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Methylene chain length and coordination geometry in triosmium clusters containing diphosphine ligands X-Ray crystal structures of $[Os_3(CO)_{10}\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 4 or 5) and $[Os_3(CO)_8\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$

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Abstract

The bis-acetonitrile compound $[Os_3(CO)_{10}(MeCN)_2]$ and the butadiene compound $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ react with dppp {dppp = $Ph_2P(CH_2)_5PPh_2$} to give only $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (**1**). Protonation of **1** with trifluoroacetic acid leads to $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-dppp})]^+$ (**2**) with the hydride bridging the same osmium atoms as the dppp. The bridging dppp compound $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (**1**) reacts with dppp at 110°C to give $[Os_3(CO)_9(\eta^1\text{-dppp})(\mu\text{-dppp})]$ (**4**) whereas $[Os_3(CO)_{10}(\mu\text{-dppm})]$ under the same conditions reacts with dppm (dppm = $Ph_2PCH_2PPh_2$) to give $[Os_3(CO)_8(\mu\text{-dppm})_2]$ (**5**). Protonation of **5** with trifluoroacetic acid gives $[(\mu\text{-}H)Os_3(CO)_8(\mu\text{-dppm})_2]^+$ (**6**) with the hydride bridging the unsubstituted Os — Os edge. The monoacetonitrile compound $[Os_3(CO)_{11}(MeCN)]$ reacts with dppp at 0°C to give two compounds: $[Os_3(CO)_{11}(\eta^1\text{-dppp})]$ (**7**) containing one coordinated and one free phosphorus atom and $[\{Os_3(CO)_{11}\}_2(\mu\text{-dppp})]$ (**8**) with one dppp ligand bridging two $Os_3(CO)_{11}$ moieties.

Solid-state structures for **1**, **5** and the previously reported cluster $[Os_3(CO)_{10}(\mu\text{-dppb})]$ (**3**) {dppb = $Ph_2P(CH_2)_4PPh_2$} are reported. Compound **1** crystallizes in the space group $P2_12_12_1$ with unit cell parameters a = 11.770(2) Å, b = 16.957(3) Å, c = 21.681(5) Å, V = 4327(2) Å^3 and Z = 4. Least-squares refinement of 6118 reflections gave a final agreement factor of R = 0.077 (R_w = 0.087). Compound **3** crystallizes in the space group $P2_1/c$ with unit cell parameters a = 12.361(2) Å, b = 16.804(2) Å, c = 20.935(2) Å, β = 116.66(1)°, V = 3886(2) Å^3 and Z = 4. Least-squares refinement of 2284 reflections gave a final agreement factor of R = 0.028 (R_w = 0.032). Compound **5** crystallizes in the space group $Pca2_1$ with unit cell parameters a = 21.398(3) Å, b = 15.684(4) Å, c = 18.219(4) Å, V = 6115(4) Å^3 and Z = 4. Least-squares refinement of 5376 reflections gave a final agreement factor of R = 0.060 (R_w = 0.062).

Keywords: Osmium; Clusters; Diphosphines; Chelates; Carbonyl; Methylene

1. Introduction

The synthesis and reactivity of triosmium clusters containing polydentate phosphines have been extensively studied by several groups [1–11]. Smith et al. [1–4] and Lewis et al. [5,6] investigated the synthesis and chemistry of the dppm derivatives of $[Os_3(CO)_{12}]$ while we have studied [8–11] the synthesis and reactivity of a series of diphosphine $[Ph_2P(CH_2)_nPPh_2$ {n = 1–4}] substituted derivatives of $[Os_3(CO)_{12}]$. As an extension of our previous work, we have now investigated the reactivity of bis(diphenylphosphino)pentane (dppp) with triosmium clusters containing lightly stabilized ligands such as $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$, $[Os_3(CO)_{10}(MeCN)_2]$ and $Os_3(CO)_{11}(MeCN)]$. We have also studied the reactions of $[Os_3(CO)_{10}(\mu\text{-dppm})]$ and $[Os_3(CO)_{10}(\mu\text{-dppp})$ with dppm and dppp, respectively,

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as well as the protonation reactions of $[Os_3(CO)_{10}(\mu$-dppp)] and $[Os_3(CO)_8(\mu$-dppm$)_2]$. We have also determined the X-ray structures of $[Os_3(CO)_{10}(\mu$-dppp)], $[Os_3(CO)_{10}(\mu$-dppb)] and $[Os_3(CO)_8(\mu$-dppm$)_2]$. The crystal structures of $[Os_3(CO)_{10}(\mu$-dppp)] and $[Os_3(CO)_{10}(\mu$-dppb)] can be compared with that of $[Os_3(CO)_{10}(\mu$-dppe)] while the structure of $[Os_3(CO)_8(\mu$-dppm$)_2]$ is comparable to that of the corresponding ruthenium compound $[Ru_3(CO)_8(\mu$-dppm$)_2]$.

2. Results and discussion

2.1. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ or $[Os_3(CO)_{10}(\eta^4\text{-}C_4H_6)]$ with dppp

The bis-acetonitrile compound $[Os_3(CO)_{10}(MeCN)_2]$ reacts with dppp at 61°C affording $[Os_3(CO)_{10}(\mu$-dppp)] (**1**) in 49% yield. The IR and $^{31}P\{^1H\}$ NMR data (Table 1) are very similar to those of $[Os_3(CO)_{10}\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 1–4) and consistent with the proposed structure [8,9]. As expected, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ −144.4 ppm showing equivalent phosphorus nuclei. The butadiene compound $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$, in which the butadiene is coordinated at an axial and an equatorial site at one osmium atom, reacts with dppp giving only the bridging dppp compound $[Os_3(CO)_{10}(\mu$-dppp)] in 30% yield. It is interesting to note that $[Ph_2P(CH_2)_5PPh_2]$ behaves differently from other diphosphines with a shorter chain length (n = 2–4). We have previously reported that the chelating butadiene compound $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ reacts with the disphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 2–4) to give two isomers of $[Os_3(CO)_{10}$(diphosphine)], known as the bridging and the chelating isomers [8]. The chelating isomers predominate for n = 2 or 3 while the bridging isomer is the major product in the case of n = 4. Dppm gives only the bridging isomer whichever starting material is used, presumably because of the strain in the four-membered ring in the chelating form and the high steric favourability of the bridging isomer. We have made a comparison (Table 2) of the yields of the product obtained from the reactions of $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1–5). It is evident that in triosmium clusters, dppm (n = 1) acts only as a bridging ligand while dppe (n = 2) acts predomi-

