Reactions of Perfluoroalkyl-substituted Phosphines with Osmium Carbonyl Clusters: Crystal Structures of Bridged, Linked and Substituted Derivatives*

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The secondary phosphine $(CF_3)_2C(OH)PH(CF_3)$ has been shown from ^1H and ^{19}F NMR and single-crystal X-ray diffraction studies to undergo P–C bond cleavage upon reaction with $[Os_3(CO)_{11}(MeCN)]$ to afford the phosphido-bridged cluster $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ **1** and the linked cluster $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$ **2**. However, its reaction with $[Os_3(CO)_{10}(MeCN)_2]$ afforded the novel molecule $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ **3** the molecular structure of which has also been established. Compound **1** was also obtained from the reaction of $(CF_3)_2C(OH)PH(CF_3)$ or $PH(CF_3)_2$ with the anionic cluster $[Os_3H(CO)_{11}]^-$. Furthermore the primary phosphines $(CF_3)_2C(OH)PH_2$ and $PH_2(CF_3)$ display similar P–C bond cleavage upon reactions with $[Os_3H(CO)_{11}]^-$ to afford the phosphido-bridged cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$. On the other hand, $(CF_3)_2C(OH)PH_2$ gave simple substitution products upon reactions with $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_3(CO)_{11}(MeCN)]$, as has been found for the tertiary phosphine $P(CF_3)_3$. Compound **2** represents the first example of two triosmium triangles linked by a terminally co-ordinated PR_2 group.

Reactions of trifluoromethyl-substituted phosphines $PH_{3-n}(CF_3)_n$ (n = 1–3) with triosmium carbonyl clusters have been relatively unexplored. In view of the electron-withdrawing effect of the CF_3 moiety, they are expected to be poor σ donors. As for the alkyl analogues, reactions of $PH(CF_3)_2$ and $PH_2(CF_3)$ with transition-metal carbonyl complexes so far reported have led to cleavage of the P–H bond to form a phosphido bridge between two metal centres.[1–7] Similarly, preferential cleavage of P–H over P–C bonds has been reported in reactions of osmium carbonyl clusters or derivatives with primary and secondary phosphines, to yield hydrido-phosphido-bridged triosmium clusters.[8–11] However, we have recently observed that the P–C bond is cleaved preferentially over the P–H bond in the reaction of the anion $[Os_3H(CO)_{11}]^-$ with $PH(C_6F_5)_2$, resulting in the formation of the bridged phosphido cluster $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(C_6F_5)\}]$.[11] We describe below reactions of triosmium carbonyl clusters with perfluoroalkyl-substituted phosphines including $(CF_3)_2C(OH)PH(CF_3)$, $(CF_3)_2C(OH)PH_2$,[12] $PH(CF_3)$ and $PH_2(CF_3)$.

Table 1 Infrared data (cm^{-1}) in cyclohexane for the substituted osmium carbonyl clusters

$[Os_3(CO)_{11}\{(CF_3)_2C(OH)PH_2\}]$	2117m, 2062s, 2049s, 2028vs, 2010m, 1999ms, 1987vw, 1979w
$[Os_3(CO)_{10}\{(CF_3)_2C(OH)PH_2\}_2]$	2103m, 2050s, 2039s, 2034w, 2020vs, 1979m
1 $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$	2112m, 2074vs, 2064s, 2031s, 2014vs, 1992w
2 $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$	2146w, 2109m, 2100s, 2076s, 2064vs, 2055s, 2022s, 1934w
3 $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$	2092m, 2061vs, 2036vs, 2014s, 1996s, 1961w
$[Os_3(CO)_{11}\{P(CF_3)_3\}]$	2122w, 2071vs, 2057s, 2036vs, 2027m, 2017m, 2011s, 2006m, 1992w
4 $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$	2115w, 2067s, 2055m, 2037vs, 2014ms, 2004mw, 1970vw

Results and Discussion

The reactions of the various substituted triosmium carbonyl clusters with the perfluoroalkyl-substituted phosphines were carried out *in vacuo*. The IR data for the new cluster derivatives isolated are given in Table 1.

