Three Isomeric Hydride Compounds formed by Protonation of Decacarbonylbis(dimethylphenylphosphine)triosmium and the *X*-Ray Structures of Two of These: 1,1- and 1,2-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ †

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The compounds 1,1- and 1,2-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ react with trifluoroacetic acid in chloroform to give the singly protonated cations 1,1- and 1,2-$[Os_3(\mu\text{-}H)(CO)_{10}(PMe_2Ph)_2]^+$, isolated in high yields as the hexafluorophosphate salts. The 1,2-isomer exists in solution as two isomers, the major one having equivalent phosphines in adjacent equatorial sites and the minor one having non-equivalent phosphines, which is quite a different isomer distribution from that of the neutral precursor. *X*-Ray crystal structures are reported for 1,1- and 1,2-$[Os_3(\mu\text{-}H)(CO)_{10}(PMe_2Ph)_2]$-$[PF_6]$. The structure of the 1,2-compound corresponds with that of the major isomer in solution. The bridged Os–Os distances are the longest, 3.064(4) and 3.062(4) Å for the two independent cations in the 1,1-isomer and 3.059(4) Å for the 1,2-isomer, and large OsOsC and OsOsP angles are found adjacent to the μ-hydride. Protonation of 1,2-$[Os_3(CO)_{10}L_2]$, where L = PPh_3 or $P(OMe)_3$, and of the 1,2,3- and 1,1,2-isomers of $[Os_3(CO)_9(PMe_2Ph)_3]$ have also been examined. There is a general marked preference for isomers with phosphines *cis* to the bridging hydride.

Yellow solutions of $[Os_3(CO)_{12}]$ in concentrated sulphuric acid contain the $[Os_3H(CO)_{12}]^+$ cation.[1,2] Substitution of carbonyl by tertiary phosphine ligands increases the basicity[1] such that protonation of $[Os_3(CO)_{12-x}L_x]$ (x = 1—3, L = PEt_3 or $PMePh_2$) under the same conditions gives solutions which contain the doubly-protonated species $[Os_3H_2(CO)_{12-x}L_x]^{2+}$. We have recently prepared a new isomer where x = 2, 1,1-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ (**1**),‡ in which both phosphines are co-ordinated to the same metal atom.[3] We have also shown that the previously known 1,2-isomers of $[M_3(CO)_{10}(PR_3)_2]$ (M = Ru or Os, PR_3 = various tertiary phosphines or trimethyl phosphite) exist in solution in two interconverting isomeric forms, (**2b**) and (**2c**), the major having non-equivalent phosphine ligands, the minor having equivalent ones.[3,4] Tachikawa and Shapley[5] have also alluded to the presence of isomers. We set out to examine the behaviour of these isomers towards protonation to see if their relative populations are significantly modified on protonation.

Here we report the protonation of compounds (**1**) and (**2**) and of 1,2,3- and 1,1,2-$[Os_3(CO)_9(PMe_2Ph)_3]$, (**3**) and (**4**), together with the *X*-ray structures of 1,1- and 1,2-$[Os_3(\mu\text{-}H)(CO)_{10}$-$(PMe_2Ph)_2][PF_6]$. The structures of protonated Os_3 clusters of this type are unknown except for a report of that of $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][OsCl_3(CO)_3]$[6] which has axial MeCN unlike the compounds described here with equatorial PMe_2Ph ligands.

Results and Discussion

Addition of a five-fold excess of CF_3CO_2H to a $CDCl_3$ solution of 1,1-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ (**1**) at room temperature gives 1,1-$[Os_3(\mu\text{-}H)(CO)_{10}(PMe_2Ph)_2]^+$ (**5**). The ^1H n.m.r. spectrum indicates a single isomer with a double doublet for the hydride [δ −19.87, J_{PH} 14 (*trans*) and 8 Hz (*cis*)]. The PMe_2Ph ligands, unlike those in (**1**), are different, giving two ^1H n.m.r. (methyl) doublets. However, the ^{31}P n.m.r. spectrum of (**5**) is a singlet (δ 4.98) which must be due to accidental coincidence rather than to exchange effects. The cation (**5**) was isolated in good yield (89%) as 1,1-$[Os_3(\mu\text{-}H)(CO)_{10}(PMe_2Ph)_2][PF_6]$ (see Table 1 and Experimental section).

Similarly the cluster 1,2-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ as a mixture of isomers (**2b**) and (**2c**) is protonated by CF_3CO_2H in $CDCl_3$ to give two isomeric cations 1,2-$[Os_3(\mu\text{-}H)(CO)_{10}$-$(PMe_2Ph)_2]^+$, (**6a**) and (**6b**). In solution the major isomer (**6a**) (90%) has equivalent phosphines with δ(^{31}P) 6.23. Its ^1H n.m.r. spectrum consists of a single methyl doublet and a hydride triple (J_{PH} = 9.3 Hz) implying C_{2v} symmetry. Two possible structures (**6a**) and (**6c**) have this symmetry but (**6a**) is favoured by the fairly low value of J_{PH}, normally associated with the *cis* P–Os–H arrangement. Isomer (**6a**) is in the crystal (see later) and no evidence for (**6c**) has been found.