Table 1
IR and ^{31}P NMR data for compounds studied

Comopound	IR ν(CO) [a] (cm^{-1})	$^{31}P\{^1H\}$NMR [d]
$[Os_3(CO)_{10}(\mu$-dppp)] (**1**)	2080 (ms); 2017 (m); 2006 (s); 1998 (s); 1968 (m); 1957 (m); 1928 (w)	−144.4 (s)
$[(\mu\text{-}H)Os_3(CO)_{10}(\mu$-dppp)][$PF_6$] (**2**)	[b] 2118 (m); 2077 (m); 2066 (ms); 2035 (s); 2020 (m); 1969 (w); 1953 (w)	−150.5 (s)
$[Os_3(CO)_9(\mu$-dppp)(η^1-dppp)] (**4**)	2058 (m); 1994 (s); 1974 (vs); 1954 (sh); 1927 (m)	−145.9 (s); −146.6 (d, J = 5.4); −151.3 (d, J = 5.4); −157.6 (s)
$[Os_3(CO)_8(\mu$-dppm$)_2]$ (**5**)	2045 (ms); 1983 (ms); 1959 (vs); 1937 (s); 1896 (w); 1885 (w)	−161.2 (m); −164.7 (m)
$[(\mu\text{-}H)Os_3(CO)_8(\mu$-dppm$)_2]^{+}$ [c] (**6**)	-	−166.0 (m) −173.9 (m)
$[Os_3(CO)_{11}(\eta^1$-dppp)] (**7**)	2104; 2052 (s); 2032 (m); 2018 (vs); 1999 (w); 1987 (w); 1976 (vw)	−157.6 (s); −150.2 (s)
$[\{Os_3(CO)_{11}\}_2(\mu$-dppp)] (**8**)	2103 (m); 2051 (vs); 2032 (s); 2018 (vs); 1999 (w); 1987 (m); 1975 (w); 1954 (w)	−150.2 (s)

[a] Recorded in cyclohexane unless stated otherwise.
[b] In dichloromethane.
[c] Generated in situ by adding CF_3CO_2H to a solution of **5**.
[d] Recorded in $CDCl_3$ relative to $P(OMe)_3$; J in Hz.

Table 2
Yields (%) of isomers isolated from the reactions of [$Os_3(CO)_{10}(\eta^4$-$C_4H_6)$] with diphosphines

Starting compound	Diphosphine	$Os_3(CO)_{10}$(diphosphine)	
		Chelating isomer	Bridging isomer
[$Os_3(CO)_{10}(\eta^4$-*cis*-$C_4H_6)$]	dppm (n = 1) [8]	–	46
[$Os_3(CO)_{10}(\eta^4$-*cis*-$C_4H_6)$]	dppe (n = 2) [8]	43	9
[$Os_3(CO)_{10}(\eta^4$-*cis*-$C_4H_6)$]	dppp (n = 3) [8]	39	3
[$Os_3(CO)_{10}(\eta^4$-*cis*-$C_4H_6)$]	dppb (n = 4) [8]	6	24
[$Os_3(CO)_{10}(\eta^4$-*cis*-$C_4H_6)$]	dppp (n = 5)	–	30

nantly as a chelating ligand, and the chelating tendency decreases as the chain length increases so that dppp (n = 5) acts only as a bridging ligand.

2.2. Protonation of [$Os_3(CO)_{10}(\mu$-dppp)]

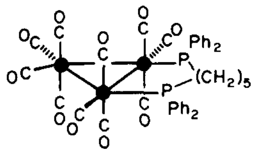
Protonation of [$Os_3(CO)_{10}\{Ph_2P(CH_2)_nPPh_2\}$] with excess CF_3CO_2H gives the cations [(μ-H)$Os_3(CO)_{10}\{\mu$-$Ph_2P(CH_2)_nPPh_2\}]^+$ with the hydride ligands in different sites depending upon the value of n [9,11]. For n = 2–4, the most stable isomer has the hydride positioned on the same Os — Os edge as the diphosphine bridge, although in the case of n = 2 or 4, other isomers were formed initially and slowly converted into the more stable form. In contrast, however, [$Os_3(CO)_{10}(\mu$-dppm)] (n = 1) is protonated at the Os

Table 3
Crystal data for compounds **1**, **3** and **5**

Compound	**1**	**3**	**5**
Formula	$C_{39}H_{30}O_{10}P_2Os_3$	$C_{38}H_{28}O_{10}P_2Os_3$	$C_{58}H_{44}O_8P_4Os_3$
Formula weight	1291.2	1277.2	1563.5
Crystal dimensions (mm^3)	0.15 × 0.28 × 0.30	0.10 × 0.21 × 0.25	0.10 × 0.35 × 0.43
Radiation, wavelength (Å)	Mo, 0.71073	Mo, 0.71073	Mo, 0.71073
Temperature (°C)	25 ± 1	25 ± 1	25 ± 1
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$Pca2_1$
a (Å)	11.770(2)	12.361(2)	21.398(3)
b (Å)	16.957(3)	16.804(2)	15.684(4)
c (Å)	21.681(5)	20.935(2)	18.219(4)
β (°)	–	116.66(1)	–
V ($Å^3$)	4327(2)	3886(2)	6115(4)
Z	4	4	4
Density (g cm^{-3})	1.92	2.12	1.70
Absorption coeff. μ (cm^{-1})	90.5	99.3	63.8
Rel. transmission coeff.	0.816–1.1222	0.402–1.000	0.558–0.999
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan rate (deg min^{-1})	8.23	1.00–16.46	8.23
Scan width (deg)	0.9 + 0.350 tan(θ)	0.5 + 0.350 tan(θ)	0.9 + 0.350 tan(θ)
hkl ranges	h: −13 to 13	h: 0 to 10	h: 0 to 19
	k: 0 to 20	k: 0 to 14	k: 0 to 26
	l: 0 to 25	l: −16 to 16	l: −22 to 22
2θ range (deg)	4.0–50.0	0.0–36.0	4.0–52.0
Structure solution	Patterson method	Patterson method	Patterson method
No. of unique data	7614	2809	6611
No. of data used in L.S. refinement with $F_o > 3.0\sigma(F_o)$	6118	2284	5376
Weighting scheme (w)	$4F_o^2/[\sigma(F_o)^2]^2$	$4F_o^2/[\sigma(F_o)^2]^2$	$4F_o^2/[\sigma(F_o)^2]^2$
No. of parameters refined	367	238	327
R [a]	0.077	0.028	0.060
R_w [b]	0.087	0.032	0.062
Esd of obs. of unit weight (GOF)	0.87	0.55	1.07
Largest shift (esd)	0.03	0.02	0.05
Highest peak in final diff. map (e $Å^{-3}$)	5.93(49)	0.62(12)	1.35(25)

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||/\Sigma_{hkl}|F_{obs}|$.
[b] $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

— Os edge not bridged by the diphosphine [11]. Addition of a 10-fold molar excess of CF_3CO_2H to a $CDCl_3$ solution of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (**1**) at room temperature gives a single isomeric form of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-dppp})]^+$ (**2**) in which the hydride gives an ^{1}H NMR triplet at δ −19.48 ppm [J(PH) = 10.5 Hz] indicating that the hydride bridges the same Os — Os edge as the dppp. Consistent with this, the $^{31}P\{^1H\}$ NMR displays a singlet at δ −150.5 ppm. The similarities of its IR, ^{1}H and $^{31}P\{^1H\}$ spectra to that of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-dppe})][PF_6]$ [9], which has been crystallographically characterized, indicates that they are isostructural and the hydride and dppp bridges the same Os — Os edge. The cation **2** has been isolated as the hexafluorophosphate salt. No ^{1}H NMR evidence for any other isomer was obtained.



