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REACTIONS OF METAL CARBONYL CLUSTER COMPLEXES WITH MULTIDENTATE PHOSPHINE LIGANDS; PREPARATION OF BIS(DIPHENYLPHOSPHINO)METHANE DERIVATIVES OF THE TRINUCLEAR COMPLEXES $M_3(CO)_{12}$ (M = Fe, Ru AND Os) AND THE X-RAY CRYSTAL STRUCTURE OF $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ (dppm = $Ph_2PCH_2PPh_2$)

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Summary

The reaction of bis(diphenylphosphino)methane (dppm) with $Fe_3(CO)_{12}$ gave the known complexes $Fe(CO)_4(dppm)$, $Fe_2(CO)_7(dppm)$, in addition to $Fe_2(CO)_5(dppm)_2$. Two new dppm derivatives of $Ru_3(CO)_{12}$, $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ and $Ru_3(CO)_6(dppm)_3$ have been isolated and spectroscopically characterised. From the reaction of $Os_3(CO)_{12}$ with dppm, the derivatives $Os_3(CO)_{10}(dppm)$, $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ and $Os_3(CO)_8(dppm)_2$ have been isolated. The crystal structure of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ has been determined.

Introduction

In recent years there has been a great deal of interest in the preparation and properties of transition metal cluster carbonyl complexes stabilised with multidentate ligands [1–26]. It has been shown that the presence of bridging or capping ligands can increase the stability of the metal atom framework and thus provide useful compounds for the study of catalysis by cluster complexes [1,3]. The bis(diphenylphosphino)methane ligand (dppm) has attracted particular attention [5–15,19,21,23] because of its tendency to act as a bridging ligand in poly-nuclear metal complexes. A recent report of a kinetic study of reaction 1 in which a monodentate dppm ligand is converted into the bidentate bridging form [27], prompts us to report the preparation and characterisation of a number of new cluster carbonyl complexes containing the dppm ligand together with the crystal structure of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$, a tri-osmium complex containing a monodentate dppm ligand.

$$Os_3(CO)_{11}(\eta^1\text{-dppm}) \rightarrow Os_3(CO)_{10}(\mu\text{-dppm}) + CO \qquad (1)$$

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Experimental

IR spectra were recorded in CH_2Cl_2 solutions in 0.5 mm NaCl cells on a Perkin–Elmer 681 spectrophotometer. NMR spectra were recorded on a Bruker WM250 instrument. Mass spectra were obtained using Fast Atom Bombardment on a VG7070E instrument using 2,4-di-t-butylphenol-glycerol suspensions. All reactions were carried out under nitrogen or argon using dry, degassed solvents and conventional Schlenk-line techniques. $Fe_3(CO)_{12}$ [28], $Ru_3(CO)_{12}$ [29] and dppm [30] were prepared by published methods, and $Os_3(CO)_{12}$ was used as received from Strem Chemicals. Microanalyses were carried out by Elemental Micro-Analysis Ltd., (Devon).

Reaction of $Fe_3(CO)_{12}$ with dppm

$Fe_3(CO)_{12}$ (2.00 g, 3.97 mmol) and dppm (3.06 g, 7.96 mmol) were heated under reflux in dichloromethane (70 cm^3) for 1 h. The resulting deep red solution was reduced in volume and ethanol (10 cm^3) was added. On cooling this solution, small brown crystals of $Fe_2(CO)_5(dppm)_2$ separated. These were filtered off under nitrogen, and the remaining solution reduced in volume. On cooling, an orange precipitate of $Fe(CO)_4(\eta^1$-dppm) separated out. The remaining solution was evaporated to dryness and the residue was recrystallised from acetone/ethanol to give red crystals of $Fe_2(CO)_7$(dppm). The three products were further purified by recrystallisation from dichloromethane/petroleum ether (60–80°C) to give:

$Fe_2(CO)_5(dppm)_2$ as large brown needles (1.47 g, 24%) (Found: C, 64.76; H, 4.54; P, 11.97; Fe, 10.7. $C_{55}H_{44}O_5P_4Fe_2$ calcd.: C, 64.73; H, 4.35; P, 12.14; Fe, 10.9%).