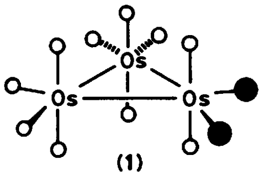
There is a major change in isomer distribution on protonation which we do not properly understand. Not only does the minor isomer (**6b**) (*ca.* 10%) correspond with the major non-protonated form (**2b**) (*ca.* 70%), but the major isomer (**6a**) has no observable non-protonated counterpart. Evidence that the neutral C_{2v} isomer is (**2c**) rather than (**2a**) is based on ^{13}C n.m.r. coalescence behaviour of compounds 1,2-$[M_3(CO)_{10}L_2]$ (M = Ru or Os, L = various tertiary phosphines) for which two-centre Cotton-type mechanisms lead to the exchange of all carbonyl ligands at the same rate.[4] This behaviour is quite unlike that of 1,2-$[Os_3(CO)_{10}\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1—4).[7] The protonated form (**6c**) is present in less than detectable amounts.

A minor isomer of (**6**) in equilibrium with (**6a**) gave two weak equal-intensity ^{31}P n.m.r. singlets (δ 7.9 and −0.7) and a double doublet hydride ^1H n.m.r. signal (Table 1). Structure (**6b**) is proposed for this minor isomer. Similar isomers were observed for the protonated forms of 1,2-$[Os_3(CO)_{10}L_2]$ [L = PPh_3 or $P(OMe)_3$] (Table 1). Protonation leads to an increase in the

† 1,1,2,2,2,2,3,3,3,3-Decacarbonyl-1,1-bis(dimethylphenylphosphine)- and 1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-bis(dimethylphenylphosphine)-1,2-μ-hydrido-*triangulo*-triosmium hexafluorophosphate respectively.

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

‡ Throughout this paper the numbers preceding the formulae of the complexes are used to indicate the metal atoms to which the phosphine ligands are bonded.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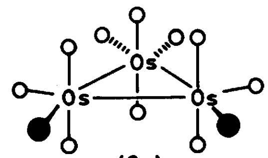
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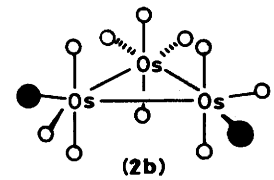
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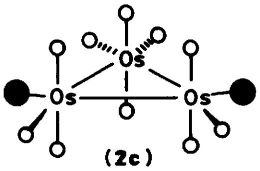
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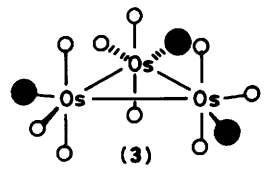
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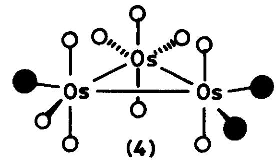
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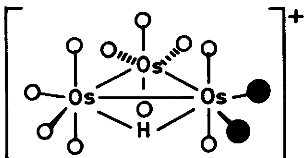
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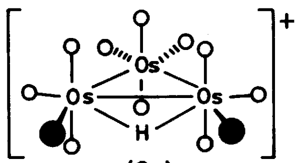
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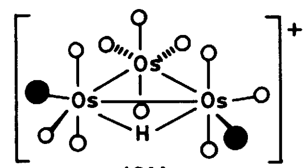
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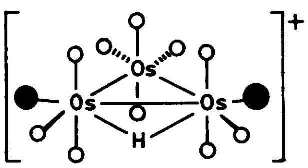
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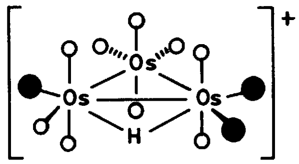
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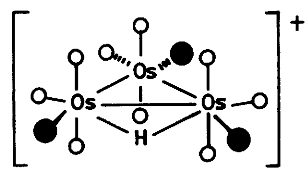
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Table 1. Spectroscopic data for protonated compounds

Compound	ν(CO)[a]/cm^{-1}	^{1}H N.m.r.[b] (δ)	^{31}P N.m.r.[c] (δ)
1,1-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] (5)	2 137m, 2 082s, 2 065m, 2 054vs, 2 044m, 2 003m, 1 996m (sh), 1 954w	1.78 (d, J_{PH} 9.8, Me) 2.24 (d, J_{PH} 9.8, Me) 7.5 (m, Ph) −19.87 [dd, J_{PH} 14 (*trans*), 8 (*cis*), OsH]	4.98 (s)
1,2-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] (6)	2 119m, 2 076m, 2 035vs, 2 022m, 1 996w	2.21 (d, J_{PH} 10.4, Me) 7.54 (m, Ph) −20.03 (t, J_{PH} 9.3, OsH) [d]	6.23 (s)[d]
		2.30 (d, J_{PH} 10, Me) 2.40 (d, J_{PH} 10, Me) 7.50 (m, Ph) −20.43 [dd, J_{PH} 14.6 (*trans*), 10.7 (*cis*), OsH] [e]	7.9 (s) −0.7 (s) [e]
1,2-[$Os_3H(CO)_{10}\{P(OMe)_3\}_2$][$PF_6$]	2 128m, 2 089m, 2 045vs, 2 033m, 2 001w	3.94 (d, J_{PH} 12.8, OMe) −20.08 (t, J_{PH} 9.3, OsH) [d]	82.7 (s)[d]
		3.90 (d, J_{PH} 11.9, OMe) −20.73 [dd, J_{PH} 29.9 (*trans*), 10.2 (*cis*), OsH] [e]	85.4 (s) 72.6 (s) [e]
1,2-[$Os_3H(CO)_{10}(PPh_3)_2$][$(CF_3CO_2)_2H$]	2 120m, 2 078m, 2 068m, 2 037vs, 2 024m, 1 998m	7.36 (m, Ph) −18.68 (t, J_{PH} 7.3, OsH)[d] −20.3 [dd, J_{PH} 11 (*cis*), 19 (*trans*), OsH][e]	
1,1,2-[$Os_3H(CO)_9(PMe_2Ph)_3$]$^+$ (7)	2 102m, 2 081vs, 2 054m, 2 030s, 1 981w, 1 944w	1.50 (d, J_{PH} 9.6, Me) 2.01 (d, J_{PH} 9.6, Me) 2.19 (d, J_{PH} 9.9, Me) 7.5 (m, Ph) −20.53 [td, J_{PH} 12.6 (*trans*), 8.6 (*cis*) OsH]	
1,2,3-[$Os_3H(CO)_9(PMe_2Ph)_3$]$^+$ (8)	2 096w, 2 062m, 2 017vs, 1 975w, 1 958w	2.33 (d, J_{PH} 10, Me) 2.35 (d, J_{PH} 10, Me) 2.54 (d, J_{PH} 10, Me) 7.48 (m, Ph) −18.93 (t, J_{PH} 9.7, OsH)	