Reactions of Primary Phosphines PH_2R [R = $(CF_3)_2C(OH)$ or CF_3.—(*a*) $(CF_3)_2C(OH)PH_2$ *with* $[Os_3(CO)_{11}(MeCN)]$. The reaction of the primary phosphine $(CF_3)_2C(OH)PH_2$ with $[Os_3(CO)_{11}(MeCN)]$ in CH_2Cl_2 at room temperature afforded a compound which displays carbonyl stretching frequencies (Table 1) comparable to those of $[Os_3(CO)_{11}(PPh_3)]$[13] and several other monosubstituted triosmium carbonyl clusters.[14–16] The ^1H NMR spectrum shows a broad OH signal at δ 1.60 and the PH signal as a doublet at δ 6.09. The ^{31}P NMR spectrum comprises a signal at δ −96.38 shifted by ≈30 ppm upfield relative to that of the free ligand, while the ^{19}F NMR contains a peak at δ 3.52. These data and the carbonyl stretching frequencies establish that the primary phosphine ligand has displaced MeCN in $[Os_3(CO)_{11}(MeCN)]$ to give $[Os_3(CO)_{11}\{(CF_3)_2C(OH)PH_2\}]$.

(*b*) $(CF_3)_2C(OH)PH_2$ *with* $[Os_3(CO)_{10}(MeCN)_2]$. The reaction of $(CF_3)_2C(OH)PH_2$ with $[Os_3(CO)_{10}(MeCN)_2]$ proceeded as that with the monosubstituted acetonitrile derivative to afford a disubstituted product $[Os_3(CO)_{10}\{(CF_3)_2C(OH)PH_2\}_2]$. The carbonyl stretching frequencies (Table 1) are typical of 1,2-disubstituted diequatorial triosmium carbonyl clusters.[13,17–19] The ^1H NMR signals due to PH and OH and the ^{19}F NMR spectrum are similar to those of the monosubstituted cluster $[Os_3(CO)_{11}\{(CF_3)_2C(OH)PH_2\}]$. The $^{31}P\text{-}\{^1H\}$ NMR spectrum however displays three peaks at δ −93.69 (s), −94.09 (s) and −99.2 (s) with the intensities of the

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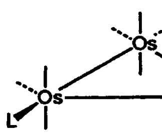
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



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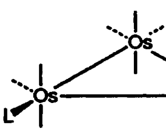

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first two signals being in the ratio of 1 : 1 and that at −99.2 being much lower. The appearance of this spectrum suggests that there are two isomers **i** and **ii** of which the former would account for the signals at δ −93.69 and −94.09 and the latter the low-intensity signal at δ −99.2 (s).

(*c*) $PH_2(CF_3)$ *with* $[Os_3(CO)_{10}(MeCN)_2]$. The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with an excess of $PH_2(CF_3)$ in CH_2Cl_2 at 58 °C gave a yellow solid as the major product. The IR, NMR and analytical data are identical to those of $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ **1**, which was also obtained from the reaction of the secondary phosphine $(CF_3)_2C(OH)PH(CF_3)$ with $[Os_3(CO)_{11}(MeCN)]$ (see below). In this case P–H cleavage occurs preferentially over that of P–C.

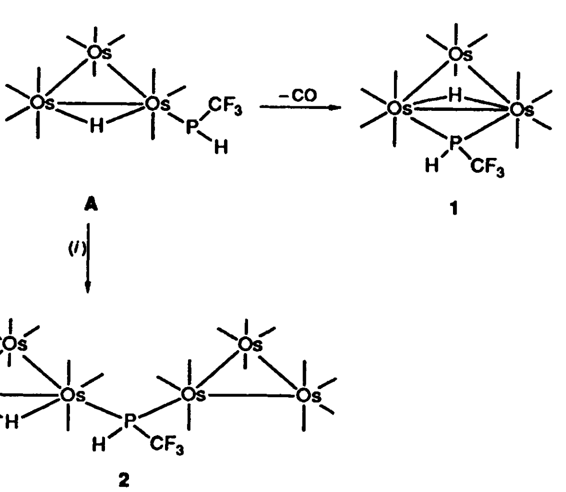
(*d*) *With* $[N(PPh_3)_2][Os_3H(CO)_{11}]$. Equimolar amounts of $[N(PPh_3)_2][Os_3H(CO)_{11}]$ and $PH_2(CF_3)$ in CH_2Cl_2 reacted at room temperature to give a yellow solution from which two major products were obtained. The first yellow solid displays carbonyl stretching frequencies at 2107m, 2065vs, 2056vs, 2025vs, 2010s, 1999s, 1984w and 1960w cm^{-1} and a ^{31}P NMR signal comprising a doublet of doublets centred at δ −135.0 with J_{PH} 381 and 421 Hz and a $^2J_{PH}$ 15 Hz. These spectral data are identical to those reported for $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$.[20,21] The second yellow product exhibits carbonyl stretching frequencies identical to those of the cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OH)]$.[22] Its ^1H NMR spectrum showed a singlet metal hydride signal at δ −12.58.[22]