$Fe(CO)_4(\eta^1$-dppm) as yellow needles (0.91 g, 14%) (Found: C, 62.96; H, 4.02; P, 11.16; Fe, 10.6. $C_{29}H_{22}O_4P_2Fe$ calcd.: C, 63.07; H, 4.02; P, 11.22; Fe, 10.1%). *M* (mass spectrometry), 552 as required for $C_{29}H_{22}O_4P_2Fe$ (based on ^{56}Fe).

$Fe_2(CO)_7$(dppm) as deep red plate-like crystals (0.96 g, 23%) (Found: C, 55.69; H, 3.21; P, 8.78; Fe, 16.9. $C_{32}H_{22}O_7P_2Fe_2$ calcd.: C, 55.53; H, 3.20; P, 8.95; Fe, 16.1%). *M* (mass spectrometry) 692, as required for $C_{32}H_{22}O_7P_2Fe_2$.

Preparation of $Ru_3(CO)_9(\mu$-dppm)(η^1-dppm)

$Me_3NO \cdot 2H_2O$ (0.021 g, 0.189 mmol) in methanol (15 cm^3) was added dropwise to a stirred solution of $Ru_3(CO)_{10}$(dppm) (0.183 g, 0.189 mmol) and dppm (0.073 g, 0.189 mmol) in dichloromethane (40 cm^3) at room temperature. The mixture was stirred at room temperature until infra-red monitoring indicated that complete reaction had occurred (4 h). The resulting solution was evaporated to dryness under reduced pressure to give a quantitative yield of $Ru_3(CO)_9(\mu$-dppm)(η^1-dppm).

Preparation of $Ru_3(CO)_6(dppm)_3$

$Ru_3(CO)_{12}$ (0.474 g, 0.741 mmol) and dppm (0.884 g, 2.30 mmol) were heated under reflux in benzene (40 cm^3) for 8 h. The resulting deep red solution was evaporated to dryness and the residue recrystallised from cold acetone/ethanol to give small red crystals of the product (0.927 g, 77%) (Found: C, 59.70; H, 3.93; P, 11.22. $C_{81}H_{66}O_6P_6Ru_3$ calcd.: C, 59.89; H, 4.10; P, 11.44%). $M = 1625$ (mass spectrometry) as required for $C_{81}H_{66}O_6P_6Ru_3$ (based on ^{101}Ru).

Preparation of $Os_3(CO)_{10}(dppm)$

$Me_3NO \cdot 2H_2O$ (0.05 g, 0.45 mmol) in methanol (10 cm^3) was added dropwise over 0.5 h to a warmed (60°C) suspension of $Os_3(CO)_{12}$ (0.203 g, 0.224 mmol) and dppm (0.086 g, 0.224 mmol) in benzene (40 cm^3). After a further hour at 60°C, the solution was evaporated to dryness, and the residue recrystallised from acetone/ethanol to yield orange needles of the product (0.205 g, 74%) (Found: C, 34.00; H, 1.80; P, 5.14. $C_{35}H_{22}O_{10}P_2Os_3$ calcd.: C, 34.04; H, 1.80; P, 5.02%). $M = 1235$ (mass spectrometry) as required for $C_{35}H_{22}O_{10}P_2Os_3$ (based on ^{190}Os).

Preparation of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ and $Os_3(CO)_8(dppm)_2$

$Os_3(CO)_{12}$ (0.301 g, 0.332 mmol) and dppm (0.257 g, 0.669 mmol) in toluene (50 cm^3) were heated under reflux for 8 h. The resulting orange solution was distilled to dryness and the residue was chromatographed on silica TLC plates using petroleum ether (60–80°C)/dichloromethane (2/1) as eluant. Three bands were obtained which were in the order: $Os_3(CO)_{10}(dppm)$ (5 mg, 1%); $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ (0.273 g, 52%) (Found: C, 45.31; H, 2.81; P, 7.81. $C_{59}H_{44}O_9P_4Os_3$ calcd.: C, 44.53; H, 2.79; P, 7.79%). $M = 1591$ (mass spectrometry) as required for $C_{59}H_{44}O_9P_4Os_3$; and $Os_3(CO)_8(dppm)_2$ (0.040 g, 14%) (Found: C, 44.66; H, 2.81; P, 7.99. $C_{58}H_{44}O_8P_4Os_3$ calcd.: C, 44.56; H, 2.84; P, 7.92%).