[a] Recorded in CH_2Cl_2. [b] Recorded in $CDCl_3$; *J* values are in Hz. [c] In $CDCl_3$ solution, relative to 85% H_3PO_4 (external). Spectra for (5) and (6) are for the cations generated *in situ* by treatment of (1) and (2) with CF_3CO_2H. [d] Major isomer. [e] Minor isomer.

barrier to isomer interconversion. There are separate ^1H n.m.r. hydride signals for (**6a**) and (**6b**) at 50 °C whereas exchange between isomers (**2b**) and (**2c**) broadens ^{31}P n.m.r. signals at room temperature (T_c *ca.* 60 °C).

In order to confirm geometries and to attempt to explain changes of isomer preference on protonation we have determined the *X*-ray crystal structures of 1,1-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] (**5**) and 1,2-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] (**6**). The structure of compound (**5**) is shown in Figure 1 while Figure 2 shows some angles associated with the equatorial ligands for cations (**5**), (**6**), and [$Os_3H(CO)_{10}(MeCN)_2$][$OsCl_3(CO)_3$].[6] Selected bond lengths and angles not given in Figure 2 are collected in Table 2. The structure based on spectroscopic evidence for cation (**5**) with both phosphines in equatorial sites at the same metal atom is confirmed. Two independent molecules with the same configuration in the unit cell differ in the conformations of the PMe_2Ph ligands. The hydride ligand was located in only one of these molecules and lies in the Os_3 plane. The Os–Os distances for the protonated edges are 3.064(4) and 3.062(4) Å for these molecules, which should be compared with 3.002(2) Å in [$Os_3H(CO)_{10}(MeCN)_2$][$OsCl_3(CO)_3$].[6] The other Os–Os lengths in (**5**) are slightly longer than the average Os–Os distance in [$Os_3(CO)_{12}$] of 2.8771 Å.[8] Protonation, and to some extent also tertiary phosphine substitution, leads to an increase in the metal–metal bond lengths.

The structure of 1,2-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$], which crystallises from solution as the major isomer (**6a**), is shown in Figure 3 with selected bond lengths and angles, other than those in Figure 2, given in Table 3. The Os–Os distances in (**6a**) are rather similar to those in cation (**5**); the hydride-bridged edge is 3.059(4) Å.

The most striking feature of the structures indicated in Figure 2 is the way the equatorial ligands *cis* to the hydride bend away from the bridged Os–Os edge. We do not believe that this is due to crowding but rather to maintain closely octahedral geometries at the bridged osmium atoms, the Os–H directions rather than the bridged Os–Os vector defining the co-ordination geometries. Cation (**6**) and [$Os_3H(CO)_{10}(MeCN)_2$]$^+$ have very similar angles between the bridged Os–Os vector and the equatorial ligands *cis* to hydride: 116.8(2) and 118.1(2)° for (**6**) compared with 118.4(7) and 117.6(9)° for the bis(acetonitrile) compound. Only when two PMe_2Ph ligands are at the same

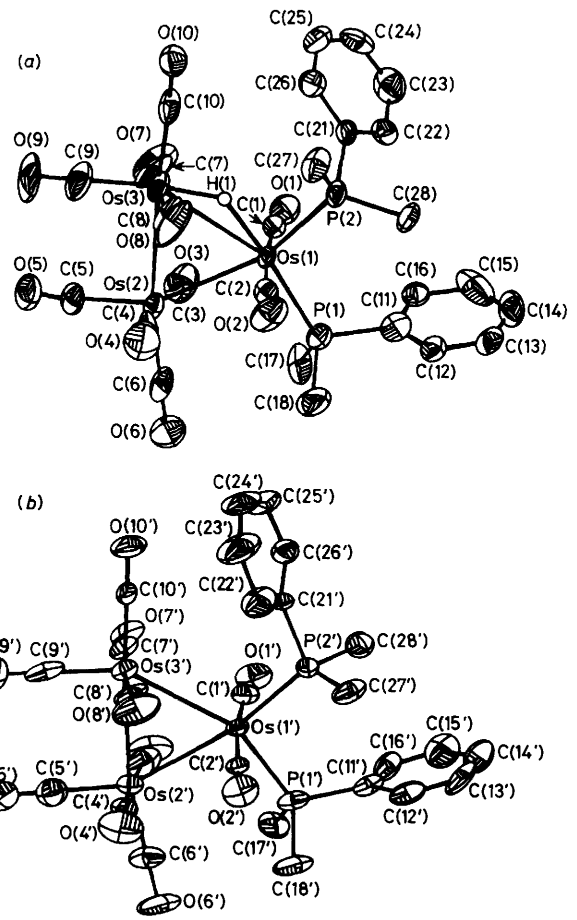

Figure 1. Molecular structure of 1,1-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] (**5**), for the two independent molecules (*a*) A and (*b*) B in the unit cell