When $(CF_3)_2C(OH)PH_2$ was allowed to react with the same anionic cluster in CH_2Cl_2 only one major product was obtained. This was identified from its IR and NMR spectral data to be $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$. Thus both the primary phosphines react in a similar manner with the anionic cluster, involving preferential P–C bond cleavage.

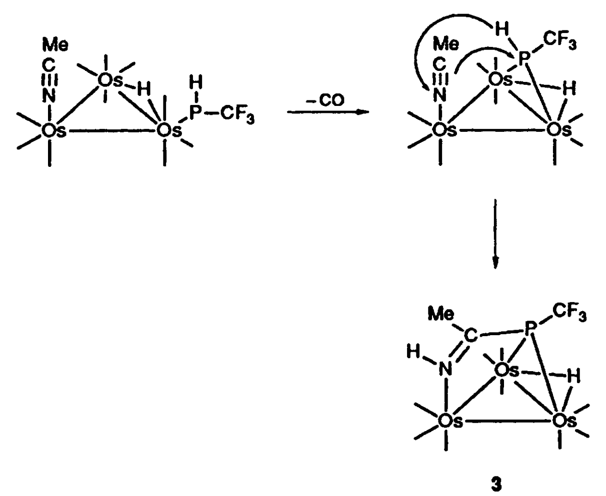
Reactions of Secondary Phosphines $PH(R)R'$ [$R = (CF_3)_2C(OH)$, $R' = CF_3$; $R = R' = CF_3$].—(*a*) $(CF_3)_2C(OH)PH(CF_3)$ *with* $[Os_3(CO)_{11}(MeCN)]$. The reaction of the secondary phosphine $(CF_3)_2C(OH)PH(CF_3)$ with $[Os_3(CO)_{11}(MeCN)]$ proceeded smoothly in CH_2Cl_2 at room temperature to afford the phosphido-bridged cluster **1** and the linked cluster **2** as shown in equation (1). The molecular structures of clusters **1** and **2** have been determined by single-crystal X-ray diffraction analysis (see below). This reaction has resulted in the P–C bond cleavage of a secondary phosphine at ambient temperature, in preference to the P–H bond. Clusters **1** and **2** are most probably derived from the intermediate $[Os_3(\mu\text{-}H)(CO)_{11}\{PH(CF_3)\}]$ **A**, which either attacks the neighbouring Os atom to form **1** or reacts with another molecule of $[Os_3(CO)_{11}(MeCN)]$ to form **2** (Scheme 1).

$$
\begin{aligned}
&[Os_3(CO)_{11}(MeCN)] + (CF_3)_2C(OH)PH(CF_3) \longrightarrow \\
&\qquad \underset{\mathbf{1}}{[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]} + \\
&\qquad \underset{\mathbf{2}}{[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]} \quad (1)
\end{aligned}
$$

