Synthesis, Single-crystal *X*-Ray Structures, and Fluxional Behaviour of 1,2-[$Os_3(CO)_{10}(\mu$-dppe)] and its Protonated Derivative 1,2-[$Os_3(\mu$-H)$(CO)_{10}$(μ-dppe)][PF_6] where dppe = $Ph_2PCH_2CH_2PPh_2$ *

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The cluster 1,2-[$Os_3(CO)_{10}(MeCN)_2$] reacts with $Ph_2PCH_2CH_2PPh_2$ (dppe) to give mainly 1,2-[$Os_3(CO)_{10}$(dppe)] (**1**) but also some 1,2-[$Os_3(CO)_{10}$(dppe-*P*)$_2$]. Variable-temperature ^{13}C-{^1H} and ^1H n.m.r. spectra for (**1**) were used to show that inversion of the OsPCCPOs ring can easily be slowed to give frozen-out spectra below −40 °C. Single-crystal *X*-ray structures of (**1**) and its protonated derivative [$Os_3H(CO)_{10}$(dppe)][PF_6] (**2**) (two independent but similar molecules in the unit cell) were determined. Although compounds (**1**) and (**2**) have closely related geometries, (**1**) has a much distorted structure in which the axial OC–Os–CO directions are not perpendicular to the Os_3 plane but are screwed with respect to each other. This screw distortion is not present in (**2**) because the μ-H ligand causes the two axial OC–Os–CO directions through adjacent Os atoms to be locked perpendicular to the Os–H directions and hence they are parallel. Ring inversion in (**2**) was also frozen out in the low-temperature n.m.r. spectra.

The diphosphine $Ph_2PCH_2CH_2PPh_2$ (dppe) has been widely used as a chelating ligand although less commonly it is known to bridge. Both co-ordination modes have been found in clusters. The cluster [$Ru_4H_4(CO)_{10}$(dppe)] has been isolated in isomeric forms with chelating [1] and bridging [2] dppe respectively, [$Ru_5C(CO)_{13}$(dppe)] contains chelating dppe [3] and [$Ru_3(CO)_{10}$(dppe)] bridging dppe.[4] We have reported the syntheses of the isomers 1,1- and 1,2-[$Os_3(CO)_{10}(PMe_2Ph)_2$] [5] and the corresponding protonated derivatives 1,1- and 1,2-[$Os_3(\mu$-H)$(CO)_{10}(PMe_2Ph)_2$][PF_6] have been structurally characterised.[6],† These isomers correspond with chelating and bridging forms, if the two monodentate ligands are replaced by a diphosphine, and we have briefly reported the syntheses of 1,1- and 1,2-[$Os_3(CO)_{10}$(dppe)] and related compounds with other diphosphines.[7] The compound [$Os_3(CO)_{10}$(dppm)] (dppm = $Ph_2PCH_2PPh_2$) has only been synthesised in the 1,2 (bridging) form. This paper reports the syntheses, *X*-ray structures, and dynamic behaviour of the 1,2 isomer of [$Os_3(CO)_{10}$(dppe)] and its protonated form 1,2-[$Os_3H(CO)_{10}$(dppe)][PF_6]. The crystal structure of [$Os_3(CO)_{10}$(dppe)] can be compared with that of the corresponding ruthenium compound[4] and the effect of protonation was also assessed.

Results and Discussion

1,2-[$Os_3(CO)_{10}$(dppe)].—The cluster [$Os_3(CO)_{10}(MeCN)_2$] reacts with dppe in refluxing chloroform to give predominantly the expected product 1,2-[$Os_3(CO)_{10}(\mu$-dppe)], (**1**), which is the subject of this paper. Some 1,2-[$Os_3(CO)_{10}$(dppe-*P*)$_2$] is also formed in low yield but this was only characterised by elemental analysis and its i.r. spectrum (see Experimental section). The i.r. spectrum around 2 000 cm^{-1} of this latter compound is very close to that of 1,2-[$Os_3(CO)_{10}(PMe_2Ph)_2$] [5] and rather different from that of compound (**1**). The cluster 1,2-[$Os_3(CO)_{10}(PMe_2Ph)_2$] exists as two interconverting isomers in solution which differ in the occupancy of equatorial sites by the PMe_2Ph ligands but neither isomer has these ligands in adjacent equatorial sites as in compound (**1**).

The ^{13}C n.m.r. spectrum of compound (**1**) at −80 °C contains five equal-intensity CO signals at δ 196.5, 192.0, 185.9, 180.1, and 174.5 (see Figure 1). Thus the symmetry of the molecule is lower than C_{2v}. The first three signals may be assigned to axial CO ligands and we propose that there is a sufficiently high barrier to inversion of the OsPCCPOs ring to give frozen-out n.m.r. signals at −80 °C. Likewise at low temperatures two equal-intensity ^1H n.m.r. multiplets at δ 3.08 and 1.80 for the PCH_2CH_2P protons of dppe (see Figure 2) confirm that there is no plane of symmetry through the diphosphine ligand. Non-planarity of such a ring is expected but the barrier to inversion is higher than normal for this ligand. The inversion process can, however, be observed in the spectra shown in Figures 1 and 2; coalescence between −80 and −20 °C shows that a time-averaged plane of symmetry is generated by ring flipping. The Scheme shows that this process (A) leads to exchange of carbonyl ligands a and b and methylene protons f and g. The carbonyls c—e are unaffected. At −20 °C the onset of another process which broadens signal d occurs (Figure 1). At 25 °C all carbonyl signals except those for c and e are broad. These further coalescences are readily explained by a second process (B) (Scheme) which is a delocalised merry-go-round CO exchange over the two bridged Os atoms. Normally this is the fastest process in dodecacarbonyltriosmium and its substituted derivatives. Compound (**1**) gives a single ^{31}P-{^1H} n.m.r. singlet down to −130 °C consistent with the molecule having C_2 symmetry as shown in the Scheme. For the clusters 1,2-[$Os_3(CO)_{10}${$Ph_2P(CH_2)_nPPh_2$}] where n = 1, 3, or 4 the ^{13}C n.m.r. spectra give no evidence for freezing-out of inversions of rings formed by the bridging diphosphine ligands.[7]

The single-crystal *X*-ray structure of compound (**1**) was determined to establish the conformation of the dppe bridge

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* 1,2-μ-[1′,2′-Bis(diphenylphosphino)ethane]-1,1,1,2,2,2,3,3,3,3-decacarbonyl-*triangulo*-triosmium and 1,2-μ-[1′,2′-bis(diphenylphosphino)ethane]-1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-μ-hydrido-*triangulo*-triosmium hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

† Throughout this paper the numbers prefixing formulae of complexes indicate the metal atoms to which the diphosphine ligands are bonded.