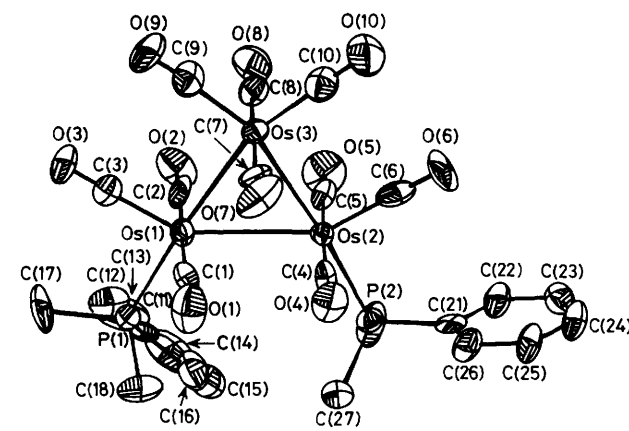

Figure 3. Molecular structure of 1,2-[$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] (**6**)

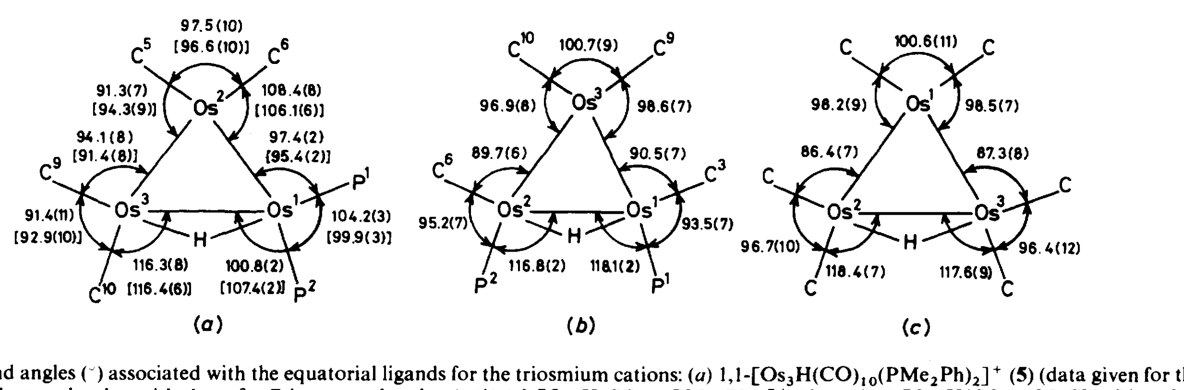

Figure 2. Bond angles (°) associated with the equatorial ligands for the triosmium cations: (*a*) 1,1-[$Os_3H(CO)_{10}(PMe_2Ph)_2$]$^+$ (**5**) (data given for the two independent molecules, with those for B in square brackets), (*b*) 1,2-[$Os_3H(CO)_{10}(PMe_2Ph)_2$]$^+$ (**6**), and (*c*) [$Os_3H(CO)_{10}(MeCN)_2$]$^+$ (ref. 6)

Table 2. Selected bond lengths (Å) and angles (°) for 1,1-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ (**5**), molecules A and B (excluding those angles in Figure 2)

Molecule A				Molecule B			
Os(2)–Os(1)	2.905(4)	Os(3)–Os(1)	3.064(4)	Os(2′)–Os(1′)	2.945(4)	Os(3′)–Os(1′)	3.062(4)
Os(3)–Os(2)	2.885(4)	H(1)–Os(1)	1.68(22)	Os(3′)–Os(2′)	2.895(4)		
H(1)–Os(3)	1.62(21)						
P(1)–Os(1)	2.358(8)	P(2)–Os(1)	2.355(6)	P(1′)–Os(1′)	2.351(7)	P(2′)–Os(1′)	2.362(6)
C(1)–Os(1)	1.889(15)	C(2)–Os(1)	1.948(16)	C(1′)–Os(1′)	1.925(16)	C(2′)–Os(1′)	1.947(15)
C(3)–Os(2)	1.931(17)	C(4)–Os(2)	1.963(18)	C(3′)–Os(2′)	1.945(19)	C(4′)–Os(2′)	1.954(18)
C(5)–Os(2)	1.945(21)	C(6)–Os(2)	1.900(28)	C(5′)–Os(2′)	1.898(21)	C(6′)–Os(2′)	1.866(26)
C(7)–Os(3)	1.932(17)	C(8)–Os(3)	1.966(17)	C(7′)–Os(3′)	1.958(17)	C(8′)–Os(3′)	1.950(18)
C(9)–Os(3)	1.890(30)	C(10)–Os(3)	1.951(22)	C(9′)–Os(3′)	1.890(20)	C(10′)–Os(3′)	1.922(24)
C(11)–P(1)	1.823(21)	C(17)–P(1)	1.838(17)	C(11′)–P(1′)	1.823(17)	C(17′)–P(1′)	1.839(21)
C(18)–P(1)	1.846(22)	C(21)–P(2)	1.825(17)	C(18′)–P(1′)	1.835(22)	C(21′)–P(2′)	1.825(25)
C(27)–P(2)	1.846(20)	C(28)–P(2)	1.835(26)	C(27′)–P(2′)	1.820(18)	C(28′)–P(2′)	1.811(18)
Os(3)–Os(1)–Os(2)	57.7	Os(3)–Os(2)–Os(1)	63.9	Os(3′)–Os(1′)–Os(2′)	57.6	Os(3′)–Os(2′)–Os(1′)	63.2
Os(2)–Os(3)–Os(1)	58.4	Os(3)–H(1)–Os(1)	136(11)	Os(2′)–Os(3′)–Os(1′)	59.2		
P(1)–Os(1)–Os(2)	97.4(2)	P(1)–Os(1)–Os(3)	155.0(1)	P(1′)–Os(1′)–Os(2′)	95.4(2)	P(1′)–Os(1′)–Os(3′)	152.6(1)
P(2)–Os(1)–Os(2)	157.6(1)	P(2)–Os(1)–Os(3)	100.8(2)	P(2′)–Os(1′)–Os(2′)	163.5(1)	P(2′)–Os(1′)–Os(3′)	107.4(2)
P(2)–Os(1)–P(1)	104.2(3)	H(1)–Os(1)–P(1)	169.7(51)	P(2′)–Os(1′)–P(1′)	99.9(3)	C(1′)–Os(1′)–P(1′)	85.1(7)
H(1)–Os(1)–Os(3)	21.3(56)	H(1)–Os(1)–P(2)	81.4(58)	C(2′)–Os(1′)–P(1′)	87.4(7)	C(1′)–Os(1′)–P(2′)	90.2(6)
C(1)–Os(1)–P(1)	87.8(7)	C(1)–Os(1)–P(2)	90.5(6)	C(2′)–Os(1′)–P(2′)	88.9(6)		
C(2)–Os(1)–P(1)	86.1(7)	C(2)–Os(1)–P(2)	87.9(6)				
C(9)–Os(3)–H(1)	173.2(62)	C(10)–Os(3)–H(1)	94.5(66)				
H(1)–Os(3)–Os(1)	22.3(64)						