Both clusters were isolated as yellow crystals on separation of the reaction products by TLC, followed by recrystallisation from dichloromethane. The spectroscopic data show signals characteristic of the CF_3P group, but not those of the CF_3C and the OH groups. Thus the ^1H NMR spectrum of **1** displays two signals centred at δ 6.77 (ddq, J_{PH} = 433.7, J_{HF} = 7.7, J_{HH} = 4.3 Hz) and −20.39 (dd, J_{PH} = 17.8, J_{HH} = 4.3 Hz). The ^{19}F NMR spectrum comprises a doublet of doublets at δ 18.87 (J_{PF} = 68.4, J_{HF} = 7.3 Hz) while the ^{31}P NMR spectrum displays a quartet at δ −25.0 (J_{PF} = 68.4 Hz). For **2** the ^1H NMR spectrum comprises a doublet of quartets at δ 5.95 (J_{PH} = 334.1, J_{HF} = 9.4 Hz) and a doublet at δ −19.33 (J_{PH} = 9.4 Hz). The ^{19}F NMR signal is quite different from that of **1**, being a doublet of doublets at δ 25.46 (J_{PF} = 43.9, J_{HF} = 9.8 Hz). Most significant of all is the $^{31}P\text{-}\{^1H\}$ NMR spectrum which contains a quartet at a very high field of δ −132.9 (J_{PF} = 44.0 Hz). Finally it is also noted that whereas the CO stretching frequencies of **1** (Table 1) are very similar to those reported for $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(C_6F_5)\}]$,[11] those for **2** are significantly different.



Scheme 1 (*i*) $[Os_3(CO)_{11}(MeCN)]$



Scheme 2

(*b*) $(CF_3)_2C(OH)PH(CF_3)$ *with* $[Os_3(CO)_{10}(MeCN)_2]$. The phosphine reacted rapidly with $[Os_3(CO)_{10}(MeCN)_2]$ in CH_2Cl_2 at room temperature to afford an orange crystalline solid and a yellow, sparingly soluble solid. The latter displayed complicated spectral data, which could not be readily rationalised. The orange solid upon recrystallisation from CH_2Cl_2 afforded diffraction-quality crystals. An X-ray structural analysis established this to be a bridged cluster $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ **3**. Its formation is interesting as it involves not only P–C(CF_3)OH bond cleavage but also the formation of a new P–C bond between the phosphorus atom and the acetonitrile molecule bound to the osmium atom. One possible route is *via* the intermediate $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)\{PH(CF_3)\}]$ followed by rearrangement reactions as shown in Scheme 2.

The NMR and IR spectral (Table 1) are consistent with this formulation. Thus the $^{31}P\text{-}\{^1H\}$ NMR spectrum comprises a quartet at δ 27.93 (J_{PF} = 73.3 Hz) and the ^{19}F NMR spectrum a doublet at δ 17.84 (J_{PF} = 73.3 Hz) both of which are comparable to those of $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$. Moreover, the ^{1}H NMR spectrum contains not only a doublet at δ −18.46 due to the bridging hydride but also two signals of intensity ratio of 1:3 at δ 2.63 and δ 2.07 attributable to NH and CH_3 respectively.

(*c*) *With* $[N(PPh_3)_2][Os_3H(CO)_{11}]$. Reaction of $[N(PPh_3)_2][Os_3(\mu\text{-}H)(CO)_{11}]$ with equimolar amounts of either phosphine in CH_2Cl_2 at room temperature afforded in each case a yellow crystalline solid which displayed IR and NMR spectral data characteristic of **1**. Thus the carbonyl stretching frequencies occur at 2112w, 2073s, 2063s, 2030vs, 2013vs and 1991w cm^{-1}. The ^{19}F NMR spectrum comprises a doublet of doublets centred at δ 18.9, the ^{31}P NMR a quartet at δ −25.0, and the ^{1}H NMR a doublet of doublet of quartets centred at δ 6.77 and a doublet of doublets centred at δ −20.39. On the basis of these data the yellow crystalline solid from these reactions has been identified as **1**.

Reactions of Tertiary Phosphine $P(CF_3)_3$.—(*a*) *With* $[Os_3(CO)_{11}(MeCN)]$. Equimolar quantities of $[Os_3(CO)_{11}(MeCN)]$ and $P(CF_3)_3$ reacted at 72 °C in CH_2Cl_2 to yield a yellow solid as the major product. The IR spectrum displays carbonyl stretching frequencies comparable to those of $[Os_3(CO)_{11}\{P(C_6F_5)_3\}]$.[15] Moreover, the ^{19}F NMR spectrum comprises a doublet at δ 17.52 (J_{PF} = 86 Hz) and the ^{31}P NMR spectrum a multiplet at δ 31.03. On the basis of the IR and NMR spectral data, the yellow solid was identified as $[Os_3(CO)_{11}\{P(CF_3)_3\}]$.