Crystal structure of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$

Orange crystals of the complex were grown from an acetone/ethanol solution. The crystals were sensitive to solvent loss and thus a suitable crystal of approximate dimensions 0.4 × 0.7 × 0.5 mm was sealed in a Lindemann capillary together with a small amount of the mother liquor. The crystals were monoclinic, space group $P2_1/n$, a 20.820(6), b 13.108(2), c 23.026(4) Å, β 108.93(2)°, V 5944 $Å^3$, D_m 1.78, D_c 1.78 g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha)$ 65.9 cm^{-1}. Intensity data were recorded on a CAD-4 diffractometer. The osmium atoms were located by the use of a Patterson map and the remaining atoms (other than hydrogen) were found by Fourier methods using the SHELX [31] program, and using 5564 unique reflections with $|F| > 5\sigma(F)$. Least-squares refinement of positional and thermal (anisotropic for Os and P, isotropic for C, H, and O) parameters converged to an agreement factor $R = 12.5\%$. After absorption corrections by the method of Stuart and Walker [32], R decreased to 10.25%. Further refinement, with Os, P, and the carbonyl C and O atoms anisotropic, and the phenyl rings constrained to regular hexagons, led to a final agreement factor R 9.77%. The atomic scattering factor for osmium was obtained from refs. 33 and 34, and for the remaining atoms the values in SHELX [31] were used. The atom coordinates are given in Table 3, and selected bond lengths and angles in Table 4. Tables of thermal parameters and lists of structure factors can be obtained from the authors on request.

Results and discussion

The reaction of dppm with $Fe_3(CO)_{12}$ results in fragmentation of the cluster, giving the substituted derivatives $Fe(CO)_4(\eta^1\text{-dppm})$, $Fe_2(CO)_7(dppm)$, and $Fe_2(CO)_5(dppm)_2$. The complex $Fe(CO)_4(\eta^1\text{-dppm})$ has previously been prepared by a radical-anion-initiated reaction between $Fe(CO)_5$ and dppm [35], and as a minor product from the photolysis of $Fe(CO)_5$ and dppm [36]. The infrared (Table

TABLE 1

INFRARED DATA

Complex	ν(CO) (cm^{-1}) (CH_2Cl_2 solution)
$Fe(CO)_4(\eta^1$-dppm)	2049s, 1972m, 1937vs,br
$Fe_2(CO)_7$(dppm)	2044vs, 1990vs, 1977s, 1940s, 1920m, 1754m
$Fe_2(CO)_5(dppm)_2$	1951m, 1902vs, 1875s, 1852m, 1693m
$Ru_3(CO)_9(\mu$-dppm)(η^1-dppm)	2048w, 1988s, 1972vs, 1938m,sh
$Ru_3(CO)_6(dppm)_3$	1994vw, 1918vs,br, 1873w, 1862w,sh
$Os_3(CO)_{10}$(dppm)	2090m, 2026sh, 2006vs, 2000vs, 1971m, 1954m, 1944m
$Os_3(CO)_9(\mu$-dppm)(η^1-dppm)	2060m, 1995s, 1975vs, 1957sh, 1929m
$Os_3(CO)_8(dppm)_2$	2047m, 1989m, 1962vs, 1937m, 1895w, 1887w,sh

1) and NMR (Table 2) data for this complex agree well with the previously published data [35], and, in addition, the mass spectrum of the complex shows a parent ion at *m/e* 552 corresponding to $[Fe(CO)_4(dppm)]^+$, and a carbonyl fragmentation pattern corresponding to $[Fe(CO)_2(dppm)]^+$, $[Fe(CO)(dppm)]^+$, and $[Fe(dppm)]^+$.