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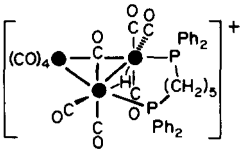

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2.3. X-Ray structures of $[Os_3(CO)_{10}(\mu\text{-dppb})]$ (3) and $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (1)

As the dppb (n = 4) compound behaves differently towards protonation from that of the dppp (n = 5) compound, we undertook solid-state structural investigations of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (**1**) and $[Os_3(CO)_{10}(\mu\text{-dppb})]$ (**3**) in order to make a direct comparison between them. We also wished to compare the geometry of **1** and **3** to that of the dppe analogue. The relevant crystal data for compounds **1**, **3** and **5** are listed in Table 3 and the molecular structures of compounds **1** and **3** are shown in Figs. 1 and 2, respectively. The two species are closely related and their structural features can be discussed together. Relevant bond distances and angles are reported in Tables 4 and 5 while the

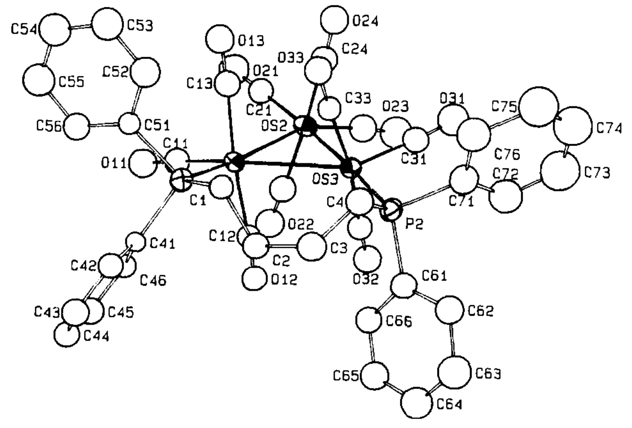


Fig. 1. Molecular structure of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (**1**).

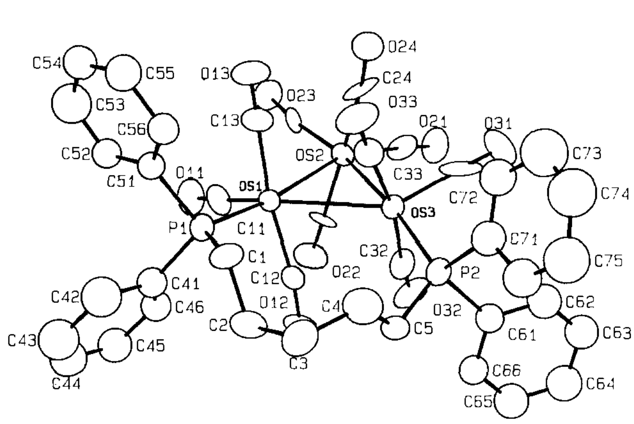


Fig. 2. Molecular structure of $[Os_3(CO)_{10}(\mu\text{-dppb})]$ (**3**).

fractional atomic coordinates are given in Tables 6 and 7 for **1** and **3**, respectively. The structures are derived from that of $[Os_3(CO)_{12}]$ [12] by replacement of an equatorial carbonyl group on each of two Os atoms by the Ph_2P groups of the diphosphine ligands. The structures are very similar to that of $[Os_3(CO)_{10}(\mu\text{-dppe})]$ [19]. The bridged Os — Os distances [Os(1) — Os(3) = 2.965(2) Å for **1** and Os(1) — Os(3) = 2.939(1) Å for **3**] are significantly longer than the non-bridged Os — Os distances [Os(1) — Os(2) = 2.865(1) Å, Os(2) — Os(3) = 2.883(2) Å for **1** and Os(1) — Os(2) = 2.864(9) Å and Os(2) — Os(3) = 2.8729(8) Å for **3**] and which

Table 4
Selected bond distances (Å) and angles (°) for **1** [a]

Bond distances	
Os1—Os2	2.865(1)
Os1—Os3	2.965(2)
Os2—Os3	2.883(2)
Os1—P1	2.337(7)
Os3—P2	2.340(8)
C1—C2	1.56(5)
C2—C3	1.59(6)
C3—C4	1.50(5)
C4—C5	1.51(5)
P—C	1.82(3) [b]
C—C(ring)	1.38(6) [b]
Os—C(CO)	1.92(3) [b]
C—C(CO)	1.13(4) [b]
Bond angles	
Os2—Os1—Os3	59.24(4)
Os1—Os2—Os3	62.10(4)
Os1—Os3—Os2	58.66(4)
C5—P2—Os3	120.0(1)
C1—P1—Os1	119.0(1)
P1—Os1—Os3	121.5(2)
P1—Os1—Os2	171.(4)
P2—Os3—Os1	121.2(2)
P2—Os3—Os2	168.0(2)
C—C—C(ring)	119.9(4)
Os—C—O	173..9(3)

[a] Numbers in parentheses are estimated standard deviations (esds).
[b] Average values.

are similar to the Os — Os distance in $[Os_3(CO)_{12}]$ [12] (2.877 Å). This contrasts with observations in $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ [13] and $[Ru_3(CO)_{10}(\mu\text{-dppe})]$ [14] in both of which the bridged Ru — Ru bonds are shorter than the unbridged ones. The bridged Os — Os edges are even significantly longer (0.09 Å and 0.06 Å, respectively) than the bridged Os — Os distance in $[Os_3(CO)_{10}(\mu\text{-dppe})]$ [19]. This is probably due to the necessity to accommodate the conformational requirements of the additional methylene groups in dppb and dppp relative to the shorter chain dppe and dppm. The Os — P bond lengths [Os(1) — P(1) = 2.337(7) Å and Os(3) — P(2) = 2.340(8) Å for **1** and Os(1) — P(1) = 2.341(4) Å and Os(3) — P(2) = 2.355(3) Å for **3**] are similar to the values of 2.328(3) Å and 2.333(3) Å for the related bonds in $[Os_3(CO)_{10}(\mu\text{-dppe})]$ [19].

Another interesting feature of the structures is the way in which the axial CO ligands are distorted. Such distortions of the CO ligands could be related to the steric requirements of the diphosphine ligands. The axial OC — Os — CO directions are far from parallel. The four ligands at each Os atom maintain approximately octahedral geometry, but these four octahedral sites are twisted as a whole with respect to the other two sites defined by the other metal atoms.

2.4. Reaction of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (1) with dppp

The reaction of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (**1**) with dppp in refluxing toluene leads to the formation of the compound $[Os_3(CO)_9(\mu\text{-dppp})(\eta^1\text{-dppp})]$ (**4**). The IR spectrum of **4** is very similar to that of $[Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})]$, whose structure has been deter-

Table 5
Selected bond (Å) distances and angles (°) for **3** [a]

Bond distances	
Os1—Os2	2.8646(9)
Os1—Os3	2.939(1)
Os2—Os3	2.8729(8)
Os1—P1	2.341(4)
Os3—P2	2.355(3)
C1—C2	1.56(2)
C2—C3	1.56(2)
C3—C4	1.53(2)
P—C	1.84(1) [b]
C—C(ring)	1.37(2) [b]
C—O(CO)	1.15(2) [b]
Bond angles	
Os2—Os1—Os3	59.33(2)
Os1—Os2—Os3	61.62(2)
Os1—Os3—Os2	59.05(2)
C1—P1—Os1	116.5(6)
P1—Os1—Os2	165.6(1)
P1—Os1—Os3	111.4(1)
P2—Os3—Os1	120.2(1)
P2—Os3—Os2	177.8(1)
C—C—C(ring)	120 (2) [b]
Os-C-O	175.6(1) [b]

[a] Numbers in parentheses are estimated standard deviations (esds).
[b] Average values.