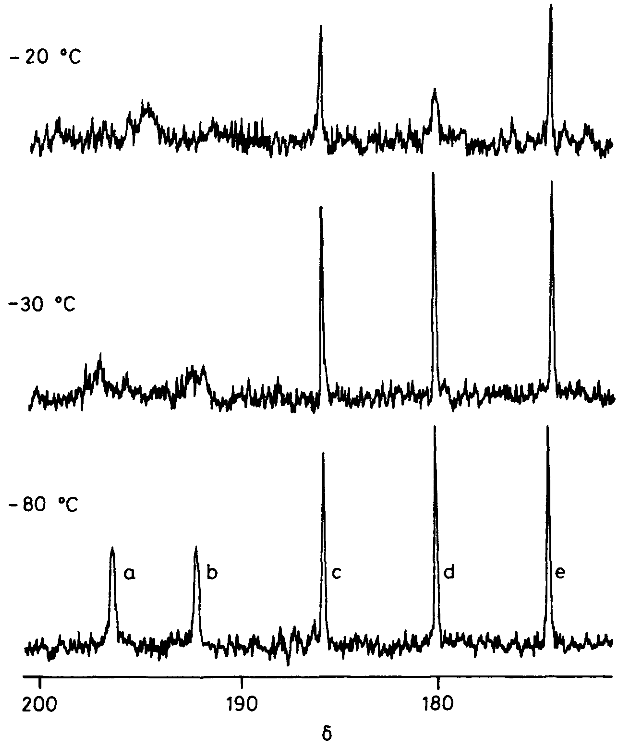


Figure 1. $^{13}C-\{^1H\}$ N.m.r. spectra of dichloromethane solutions of 1,2-[$Os_3(CO)_{10}$(dppe)] (**1**). The assignments relate to the left-hand molecules in the Scheme

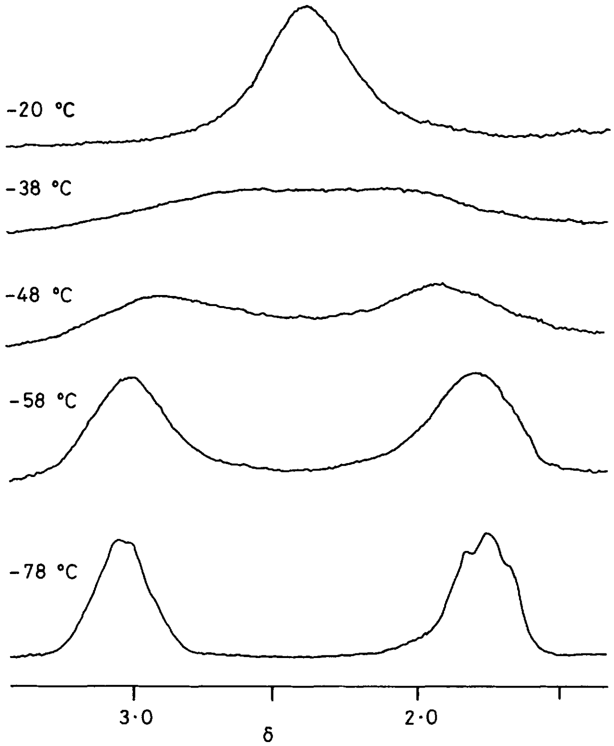


Figure 2. Proton n.m.r. spectra for CD_2Cl_2 solutions of 1,2-[$Os_3(CO)_{10}$(dppe)] (**1**) showing the methylene signals of the dppe ligand

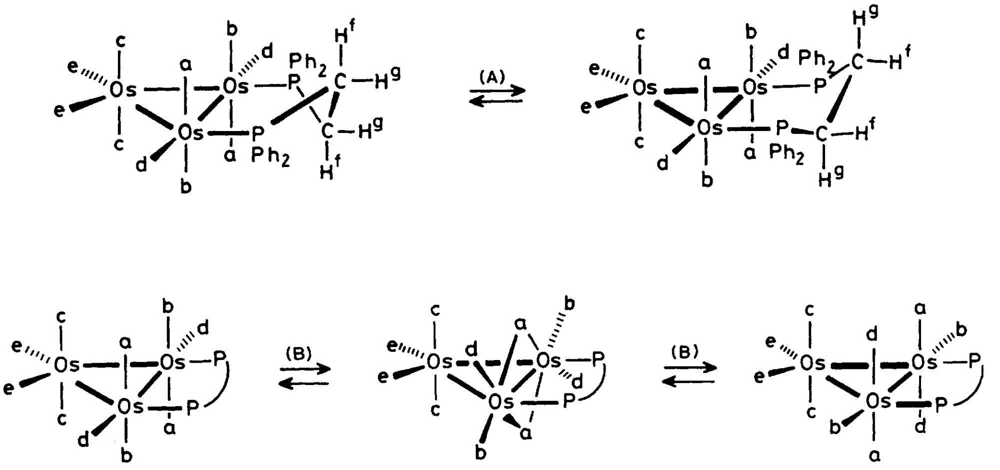
Table 1. Selected bond lengths (Å) and angles (°) for [$Os_3(CO)_{10}$(dppe)] (**1**)

Os(1)–Os(2)	2.891(1)	Os(1)–P(1)	2.328(3)
Os(2)–Os(3)	2.878(1)	Os(2)–P(2)	2.333(3)
Os(1)–Os(3)	2.871(1)		
		P(1)–C(1)	1.81(1)
C(1)–C(2)	1.59(1)	P(1)–C(111)	1.82(1)
		P(1)–C(121)	1.83(1)
		P(2)–C(2)	1.83(3)
		P(2)–C(211)	1.82(1)
Os–C (carbonyl)	1.92(1) (mean)	P(2)–C(221)	1.86(1)
C–O (carbonyl)	1.14(2) (mean)		
Phenyl rings			
C–C (ring 111)	1.40(2)	C–C (ring 211)	1.40(2)
C–C (ring 121)	1.40(2)	C–C (ring 221)	1.39(2)
Os(3)–Os(1)–Os(2)	59.9(1)	P(1)–Os(1)–Os(3)	158.3(1)
Os(2)–Os(3)–Os(1)	60.4(1)	P(1)–Os(1)–Os(2)	101.2(1)
Os(3)–Os(2)–Os(1)	59.7(1)	P(2)–Os(2)–Os(3)	156.3(1)
		P(2)–Os(2)–Os(1)	100.5(1)
C(1)–P(1)–Os(1)	116.6(3)		
C(111)–P(1)–Os(1)	112.8(4)	C(1)–C(2)–P(2)	111.9(7)
C(121)–P(1)–Os(1)	117.5(4)	C(2)–C(1)–P(1)	111.1(9)
C(2)–P(2)–Os(2)	116.3(4)		
C(211)–P(2)–Os(2)	118.4(4)		
C(221)–P(2)–Os(2)	113.9(4)		

