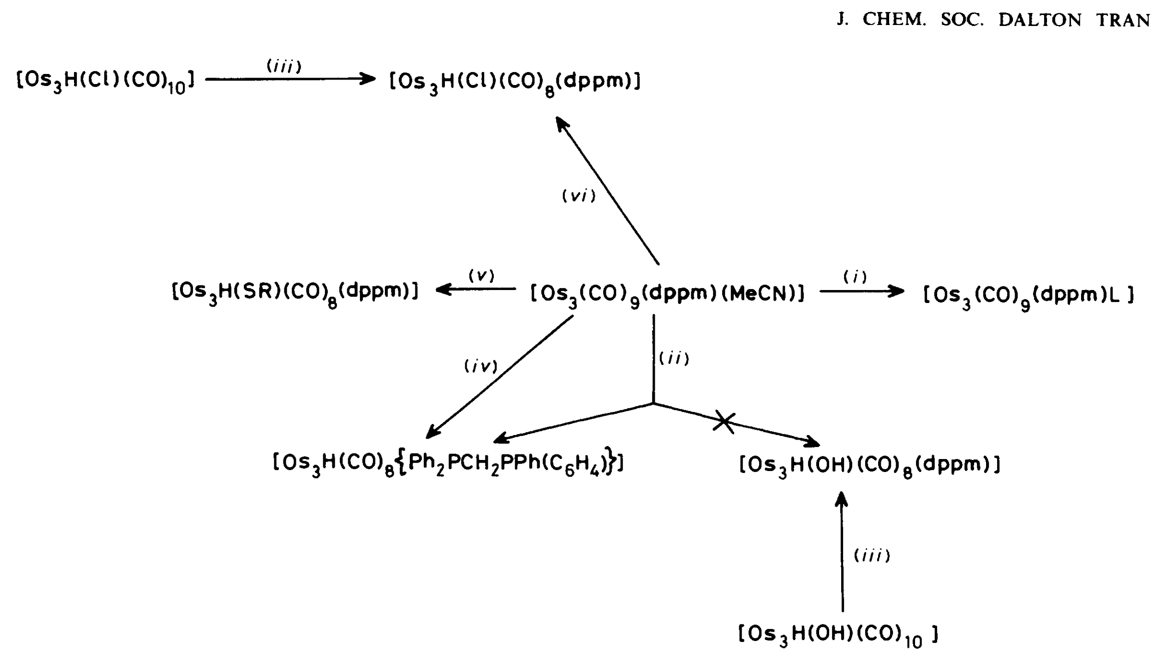
Table 3. Bond lengths (Å) and angles (°) for $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ (**3**)