Table 6
Fractional atomic coordinates for **1**

Atom	x	y	z	B (Å²) [a]
Os1	0.05313(8)	0.86733(7)	0.87258(5)	2.78(2)
Os2	0.26815(9)	0.87649(7)	0.93413(5)	3.13(2)
Os3	0.0824(1)	0.96762(7)	0.98345(5)	3.11(2)
P1	−0.1110(6)	0.8740(5)	0.8121(3)	3.5(1)
P2	−0.0745(7)	1.0184(5)	1.0364(3)	3.7(2)
O11	0.142(2)	0.717(2)	0.816(1)	6.7(7)
O12	−0.085(2)	0.785(1)	0.976(1)	5.6(5)
O13	0.168(2)	0.976(2)	0.778(1)	8.7(8)
O21	0.432(2)	0.892(2)	1.040(1)	6.3(6)
O22	0.178(2)	0.718(1)	0.982(1)	5.5(6)
O23	0.424(2)	0.796(1)	0.841(1)	6.8(6)
O24	0.329(2)	1.039(1)	0.877(1)	5.6(6)
O31	0.248(3)	1.069(2)	1.055(2)	10.5(9)
O32	0.090(2)	0.836(1)	1.080(1)	5.9(6)
O33	0.055(3)	1.085(2)	0.879(1)	8.4(8)
C1	−0.223(3)	0.942(2)	0.834(1)	4.0(7)
C2	−0.294(2)	0.908(2)	0.888(2)	6 (1)
C3	−0.347(3)	0.984(3)	0.921(1)	6 (1)
C4	−0.266(3)	1.030(2)	0.960(2)	5.6(8)
C5	−0.215(2)	0.989(2)	1.016(1)	3.7(6)
C11	0.102(3)	0.774(2)	0.838(2)	5.2(8)
C12	−0.032(2)	0.822(1)	0.940(1)	3.4(6)
C13	0.125(3)	0.936(2)	0.812(2)	5.6(8)
C21	0.372(3)	0.889(2)	1.001(1)	4.1(6)
C22	0.211(2)	0.777(1)	0.965(1)	3.2(6)
C23	0.367(2)	0.817(2)	0.878(1)	4.5(6)
C24	0.305(3)	0.981(2)	0.901(1)	4.5(6)
C31	0.194(3)	1.029(2)	1.030(2)	5.1(7)
C32	0.082(3)	0.882(2)	1.043(1)	4.4(7)
C33	0.067(3)	1.038(2)	0.916(1)	4.1(6)
C41	−0.183(3)	0.782(2)	0.803(2)	4.8(7) *
C42	−0.277(4)	0.784(3)	0.759(2)	8 (1) *
C43	−0.331(4)	0.703(3)	0.748(2)	8 (1) *
C44	−0.297(4)	0.640(3)	0.774(2)	8 (1) *
C45	−0.209(3)	0.636(3)	0.817(2)	6.8(9) *
C46	−0.160(3)	0.719(2)	0.828(2)	5.3(8) *
C51	−0.081(3)	0.902(2)	0.733(1)	3.7(6) *
C52	−0.040(3)	0.846(2)	0.692(1)	4.3(6) *
C53	−0.011(4)	0.871(3)	0.635(2)	8 (1) *
C54	−0.019(3)	0.948(2)	0.617(2)	5.2(8) *
C55	−0.060(3)	1.005(2)	0.655(2)	6.0(9) *
C56	−0.092(3)	0.981(2)	0.717(1)	4.5(6) *
C61	−0.070(3)	0.994(2)	1.118(1)	4.2(6) *
C62	−0.011(3)	1.036(3)	1.161(2)	6.5(9) *
C63	−0.003(3)	1.019(3)	1.223(2)	6.3(9) *
C64	−0.057(4)	0.954(3)	1.245(2)	7 (1) *
C65	−0.118(4)	0.912(3)	1.203(2)	7 (1) *
C66	−0.123(3)	0.928(2)	1.140(2)	4.7(7) *
C71	−0.093(3)	1.129(2)	1.038(2)	5.6(7) *
C72	−0.007(4)	1.172(2)	1.015(2)	6.6(9) *
C73	−0.023(5)	1.255(3)	1.023(3)	10 (2) *
C74	−0.121(4)	1.283(4)	1.049(2)	10 (1) *
C75	−0.199(4)	1.239(3)	1.075(2)	8 (1) *
C76	−0.180(3)	1.160(2)	1.070(2)	6.5(9) *

[a] Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Table 7
Fractional atomic coordinates for **3**

Atom	x	y	z	B (Å^2) [a]
Os1	0.27610(5)	0.13234(4)	0.22764(3)	2.48(2)
Os2	0.21623(6)	0.09386(4)	0.08227(3)	3.16(2)
Os3	0.46157(5)	0.13759(4)	0.17626(3)	2.80(2)
P1	0.3441(3)	0.1929(2)	0.3398(2)	2.8(1)
P2	0.6636(3)	0.1687(3)	0.2556(2)	3.2(1)
O11	0.0488(9)	0.0655(7)	0.2264(6)	5.4(3)*
O12	0.4214(8)	−0.0193(6)	0.2960(5)	4.0(2)*
O13	0.1370(9)	0.2836(7)	0.1531(5)	4.8(3)*
O21	−0.058(1)	0.1002(8)	0.0177(6)	6.8(3)*
O22	0.223(1)	−0.0713(8)	0.1465(6)	6.3(3)*
O23	0.266(1)	0.0175(8)	−0.0334(7)	7.4(3)*
O24	0.2088(9)	0.2664(7)	0.0305(6)	5.3(3)*
O31	0.497(1)	0.1546(8)	0.0433(6)	6.3(3)*
O32	0.5040(9)	−0.0432(7)	0.1770(6)	5.3(3)*
O33	0.4124(8)	0.3139(6)	0.1894(5)	4.3(2)*
C1	0.490(1)	0.2451(9)	0.3739(7)	3.2(3)*
C2	0.593(1)	0.1819(9)	0.3963(7)	3.3(3)*
C3	0.711(1)	0.218(1)	0.3985(8)	4.6(4)*
C4	0.701(1)	0.246(1)	0.3269(8)	3.8(4)*
C11	0.134(1)	0.093(1)	0.2257(8)	4.0(4)*
C12	0.374(1)	0.0401(9)	0.2716(7)	3.4(4)*
C13	0.190(1)	0.229(1)	0.1778(8)	4.1(4)*
C21	0.045(1)	0.095(1)	0.0413(8)	4.4(4)*
C22	0.224(1)	−0.010(1)	0.1247(9)	5.4(5)*
C23	0.247(1)	0.050(1)	0.0093(9)	5.3(4)*
C24	0.214(1)	0.203(1)	0.0498(8)	4.9(4)*
C31	0.490(1)	0.148(1)	0.0975(8)	4.2(4)*
C32	0.489(1)	0.024(1)	0.1789(8)	4.0(4)*
C33	0.426(1)	0.2466(9)	0.1837(7)	3.3(3)*
C41	0.360(1)	0.1299(8)	0.4145(6)	2.3(3)*
C42	0.427(1)	0.1569(9)	0.4845(7)	3.3(3)*
C43	0.439(1)	0.1114(9)	0.5404(8)	4.0(4)*
C44	0.387(1)	0.0388(9)	0.5300(8)	3.6(4)*
C45	0.320(1)	0.009(1)	0.4632(8)	4.3(4)*
C46	0.308(1)	0.0549(9)	0.4051(7)	3.4(4)*
C51	0.241(1)	0.2696(9)	0.3406(7)	2.7(3)*
C52	0.241(1)	0.344(1)	0.3137(8)	4.7(4)*
C53	0.155(1)	0.400(1)	0.3057(8)	5.5(4)*
C54	0.068(1)	0.382(1)	0.3253(8)	5.3(4)*
C55	0.066(2)	0.311(1)	0.3538(9)	5.6(5)*
C56	0.152(1)	0.253(1)	0.3596(7)	4.0(4)*
C61	0.770(1)	0.091(1)	0.3095(7)	3.6(4)*
C62	0.892(1)	0.102(1)	0.3318(8)	4.4(4)*
C63	0.975(2)	0.044(1)	0.3806(9)	5.9(5)*
C64	0.933(1)	−0.020(1)	0.4015(9)	5.5(5)*
C65	0.811(1)	−0.031(1)	0.3754(8)	4.6(4)*
C66	0.729(1)	0.0232(9)	0.3304(7)	3.8(4)*
C71	0.736(1)	0.212(1)	0.2048(8)	4.4(4)*
C72	0.776(1)	0.164(1)	0.1661(9)	6.3(5)*
C73	0.822(2)	0.198(1)	0.121(1)	7.9(6)*
C74	0.831(2)	0.277(1)	0.123(1)	7.8(6)*
C75	0.795(2)	0.326(1)	0.156(1)	7.6(6)*
C76	0.746(1)	0.294(1)	0.2000(9)	5.7(5)*
H42	0.464	0.208	0.492	6.0
H43	0.486	0.131	0.588	6.0
H44	0.396	0.008	0.570	6.0
H45	0.283	−0.041	0.456	6.0
H46	0.263	0.036	0.358	6.0
H52	0.304	0.357	0.301	6.0
H53	0.159	0.452	0.289	6.0
H54	0.006	0.420	0.318	6.0
H55	0.005	0.299	0.368	6.0