Table 3. Selected bond lengths (Å) and angles (°) for 1,2-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ (**6**) (excluding those angles in Figure 2)

Os(2)–Os(1)	3.059(4)	Os(3)–Os(1)	2.902(4)
Os(3)–Os(2)	2.891(4)	C(1)–Os(1)	1.934(27)
C(2)–Os(1)	1.887(26)	C(3)–Os(1)	1.906(23)
C(4)–Os(2)	1.946(22)	C(5)–Os(2)	1.929(23)
C(6)–Os(2)	1.854(23)	C(7)–Os(3)	1.940(22)
C(8)–Os(3)	1.939(21)	C(9)–Os(3)	1.947(25)
C(10)–Os(3)	1.840(27)	P(1)–Os(1)	2.365(7)
P(2)–Os(2)	2.364(6)	C(11)–P(1)	1.819(14)
C(17)–P(1)	1.871(24)	C(18)–P(1)	1.777(23)
C(21)–P(2)	1.819(11)	C(27)–P(2)	1.868(26)
C(28)–P(2)	1.832(25)		
Os(3)–Os(1)–Os(2)	58.0	Os(3)–Os(2)–Os(1)	58.3
Os(2)–Os(3)–Os(1)	63.7	P(1)–Os(1)–Os(2)	118.1(2)
P(1)–Os(1)–Os(3)	176.0(1)	C(2)–Os(1)–P(1)	90.5(10)
C(1)–Os(1)–P(1)	88.6(8)	C(3)–Os(1)–P(1)	93.5(7)
P(2)–Os(2)–Os(1)	116.8(2)	P(2)–Os(2)–Os(3)	174.6(1)
C(4)–Os(2)–P(2)	87.3(8)	C(5)–Os(2)–P(2)	89.4(8)
C(6)–Os(2)–P(2)	95.2(7)		

osmium atom does repulsion between these ligands reduce this angle: 100.8(2)° for P(2)Os(1)Os(3) in cation (**5**) [107.4(2)° for the other molecule in the unit cell]. Hence the PMe_2Ph ligands probably favour these *cis* sites in the protonated forms because these are the least crowded whereas repulsion between the PMe_2Ph ligands in the non-protonated form (**2a**) prevents this isomer being observed.

The tris(phosphine) compounds 1,1,2- and 1,2,3-$[Os_3(CO)_9(PMe_2Ph)_3]$, (**4**) and (**3**), react as expected with trifluoroacetic acid under the same conditions as the bis(phosphine) compounds to give 1,1,2-$[Os_3H(CO)_9(PMe_2Ph)_3]^+$ (**7**) and the 1,2,3-isomer, cation (**8**). These exist as single isomers with the structures shown (^1H n.m.r. evidence). The ^1H n.m.r. hydride signal for cation (**7**) is a triplet (J_{PH} 12.6 Hz) of doublets (J_{PH} 8.6 Hz) suggesting that there are two phosphorus nuclei *trans* and one *cis* to the hydride. All three phosphorus nuclei were shown to be different. For cation (**8**) the hydride n.m.r. signal is a triplet (J_{PH} 9.7 Hz) with two PMe_2Ph ligands *cis* to the hydride. The geometry therefore is not based on that of the unprotonated form (**3**) but as in (**6a**) the phosphines have been induced to be *cis* to the hydride ligand. Complex cations related to (**8**) have been described previously.[1]

Experimental

The compounds 1,1- and 1,2-$[Os_3(CO)_{10}L_2]$ [L = PMe_2Ph, $P(OMe)_3$, or PPh_3] and 1,1,2- and 1,2,3-$[Os_3(CO)_9(PMe_2Ph)_3]$, compounds (**1**)—(**4**), were prepared from $[Os_3(CO)_{10}(\eta^4\text{-}C_4H_6)]$ (C_4H_6 = *S-cis*-buta-1,3-diene) or $[Os_3(CO)_{10}(MeCN)_2]$ according to published procedures.[2,4] Hydrogen-1 n.m.r. (200.057 MHz) and ^{31}P n.m.r. spectra (80.984 MHz) were recorded on a Varian XL200 spectrometer and i.r. spectra (CH_2Cl_2 solutions) on a Perkin-Elmer PE983 spectrometer.