and how this relates to the geometry of the cluster as a whole. We also wished to compare the geometry to that of the protonated form (see later). Selected bond lengths and angles are in Table 1, while Figure 3 shows the molecular structure. The 1,2 configuration is established and the structure is closely similar to that of 1,2-[$Ru_3(CO)_{10}$(dppe)].[4] The bridged Os(1)–Os(2) distance of 2.891(1) Å is slightly longer than the non-bridged ones [2.871(1) and 2.878(1) Å] which are similar to the Os–Os distance in [$Os_3(CO)_{12}$] (2.877 Å).[8] Bridging the metal atoms by $Ph_2PCH_2PPh_2$ (dppm) in the clusters 1,2-[$Ru_3(CO)_{10}$(dppm)][9] and [$Ru_3(CO)_8(dppm)_2$][10] leads to shorter Ru–Ru distances than for the unbridged ones.

The main features of the structure are the non-planarity of the Os(1)P(1)C(1)C(2)P(2)Os(2) ring and how the chirality of this arrangement is linked to the chirality of the cluster as a whole which results from the screwed arrangement of the carbonyl framework. 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. The metal–metal directions are less important in defining the co-ordination geometries than the metal–ligand directions. This type of distortion is common and appears to a small extent in the structure of [$Os_3(CO)_{12}$][8] but is particularly pronounced in this compound. Transfer of axial ligands between metal atoms by a delocalised conical rotation not affecting the equatorial CO ligands, which would relate to this screw distortion, has been discussed.[9–11] This process is slow even in [$Ru_3(CO)_{10}$(dppm)] and we did not examine high-temperature ^{13}C n.m.r. spectra from which this might be apparent.

1,2-[$Os_3H(CO)_{10}$(dppe)][PF_6].—Addition of an excess of CF_3CO_2H to a $CDCl_3$ solution of compound (**1**) at −50 °C gave immediately a ^1H n.m.r. spectrum containing two hydride signals: δ −19.48 (d, J_{PH} = 14.3 Hz) and −21.31 (t, J_{PH} = 17.0 Hz). The doublet signal was the minor component and became



Scheme.

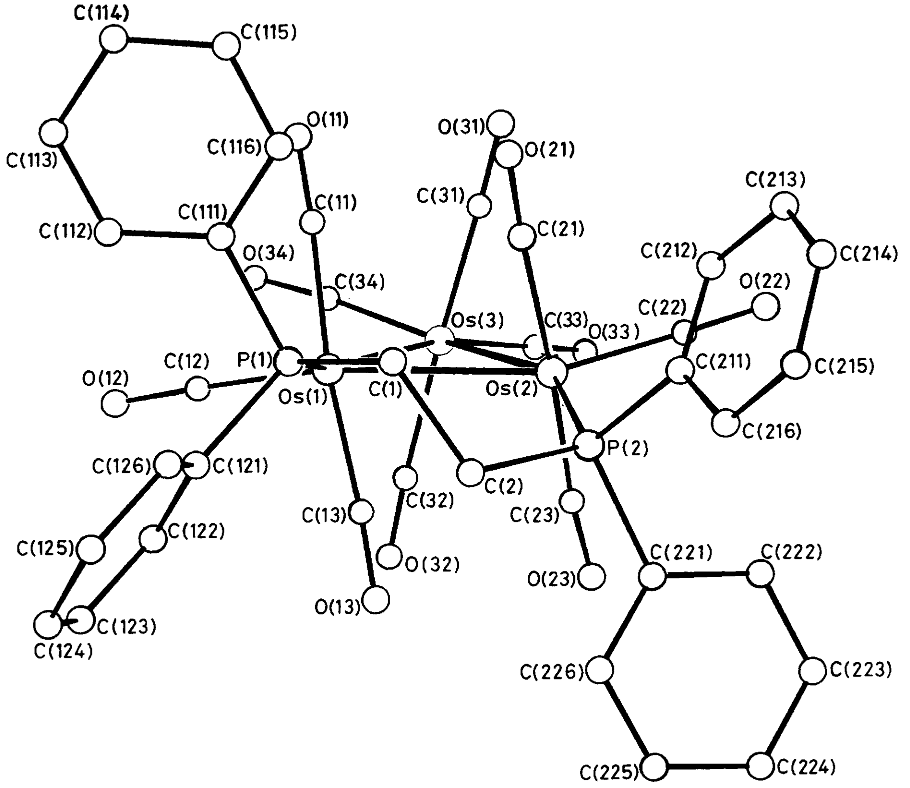


Figure 3. Molecular structure of 1,2-[$Os_3(CO)_{10}$(dppe)] (**1**)

even weaker on warming the solution to 22 °C for 48 h. The isolated salt 1,2-[$Os_3H(CO)_{10}$(dppe)][PF_6] (**2**), when redissolved in $CDCl_3$, gave only the triplet signal at δ −21.31. We believe that the hydride doublet results from a species with the hydride spanning one of the Os–Os edges not bridged by dppe. On the other hand the isolated cation (**2**) has the hydride and the dppe ligand bridging the same edge. The ^1H n.m.r. spectrum of (**2**) in $CDCl_3$ at −79 °C contains two equal-intensity multiplets for the CH_2CH_2 group (δ 2.23 and 4.60) which coalesce at about 10 °C to give a broad singlet (δ 3.5) at 25 °C. As for the parent cluster (**1**), we assign this as a ring-flipping process but this is somewhat slower for the protonated compound (**2**).

The single-crystal molecular structures of the two independent molecules (a and b) of [$Os_3H(CO)_{10}$(dppe)][PF_6] (**2**) in the unit cell are shown in Figures 4 and 5. Selected bond lengths and angles for molecules a and b are given in Table 2. The geometries of molecules a and b are very similar although there is an approximately 90° rotation of the phenyl ring C(211)—C(216) about the P–Ph bond on going from one molecule to the other. The bridging hydride ligand was not located in either molecule but the structures are consistent with this ligand bridging Os(1) and Os(2). The positions shown in Figures 4 and 5 were calculated by minimising repulsions to the adjacent ligands and may be regarded as approximately correct (see Experimental section). One effect of protonation is to increase all Os–Os distances but especially that of Os(1)–Os(2) [3.058(1) and 3.060(1) Å for molecules a and b respectively]. The other major effect is to remove the screw distortion found for compound (**1**); the axial OC–Os–CO directions are closely perpendicular to the Os_3 plane in (**2**) and the equatorial ligands lie in this plane. Figure 6 shows projections through the bridged metal atoms, Os(1) and Os(2), showing how the essentially eclipsed arrangement in cluster (**2**) [Figure 6(*b*)] compares with the significant distortion found in (**1**) [Figure 6(*a*)] which has torsional angles about the Os(1)–Os(2) pair of atoms of around 27°. We can see that this eclipsed geometry about the Os(1)–Os(2) pair results in the phenyl groups being eclipsed as well and these are positioned equally above and below the Os_3 plane. In contrast the phenyl groups in compound (**1**) adopt distinctly axial and equatorial positions.