Table 7 (continued).

Atom	x	y	z	B (Å^2) [a]
H56	0.149	0.202	0.378	6.0
H62	0.922	0.146	0.316	6.0
H63	1.060	0.051	0.397	6.0
H64	0.989	−0.056	0.435	6.0
H65	0.782	−0.078	0.388	6.0
H66	0.645	0.015	0.315	6.0
H72	0.773	0.108	0.171	6.0
H73	0.842	0.163	0.092	6.0
H74	0.866	0.299	0.095	6.0
H75	0.805	0.381	0.152	6.0
H76	0.720	0.329	0.226	6.0

[a] Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

mined by single-crystal X-ray crystallography indicating coordination of the second dppm to the third osmium atom in a unidentate fashion [4]. Evidence for equatorial substitution at the uncomplexed osmium atom and the pendent mode of the η^1-dppp ligand are provided by $^{31}P\{^1H\}$ NMR data. The $^{31}P\{^1H\}$ NMR spectrum at 24°C shows an ABMX-type pattern with one of these resonances [δ −157.6 (s) ppm] in the same location as that of the free ligand while the others [δ −151.3 {d, J(PP) = 5.5 Hz}; −146.6 {d, J(PP) = 5.5 Hz}; 145.9 (s) ppm] have a downfield coordination shift. The spectroscopic data therefore show that $[Os_3(CO)_9(\mu$-dppp$)(\eta^1$-dppp$)]$ has a structure similar to that of $[Os_3(CO)_{10}(\mu$-dppm$)(\eta^1$-dppm$)]$ [4], the only difference being the latter is more fluxional than the former as

Table 8
Selected bond distances (Å) and angles (°) for **5** [a]

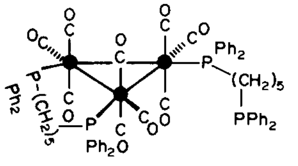
Bond distances	
Os1—Os2	2.860(1)
Os1—Os3	2.854(1)
Os2—Os3	2.875(1)
Os1—P1	2.319(5)
Os3—P2	2.314(5)
Os2—P3	2.304(5)
Os1—P4	2.302(6)
P—C	1.83(2) [b]
C—C(ring)	1.49(4) [b]
Os—C(CO)	1.87(3) [b]
C—O	1.19(3) [b]
Bond angles	
Os2—Os1—Os3	60.41(3)
Os1—Os2—Os3	59.70(3)
Os1—Os3—Os2	59.89(3)
C1—P1—Os1	112.3(6)
C1—P2—Os3	114.3(6)
C2—P4—Os1	110.2(8)
C—C—C(ring)	119.9(3) [b]
Os—C—O	174.4(2) [b]

[a] Number in parentheses are estimated standard deviations (esds).
[b] Average values.

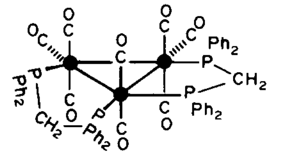
indicated by a frozen-out $^{31}P\{^1H\}$ NMR spectrum for $[Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})]$ obtained at −33°C which on warming to +95°C led to the two phosphorus atoms of μ-dppm becoming equivalent and thus indicating a fluxional process in which the η^1-dppm ligand can move between the two equatorial sites on the unique osmium atom [4]. Similar fluxional behaviour has also been observed in the complexes $[Os_3(CO)_9(\mu\text{-dppm})(PPh_3)]$ [5] and $[Os_3(CO)_9\text{-}\{P(OMe)_3\}(PPh_3)_2]$ [15].

2.5. Reaction of $[Os_3(CO)_{10}(\mu\text{-dppm})]$ with dppm

The reaction of $[Os_3(CO)_{10}(\mu\text{-dppm})]$ with dppm at 110°C yields $Os_3(CO)_8(\mu\text{-dppm})_2]$ (**5**) as the sole product in 67% yield. The compound has previously been reported as a minor product (14% yield) from the reaction between $[Os_3(CO)_{12}]$ and dppm as characterized by spectroscopic data [4]. We have characterized this compound by both spectroscopic and X-ray crystal structure analysis. The IR and NMR data for this complex agree well with the previously reported data [4].



4



5

2.6. X-Ray structure of $[Os_3(CO)_8(\mu\text{-dppm})_2]$ (5)

In order to verify the structure of **5** and to study the effect of the substitution of two dppm ligands on the metal triangle, a single-crystal X-ray analysis was undertaken. The molecular structure of **5** is shown in Fig. 3. Selected bond lengths and angles are presented in Table 8 and fractional atomic coordinates in Table 9.

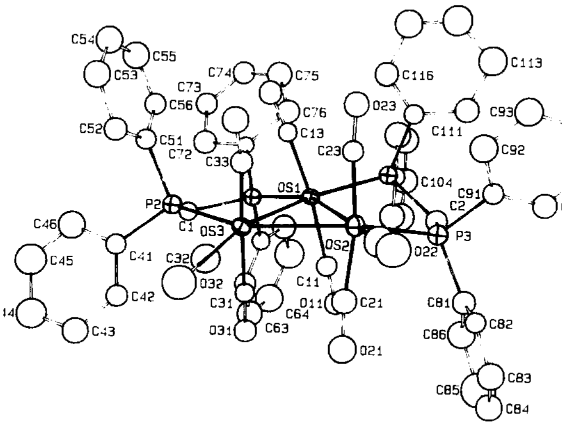


Fig. 3. Molecular structure of $[Os_3(CO)_8(\mu\text{-dppm})_2]$ (**5**).