Preparation of 1,1-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ (**5**).—Addition of CF_3CO_2H (0.011 cm^3, 5 mol per mol Os_3) to an orange solution of 1,1-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ (0.033 g) in $CDCl_3$ (0.5 cm^3) gave a yellow solution and the ^1H n.m.r. spectrum indicated complete protonation. The residue, after the removal of solvent under vacuum, was dissolved in methanol (5 cm^3) and a methanolic solution of ammonium hexafluorophosphate (0.007 g) was added followed by a few drops of water to give a precipitate which was recrystallised from CH_2Cl_2–Et_2O to give yellow crystals of compound (**5**) (0.033 g, 89%) (Found: C, 24.5; H, 1.95; P, 7.05. $C_{26}H_{23}F_6O_{10}Os_3P_3$ requires C, 24.55; H, 1.85; P, 7.3%).

Preparation of 1,2-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ (**6**).—The ^1H and ^{31}P n.m.r. spectra of a solution of CF_3CO_2H (0.034 cm^3, 5 mol per mol Os_3) and 1,2-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ (0.099 g) in $CDCl_3$ (2.5 cm^3) indicated complete protonation. The solvent was removed under vacuum and the residue dissolved in methanol and a methanolic solution of $[NH_4][PF_6]$ (0.021 g) added to give a yellow solid. Recrystallisation from

Table 4. Fractional atomic co-ordinates (× 10^4) for 1,1-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ (**5**)

Atom	*x*	*y*	*x*	Atom	*x*	*y*	*z*
Os(1)	1 975(1)	7 645(1)	331(1)	O(2′)	4 942(9)	1 454(8)	6 207(9)
Os(2)	3 195(1)	9 022(1)	631(1)	C(3′)	1 551(12)	1 138(13)	3 615(15)
Os(3)	1 547(1)	8 688(1)	1 400(1)	O(3′)	1 083(9)	1 391(9)	2 828(9)
P(1)	2 895(3)	7 213(3)	−432(3)	C(4′)	3 212(13)	213(10)	6 248(14)
P(2)	593(3)	6 812(3)	213(3)	O(4′)	3 748(11)	−67(9)	6 953(10)
C(1)	2 527(11)	6 833(10)	1 553(12)	C(5′)	1 382(13)	−143(12)	5 395(14)
O(1)	2 880(9)	6 281(8)	2 267(9)	O(5′)	808(11)	−624(9)	5 663(12)
C(2)	1 434(11)	8 398(9)	−1 006(13)	C(6′)	2 854(13)	4(11)	4 491(13)
O(2)	1 112(10)	8 797(8)	−1 792(9)	O(6′)	3 204(10)	−402(9)	4 203(11)
C(3)	3 873(11)	8 122(11)	1 705(12)	C(7′)	899(12)	2 182(11)	4 378(13)
O(3)	4 381(8)	7 636(9)	2 299(10)	O(7′)	390(9)	2 427(8)	3 612(9)
C(4)	2 472(14)	9 818(11)	−590(15)	C(8′)	2 879(13)	1 520(12)	6 825(14)
O(4)	2 078(12)	10 306(9)	−1 312(11)	O(8′)	3 501(11)	1 345(10)	7 469(10)
C(5)	3 704(12)	9 793(10)	1 320(13)	C(9′)	977(12)	1 082(12)	6 264(13)
O(5)	3 997(10)	10 177(9)	1 787(11)	O(9′)	455(10)	598(8)	6 667(10)
C(6)	4 116(16)	9 228(11)	−105(16)	C(10′)	1 533(12)	2 718(10)	5 953(13)
O(6)	4 670(13)	9 318(12)	−541(14)	O(10′)	1 350(10)	3 228(9)	6 148(12)
C(7)	2 392(11)	8 040(14)	2 607(13)	C(11′)	4 752(10)	2 890(10)	2 675(11)
O(7)	2 897(11)	7 619(12)	3 295(10)	C(12′)	5 686(12)	3 102(11)	3 064(11)
C(8)	806(15)	9 321(12)	71(13)	C(13′)	6 116(13)	3 789(13)	2 538(14)
O(8)	306(10)	9 652(9)	−669(10)	C(14′)	5 653(16)	4 261(13)	1 612(13)
C(9)	1 779(13)	9 607(15)	1 815(15)	C(15′)	4 760(15)	4 050(13)	1 173(13)
O(9)	1 880(11)	10 208(10)	2 009(13)	C(16′)	4 328(12)	3 359(11)	1 714(11)
C(10)	462(12)	8 322(13)	1 973(15)	C(17′)	3 373(14)	1 653(10)	2 435(12)
O(10)	−171(10)	8 171(10)	2 278(11)	C(18′)	5 011(14)	1 230(12)	4 083(16)
C(11)	2 493(10)	6 255(10)	−661(13)	C(21′)	3 542(11)	4 029(10)	5 081(13)
C(12)	2 083(14)	6 238(11)	−1 581(13)	C(22′)	3 834(14)	3 751(14)	6 125(13)
C(13)	1 843(12)	5 472(12)	−1 672(14)	C(23′)	3 439(16)	4 134(16)	6 614(16)
C(14)	1 948(15)	4 762(12)	−910(18)	C(24′)	2 852(16)	4 708(16)	6 140(22)
C(15)	2 366(14)	4 763(13)	26(20)	C(25′)	2 588(13)	5 006(14)	5 101(22)
C(16)	2 676(12)	5 508(11)	190(14)	C(26′)	2 928(12)	4 671(11)	4 572(17)
C(17)	4 112(10)	7 027(11)	273(15)	C(27′)	5 259(11)	3 602(12)	5 010(13)
C(18)	3 008(16)	7 942(11)	−1 675(15)	C(28′)	3 933(15)	4 375(11)	3 183(13)
C(21)	502(11)	6 040(10)	1 423(12)				
C(22)	830(13)	5 268(9)	1 756(13)	P(3)	8 488(4)	2 590(4)	4 927(4)
C(23)	761(14)	4 710(12)	2 682(17)	F(11)	8 729(11)	2 900(11)	5 802(11)
C(24)	401(15)	4 896(12)	3 291(16)	F(12)	8 205(17)	2 256(16)	4 049(15)
C(25)	56(17)	5 670(12)	2 975(14)	F(13)	8 393(18)	1 732(12)	5 749(14)
C(26)	90(15)	6 234(12)	2 050(15)	F(14)	8 512(24)	3 393(14)	4 142(15)
C(27)	−448(11)	7 434(12)	−252(13)	F(15)	7 489(12)	2 690(20)	4 828(15)
C(28)	318(13)	6 216(13)	−618(13)	F(16)	9 468(12)	2 458(21)	5 092(17)
Os(1′)	3 322(1)	2 274(1)	4 414(1)	P(4)	2 845(7)	2 410(5)	−643(5)
Os(2′)	2 330(1)	646(1)	4 953(1)	F(21)	2 026(16)	2 890(16)	−1 409(14)
Os(3′)	1 852(1)	1 840(1)	5 637(1)	F(22)	3 745(21)	2 062(20)	190(18)
P(1′)	4 126(3)	2 010(3)	3 417(3)	F(23)	2 569(11)	2 655(12)	181(11)
P(2′)	4 023(3)	3 575(2)	4 405(3)	F(24)	3 012(33)	2 216(17)	−1 470(17)
C(1′)	2 449(11)	2 803(9)	3 173(12)	F(25)	3 450(17)	3 219(16)	−938(18)
O(1′)	1 985(9)	3 164(8)	2 419(9)	F(26)	2 258(32)	1 647(17)	−293(25)
C(2′)	4 322(11)	1 750(9)	5 559(12)				