The di-iron derivative, $Fe_2(CO)_7$(dppm) has previously been prepared by the thermally initiated reaction between $Fe_2(CO)_9$ and dppm [37]. The infrared data (Table 1) agree well with those previously published [37], and we also report here the ^{1}H and ^{31}P NMR spectroscopic data (Table 2). This complex was previously also characterised by an X-ray crystal structure analysis which showed the molecule to consist of two $Fe(CO)_3$ units linked by an Fe–Fe bond bridged by the dppm ligand and a carbonyl ligand [37].

The complex $Fe_2(CO)_5(dppm)_2$ was characterised by microanalysis, and by infrared and NMR spectroscopic data (Tables 1 and 2). The singlet resonance at 67.3 ppm in the ^{31}P NMR spectrum indicates that both dppm ligands bridge the

TABLE 2

^{1}H AND ^{31}P NMR DATA

Complex	$\delta(^1H)$ (CD_2Cl_2 solution) [a]	$\delta(^{31}P\{^1H\})$ [b]
$Fe(CO)_4(\eta^1$-dppm)	3.36 (dd, *J*(PH) 9.3, *J*(P^1H) 1.5)	65.5 (d, *J*(PP) 79.3), −26.2(d)
$Fe_2(CO)_7$(dppm)	3.57 (t, *J*(PH) 11.4)	62.1 (s)
$Fe_2(CO)_5(dppm)_2$	3.58 (m)	67.3 (s)
$Ru_3(CO)_9(\mu$-dppm) (η^1-dppm)	4.25 (m) 4.45 (t, *J*(PH) 11.0)	27.6 (d, *J*(PP) 58), 21.5 (d, *J*(PP) 52), 18.2 (d, *J*(PP) 52), −25.5 (d, *J*(PP) 58)
$Ru_3(CO)_6(dppm)_3$	3.89 (t, *J*(PH) 8.8)	22.3 (s)
$Os_3(CO)_{10}$(dppm)	5.09 (t, *J*(PH) 10.7)	−27.0 (s)
$Os_3(CO)_9(\mu$-dppm) (η^1-dppm)	3.43 (dd, *J*(PH) 8.1, *J*(P^1H) 1.5), 4.94 (t, *J*(PH) 10.5)	−12.0 (dd, *J*(PP^1) 59.6, *J*(PP″) 2.9), −24.5(dd, *J*(P″P‴) 54.7, *J*(P″P) 2.9), −27.3 (d, *J*(P′P) 59.6), −27.9 (d, *J*(P‴P″) 54.7) (at −33°C)
$Os_3(CO)_8(dppm)_2$	4.84 (t, *J*(PH) 9.8)	AA′BB′ spectrum centred at −22.2

[a] Chemical shifts relative to TMS; all coupling constants given in Hz. dd = doublet of doublets t = triplet, m = multiplet. [b] Chemical shifts relative to 85% H_3PO_4; CD_2Cl_2 solution.

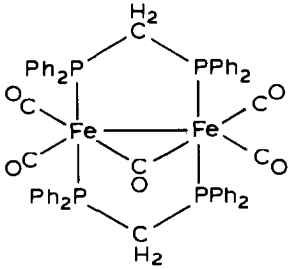

Fig. 1. Proposed structure for $Fe_2(CO)_5(dppm)_2$.

Fe–Fe bond, while the band at 1693 cm^{-1} in the infrared spectrum indicates the presence of a bridging carbonyl ligand. The structure of this complex is thus established as that shown in Fig. 1. This complex is analogous to the previously reported complexes $Fe_2(CO)_5(Me_2PCH_2PMe_2)_2$ [38], and $Fe_2(CO)_5\{(PR_2)_2)NMe\}_2$ (R = F, OMe) [39,40], which have very similar infrared spectra to that observed for $Fe_2(CO)_5(dppm)_2$. This further confirms the structure proposed, since the structure of $Fe_2(CO)_5\{(PF_2)_2NMe\}_2$ has been determined by X-ray crystallography [41]. The complex $Fe_2(CO)_5(dppm)_2$ has recently been reported as a product of the reaction between dppm and $Fe_2(CO)_7(dppm)$ under photochemical conditions [42].