We believe that the differences shown in Figure 6 result from a necessity for the bridging hydride ligand in compound (**2**) to occupy a particular co-ordination site at the metal atoms to which it is bonded. Thus the ligands C(12)O(12) and C(22)O(22) orientate to be *trans* to the hydride and hence must lie in the metal plane. This produces the essentially eclipsed configuration shown in Figure 6(*b*). The differences between

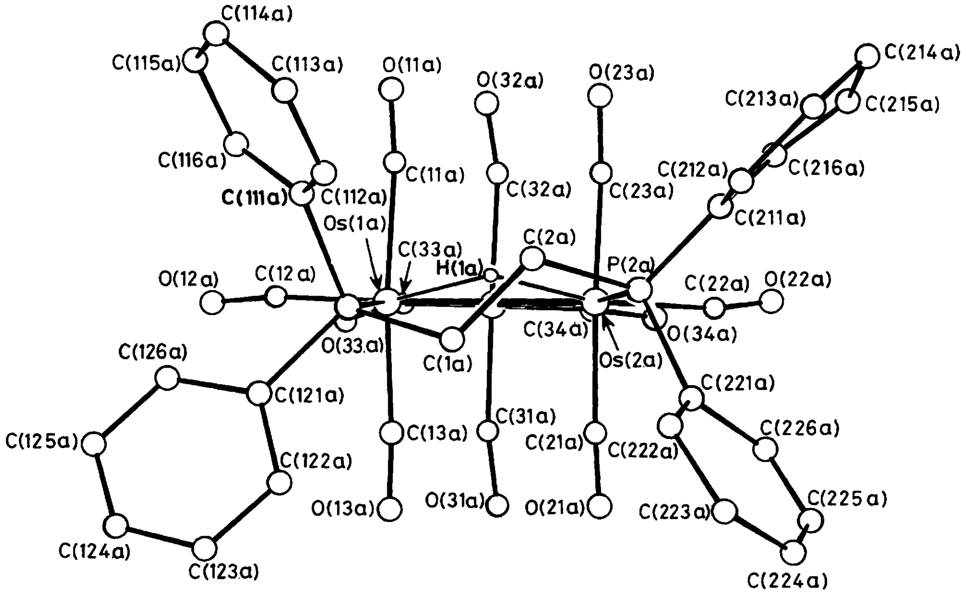


Figure 4. Molecular structure of 1,2-$[Os_3H(CO)_{10}(dppe)][PF_6]$ (**2**), molecule a

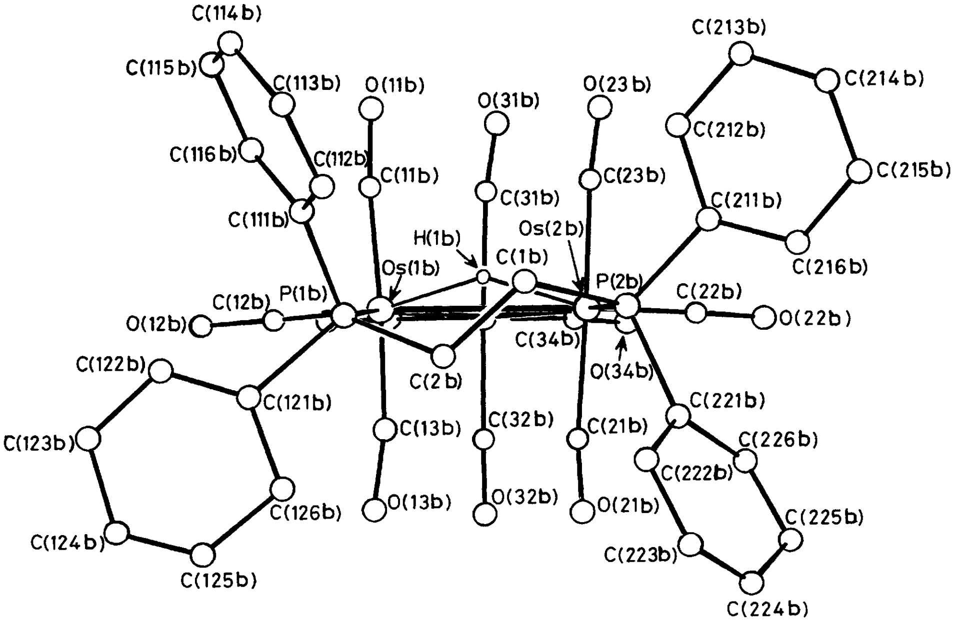


Figure 5. Molecular structure of 1,2-$[Os_3H(CO)_{10}(dppe)][PF_6]$ (**2**), molecule b

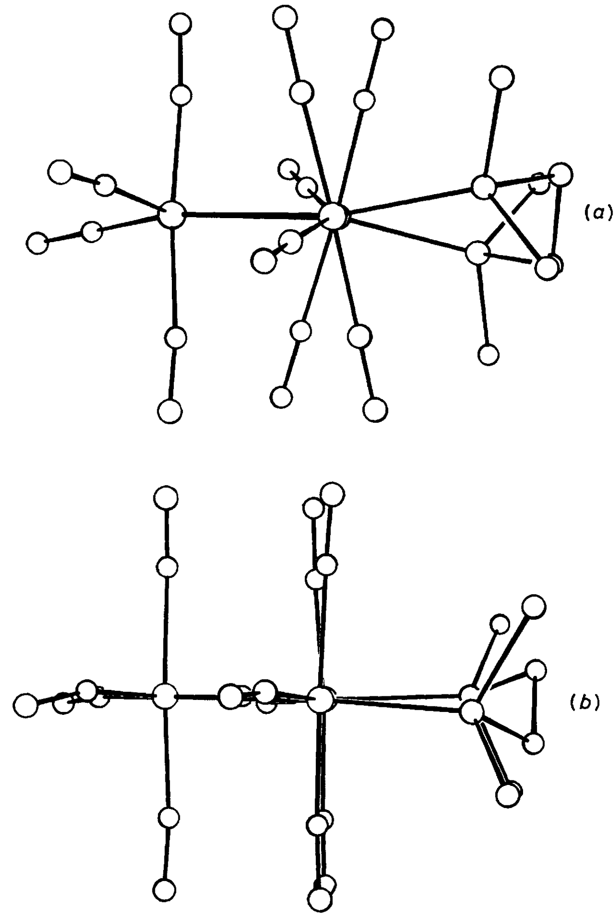


Figure 6. Projections perpendicular to the Os(1)–Os(2) direction for compounds (**1**) (*a*) and (**2**) (molecule a) (*b*)