CH_2Cl_2–Et_2O gave compound (**6**) as yellow crystals (0.100 g, 89%) (Found: C, 24.5; H, 1.9; P, 7.2. $C_{26}H_{23}F_6O_{10}Os_3P_3$ requires C, 24.55; H, 1.85; P, 7.3%).

Preparation of 1,2-$[Os_3H(CO)_{10}\{P(OMe)_3\}_2][PF_6]$.—$CF_3CO_2H$ (0.070 cm^3) was added to a solution of the neutral compound (0.100 g) in toluene (3 cm^3). A similar work-up to that above gave, after recrystallisation from CH_2Cl_2–Et_2O, the product as yellow crystals (0.084 g, 74%) (Found: C, 15.45; H, 1.5; P, 7.3. $C_{16}H_{19}F_6O_{16}Os_3P_3$ requires C, 15.45; H, 1.55; P, 7.45%).

Protonation of 1,2-$[Os_3(CO)_{10}(PPh_3)_2]$.—CF_3CO_2H (0.013 cm^3) was added to a solution of the neutral compound (0.045 g) in $CDCl_3$ (0.5 cm^3). After recording the ^1H n.m.r. spectrum the solvent was removed and the residue recrystallised from CH_2Cl_2–Et_2O as yellow crystals of 1,2-$[Os_3H(CO)_{10}(PPh_3)_2][(CF_3CO_2)_2H]$ (0.045 g, 92%) (Found: C, 37.45; H, 2.2. $C_{50}H_{32}F_6O_{14}Os_3P_2$ requires C, 37.45; H, 2.0%).

Preparation of 1,1,2-$[Os_3H(CO)_9(PMe_2Ph)_3][PF_6]$ (**7**).—The ^1H n.m.r. spectrum of a solution of CF_3CO_2H (0.006 cm^3, 5 mol per mol Os_3) and 1,1,2-$[Os_3(CO)_9(PMe_2Ph)_3]$ (0.015 g) in $CDCl_3$ (0.5 cm^3) showed that protonation had occurred. Isolation of the hexafluorophosphate salt as above gave a yellow solid (0.012 g, 71%) (Found: C, 27.05; H, 2.25. $C_{33}H_{34}F_6O_9Os_3P_4$ requires C, 28.65; H, 2.5%).

Preparation of 1,2,3-$[Os_3H(CO)_9(PMe_2Ph)_3][PF_6]$ (**8**).—Protonation of 1,2,3-$[Os_3(CO)_9(PMe_2Ph)_3]$ (0.054 g) under the same conditions as above gave compound (**8**) as yellow crystals (0.045 g, 75%) from a CH_2Cl_2–Et_2O mixture (Found:

Table 5. Fractional atomic co-ordinates (× 10^4) for 1,2-$[Os_3H(CO)_{10}(PMe_2Ph)_2][PF_6]$ (**6**)