The syntheses of $Ru_3(CO)_{10}(dppm)$ [5,11] and $Ru_3(CO)_8(dppm)_2$ [7,8] have previously been reported. We have prepared the more highly substituted cluster $Ru_3(CO)_6(dppm)_3$ by refluxing $Ru_3(CO)_{12}$ with three equivalents of dppm in benzene. The spectroscopic data for this complex (Tables 1 and 2) are fully consistent with the structure shown in Fig. 2, in which all the equatorial carbonyl ligands in $Ru_3(CO)_{12}$ have been substituted by the phosphine ligands. The complex $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ is not isolated from the direct reaction of dppm with $Ru_3(CO)_{12}$ (c.f. $Os_3(CO)_{12}$ below), however, the complex may be obtained from $Ru_3(CO)_{10}(dppm)$ by treatment with Me_3NO in the presence of dppm. We have not succeeded in isolating the product in an analytically pure form since, in solution at room temperature, it readily undergoes further substitution to give $Ru_3(CO)_8(dppm)_2$ [27]. However, the infrared and ^{31}P NMR spectroscopic data (Tables 1 and 2) clearly

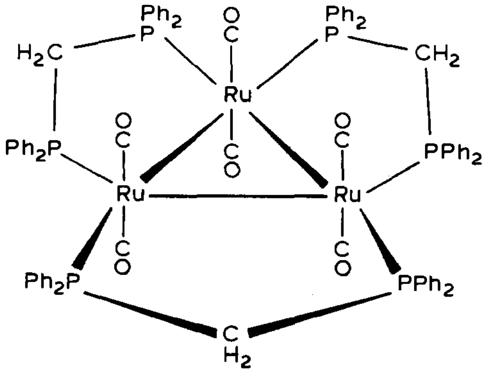

Fig. 2. Proposed structure for $Ru_3(CO)_6(dppm)_3$.