Table 2. Selected bond lengths (Å) and angles (°) for $[Os_3H(CO)_{10}(dppe)][PF_6]$ (**2**)

Molecule a		Molecule b	
Os(1a)–Os(2a)	3.058(1)	Os(1b)–Os(2b)	3.060(1)
Os(1a)–Os(3a)	2.896(1)	Os(1b)–Os(3b)	2.890(1)
Os(2a)–Os(3a)	2.893(1)	Os(2b)–Os(3b)	2.895(1)
Os(1a)–P(1a)	2.371(5)	Os(1b)–P(1b)	2.373(5)
Os(2a)–P(2a)	2.378(5)	Os(2b)–P(2b)	2.376(5)
P(1a)–C(1a)	1.87(2)	P(1b)–C(1b)	1.83(2)
P(2a)–C(2a)	1.85(2)	P(2b)–C(2b)	1.87(2)
P(1a)–C(111a)	1.82(2)	P(1b)–C(111b)	1.85(2)
P(1a)–C(121a)	1.80(2)	P(1b)–C(121b)	1.82(2)
P(2a)–C(211a)	1.84(2)	P(2b)–C(211b)	1.80(2)
P(2a)–C(221a)	1.83(2)	P(2b)–C(221b)	1.84(3)
C(1a)–C(2a)	1.56(3)	C(1b)–C(2b)	1.57(3)
Os–C (carbonyl) (mean)	1.92(2)		1.89(3)
C–O (carbonyl) (mean)	1.13(3)		1.16(3)
Phenyl rings (mean values)			
C–C (ring 11)	1.40(3)		1.40(4)
C–C (ring 12)	1.41(4)		1.41(4)
C–C (ring 21)	1.41(3)		1.41(3)
C–C (ring 22)	1.40(3)		1.40(4)
P–F (PF_6 ions)	1.56(2)		1.58(2)
Os(3a)–Os(1a)–Os(2a)	58.1(1)	Os(3b)–Os(1b)–Os(2b)	58.1(1)
Os(3a)–Os(2a)–Os(1a)	58.2(2)	Os(3b)–Os(2b)–Os(1b)	58.0(1)
Os(1a)–Os(3a)–Os(2a)	63.8(1)	Os(1b)–Os(3b)–Os(2b)	63.9(1)
Os(1a)–Os(2a)–P(2a)	103.7(1)	Os(1b)–Os(2b)–P(2b)	103.6(1)
Os(2a)–Os(1a)–P(1a)	102.7(1)	Os(2b)–Os(1b)–P(1b)	101.9(1)
P(1a)–Os(1a)–C(12a)	101.7(7)	P(1b)–Os(1b)–C(12b)	100(1)
P(2a)–Os(2a)–C(22a)	103.8(8)	P(2b)–Os(2b)–C(22b)	101.4(7)

compounds (**1**) and (**2**) do not appear to arise from an increase in the Os(1)Os(2)P(2) and Os(2)Os(1)P(1) angles on protonation since these increase from an average of 100.9 to an average of 103.0° on protonation, a very small difference. The increased Os(1)–Os(2) distance in (**2**) would, however, have the effect of prizing the PPh_2 groups apart and possibly reducing flexibility in the OsPCCPOs ring which might favour a more closely planar Os_2P_2 set of atoms.

In spite of the CH_2CH_2 group in (**2**) being the only set of atoms that remove molecular C_{2v} symmetry, we have found that the rates of ring inversion in (**2**) are somewhat slower than in (**1**) (see above).

Experimental

I.r. spectra were recorded of solutions in CaF_2 cells on a Perkin-Elmer PE983 spectrometer. N.m.r. spectra (Varian XL200) were recorded with chemical shifts relative to $P(OMe)_3$ (^{31}P) or $SiMe_4$ (^1H, ^{13}C), ^{13}C n.m.r. spectra (natural abundance) for solutions containing *ca.* 0.05 mol dm^{-3} $[Cr(acac)_3]$ (acac = acetylacetonate) as a shiftless relaxation reagent. The starting cluster $[Os_3(CO)_{10}(MeCN)_2]$ was prepared as reported[12] and dppe was purchased from Strem Chemicals Inc.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with* $Ph_2PCH_2CH_2PPh_2$ (dppe).—A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.288 g) and dppe (0.185 g, 1 mol per mol Os_3) in chloroform (40 cm^3) was refluxed under nitrogen for 3 h. The solvent was removed under vacuum and the residue separated by t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (10:3 v/v)] to give $[Os_3(CO)_{11}(dppe\text{-}P)]$ as yellow crystals from hexane (0.040 g, 10%) {possibly derived from $[Os_3(CO)_{11}(MeCN)]$ impurity in $[Os_3(CO)_{10}(MeCN)_2]$} (Found: C, 35.25; H, 2.15; P, 4.8. $C_{37}H_{24}O_{11}Os_3P_2$ requires C, 34.8; H, 1.9; P, 4.85%), ν(CO) (cyclo-C_6H_{12}) at 2 106w, 2 052s, 2 033s, 2 017s, 2 000w 1 987m, 1 976w, and 1 957w cm^{-1}; $^{31}P\text{-}\{^1H\}$ n.m.r. ($CDCl_3$) δ −154.0 (d) and −147.0 (d) (J = 39.1 Hz). The compound 1,2-$[Os_3(CO)_{10}(\mu\text{-dppe})]$ (**1**) was obtained as yellow crystals (0.250 g, 43%) from pentane–dichloromethane mixtures (Found: C, 34.65; H, 1.85; P, 4.9. $C_{36}H_{24}O_{10}Os_3P_2$ requires C, 34.6; H, 1.95; P, 4.95%), ν(CO) (cyclo-C_6H_{12}) at 2 086m, 2 023m, 2 013vs, 1 999vs, 1 974m, 1 958m, 1 941w, and 1 932w cm^{-1}. N.m.r.: $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ −138.6 (s); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$, −20 °C), 194.1 (s), 185.9 (s), 180.1 (s), 174.5 (s) (CO signals, intensity ratio 2:1:1:1); ^1H (CD_2Cl_2, −78 °C), 3.08 (m) and 1.80 (m) (CH_2 signals). The compound 1,2-$[Os_3(CO)_{10}(dppe\text{-}P)_2]$ was obtained as red crystals from hexane (0.027 g, 5%) (Found: C, 44.75; H, 3.05; P, 7.5. $C_{62}H_{48}O_{10}Os_3P_4$ requires C, 45.2; H, 2.95; P, 7.5%), ν(CO) (cyclo-C_6H_{12}) at 2 082w, 2 025s, 2 010 (sh), 1 997vs, 1 965m, and 1 953 (sh) cm^{-1}.