Os(1)–Os(2)	3.104(1)	Os(2)–C(21)	1.917(16)	Os(1)–H(1)	2.10(9)	P(2)–C(10)	1.743(14)
Os(1)–Os(3)	2.832(1)	Os(2)–C(22)	1.897(18)	Os(2)–H(1)	1.92(9)	P(1)–C(101)	1.841(14)
Os(2)–Os(3)	2.839(1)	Os(2)–C(23)	1.960(16)	Os(1)–P(1)	2.366(3)	P(1)–C(111)	1.832(14)
Os(1)–C(11)	1.908(13)	Os(3)–C(31)	1.874(14)	Os(2)–P(2)	2.357(4)	P(2)–C(201)	1.839(16)
Os(1)–C(12)	1.887(12)	Os(3)–C(32)	1.908(14)	Os(3)–C(10)	2.226(14)	P(2)–C(211)	1.815(16)
Os(1)–C(13)	1.963(13)	Os(3)–C(33)	1.902(15)	P(1)–C(10)	1.797(14)		
Os(2)–Os(1)–Os(3)	56.9(1)	Os(2)–Os(3)–C(31)	164.3(4)	Os(3)–Os(1)–P(1)	71.0(1)	C(21)–Os(2)–C(23)	94.8(6)
Os(1)–Os(2)–Os(3)	56.7(1)	Os(2)–Os(3)–C(32)	101.4(4)	Os(1)–Os(2)–P(2)	89.4(1)	C(21)–Os(2)–P(2)	94.7(5)
Os(1)–Os(3)–Os(2)	66.4(1)	Os(2)–Os(3)–C(33)	89.0(4)	Os(3)–Os(2)–P(2)	70.5(1)	C(22)–Os(2)–C(23)	88.3(7)
Os(2)–Os(1)–C(11)	115.5(4)	Os(1)–H(1)–Os(2)	101.0(35)	H(1)–Os(1)–C(11)	78.1(24)	C(22)–Os(2)–P(2)	90.0(5)
Os(2)–Os(1)–C(12)	147.0(4)	Os(1)–P(1)–C(10)	101.7(5)	H(1)–Os(1)–C(12)	175.4(20)	C(23)–Os(2)–P(2)	170.5(4)
Os(2)–Os(1)–C(13)	87.7(4)	Os(1)–P(1)–C(101)	117.5(5)	H(1)–Os(1)–C(13)	89.3(26)	C(31)–Os(3)–C(32)	93.9(6)
Os(3)–Os(1)–C(11)	164.2(4)	Os(1)–P(1)–C(111)	115.9(5)	H(1)–Os(1)–P(1)	92.7(25)	C(31)–Os(3)–C(33)	93.9(6)
Os(3)–Os(1)–C(12)	91.3(4)	C(10)–P(1)–C(101)	105.9(6)	H(1)–Os(2)–C(21)	76.2(26)	C(31)–Os(3)–C(10)	97.2(6)
Os(3)–Os(1)–C(13)	99.9(4)	C(10)–P(1)–C(111)	115.1(7)	H(1)–Os(2)–C(22)	174.0(24)	C(32)–Os(3)–C(33)	92.3(6)
Os(1)–Os(2)–C(21)	117.8(5)	C(101)–P(1)–C(111)	101.0(6)	H(1)–Os(2)–C(23)	87.6(29)	C(10)–P(2)–C(201)	105.9(7)
Os(1)–Os(2)–C(22)	142.3(5)	Os(2)–P(2)–C(10)	102.1(5)	H(1)–Os(2)–P(2)	94.8(29)	C(10)–P(2)–C(211)	114.2(7)
Os(1)–Os(2)–C(23)	86.3(5)	Os(2)–P(2)–C(201)	117.6(5)	C(11)–Os(1)–C(12)	97.5(6)	C(201)–P(2)–C(211)	99.7(8)
Os(3)–Os(2)–C(21)	163.4(5)	Os(2)–P(2)–C(211)	117.4(5)	C(11)–Os(1)–C(13)	93.2(6)	Os(3)–C(10)–P(1)	97.6(6)
Os(3)–Os(2)–C(22)	87.8(5)	Os(2)–Os(1)–H(1)	37.4(23)	C(11)–Os(1)–P(1)	96.0(4)	Os(3)–C(10)–P(2)	98.5(6)
Os(3)–Os(2)–C(23)	100.1(4)	Os(3)–Os(1)–H(1)	93.3(24)	C(12)–Os(1)–C(13)	89.7(5)	P(1)–C(10)–P(2)	116.6(7)
Os(1)–Os(3)–C(31)	98.2(4)	Os(1)–Os(2)–H(1)	41.6(26)	C(12)–Os(1)–P(1)	89.1(4)	C(32)–Os(3)–C(10)	97.2(6)
Os(1)–Os(3)–C(32)	167.7(4)	Os(3)–Os(2)–H(1)	97.2(25)	C(13)–Os(1)–P(1)	170.8(4)	C(33)–Os(3)–C(10)	164.9(5)
Os(1)–Os(3)–C(33)	89.3(4)	Os(2)–Os(1)–P(1)	88.4(1)	C(21)–Os(2)–C(22)	99.9(7)		

species are similar to those of the chloro-analogues discussed above, indicating that they have a similar structure.

There are several possible isomeric structures for these $[Os_3H(X)(CO)_8(L\text{–}L)]$ (X = Cl or SR) derivatives. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra show an AB pattern for the two phosphorus atoms of the diphosphine ligand. For all the species the ^1H n.m.r. spectra showed a high-field doublet, consistent with a bridging metal hydride coupled to only one phosphorus atom of the diphosphine. The hydrogen–phosphorus coupling constants of 25—35 Hz are typical of two-bond *trans* HOsP values for such systems. Based on the n.m.r. evidence, the 18-electron rule, and the structures of other similar systems, the most likely arrangement of the ligands in $[Os_3H(X)(CO)_8(L\text{–}L)]$ is with the H and X groups bridging one Os–Os edge and the diphosphine bridging one of the other edges [Figure 3(*a*)]. Another possible ligand arrangement is to have one phosphorus at an axial site of the rear Os atom [Figure 3(*b*)], but this seems less likely as it has previously been shown that phosphine ligands prefer to occupy equatorial sites.[9]