TABLE 3

ATOMIC COORDINATES FOR $Os_3(CO)_9(dppm)(\eta^1\text{-dppm})$

Atom	x	y	z
Os(1)	0.3894(1)	0.0911(1)	0.1943(1)
Os(2)	0.4664(1)	−0.0891(1)	0.1903(0)
Os(3)	0.5180(1)	0.0587(1)	0.2874(1)
P(1)	0.3139(3)	0.0532(5)	0.0982(3)
P(2)	0.3769(3)	−0.1662(5)	0.1140(3)
P(3)	0.6110(4)	−0.0267(7)	0.3544(4)
P(4)	0.6559(4)	−0.2378(7)	0.4195(4)
C(1)	0.3513(12)	0.2058(16)	0.2198(13)
O(1)	0.3281(15)	0.2736(16)	0.2367(12)
C(2)	0.4416(15)	0.1851(20)	0.1628(12)
O(2)	0.4698(11)	0.2429(15)	0.1427(10)
C(3)	0.3437(15)	−0.0023(17)	0.2338(13)
O(3)	0.3073(10)	−0.0563(15)	0.2471(10)
C(4)	0.5333(12)	−0.1887(18)	0.1946(14)
O(4)	0.5749(10)	−0.2461(18)	0.1951(10)
C(5)	0.4951(14)	−0.0016(19)	0.1361(12)
O(5)	0.5133(11)	0.0378(13)	0.0997(9)
C(6)	0.4408(10)	−0.1598(23)	0.2526(12)
O(6)	0.4261(9)	−0.2109(14)	0.2867(8)
C(7)	0.5718(18)	0.1031(33)	0.2395(17)
O(7)	0.6072(12)	0.1309(20)	0.2143(11)
C(8)	0.4616(14)	0.0083(19)	0.3315(13)
O(8)	0.4324(10)	−0.0210(15)	0.3625(8)
C(9)	0.5264(18)	0.1860(15)	0.3274(12)
O(9)	0.5285(14)	0.2659(15)	0.3472(12)
C(10)	0.2973(14)	−0.0853(21)	0.0827(13)
C(11)	0.5880(14)	−0.1574(22)	0.3696(13)
C(21)	0.2232(10)	0.0942(14)	0.0813(8)
C(22)	0.1802(10)	0.0995(14)	0.0207(8)
C(23)	0.1125(10)	0.1286(14)	0.0080(8)
C(24)	0.0880(10)	0.1525(14)	0.0560(8)
C(25)	0.1311(10)	0.1473(14)	0.1166(8)
C(26)	0.1987(10)	0.1181(14)	0.1293(8)
C(31)	0.3295(9)	0.1030(10)	0.0304(9)
C(32)	0.3481(9)	0.0423(10)	−0.0113(9)
C(33)	0.3611(9)	0.0870(10)	−0.0613(9)
C(34)	0.3554(9)	0.1924(10)	−0.0697(9)
C(35)	0.3368(9)	0.2531(10)	−0.0280(9)
C(36)	0.3238(9)	0.2084(10)	0.0220(9)
C(41)	0.3918(7)	−0.2091(12)	0.0450(7)
C(42)	0.4527(7)	−0.1917(12)	0.0336(7)
C(43)	0.4594(7)	−0.2201(12)	−0.0225(7)
C(44)	0.4052(7)	−0.2660(12)	−0.0673(7)
C(45)	0.3442(7)	−0.2835(12)	−0.0560(7)
C(46)	0.3375(7)	−0.2550(12)	0.0001(7)
C(51)	0.3453(8)	−0.2823(15)	0.1393(8)
C(52)	0.3898(8)	−0.3650(15)	0.1499(8)
C(53)	0.3760(8)	−0.4530(15)	0.1778(8)
C(54)	0.3178(8)	−0.4583(15)	0.1951(8)
C(55)	0.2734(8)	−0.3756(15)	0.1845(8)
C(56)	0.2871(8)	−0.2876(15)	0.1566(8)
C(61)	0.6851(13)	−0.0407(17)	0.3269(11)
C(62)	0.7045(13)	−0.1299(17)	0.3041(11)

TABLE 3 (continued)

Atom	*x*	*y*	*z*
C(63)	0.7618(13)	−0.1301(17)	0.2853(11)
C(64)	0.7997(13)	−0.0411(17)	0.2894(11)
C(65)	0.7803(13)	0.0482(17)	0.3122(11)
C(66)	0.7230(13)	0.0484(17)	0.3310(17)
C(71)	0.6496(8)	0.0250(16)	0.4342(10)
C(72)	0.6075(8)	0.0733(16)	0.4621(10)
C(73)	0.6330(8)	0.1014(16)	0.5237(10)
C(74)	0.7006(8)	0.0814(16)	0.5575(10)
C(75)	0.7427(8)	0.0332(16)	0.5296(10)
C(76)	0.7172(8)	0.0050(16)	0.4697(10)
C(81)	0.6354(10)	−0.3594(20)	0.3786(9)
C(82)	0.6902(10)	−0.4202(20)	0.3782(9)
C(83)	0.6789(10)	−0.5147(20)	0.3488(9)
C(84)	0.6126(10)	−0.5484(20)	0.3197(9)
C(85)	0.5578(10)	−0.4876(20)	0.3200(9)
C(86)	0.5691(10)	−0.3931(20)	0.3495(9)
C(91)	0.6232(11)	−0.2642(19)	0.4836(11)
C(92)	0.6096(11)	−0.3614(19)	0.5012(11)
C(93)	0.5928(11)	−0.3742(19)	0.5547(11)
C(94)	0.5879(11)	−0.2898(19)	0.5906(11)
C(95)	0.6033(11)	−0.1925(19)	0.5729(11)
C(96)	0.6201(11)	−0.1797(19)	0.5194(11)

show the presence of a bridging dppm ligand and a unidentate dppm ligand. It is also most probable that all three phosphine groups are coordinated at equatorial sites, to give a complex analogous to that of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ whose structure is described below.