Protonation of 1,2-$[Os_3(CO)_{10}(\mu\text{-dppe})]$ (**1**).—Trifluoroacetic acid (0.040 cm^3, 16 mol per mol Os_3) was added to an orange-yellow solution of compound (**1**) (0.040 g) in $CDCl_3$ (0.5

Table 3. Fractional atomic co-ordinates for [$Os_3(CO)_{10}$(dppe)] (**1**)

Atom	*x*	*y*	*z*
Os(1)	0.236 26(2)	0.307 19(3)	0.148 41(4)
Os(2)	0.301 69(3)	0.088 18(4)	0.022 94(4)
Os(3)	0.318 30(3)	0.269 36(4)	−0.109 08(5)
P(1)	0.206 4(2)	0.298 4(2)	0.364 3(3)
P(2)	0.236 7(2)	−0.033 2(2)	0.154 3(3)
C(11)	0.341 9(7)	0.424 7(10)	0.205 8(11)
O(11)	0.402 2(5)	0.497 4(7)	0.244 9(10)
C(12)	0.187 6(6)	0.439 0(9)	0.162 5(11)
O(12)	0.155 6(5)	0.516 6(7)	0.170 1(10)
C(13)	0.139 3(7)	0.176 6(9)	0.077 0(11)
O(13)	0.077 9(5)	0.104 7(7)	0.039 6(9)
C(21)	0.383 3(6)	0.193 3(10)	0.157 8(13)
O(21)	0.433 4(5)	0.248 6(7)	0.237 2(10)
C(22)	0.375 9(7)	−0.009 9(10)	−0.072 3(13)
O(22)	0.423 2(6)	−0.064 6(9)	−0.126 7(12)
C(23)	0.219 1(8)	−0.005 0(11)	−0.115 7(13)
O(23)	0.174 0(7)	−0.066 3(9)	−0.199 5(10)
C(31)	0.430 2(8)	0.314 9(12)	−0.038 3(13)
O(31)	0.497 0(6)	0.347 2(10)	−0.003 2(12)
C(32)	0.202 8(9)	0.211 1(13)	−0.169 6(12)
O(32)	0.138 8(6)	0.179 0(11)	−0.214 3(11)
C(33)	0.358 8(9)	0.196 1(14)	−0.283 9(14)
O(33)	0.382 5(7)	0.159 2(12)	−0.393 7(11)
C(34)	0.322 1(8)	0.434 6(12)	−0.094 5(13)
O(34)	0.323 2(7)	0.534 3(9)	−0.088 0(12)
C(1)	0.224 7(7)	0.165 2(9)	0.395 3(11)
C(2)	0.172 6(7)	0.038 7(9)	0.295 8(11)
C(111)	0.270 1(7)	0.428 6(9)	0.491 4(10)
C(112)	0.241 9(7)	0.539 1(9)	0.544 2(11)
C(113)	0.295 3(8)	0.646 0(11)	0.632 0(13)
C(114)	0.374 4(8)	0.638 3(12)	0.663 3(14)
C(115)	0.399 2(8)	0.527 9(13)	0.611 3(14)
C(116)	0.347 5(8)	0.424 6(11)	0.525 9(12)
C(121)	0.099 7(6)	0.300 7(9)	0.429 1(11)
C(122)	0.040 4(7)	0.311 1(11)	0.353 2(13)
C(123)	−0.041 1(8)	0.314 1(13)	0.405 7(13)
C(124)	−0.061 8(8)	0.309 3(13)	0.533 6(15)
C(125)	−0.002 2(9)	0.298 0(14)	0.609 7(14)
C(126)	0.080 7(8)	0.295 7(12)	0.558 3(13)
C(211)	0.301 7(7)	−0.090 1(9)	0.235 9(12)
C(212)	0.388 3(7)	−0.048 6(11)	0.237 0(14)
C(213)	0.438 6(9)	−0.092 0(14)	0.304 6(16)
C(214)	0.398 6(10)	−0.175 3(15)	0.371 5(18)
C(215)	0.309 6(10)	−0.222 1(16)	0.363 2(20)
C(216)	0.264 9(8)	−0.182 2(15)	0.290 9(18)
C(221)	0.161 0(6)	−0.177 6(8)	0.061 5(11)
C(222)	0.199 0(7)	−0.271 4(10)	−0.030 7(13)
C(223)	0.145 1(8)	−0.381 5(11)	−0.103 9(14)
C(224)	0.057 0(8)	−0.397 8(10)	−0.089 3(12)
C(225)	0.024 8(7)	−0.303 4(12)	−0.001 1(14)
C(226)	0.078 2(7)	−0.192 4(10)	0.073 3(12)

Table 4. Fractional atomic co-ordinates for [$Os_3H(CO)_{10}$(dppe)][PF_6] (**2**)