Refluxing $[Os_3(CO)_9(dppm)(MeCN)]$ (**1**) in methanol does not lead to the expected product $[Os_3H(OMe)(CO)_8(dppm)]$ but instead gives the cyclometallated complex $[Os_3H(CO)_8\text{-}\{Ph_2PCH_2PPh(C_6H_4)\}]$.[4] The same product is obtained when (**1**) is refluxed in diethyl ether containing a few drops of water, no $[Os_3H(OH)(CO)_8(dppm)]$ (**4**) being produced. Compound (**4**) can however be prepared by heating $[Os_3H(OH)(CO)_{10}]$ and dppm together in cyclohexane. Its n.m.r. and i.r. spectra clearly show a different structure from the chloro-analogue $[Os_3H(Cl)(CO)_8(dppm)]$ discussed earlier. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows only a singlet indicating that the two phosphorus atoms are equivalent. In the ^1H n.m.r. the high-field metal hydride signal appears as a broad triplet with equal coupling to the two phosphorus atoms of the dppm. The signal due to the hydrogen of the OH group at δ 0.44 is well resolved



Scheme 1. The reactions of [$Os_3(CO)_9$(dppm)(MeCN)] (**1**): (*i*) L = PPh_3, $P(OMe)_3$, or Bu^{t}NC; (*ii*) H_2O–Et_2O; (*iii*) dppm; (*iv*) MeOH; (*v*) RSH (R = Me, Et, Ph, or Bu^t); (*vi*) HCl

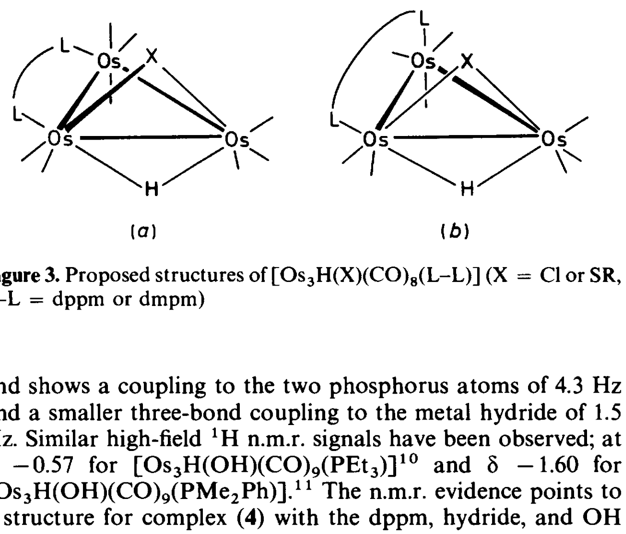


Figure 3. Proposed structures of [$Os_3H(X)(CO)_8$(L–L)] (X = Cl or SR, L–L = dppm or dmpm)

and shows a coupling to the two phosphorus atoms of 4.3 Hz and a smaller three-bond coupling to the metal hydride of 1.5 Hz. Similar high-field ^1H n.m.r. signals have been observed; at δ −0.57 for [$Os_3H(OH)(CO)_9(PEt_3)$][10] and δ −1.60 for [$Os_3H(OH)(CO)_9(PMe_2Ph)$].[11] The n.m.r. evidence points to a structure for complex (**4**) with the dppm, hydride, and OH group all bridging the same Os–Os edge of an Os_3 triangle. In order to confirm this and to establish the full molecular structure a single-crystal *X*-ray study was carried out. The molecular structure is shown in Figure 4 and bond parameters are given in Table 4.

The three osmium atoms form a closed triangle with the dppm and the oxygen of the OH group bridging one edge. The two phosphorus atoms of the dppm lie essentially in the plane of the Os_3 triangle as the angle between the planes defined by Os(1)Os(2)Os(3) and Os(2)Os(3)P(1)P(2) is only 2.5°. The bridged Os–Os bond [2.774(1) Å] is appreciably shorter than the other two [2.826(1) and 2.856(1) Å]. This can be attributed to the presence of the bridging dppm. A similar shortening of dppm-bridged M–M bonds is observed in both [$Ru_3(CO)_{10}$(dppm)][12] and [$Ru_3(CO)_8(dppm)_2$].[13] The metal hydride was not directly located but the distribution of the carbon monoxide ligands indicates that it bridges the same Os–Os edge as the dppm and OH group, on the opposite side of the Os_3 plane to the oxygen of the OH. This is in agreement with the n.m.r. data discussed earlier, and with the arrangement of the ligand polyhedron. The pseudoaxial carbonyls, C(21)O(21) and C(31)-O(31), bend away from the Os(2)–Os(3) edge [Os(3)–Os(2)–C(21) 123.1(4) and Os(2)–Os(3)–C(31) 125.3(4)°] giving room for the hydride.