The structure of **5** is derived from $[Os_3(CO)_{12}]$ [12] by replacement of two equatorial carbonyl groups on one osmium atom and one equatorial carbonyl group on each of the other two osmium atoms by two bidentate dppm ligands, in such a way that each ligand bridges two osmium atoms and one osmium–osmium bond remains unbridged. The structure is very similar to that of $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ [16]. The bridged Os—Os distances [Os(1)—Os(2) = 2.860(1) Å and Os(1)—Os(3) = 2.854(1) Å] are slightly shorter than the non-bridged Os(3)—Os(2) distance of 2.875(1) Å which is similar to the Os—Os distance in $[Os_3(CO)_{12}]$(2.877 Å)] [12]. A similar shortening of the dppm bridged M—M bonds was observed in $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ [16] {supported bonds Ru(1)—Ru(2) = 2.826(2) Å, Ru(1)—Ru(3) = 2.833(2) Å; unsupported bond Ru(2)—Ru(3) = 2.858(2) Å} and $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ [13] {supported bond Ru(1)—Ru(2) = 2.834(1) Å; unsupported bonds Ru(1)—Ru(3) = 2.841(1) Å, Ru(2)—Ru(3) = 2.860(1) Å}. The axial Os—C bond lengths (average 1.903 Å) are longer than the equatorial bonds (average 1.76 Å). This type of distortion is common and was observed in $[Os_3(CO)_{12}]$ [12]. Additional distortions occur in the present case since the phosphorus atoms are tilted away from the plane of the metal triangle, forcing one below and the other above the plane of the metal triangle. As a result, the axial CO ligands are twisted from their normal orthogonal positions.

2.7. Protonation of $[Os_3(CO)_8(\mu\text{-dppm})_2]$ (5)

Addition of a 10-fold excess of CF_3CO_2H to a $CDCl_3$ solution of **5** at room temperature gave quantitative conversion to $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-dppm})_2]^+$ (**6**). The ^1H NMR spectra at room temperature and at −50°C contained a hydride triplet at δ −19.42 ppm [J(PH) = 14.4 Hz] implying that the hydride bridges the Os—Os edge not bridged by the dppm ligands and that cation **6** exists as a single isomer. The hydride ligand is coupled to two equivalent ^{31}P nuclei and the size of the coupling suggests a transoid relationship with the two ^{31}P nuclei. The $^{31}P\{^1H\}$ NMR spectra at room temperature and at −50°C showed an AA′BB′ pattern consistent with the proposed structure for **6**. Protonation at the dppm-bridged Os—Os edges is not consistent with the observation of a hydride triplet in the ^1H NMR spectrum. If the hydride spans one of the dppm-bridged Os—Os edges, the hydride signal should appear as a doublet of double doublets because of its expected coupling with three non-equivalent ^{31}P nuclei. As reported earlier for $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-dppm})]^+$ [11], $[(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-dppm})]^+$ [17] and $[(\mu\text{-H})Ru_3(CO)_8(\mu\text{-dppm})_2]^+$ [18], cation **6** does not coordinate the hydride at the dppm-bridged Os—Os edge because of steric constraints. But if all the M—M edges are dppm-bridged as in $[(\mu\text{-H})Ru_3(CO)_6(\mu\text{-}$

Table 9
Fractional atomic coordinates for **5**

Atom	x	y	z	B (Å^2) [a]
Os1	0.14756(3)	0.27452(5)	0.700	2.48(1)
Os2	0.04041(4)	0.17039(5)	0.67226(6)	3.06(2)
Os3	0.03427(3)	0.35181(5)	0.65090(5)	2.60(1)
P1	0.2098(2)	0.3944(4)	0.6859(3)	2.9(1)
P2	0.0770(2)	0.4862(4)	0.6665(3)	3.1(1)
P3	0.0988(2)	0.0469(4)	0.6712(4)	3.5(1)
P4	0.2011(3)	0.1582(4)	0.7444(3)	3.1(1)
O11	0.1957(7)	0.220(1)	0.544(1)	4.7(4) *
O13	0.1020(7)	0.352(1)	0.842(1)	4.6(4) *
O21	0.0466(8)	0.168(1)	0.499(1)	6.3(5) *
O22	−0.0845(9)	0.084(1)	0.654(1)	8.6(6) *
O23	0.0244(7)	0.189(1)	0.836(1)	4.9(4) *
O31	0.0957(7)	0.344(1)	0.4982(9)	4.5(3) *
O32	−0.086(1)	0.397(1)	0.576(1)	8.9(6) *
O33	0.0380(8)	0.642(1)	0.295(1)	5.6(4) *
C1	0.1636(8)	0.491(1)	0.654(1)	3.1(4) *
C2	0.187(1)	0.064(1)	0.686(1)	4.4(5) *
C11	0.175(1)	0.238(1)	0.600(1)	4.1(5) *
C13	0.1175(9)	0.319(1)	0.789(1)	3.1(4) *
C21	0.045(1)	0.175(2)	0.566(2)	5.1(6) *
C22	−0.032(1)	0.114(2)	0.659(2)	7.4(8) *
C23	0.032(1)	0.187(1)	0.772(1)	3.7(5) *
C31	0.0718(9)	0.345(1)	0.556(1)	3.1(4) *
C32	−0.034(1)	0.380(2)	0.607(2)	6.3(7) *
C33	−0.006(1)	0.351(1)	0.740(1)	3.8(5) *
C41	0.057(1)	0.566(1)	0.602(1)	3.7(5) *
C42	0.037(1)	0.545(1)	0.531(1)	4.1(5) *
C43	0.026(1)	0.604(2)	0.474(2)	6.1(7) *
C44	0.034(1)	0.685(2)	0.489(2)	8.1(9) *
C45	0.058(2)	0.710(2)	0.562(2)	9 (1) *
C46	0.068(1)	0.651(2)	0.620(2)	6.5(7) *
C51	0.061(1)	0.537(1)	0.754(1)	3.5(4) *
C52	−0.001(1)	0.563(2)	0.764(1)	4.5(5) *
C53	−0.016(1)	0.598(2)	0.835(2)	5.8(7) *
C54	0.031(1)	0.606(2)	0.886(2)	5.9(7) *
C55	0.090(1)	0.584(2)	0.872(2)	6.2(7) *
C56	0.105(1)	0.546(2)	0.807(1)	4.2(5) *
C61	0.2702(9)	0.389(1)	0.618(1)	3.4(4) *
C62	0.262(1)	0.404(2)	0.548(1)	4.7(5) *
C63	0.306(1)	0.401(2)	0.496(2)	7.1(8) *
C64	0.370(2)	0.387(2)	0.517(2)	9 (1) *
C65	0.393(2)	0.366(2)	0.593(2)	10 (1) *
C66	0.327(1)	0.364(2)	0.640(2)	6.1(6) *
C71	0.253(1)	0.432(1)	0.763(1)	2.7(4) *
C72	0.280(1)	0.517(2)	0.760(2)	5.5(6) *
C73	0.321(1)	0.537(2)	0.823(2)	5.3(6) *
C74	0.332(1)	0.479(2)	0.879(2)	5.3(6) *
C75	0.306(1)	0.401(2)	0.881(2)	6.5(7) *
C76	0.263(1)	0.365(2)	0.823(2)	5.8(7) *
C81	0.094(1)	−0.010(2)	0.582(1)	4.6(5) *
C82	0.0375(9)	−0.038(1)	0.562(1)	3.3(4) *
C83	0.022(1)	−0.073(2)	0.495(2)	5.6(6) *
C84	0.073(1)	−0.073(2)	0.444(2)	5.4(6) *
C85	0.126(2)	−0.050(3)	0.457(3)	11 (1) *
C86	0.145(1)	−0.007(2)	0.530(2)	7.1(8) *
C91	0.080(1)	−0.036(1)	0.738(1)	3.6(5) *
C92	0.040(1)	−0.016(2)	0.797(2)	6.0(7) *
C93	0.038(1)	−0.078(2)	0.852(2)	6.0(7) *
C94	0.069(1)	−0.159(2)	0.840(2)	7.8(9) *
C95	0.107(1)	−0.180(2)	0.783(2)	5.7(6) *
C96	0.110(1)	−0.116(2)	0.729(2)	5.1(6) *
C101	0.2849(9)	0.160(1)	0.742(1)	3.2(4) *
C102	0.312(1)	0.163(2)	0.679(2)	6.6(7) *
C103	0.388(1)	0.161(2)	0.676(2)	9.0(9) *
C104	0.420(1)	0.166(2)	0.736(2)	7.0(8) *
C105	0.389(2)	0.171(2)	0.802(2)	7.7(9) *
C106	0.313(1)	0.172(2)	0.808(2)	7.2(8) *
C111	0.188(1)	0.125(2)	0.838(1)	3.9(5) *
C112	0.194(1)	0.038(2)	0.853(2)	5.6(6) *
C113	0.184(1)	0.003(2)	0.927(2)	7.7(8) *
C114	0.170(2)	0.068(2)	0.978(2)	7.9(9) *
C115	0.169(1)	0.149(2)	0.966(2)	7.0(8) *
C116	0.175(1)	0.178(2)	0.891(2)	5.2(6) *