We have previously reported in a preliminary communication the preparation of $Os_3(CO)_{10}(dppm)$ and its thermolysis in refluxing toluene to give the coordinately unsaturated cluster $Os_3(CO)_8(H)\{Ph_2PCH_2P(Ph)C_6H_4\}$ [26]. The experimental details for the preparation of $Os_3(CO)_{10}(dppm)$ are reported here, together with those of the more highly substituted derivatives $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ and $Os_3(CO)_8(dppm)_2$. All attempts to prepare $Os_3(CO)_6(dppm)_3$ were unsuccessful. The complex $Os_3(CO)_{10}(dppm)$ has also been prepared by treatment of $Os_3(CO)_{10}(C_4H_6)$ (C_4H_6 = *cis*- or *trans*-butadiene) with dppm [43].

In contrast to the high yield preparation of $Ru_3(CO)_8(dppm)_2$ [7,8], the thermal reaction between $Os_3(CO)_{12}$ and two equivalents of dppm results in a mixture of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ and $Os_3(CO)_8(dppm)_2$. The spectroscopic data for $Os_3(CO)_8(dppm)_2$ (Tables 1 and 2) indicate that this complex has the same structure as the crystallographically characterised ruthenium analogue $Ru_3(CO)_8(dppm)_2$ [7–9].

The complex $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ has been characterised both spectroscopically and by an X-ray crystal structure analysis. The mass spectrum of this complex shows a parent ion at *m/e* 1591, as expected, and the stepwise loss of nine carbonyl groups is also observed. Evidence for the uncoordinated phosphine group in the η^1-dppm ligand is provided by both ^1H and ^{31}P NMR data. Thus, the methylene protons of the η^1-dppm ligand give rise to a doublet of doublets at 3.43

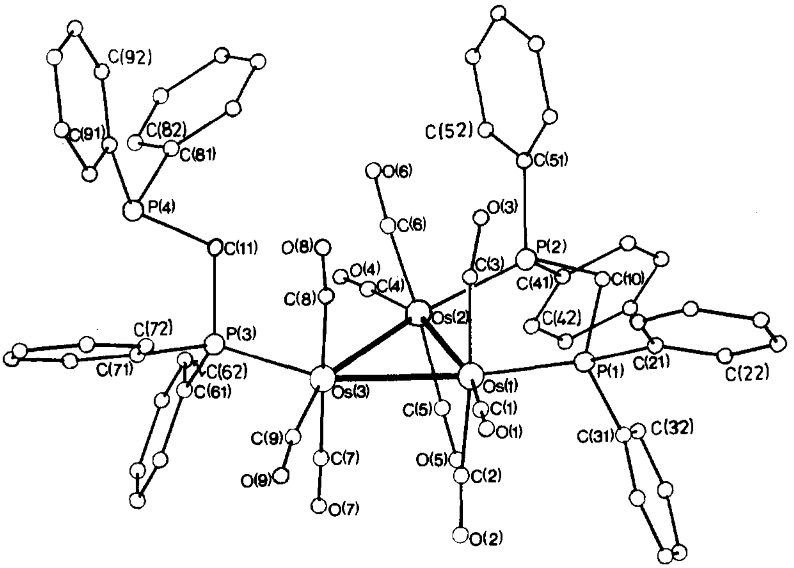

Fig. 3. Molecular structure of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ with H atoms omitted.

ppm in the ^1H NMR spectrum, similar to that observed in $Fe(CO)_4(\eta^1\text{-dppm})$. The coupling constants of 8.1 and 1.5 Hz $\{J(PH)\}$ are also in agreement with coupling to a coordinated and uncoordinated phosphorus atom respectively. The ^{31}P NMR spectrum at −33°C shows an ABLX type pattern. On warming the two phosphorus atoms of the μ-dppm group (P_A and P_B) become equivalent (at +95°C), indicating a