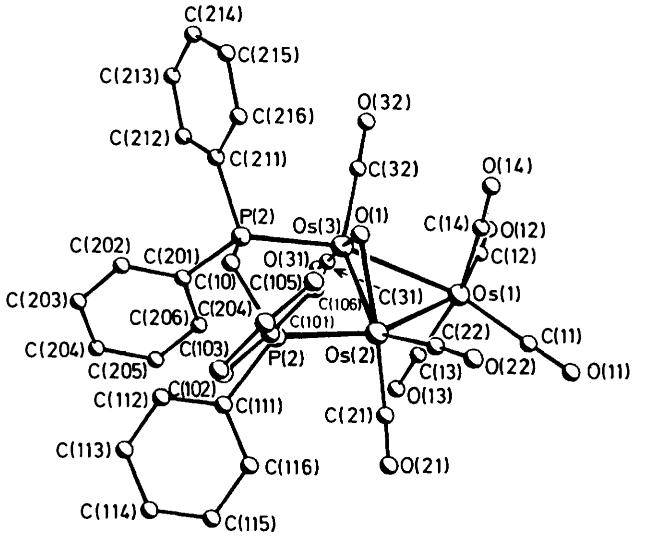


Figure 4. The molecular structure of [$Os_3H(OH)(CO)_8$(dppm)] (**4**) showing the atom numbering scheme adopted. Hydrogen atoms have been omitted for clarity

The structure of a similar molecule of this general type [$Os_3X(Y)(CO)_8$(dppm)] where X = Y = H has recently been reported.[5] In this compound the two hydrides and the dppm bridge a formal Os=Os double bond. The Os=Os distance is 2.681(1) Å compared to 2.744(1) Å for the Os–Os single bond in complex (**4**). The formal electron count for the former complex is 46 electrons unlike complex (**4**) which is a 48-electron system. In both cases it is better not to consider the Os–Os interaction as either a double or single bond but as a four-centre delocalised bond involving both Os atoms and the X and Y bridgehead atoms.

Attempts to prepare the dmpm analogue of (**4**) by the reaction of [$Os_3H(OH)(CO)_{10}$] with dmpm led only to decomposition.

Table 4. Bond lengths (Å) and angles (°) for $[Os_3H(OH)(CO)_8(dppm)]$ (4)

Os(1)–Os(2)	2.856(1)	Os(1)–C(14)	1.960(15)	Os(2)–O(1)	2.167(8)	P(2)–C(10)	1.855(11)
Os(1)–Os(3)	2.826(1)	Os(2)–C(21)	1.845(13)	Os(3)–O(1)	2.157(8)	P(1)–C(101)	1.827(8)
Os(2)–Os(3)	2.774(1)	Os(2)–C(22)	1.877(15)	Os(2)–P(1)	2.360(3)	P(1)–C(111)	1.837(8)
Os(1)–C(11)	1.929(16)	Os(3)–C(31)	1.858(14)	Os(3)–P(2)	2.339(3)	P(2)–C(201)	1.821(7)
Os(1)–C(12)	1.964(19)	Os(3)–C(32)	1.870(14)	P(1)–C(10)	1.869(10)	P(2)–C(211)	1.829(8)
Os(1)–C(13)	1.925(15)						