Atom	*x*	*y*	*z*
Os(1a)	0.147 60(4)	0.379 10(5)	0.046 22(3)
Os(2a)	0.080 98(4)	0.208 90(5)	0.014 62(3)
Os(3a)	0.089 02(5)	0.331 50(5)	−0.056 28(3)
P(1a)	0.175 7(2)	0.375 5(3)	0.132 8(2)
P(2a)	0.096 8(3)	0.140 4(3)	0.090 4(2)
Os(1b)	0.421 72(4)	−0.203 85(5)	−0.044 11(3)
Os(2b)	0.331 15(4)	−0.362 28(5)	−0.074 08(3)
Os(3b)	0.413 67(5)	−0.324 69(6)	0.027 59(3)
P(1b)	0.410 5(3)	−0.144 8(3)	−0.121 7(2)
P(2b)	0.284 2(3)	−0.354 6(3)	−0.161 3(2)
P(3a)	0.625 1(4)	0.191 6(5)	0.316 3(2)
F(1a)	0.633 1(11)	0.114 4(11)	0.286 8(6)
F(2a)	0.559 6(8)	0.152 7(10)	0.331 1(5)
F(3a)	0.685 4(10)	0.156 2(12)	0.363 2(5)
F(4a)	0.690 3(8)	0.232 4(10)	0.300 3(6)
F(5a)	0.622 4(10)	0.267 4(12)	0.348 2(6)
F(6a)	0.567 6(8)	0.229 1(13)	0.270 0(5)
P(3b)	0.164 4(4)	0.186 4(4)	0.298 5(2)
F(1b)	0.171 6(8)	0.128 2(8)	0.256 1(4)
F(2b)	0.133 3(9)	0.257 1(9)	0.258 3(4)
F(3b)	0.193 8(9)	0.115 3(9)	0.337 0(5)
F(4b)	0.157 3(8)	0.245 9(9)	0.339 5(4)
F(5b)	0.081 7(9)	0.157 3(10)	0.289 0(6)
F(6b)	0.246 2(8)	0.217 9(10)	0.306 4(6)
C(11a)	0.244 4(12)	0.337 1(16)	0.048 6(8)
O(11a)	0.302 7(10)	0.315 4(13)	0.053 6(7)
C(12a)	0.180 3(12)	0.489 0(16)	0.036 3(8)
O(12a)	0.197 7(8)	0.553 8(11)	0.029 1(6)
C(13a)	0.048 8(9)	0.417 5(12)	0.042 1(6)
O(13a)	−0.008 2(7)	0.441 3(9)	0.043 0(5)
C(21a)	0.175 1(11)	0.170 2(14)	0.011 5(7)
O(21a)	0.232 1(9)	0.145 2(11)	0.010 9(6)
C(22a)	0.032 6(12)	0.131 5(17)	−0.032 8(9)
O(22a)	0.003 0(9)	0.087 7(13)	−0.064 2(6)
C(23a)	−0.017 9(11)	0.249 0(14)	0.011 7(7)
O(23a)	−0.074 8(8)	0.266 6(11)	0.011 9(6)
C(31a)	−0.011 4(11)	0.367 0(14)	−0.059 3(7)
O(31a)	−0.069 1(8)	0.387 4(10)	−0.062 7(5)
C(32a)	0.189 8(11)	0.295 9(15)	−0.054 9(7)
O(32a)	0.246 0(8)	0.278 3(11)	−0.055 2(5)
C(211a)	0.143 0(10)	0.039 4(13)	0.098 8(7)
C(212a)	0.161 8(10)	0.003 0(14)	0.145 2(7)
C(213a)	0.195 6(11)	−0.075 3(16)	0.152 3(8)
C(214a)	0.204 0(12)	−0.118 5(17)	0.112 5(9)
C(215a)	0.182 9(12)	−0.082 9(16)	0.067 0(8)
C(216a)	0.151 1(10)	−0.002 3(15)	0.059 1(7)
C(221a)	0.012 6(9)	0.121 8(13)	0.107 0(6)
C(222a)	0.012 6(10)	0.129 6(13)	0.155 5(7)
C(223a)	−0.049 8(11)	0.104 5(15)	0.167 0(8)
C(224a)	−0.113 9(12)	0.076 8(16)	0.131 4(8)
C(225a)	−0.114 7(12)	0.067 3(16)	0.082 9(9)
C(226a)	−0.051 6(11)	0.091 9(14)	0.069 5(7)
C(11b)	0.341 6(13)	−0.148 0(17)	−0.032 2(8)
O(11b)	0.290 9(9)	−0.115 1(12)	−0.025 4(6)
C(12b)	0.486 6(17)	−0.125 0(21)	−0.001 8(11)
O(12b)	0.532 2(16)	−0.082 1(20)	0.021 8(10)
C(13b)	0.502 9(16)	−0.259 4(20)	−0.049 4(10)
O(13b)	0.560 2(12)	−0.288 6(15)	−0.050 8(8)
C(21b)	0.418 6(13)	−0.412 1(16)	−0.080 0(8)
O(21b)	0.470 7(9)	−0.445 0(12)	−0.085 8(6)
C(22b)	0.295 4(12)	−0.466 5(17)	−0.062 8(8)
O(22b)	0.279 0(9)	−0.530 9(13)	−0.052 1(6)
C(23b)	0.244 4(12)	−0.316 4(16)	−0.067 1(8)
O(23b)	0.186 4(9)	−0.289 6(12)	−0.066 1(6)
C(31b)	0.324 4(12)	−0.273 2(15)	0.034 7(8)
O(31b)	0.270 7(8)	−0.247 6(11)	0.038 4(6)
C(32b)	0.500 0(12)	−0.378 2(15)	0.020 5(8)
O(32b)	0.554 4(9)	−0.412 9(12)	0.020 8(6)
C(33b)	0.473 8(14)	−0.265 9(18)	0.083 3(10)
O(33b)	0.513 0(11)	−0.228 5(14)	0.114 1(7)
C(34b)	0.391 7(12)	−0.419 7(18)	0.057 1(9)
O(34b)	0.377 1(9)	−0.476 8(12)	0.075 4(6)
C(1b)	0.381 8(10)	−0.221 2(13)	−0.170 6(7)
C(2b)	0.297 9(10)	−0.250 0(13)	−0.184 1(7)
C(111b)	0.345 2(10)	−0.057 8(14)	−0.142 2(7)
C(112b)	0.309 0(14)	−0.047 4(19)	−0.193 0(9)
C(113b)	0.259 4(16)	0.021 4(22)	−0.205 7(11)
C(114b)	0.251 0(16)	0.075 5(21)	−0.170 1(11)
C(115b)	0.290 5(13)	0.064 3(17)	−0.121 4(9)
C(116b)	0.338 4(10)	−0.003 9(15)	−0.105 9(7)