Atom	*x*	*y*	*x*	Atom	*x*	*y*	*z*
Os(1)	8 287(1)	3 163(1)	1 759(1)	C(11)	6 185(9)	2 713(10)	2 800(7)
Os(2)	8 343(1)	5 263(1)	1 745(1)	C(12)	6 302(9)	2 205(10)	3 528(7)
Os(3)	9 989(1)	4 161(1)	1 608(1)	C(13)	5 820(9)	2 435(10)	4 250(7)
P(1)	6 845(3)	2 446(3)	1 869(4)	C(14)	5 223(9)	3 172(10)	4 244(7)
P(2)	6 922(3)	5 997(3)	1 806(3)	C(15)	5 107(9)	3 680(10)	3 517(7)
C(1)	8 114(16)	3 218(13)	563(16)	C(16)	5 588(9)	3 451(10)	2 795(7)
O(1)	7 928(16)	3 261(11)	−152(11)	C(17)	6 938(17)	1 181(14)	1 912(20)
C(2)	8 410(20)	3 157(12)	2 933(15)	C(18)	6 085(19)	2 629(22)	1 020(15)
O(2)	8 445(14)	3 113(11)	3 672(9)	C(21)	7 057(8)	7 176(6)	1 498(8)
C(3)	8 938(15)	2 045(13)	1 728(14)	C(22)	7 185(8)	7 849(6)	2 098(8)
O(3)	9 362(11)	1 392(8)	1 688(12)	C(23)	7 354(8)	8 741(6)	1 853(8)
C(4)	8 221(16)	5 255(11)	535(12)	C(24)	7 394(8)	8 960(6)	1 006(8)
O(4)	8 116(14)	5 308(10)	−162(9)	C(25)	7 267(8)	8 287(6)	405(8)
C(5)	8 404(17)	5 265(12)	2 948(13)	C(26)	7 098(8)	7 395(6)	651(8)
O(5)	8 435(16)	5 292(12)	3 668(10)	C(27)	6 055(17)	5 532(15)	1 064(18)
C(6)	9 039(12)	6 283(14)	1 667(14)	C(28)	6 392(17)	6 050(14)	2 842(16)
O(6)	9 469(12)	6 962(10)	1 607(13)				
C(7)	9 829(12)	4 172(16)	406(13)	P(3)	3 608(4)	4 217(5)	10 702(4)
O(7)	9 823(12)	4 208(14)	−309(9)	F(1)	3 149(13)	3 890(12)	9 865(10)
C(8)	10 084(14)	4 155(15)	2 816(12)	F(2)	4 102(13)	4 528(14)	11 529(11)
O(8)	10 167(11)	4 133(12)	3 523(9)	F(3)	4 509(14)	4 177(26)	10 292(13)
C(9)	10 824(16)	3 136(15)	1 529(15)	F(4)	2 741(15)	4 051(29)	11 140(16)
O(9)	11 253(11)	2 529(11)	1 445(11)	F(5)	3 782(23)	3 212(15)	10 975(18)
C(10)	10 801(16)	5 113(16)	1 565(18)	F(6)	3 455(25)	5 147(12)	10 530(18)
O(10)	11 306(11)	5 738(13)	1 518(14)				

Table 6. Crystal data, intensity data collection parameters, and details of refinement

Crystal data		
Compound	(**5**)	(**6**)
Stoicheiometry	$[C_{26}H_{23}O_{10}Os_3P_2]$-$[PF_6]$	$[C_{26}H_{23}O_{10}Os_3P_2]$-$[PF_6]$
M	1 272.6	1 272.6
a/Å	14.929(3)	14.624(2)
b/Å	17.517(4)	14.750(3)
c/Å	14.903(3)	16.011(4)
α/°	67.69(2)	90
β/°	105.90(2)	90
γ/°	98.29(2)	90
U/Å^3	3 464.1	3 453.6
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
D_c/g cm^{-3}	2.440	2.447
Z	4	4
F(000)	2 344	2 344
μ/cm^{-1}	107.7	107.4
Data collection		
$\theta_{min., max.}$	1.5, 25	1.5, 25
Total data measured	12 679	3 579
Total unique data	12 184	3 401
Total observed data [$F_o > 3\sigma(F_o)$]	8 179	2 618
Refinement		
No. of parameters:	468 in block 1, 464 in block 2	409
Absorption correction	ψ-scan and DIFABS	ψ-scan and DIFABS
Weighting scheme parameter *g* in $w = 1/[\sigma^2(F_o) + g(F_o)^2]$	unit weights	0.0005
$R = [\Sigma\Delta F/\Sigma(F_o)]$	0.0399	0.0360
$R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$	0.0472	0.0399

C, 28.35; H, 2.4; P, 8.8. $C_{33}H_{34}F_6O_9Os_3P_4$ requires C, 28.65; H, 2.5; P, 8.95%).

Crystal Structure Determinations.—Suitable single crystals of compounds (**5**) and (**6**) were sealed in thin-walled glass capillaries. The orientation matrices, unit-cell parameters, and the intensity data were obtained following previously described procedures[9] using an Enraf-Nonius CAD4 diffractometer and monochromatised Mo-K_α radiation (λ = 0.710 69 Å) at 273 K. The Os atoms were located by Patterson Search (SHELX 84)[10] and the lighter atoms by difference electron-density syntheses (SHELX 76).[11] The structures were refined by full-matrix least-squares methods with neutral-atom scattering factors based on parameters in ref. 12. Structure (**5**) was refined in two blocks with the six Os atoms common in each block. All non-H atoms were anisotropic, the bridging H in one independent cation isotropic, and the phenyl H atoms riding on their parent carbons but with one common value of $U_{iso.}$ refined for the five H atoms in each ring. In structure (**6**), all the H atoms were ignored, the two phenyl rings refined as rigid, regular hexagons (C–C 1.395 Å) and all non-hydrogen atoms treated anisotropically. Atomic co-ordinates for compounds (**5**) and (**6**) are given in Tables 4 and 5 respectively. Atomic parameters and the derived molecular geometry for compound (**6**) presented in the text are those which correspond to the enantiomorph giving lower *R* and *R'* values (0.0360 *vs.* 0.0434 and 0.0399 *vs.* 0.0505 respectively). The crystal data and other details of intensity data collection and structure refinement are given in Table 6.

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