Os(3)–Os(1)–Os(2)	58.4(1)	C(14)–Os(1)–C(12)	94.4(7)	O(1)–Os(2)–Os(1)	84.6(2)	O(1)–Os(3)–Os(1)	85.5(2)
Os(3)–Os(2)–Os(1)	60.2(1)	C(14)–Os(1)–C(13)	164.9(6)	O(1)–Os(2)–Os(3)	49.9(2)	O(1)–Os(3)–Os(2)	50.3(2)
Os(2)–Os(3)–Os(1)	61.3(1)	C(10)–P(1)–Os(2)	109.4(4)	C(21)–Os(2)–Os(1)	93.1(4)	C(31)–Os(3)–Os(1)	93.2(4)
C(11)–Os(1)–Os(2)	98.7(5)	C(101)–P(1)–Os(2)	118.0(3)	C(21)–Os(2)–Os(3)	123.1(4)	C(31)–Os(3)–Os(2)	125.3(4)
C(11)–Os(1)–Os(3)	157.1(5)	C(101)–P(1)–C(10)	99.0(4)	C(21)–Os(2)–O(1)	172.7(5)	C(31)–Os(3)–O(1)	175.4(5)
C(12)–Os(1)–Os(2)	155.4(5)	C(111)–P(1)–Os(2)	117.7(3)	C(22)–Os(2)–Os(1)	99.5(5)	C(32)–Os(3)–Os(1)	100.8(4)
C(12)–Os(1)–Os(3)	97.1(5)	C(111)–P(1)–C(10)	108.1(4)	C(22)–Os(2)–Os(3)	140.2(5)	C(32)–Os(3)–Os(2)	140.7(4)
C(12)–Os(1)–C(11)	105.9(7)	C(111)–P(1)–C(101)	102.6(4)	C(22)–Os(2)–O(1)	97.7(5)	C(32)–Os(3)–O(1)	96.7(5)
C(13)–Os(1)–Os(2)	82.3(4)	C(10)–P(2)–Os(3)	110.2(4)	C(22)–Os(2)–C(21)	89.5(6)	C(32)–Os(3)–C(31)	87.9(6)
C(13)–Os(1)–Os(3)	83.9(4)	C(201)–P(2)–Os(3)	120.2(2)	P(1)–Os(2)–Os(1)	155.1(1)	P(2)–Os(3)–Os(1)	156.0(1)
C(13)–Os(1)–C(11)	94.9(6)	C(201)–P(2)–C(10)	102.0(5)	P(1)–Os(2)–Os(3)	94.9(1)	P(2)–Os(3)–Os(2)	94.8(1)
C(13)–Os(1)–C(12)	93.5(7)	C(211)–P(2)–Os(3)	112.8(3)	P(1)–Os(2)–O(1)	79.8(2)	P(2)–Os(3)–O(1)	80.2(2)
C(14)–Os(1)–Os(2)	85.1(5)	C(211)–P(2)–C(10)	102.9(4)	P(1)–Os(2)–C(21)	100.0(4)	P(2)–Os(3)–C(21)	99.5(4)
C(14)–Os(1)–Os(3)	82.4(4)	C(211)–P(2)–C(201)	107.1(3)	P(1)–Os(2)–C(22)	101.7(5)	P(2)–Os(3)–C(32)	100.0(4)
C(14)–Os(1)–C(11)	95.2(6)	P(2)–C(10)–P(1)	116.8(6)				

Experimental

None of the compounds reported here is particularly air sensitive, but all reactions were carried out under an atmosphere of dry nitrogen using dried, distilled solvents. Products were separated in the air by t.l.c. with plates coated with 0.25 mm of Merck Kieselgel 60 F_{254} and using dichloromethane–hexane (1 : 1) as eluant unless otherwise stated.

Proton, ^{13}C, and ^{31}P n.m.r. data were obtained on Bruker WH400, WM250 or Varian XL100 instruments. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer between 2 150 and 1 700 cm^{-1}, mass spectra on a AEI MS12 spectrometer.

The complexes $[Os_3(CO)_{11}(MeCN)]$,[7] $[Os_3(CO)_{10}(dppm)]$,[4] and $[Os_3H(X)(CO)_{10}]$ (X = Cl or OH) were prepared by the literature methods.

Preparations.—$[Os_3(CO)_{10}(dmpm)]$. A solution of $[Os_3(CO)_{11}(MeCN)]$ (100 mg) and dmpm (20 cm^3) in dichloromethane (20 cm^3) was refluxed for 6 h. The volume of solvent was then reduced and the products separated by t.l.c. to give $[Os_3(CO)_{10}(dmpm)]$ (75 mg, 70%) [Found: C, 17.9; H, 1.6%; *M* 992 (^{192}Os). $C_{15}H_{14}O_{10}Os_3P_2$ requires C, 18.3; H, 1.4%; *M* 992].

$[Os_3(CO)_9(dppm)(MeCN)]$. The complex $[Os_3(CO)_{10}(dppm)]$ (30 mg) and Me_3NO (2.0 mg) were stirred together in acetonitrile (5 cm^3) until the i.r. spectrum showed no bands due to the starting material (*ca.* 0.5 h). The solution was filtered through a short silica column and the solvent removed under vacuum to leave $[Os_3(CO)_9(dppm)(MeCN)]$ as a yellow solid (27 mg, 89%). The complex $[Os_3(CO)_9(dmpm)(MeCN)]$ was prepared using the same procedure except that the solution was stirred for *ca.* 3 h prior to filtration.