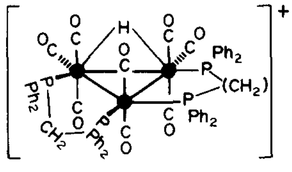
[a] Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

dppm)$_3$]$^+$, there is no alternative and the hydride and dppm bridge the same Ru—Ru edge [9]. The hydride is above and the dppm below the Ru plane in order to accommodate the steric requirements of the metal. The hydride vector imparts a significant distortion to the Ru_3(dppm)$_3$ framework.

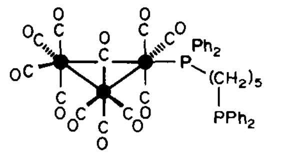
2.8. Reactions of [$Os_3(CO)_{11}$(MeCN)] with dppp

The reaction of the mono-acetonitrile compound [$Os_3(CO)_{11}$(MeCN)] with dppp proceeds smoothly at 0°C. The yields of products obtained depend on the molar ratio of the reactants. Using a 1 : 1 molar ratio of [$Os_3(CO)_{11}$(MeCN)] to dppp, two series of compounds were obtained: the major product is characterized as [$Os_3(CO)_{11}$(η^1-dppp)] (**7**) in which only one phosphorus atom of dppp is coordinated to the Os_3 triangle; the other product as non-coordinated and minor, characterized as [{$Os_3(CO)_{11}$}$_2$(μ-dppp)] (**8**) with the dppp ligand bridging two $Os_3(CO)_{11}$ clusters. With a 1 : 0.5 molar ratio of [$Os_3(CO)_{11}$(MeCN)] to dppp, the reaction proceeds cleanly at 0°C to give **8** as the sole product.

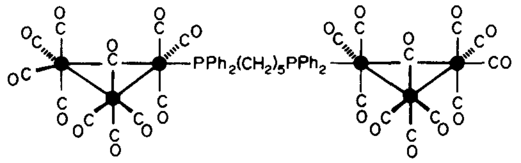
Both compounds **7** and **8** have been characterized by IR and ^{31}P{^{1}H} NMR spectroscopy, and by elemental analysis. The IR spectrum of **7** shows a carbonyl stretching pattern very similar to those of [$Os_3(CO)_{11}$-{η^1-$Ph_2P(CH_2)_nPPh_2$}] (n = 1–4) indicating that they are isostructural [10]. The pendent mode of the η^1-dppp ligand is demonstrated by the ^{31}P{^{1}H} NMR data. Thus the ^{31}P{H} NMR spectrum of **7** contains two singlets at δ −157.6 ppm and −150.2 ppm, the low-field signal being unshifted from that of the free ligand. The IR and ^{31}P{^{1}H} NMR data of **8** are fully consistent with the proposed structure in which the dppp ligand bridges between two $Os_3(CO)_{11}$ clusters. These compounds are analogous to the previously reported compounds [$M_3(CO)_{11}${η^1-$Ph_2P(CH_2)_nPPh_2$}] (M = Ru, n = 2 [14]; M = Os, n = 1–4 [8]) [{$M_3(CO)_{11}$}$_2${μ-Ph_2P-



6



7



8

Form 3.

$(CH_2)_nPPh_2\}]$ (M = Ru, $n = 2$ [14]; M = Os, $n = 2$–4 [8]).

3. Experimental details

All reactions were carried out under nitrogen using dry, degassed solvents. IR spectra were recorded on a Perkin-Elmer 1420 spectrometer. NMR spectra were recorded on an IBM NR80, Bruker AC-200 or Bruker AMX-360 spectrometer. Chemical shifts are relative to $SiMe_4$ (^{1}H) or $P(OMe)_3$ (^{31}P). The starting clusters $[Os_3(CO)_{10}(MeCN)_2]$ [20], $[Os_3(CO)_{11}(MeCN)]$ [20] and $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ [21] were prepared as described in the literature. $[Os_3(CO)_{12}]$ was purchased from Strem Chemicals and the diphosphines were purchased from Aldrich and used as received.

3.1. Reaction of $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ with dppp {dppp = $Ph_2P(CH_2)_5PPh_2$}

A solution of $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ (0.250 g) and dppp (0.122 g, 1 mol per mol Os_3) in chloroform (50 cm^3) was heated to reflux for 9 h. The solvent was removed under vacuum and the residue separated by TLC [SiO_2; eluant, hexane/dichloromethane (10:3, v/v] to give unchanged $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ (0.005 g), $[Os_3(CO)_{10}(\mu\text{-}trans\text{-}C_4H_6)]$ (0.013 g, 5%) and $[Os_3(CO)_{10}(\mu\text{-dppp})]$(**1**) as red crystals (0.108 g, 30%) from a dichloromethane/hexane mixture at −20°C (Anal. Found: C, 35.45; H, 2.45; P, 4.95%. Calc. for $C_{39}H_{30}O_{10}P_2Os_3$: C, 36.25; H, 2.35; P, 4.80%).