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$

Os(1)–Os(2)	2.872(2)	Os(2)–C(5)	1.927(29)
Os(1)–Os(3)	2.866(2)	Os(2)–C(6)	1.924(29)
Os(2)–Os(3)	2.890(2)	Os(3)–C(7)	1.903(44)
Os(1)–P(1)	2.315(6)	Os(3)–C(8)	1.903(33)
Os(2)–P(2)	2.336(6)	Os(3)–C(9)	1.887(22)
Os(3)–P(3)	2.333(8)	P(1)–C(10)	1.861(28)
Os(1)–C(1)	1.881(25)	P(2)–C(10)	1.902(28)
Os(1)–C(2)	1.931(31)	P(3)–C(11)	1.843(30)
Os(1)–C(3)	1.948(30)	P(4)–C(11)	1.837(27)
Os(2)–C(4)	1.889(26)		
Os(2)–Os(1)–Os(3)	60.5(0)	Os(3)–Os(2)–C(5)	89.2(7)
Os(1)–Os(2)–Os(3)	59.7(0)	Os(3)–Os(2)–C(6)	82.5(8)
Os(1)–Os(3)–Os(2)	59.9(0)	C(2)–Os(1)–P(1)	93.9(8)
Os(1)–Os(2)–P(2)	93.6(2)	C(3)–Os(1)–P(1)	91.6(7)
Os(3)–Os(2)–P(2)	151.4(2)	C(5)–Os(2)–P(2)	96.3(7)
Os(2)–Os(1)–P(1)	90.3(2)	C(6)–Os(2)–P(2)	90.3(7)
Os(3)–Os(1)–P(1)	149.7(2)	C(7)–Os(3)–P(3)	90.6(11)
Os(2)–Os(3)–P(3)	102.1(2)	C(8)–Os(3)–P(3)	90.3(8)
Os(3)–Os(1)–C(2)	82.7(7)	P(1)–C(10)–P(2)	112.7(14)
Os(3)–Os(1)–C(3)	92.1(7)	P(3)–C(11)–P(4)	117.2(15)

fluxional process in which the η^1-dppm ligand can move rapidly on the NMR timescale between the two equatorial sites available on the third Os atom. Similar fluxional behaviour has been observed also in the complexes $Os_3(CO)_9(dppm)(PPh_3)$ [44], $Os_3(CO)_9\{P(OMe)_3\}(PPh_3)_2$ [45], and $Os_3(CO)_7\{P(OMe)_3\}_5$ [46].

The structure of $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ is shown in Fig. 3, and selected bond lengths and angles are given in Table 4. The molecule consists of a triangle of osmium atoms with one Os–Os bond bridged by a dppm ligand, coordinated at equatorial sites, and the unidentate dppm ligand coordinated to the third Os atom, also at an equatorial site. There is a significant distortion of the Os_3 triangle. In contrast to $Ru_3(CO)_{10}(dppm)$ [6] and $Ru_3(CO)_8(dppm)_2$ [9] in which the dppm-bridged Ru–Ru bonds are significantly shorter than the unbridged Ru–Ru bonds, the unbridged Os(1)–Os(3) bond (2.866(2) Å) is the shortest Os–Os bond, while the unbridged Os(2)–Os(3) bond is the longest (2.890(2) Å).

The axial Os–C bond lengths (average 1.923 Å) are longer than the equatorial bonds (av. 1.886 Å). This is in full agreement with the variations previously found in $Ru_3(CO)_{12}$ [47] and $Os_3(CO)_{12}$ [48]. Additional distortions of the carbonyl ligands can be related to the presence of the dppm ligands. The phosphorus atoms P(1) and P(2) are tilted away from the plane of the Os_3 triangle, forcing P(1) below and P(2) above the plane of the metal triangle. This favoured conformation of the five-membered ring contributes to the tilting of the axial carbonyl ligands away from the precise orthogonal positions. Similar distortions are found in $Ru_3(CO)_{10}(dppm)$ [6].

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