$[Os_3(CO)_9(dppm)(PPh_3)]$. The complex $[Os_3(CO)_9(dppm)(MeCN)]$ (28 mg) and PPh_3 (7 mg) were stirred together in dichloromethane for 0.25 h. T.l.c. of the resulting solution gave a single orange band characterised as $[Os_3(CO)_9(dppm)(PPh_3)]$ (26 mg, 79%) (Found: C, 42.6; H, 2.9. $C_{52}H_{37}O_9Os_3P_3$ requires C, 42.5; H, 2.5%). Other phosphine, phosphite, and isonitrile derivatives $[Os_3(CO)_9(dppm)L]$ [L = $P(C_6H_4OMe\text{-}p)_3$, $P(OMe)_3$, or Bu^tNC] and $[Os_3(CO)_9(dmpm)L]$ [L = $P(OMe)_3$] were prepared in the same way: $[Os_3(CO)_9(dppm)\{P(C_6H_4OMe\text{-}p)_3\}]$ (Found: C, 42.6; H, 3.2. $C_{55}H_{43}O_{12}Os_3P_3$ requires C, 42.4, H, 2.8%); $[Os_3(CO)_9(dppm)(Bu^tNC)]$ (Found: C, 36.2; H, 2.4; N, 0.9. $C_{39}H_{31}NO_9Os_3P_2$ requires C, 36.3; H, 2.4; N, 1.1%); and $[Os_3(CO)_9(dmpm)\{P(OMe)_3\}]$ [Found: *M* 1 088 (^{192}Os). Requires *M* 1 088].

$[Os_3H(CO)_9(Me_2PCHPMe_2)]$. The complex $[Os_3(CO)_{10}(dmpm)]$ (42 mg) was refluxed in *p*-xylene (20 cm^3) for 1.5 h. The solvent was removed and the product recrystallised from CH_2Cl_2–hexane at −20 °C, giving $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ (28 mg, 69%). *X*-Ray quality crystals were obtained by this method.

$[Os_3H(OH)(CO)_8(dppm)]$. The complex $[Os_3H(OH)(CO)_{10}]$ (40 mg) and dppm (18 mg) were refluxed together in hexane (40 cm^3) for 5 h. T.l.c. gave as the major product $[Os_3H(OH)(CO)_8(dppm)]$ (40 mg, 70%) (Found: C, 32.6; H, 2.0. $C_{33}H_{24}O_9Os_3P_2$ requires C, 33.1; H, 2.0%). Suitable crystals for *X*-ray diffraction were obtained by recrystallisation from dichloromethane–ethanol.

Reactions.—$[Os_3(CO)_9(dmpm)(MeCN)]$ *with* C_2H_4. (*a*) The complex $[Os_3(CO)_9(dmpm)(MeCN)]$ (30 mg) was dissolved in dichloromethane (10 cm^3) and C_2H_4 bubbled through the solution for 5 min. The i.r. spectrum showed only bands due to $[Os_3(CO)_9(dmpm)(C_2H_4)]$. The solvent was removed and the residue dissolved in acetonitrile. The i.r. spectrum showed only bands due to $[Os_3(CO)_9(dmpm)(MeCN)]$ and was unchanged on bubbling C_2H_4 through the solution for 15 min.

(*b*) The complex was dissolved in octane and C_2H_4 bubbled through for 5 min. The solution was then refluxed for a further 5 min. The i.r. spectrum showed mainly bands due to $[Os_3H(CO)_9(Me_2PCHPMe_2)]$.

$[Os_3(CO)_9(dppm)(MeCN)]$ *with* HCl. Hydrogen chloride gas was bubbled through a solution of $[Os_3(CO)_9(dppm)(MeCN)]$ (25 mg) in cyclohexane (10 cm^3) for 1 min. The solution was then refluxed for 1.5 h. T.l.c. gave, as the major product, an orange band, characterised as $[Os_3H(Cl)(CO)_8(dppm)]$ (12 mg, 48%) (Found: C, 32.2; H, 2.2. $C_{33}H_{23}ClO_8Os_3P_2$ requires C, 32.6; H, 1.9%). The complex $[Os_3H(Cl)(CO)_8(dmpm)]$ was prepared by the same method [Found: *M* 974 (^{192}Os). Requires *M* 974].