3.2. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with dppp

A solution of the bis-acetonitrile compound (0.445 g) and dppp (0.31 g, 1.5 mol per mol Os_3) in chloroform (100 cm^3) was refluxed for 3 h. Removal of the solvent under reduced pressure and separation by TLC [SiO_2; eluant, hexane/dichloromethane (10:3 v/v)] gave three bands of which two yielded $[Os_3(CO)_{11}(\eta^1\text{-dppp})]$ {possibly derived from some $[Os_3(CO)_{11}(MeCN)]$ impurity in $[Os_3(CO)_{10}(MeCN)_2]$} as yellow crystals (0.037 g, 6%) from hexane/CH_2Cl_2 at −20°C and $[Os_3(CO)_{10}(\mu\text{-dppp})]$(**1**) as red crystals (0.300 g, 49%) from hexane/CH_2Cl_2 at −20°C. The third band gave a trace amount of an uncharacterized compound.

3.3. Reaction of $[Os_3(CO)_{11}(MeCN)]$ with dppp

(a) To a dichloromethane solution (25 cm^3) of the mono-acetonitrile compound (0.200 g) at 0°C was added dppp (0.096 g, 1 mol per mol Os_3) and the reaction mixture was allowed to stir for 1 h. The reaction mixture was slowly warmed to room temperature and the solvent was removed under reduced pressure. TLC separation [SiO_2; eluant, hexane/CH_2Cl_2 (10:1 v/v) gave three bands yielding $[Os_3(CO)_{11}(\eta^1\text{-dppp})]$(**7**) as yellow crystals (0.172 g, 60%) from hexane/CH_2Cl_2 at −20°C (Anal. Found: C, 36.85; H, 2.65; P, 4.95%. Calc. for $C_{40}H_{30}Os_3P_2$: C, 36.40; H, 2.30; P, 4.70%) and $[\{Os_3(CO)_{11}\}_2(\mu\text{-dppp})]$(**8**) (0.072 g, 15%) as yellow crystals from hexane/CH_2Cl_2 at −20°C (Anal. Found: C, 28.05; H, 1.55; P, 2.95%. Calc. for $C_{51}H_{30}O_{22}Os_6P_2$: C, 27.85; H, 1.40; P, 2.80%) and a trace amount of an uncharacterized compound.

(b) A similar reaction of the MeCN compound (0.200 g) and dppp (0.048 g, 0.5 mol per mol Os_3) in dichloromethane gave $[\{Os_3(CO)_{11}\}_2(\mu\text{-dppp})]$ (0.184 g, 77%).

3.4. Protonation of $[Os_3(CO)_{10}(\mu\text{-dppp})]$

Trifluoroacetic acid (0.031 cm^3, 10 mol per mol Os_3) was added to a solution of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (0.052 g) in $CDCl_3$ (0.5 cm^3). The ^{1}H NMR spectrum indicated the immediate formation of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-dppp})]^+$. The residue, after removal of solvent under reduced pressure, was dissolved in methanol (5 cm^3) and a methanolic solution of NH_4PF_6 (0.010 g) was added followed by a few drops of water to give a yellow precipitate. The residue was extracted with CH_2Cl_2 and recrystallized from a diethyl ether/CH_2Cl_2 mixture to give $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-dppp})][PF_6]$(**2**) as pale yellow crystals (0.040 g, 49%) (Anal. Found: C, 33.85; H, 2.45; P, 6.65%. Calc. for $C_{39}H_{31}F_6O_{10}Os_3P_2$: C, 32.60; H, 2.20; P, 6.45%); ^{1}H NMR ($CDCl_3$) δ: 7.52 (m, C_6H_5); 2.92 (m, CH_2); 1.63 (m, CH_2); −19.48 {t, OsH, J(PH) = 8.5 Hz} ppm.

3.5. Reaction of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ with dppp

A toluene solution (30 cm^3) of $[Os_3(CO)_{10}(\mu\text{-dppp})]$ (0.100 g) and dppp (0.034 g, 1 mol per mol Os_3) was refluxed for 3.5 h. The solvent was removed under reduced pressure and the residue separated by TLC [SiO_2; eluant, hexane/dichloromethane (2:1, v/v)] to give [$Os_3(CO)_9(\mu$-dppp)(η^1-dppp)](4) (0.045 g, 34%) as red crystals after recrystallization from hexane CH_2Cl_2 at −20°C (Anal. Found: C, 47.55; H, 3.75; P, 7.30%. Calc. for $C_{67}H_{60}O_9Os_3P_4$: C, 47.25; H, 3.55; P, 7.25%).

3.6. Reaction of [$Os_3(CO)_{10}(\mu$-dppm)] with dppm

A toluene solution (40 cm^3) of [$Os_3(CO)_{10}(\mu$-dppm)] (0.105 g) and dppm (0.032 g, 1 mol per mol Os_3) was heated under reflux for 2 h. Work-up as above gave [$Os_3(CO)_8(\mu$-dppm$)_2$](5) as orange crystals (0.086 g, 68%) from hexane/CH_2Cl_2 at −20°C (Anal. Found: C, 44.90; H, 3.15; P, 7.95%. Calc. for $C_{58}H_{44}O_8Os_3P_4$: C, 44.55; H, 2.85; P, 7.90%); ^{1}H NMR ($CDCl_3$) δ: 7.35 (m, C_6H_5); 4.84 {t, CH_2, J(PH) = 9.8 Hz} ppm.

3.7. Protonation of [$Os_3(CO)_8(\mu$-dppm$)_2$] with CF_3CO_2H

Trifluoroacetic acid (0.018 cm^3, 10 mol per mol Os_3) was added to a $CDCl_3$ solution (0.5 cm^3) of [$Os_3(CO)_8(\mu$-dppm$)_2$] (0.035 g) in an NMR tube. The ^{1}H and ^{31}P NMR spectra indicated complete protonation to give [(μ-H)$Os_3(CO)_8(\mu$-dppm$)_2$]$^+$ (6); ^{1}H NMR ($CDCl_3$) δ: 7.17 (m, C_6H_5); 4.94 {t, CH_2, J(PH) = 9.0 Hz}; −19.42 {t, OsH, J(PH) = 14.4 Hz} ppm.

3.8. X-Ray structure determinations of 1, 3 and 5

Crystals of **1**, **3** and **5** for X-ray examination were obtained from saturated solutions of each in hexane/dichloromethane solvent systems at −20°C. Suitable crystals of each were mounted on glass fibres, placed in a goniometer bead on an Enraf-Nonius CAD4 diffractometer and centred optically. Unit cell parameters and an orientation matrix for data collection were obtained by using the centering program in the CAD4 system. Details of the crystal data are given in Table 3. For each crystal the actual scan range was calculated by scan width = scan range + 0.35 tanθ and measured by using the moving crystal-moving counter technique at the beginning and end of each scan. Two or three representative reflections were monitored every 2 h as a check on instrument and crystal stability and an additional two reflections were monitored for crystal orientation control. Lorentz, polarization and decay corrections were applied as was an empirical absorption correction based on a series of ψ scans. Each of the structures was solved by the Patterson method using SHELXS-86 [22] which revealed the positions of the metal atoms. For compound **1**, all non-hydrogen atoms were refined anisotropically, while for compounds **3** and **5** the osmium and phosphorus atoms only were refined anisotropically. Scattering factors were taken from Cromer and Waber [23]. Anomalous dispersion corrections were those of Cromer [24]. All calculations were carried out on a DEC MicroVAX II computer using the MOLEN system of programs.

4. Supplementary material available

Tables 10–12, listing complete bond distances and angles; Tables 13–15, listing anisotropic displacement parameters; and Tables 16–18, listing calculated and observed structure factors for **3**, **1** and **5**.

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