Table 4 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(33a)	0.103 8(12)	0.432 8(16)	−0.086 1(8)	C(121b)	0.498 6(11)	−0.106 6(16)	−0.126 8(8)
O(33a)	0.112 0(8)	0.493 1(12)	−0.103 8(6)	C(122b)	0.520 6(14)	−0.023 1(19)	−0.114 1(9)
C(34a)	0.044 0(12)	0.267 3(16)	−0.112 6(8)	C(123b)	0.593 8(16)	0.002 4(21)	−0.116 5(10)
O(34a)	0.010 6(9)	0.225 2(12)	−0.144 5(6)	C(124b)	0.638 6(14)	−0.049 5(20)	−0.129 0(10)
C(1a)	0.126 8(10)	0.286 4(13)	0.149 6(7)	C(125b)	0.616 4(15)	−0.131 6(21)	−0.142 9(10)
C(2a)	0.159 3(9)	0.201 7(13)	0.141 6(6)	C(126b)	0.544 3(14)	−0.161 4(19)	−0.142 3(10)
C(111a)	0.273 3(9)	0.362 6(13)	0.170 5(6)	C(211b)	0.185 4(9)	−0.366 1(13)	−0.192 5(7)
C(112a)	0.291 3(11)	0.316 5(15)	0.214 1(8)	C(212b)	0.133 1(13)	−0.304 3(17)	−0.188 9(9)
C(113a)	0.368 6(13)	0.314 4(17)	0.244 9(9)	C(213b)	0.055 2(13)	−0.311 9(17)	−0.215 9(9)
C(114a)	0.423 3(14)	0.351 9(19)	0.231 1(10)	C(214b)	0.030 0(12)	−0.378 0(16)	−0.248 1(8)
C(115a)	0.404 2(13)	0.400 9(17)	0.187 8(9)	C(215b)	0.079 4(13)	−0.440 0(17)	−0.249 6(9)
C(116a)	0.329 6(12)	0.406 2(16)	0.158 6(8)	C(216b)	0.157 1(13)	−0.433 3(18)	−0.222 7(9)
C(121a)	0.142 5(9)	0.462 4(13)	0.158 3(6)	C(221b)	0.328 7(11)	−0.427 2(15)	−0.192 2(7)
C(122a)	0.077 5(11)	0.458 7(16)	0.171 8(8)	C(222b)	0.354 4(10)	−0.401 2(14)	−0.230 1(7)
C(123a)	0.053 5(12)	0.533 2(16)	0.190 2(8)	C(223b)	0.391 6(13)	−0.460 2(18)	−0.250 6(9)
C(124a)	0.098 3(12)	0.604 6(17)	0.197 1(8)	C(224b)	0.403 9(14)	−0.535 9(20)	−0.232 2(10)
C(125a)	0.158 9(12)	0.605 7(17)	0.183 0(8)	C(225b)	0.372 3(14)	−0.566 8(19)	−0.197 7(10)
C(126a)	0.183 0(11)	0.535 2(15)	0.163 8(7)	C(226b)	0.339 0(13)	−0.508 8(18)	−0.173 4(9)

cm^3) at −50 °C. The ^{1}H n.m.r. spectrum showed the immediate formation of two hydrido-species [δ −19.48 (d) and −21.31 (t)]. The solvent was removed under vacuum after 48 h, the residue dissolved in methanol, and a methanolic solution of NH_4PF_6 (0.008 g) added followed by a few drops of water to give a pale yellow precipitate. Extraction of this with dichloromethane and recrystallisation from dichloromethane–diethyl ether mixtures gave 1,2-[$Os_3H(CO)_{10}$(μ-dppe)][PF_6] (**2**) (0.27 g, 60%) as pale yellow crystals (Found: C, 30.9; H, 1.85; P, 6.8. $C_{36}H_{25}F_6O_{10}Os_3P_3$ requires C, 31.0; H, 1.85; P, 6.65%), ν(CO) (CH_2Cl_2) at 2 121m, 2 078vs, 2 068ms, 2 038vs, and 2 020vs cm^{-1}; ^{1}H n.m.r. (CD_2Cl_2, −79 °C), δ 2.23 (m, CH_2), 4.60 (m, CH_2), 7.49 (m, Ph), and −21.32 (t, OsH, J_{PH} = 17.0 Hz).

Crystallographic Studies.—*Crystal data for* [$Os_3(CO)_{10}$(dppe)] (**1**). $C_{36}H_{24}O_{10}Os_3P_2$, $M = 1\,249.1$, triclinic, $a = 16.558(3)$, $b = 11.777(3)$, $c = 10.617(2)$ Å, $\alpha = 110.19(3)$, $\beta = 84.27(2)$, $\gamma = 104.70(3)°$, $U = 1\,879.4$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 2.21$ g cm^{-3}, $F(000) = 1\,155.9$, μ(Mo-K_α) = 98.38 cm^{-1}, $\lambda = 0.710\,69$ Å.

Crystal data for [$Os_3H(CO)_{10}$(dppe)][PF_6] (**2**). $C_{36}H_{25}F_6O_{10}Os_3P_3$, $M = 1\,395.1$, monoclinic, $a = 18.856(3)$, $b = 16.294(3)$, $c = 28.747(5)$ Å, $\beta = 108.96(3)°$, $U = 8\,353.0$ Å^3, space group $P2_1/c$, $Z = 8$, $D_c = 2.22$ g cm^{-3}, $F(000) = 5\,183.5$, μ(Mo-K_α) = 89.13 cm^{-1}, $\lambda = 0.710\,69$ Å.

Data collection. Unit-cell parameters and intensity data for both structures were collected at room temperature on a Phillips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation in the range $3 \leqslant \theta \leqslant 25°$. The method of data collection and processing was similar to that described previously.[13] A semi-empirical absorption correction based on a pseudo-ellipsoid model[14] was applied to each data set; 370 azimuthal scan data from 10 independent reflections for each crystal gave relative transmission factors of 1.00—0.415 for compound (**1**) and 1.00—0.200 for compound (**2**). Equivalent reflections were merged to give 5 422 and 8 127 unique data with $I \geqslant 3\sigma(I)$ for (**1**) and (**2**) respectively.

Structure solution and refinement.[15] For both compounds the Os atoms in the asymmetric unit [two unique molecules per asymmetric unit for compound (**2**)] were located from a Patterson map. All remaining non-hydrogen atoms were located by subsequent refinement and Fourier difference synthesis. In compound (**2**) the position of the hydrogen atom bridging Os(1)–Os(2) in each molecule was calculated using the program HYDEX.[16] For compound (**1**), the positions of the methylene hydrogen atoms in the dppe bridge were calculated and then refined as a rigid group with an overall thermal parameter. Complex neutral-atom scattering factors[17] and weights, $w = 1/[\sigma^2(F_o)]$, were used in final refinements. For compound (**2**), blocked, full-matrix least squares with Os, P, F atoms anisotropic, and C and O atoms isotropic; for compound (**1**), blocked, full-matrix least squares with all non-hydrogen atoms anisotropic, and the four methylene hydrogen atoms refined with an isotropic group thermal parameter, riding on their respective C atoms with C–H of 1.08 Å. The final values of R and R' were 0.0438 and 0.0439 for (**1**) and 0.0585 and 0.0570 for (**2**). The final difference maps for each compound contained several residual peaks of *ca.* 2 e Å^{-3} in the vicinity of the osmium atoms and several of *ca.* 1 e Å^{-3} in possible positions for H atoms bonded to phenyl carbon atoms.

Refined atomic positional parameters are in Tables 3 and 4 for compounds (**1**) and (**2**) respectively. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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