With EtSH. The complex $[Os_3(CO)_9(dppm)(MeCN)]$ (30 mg) and excess of EtSH were refluxed together in dichloromethane for 5 h. T.l.c. [hexane–ethyl acetate (5:1) as eluant]

Table 5. Atomic co-ordinates (× 10^4) for $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	6 722(1)	3 027(1)	2 350(1)	O(23)	7 167(11)	395(7)	3 062(9)
Os(2)	5 100(1)	1 725(1)	3 340(1)	C(31)	4 260(14)	2 922(9)	149(10)
Os(3)	4 375(1)	2 318(1)	1 350(1)	O(31)	4 166(11)	3 254(7)	−609(7)
H(1)	6 479(89)	2 516(59)	3 741(61)	C(32)	2 766(14)	1 744(10)	953(10)
C(11)	7 987(13)	3 634(9)	3 249(10)	O(32)	1 827(11)	1 366(9)	680(8)
O(11)	8 778(12)	4 013(8)	3 760(9)	C(33)	5 352(13)	1 426(9)	895(10)
C(12)	7 071(12)	3 521(8)	1 151(9)	O(33)	5 994(10)	904(7)	660(8)
O(12)	7 277(11)	3 819(7)	422(7)	P(1)	5 008(3)	4 001(2)	2 373(2)
C(13)	7 940(12)	2 115(8)	2 181(9)	P(2)	3 416(3)	2 723(2)	3 295(2)
O(13)	8 687(10)	1 660(7)	2 034(8)	C(10)	3 612(13)	3 321(9)	2 249(10)
C(21)	5 410(16)	1 639(11)	4 772(12)	C(101)	4 688(14)	4 753(9)	1 329(9)
O(21)	5 471(12)	1 574(10)	5 612(7)	C(111)	5 178(14)	4 714(9)	3 450(10)
C(22)	3 843(16)	862(11)	3 031(12)	C(201)	1 728(16)	2 336(10)	3 064(12)
O(22)	3 112(13)	339(8)	2 836(11)	C(211)	3 362(16)	3 334(11)	4 421(11)
C(23)	6 444(14)	908(10)	3 134(10)				

Table 6. Atomic co-ordinates (× 10^4) for $[Os_3H(OH)(CO)_8(dppm)]$ (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	8 820(1)	1 643(1)	4 031(1)	C(102)	3 824(6)	5 295(6)	3 653(3)
Os(2)	6 941(1)	2 928(1)	4 002(1)	C(103)	3 535(6)	6 407(6)	3 481(3)
Os(3)	6 809(1)	1 043(1)	3 293(1)	C(104)	4 103(6)	7 008(6)	3 158(3)
O(1)	6 654(7)	2 818(7)	3 069(3)	C(105)	4 960(6)	6 498(6)	3 005(3)
C(11)	9 839(13)	2 537(14)	4 593(7)	C(106)	5 249(6)	5 386(6)	3 177(3)
O(11)	10 456(10)	3 046(13)	4 917(5)	C(111)	4 293(6)	2 973(7)	4 214(3)
C(12)	9 632(15)	371(15)	3 831(7)	C(112)	3 347(6)	2 349(7)	4 051(3)
O(12)	10 051(11)	−358(12)	3 687(8)	C(113)	2 756(6)	2 149(7)	4 450(3)
C(13)	8 346(12)	781(13)	4 600(6)	C(114)	3 110(6)	2 575(7)	5 013(3)
O(13)	8 096(10)	226(11)	4 939(5)	C(115)	4 055(6)	3 199(7)	5 177(3)
C(14)	8 898(12)	2 565(13)	3 361(6)	C(116)	4 647(6)	3 398(7)	4 777(3)
O(14)	8 908(9)	3 051(10)	2 961(5)	C(201)	4 074(6)	290(7)	3 216(2)
C(21)	7 142(11)	2 828(11)	4 794(5)	C(202)	2 987(6)	224(7)	2 933(2)
O(21)	7 236(9)	2 764(10)	5 283(4)	C(203)	2 288(6)	−316(7)	3 201(2)
C(22)	7 534(12)	4 390(12)	4 099(6)	C(204)	2 676(6)	−789(7)	3 752(2)
O(22)	7 905(12)	5 268(9)	4 196(6)	C(205)	3 763(6)	−723(7)	4 034(2)
C(31)	6 924(11)	−455(11)	3 543(6)	C(206)	4 462(6)	−183(7)	3 766(2)
O(31)	6 978(11)	−1 409(10)	3 682(5)	C(211)	4 539(7)	955(6)	2 125(3)
C(32)	7 207(11)	557(11)	2 635(6)	C(212)	4 143(7)	−95(6)	1 897(3)
O(32)	7 427(10)	296(13)	2 224(5)	C(213)	3 969(7)	−309(6)	1 305(3)
P(1)	5 094(2)	3 329(2)	3 709(1)	C(214)	4 193(7)	527(6)	941(3)
P(2)	4 955(2)	1 154(2)	2 911(1)	C(215)	4 589(7)	1 578(6)	1 169(3)
C(10)	4 481(9)	2 610(9)	3 002(4)	C(216)	4 763(7)	1 791(6)	1 761(3)
C(101)	4 681(6)	4 784(6)	3 500(3)				

gave two bands characterised as $[Os_3(CO)_{10}(dppm)]$ and $[Os_3H(SEt)(CO)_8(dppm)]$ (21 mg, 70%). Other thiol derivatives $[Os_3H(SR)(CO)_8(dppm)]$ (R = Me, Et, Bu^t, or Ph) and $[Os_3H(SR)(CO)_8(dmpm)]$ (R = Me, Et, or Ph) were prepared by the same procedure {Found for $[Os_3H(SEt)(CO)_8(dmpm)]$: *M* 998 (^{192}Os). Requires *M* 998}.

Crystal Structure Determination of $[Os_3H(CO)_9(Me_2PCHPMe_2)]$ (**3**).—A suitable yellow, block-shaped crystal was mounted on a glass fibre with epoxy-resin.

Crystal data. $C_{14}H_{14}O_9Os_3P_2$, $M = 958.79$, monoclinic, $a = 10.393(1)$, $b = 15.921(2)$, $c = 13.516(1)$ Å, $\beta = 98.98(1)°$, $U = 2\,209.0$ Å^3 (by least-squares refinement on diffractometer angles for 50 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $Z = 4$, $D_c = 2.88$ g cm^{-3}, $F(000) = 1\,712$. Yellow blocks. Crystal dimensions (distance to faces from centre): 0.238 (100, $\bar{1}$00) × 0.076 (010, 0$\bar{1}$0) × 0.160 (1$\bar{1}\bar{1}$, $\bar{1}$11) mm, μ(Mo-K_α) = 173.80 cm^{-1}.

Data collection and processing.[14] Stoe-Siemens AED diffractometer, 24-step ω—θ mode with ω scan width = 0.05° for each step, scan time 0.5—2.0 s per step, graphite-monochromated Mo-K_α radiation. 8 558 Reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $+h$, $\pm k$, $\pm l$), 3 888 unique [merging R = 0.035 after empirical absorption correction based on an ellipsoid fit of 300 azimuthal scan data (maximum, minimum transmission factors = 0.04, 0.01)] giving 3 451 with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Direct methods (Os atoms) followed by Fourier difference techniques. Blocked-cascade least-squares refinement with Os, P, and O atoms anisotropic. Hydride H directly located and refined freely. Methyl H in calculated positions with one, overall refined U_{iso} [= 0.057(11) Å^2]; methyls treated as rigid groups. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0007\,F_o^2]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R' values were 0.049 and 0.049. Programs and computers used and sources of scattering factor data are given in ref. 14. Final atomic co-ordinates are listed in Table 5.

Crystal Structure Determination of [$Os_3H(OH)(CO)_8$-(dppm)] (**4**).—A suitable yellow crystal was mounted on a glass fibre with epoxy-resin.

Crystal data. $C_{33}H_{24}O_9Os_3P_2$, M = 1 197.06, monoclinic, a = 12.975(3), b = 11.790(1), c = 23.904(4) Å, β = 105.36(2)°, U = 3 526.1 $Å^3$ (by least-squares refinement on diffractometer angles for 54 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), Z = 4, D_c = 2.25 g cm^{-3}, $F(000)$ = 2 208. Yellow hexagonal plates. Crystal dimensions (distance to faces from centre): 0.167 (101, $\bar{1}0\bar{1}$) × 0.053 ($10\bar{1}$, $\bar{1}01$) × 0.310 (012, $0\bar{1}\bar{2}$) × 0.302 ($01\bar{2}$, $0\bar{1}2$) mm, μ(Mo-K_α) = 115.44 cm^{-1}.

Data collection and processing.[14] As for complex (**3**) except ω scan width = 0.04°. 13 378 Reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $\pm h$, $+k$, $\pm l$), 6 202 unique [merging R = 0.026 after absorption correction (maximum, minimum transmission factors = 0.336, 0.060)], giving 5 359 with $F > 5\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Direct methods (Os atoms) followed by Fourier difference techniques. Full-matrix least-squares refinement with Os, P, O, and methylene C atoms anisotropic. Phenyl rings refined as regular hexagons (C–C 1.395 Å). Phenyl and methylene H in calculated positions with one, overall, refined U_{iso} [= 0.074(10) $Å^2$]. The weighting scheme $w = 1/[\sigma^2(F) + 0.0016F_o^2]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R' values were 0.050 and 0.051. Programs and computers used and sources of scattering factor data are given in ref. 14. Final atomic co-ordinates are presented in Table 6.

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