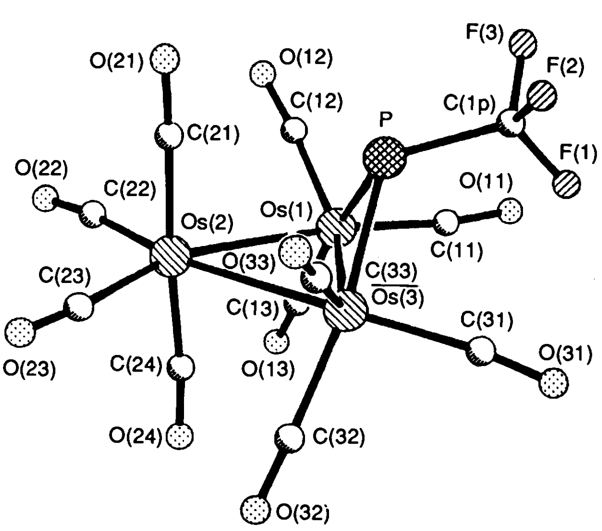


Fig. 1 Molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ **1**

(*b*) *With* $[Os_3(CO)_{10}(MeCN)_2]$. Reaction of $P(CF_3)_3$ with $[Os_3(CO)_{10}(MeCN)_2]$ in approximately 1:2 molar ratio in CH_2Cl_2 at 28 °C yielded a yellow residue which upon TLC using CH_2Cl_2–hexane (1:5) resolved into two bands. The minor band at R_f = 0.8 was identified from its IR and ^{19}F NMR spectra to be $[Os_3(CO)_{11}\{P(CF_3)_3\}]$. The major band at R_f = 0.94 gave an orange solid. Its ^{19}F NMR spectrum comprises signals at δ 18.1 (d, $^2J_{PF}$ = 85) and 17.8 (d, $^2J_{PF}$ = 87 Hz). The ^{31}P NMR spectrum shows a multiplet centred at δ 30.8 with J_{PF} = 85 Hz. A single-crystal X-ray structural study reveals that in the solid state the compound isolated from the major band is the diequatorially substituted $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$ **4** (see below).

(*c*) *With* $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. Reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with an excess of $P(CF_3)_3$ in hexane at 50 °C gave a purplish brown solution. Thin-layer chromatography of the solid obtained after removal of solvent afforded a major band which displays carbonyl stretching frequencies (2090m, 2052s, 2010s, 2003m, 1989m, 1973m and 1959 cm^{-1}) comparable to those of $[Os_3(\mu\text{-}H)_2(CO)_9(PPh_3)]$. Moreover, the ^{1}H NMR spectrum shows a doublet at δ −16.79 (J_{PH} = 1.47 Hz), typical of bridging hydride. The ^{19}F NMR spectrum consists of a doublet at δ 17.92 ($^2J_{PF}$ = 85.13 Hz) while the ^{31}P-{^{1}H} spectrum comprises a multiplet centred at δ 42.78. These reflect an upfield shift of the ^{19}F signal and downfield shift of the ^{31}P signal from those of the free ligand. Thus on the basis of these spectral data the compound from the major band is most likely the dihydro derivative $[Os_3(\mu\text{-}H)_2(CO)_9\{P(CF_3)_3\}]$.

Structures of $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ **1** *and* $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$ **2**.—The molecular structures of compounds **1** and **2** are shown in Figs. 1 and 2 respectively, while the atomic coordinates are given in Tables 2 and 3 and selected bond lengths and angles in Tables 4 and 5.

The structure of compound **1** consists of the triosmium framework, a μ-$PH(CF_3)$ group, ten terminally bound carbonyl groups and a μ-hydride which most probably bridges the same

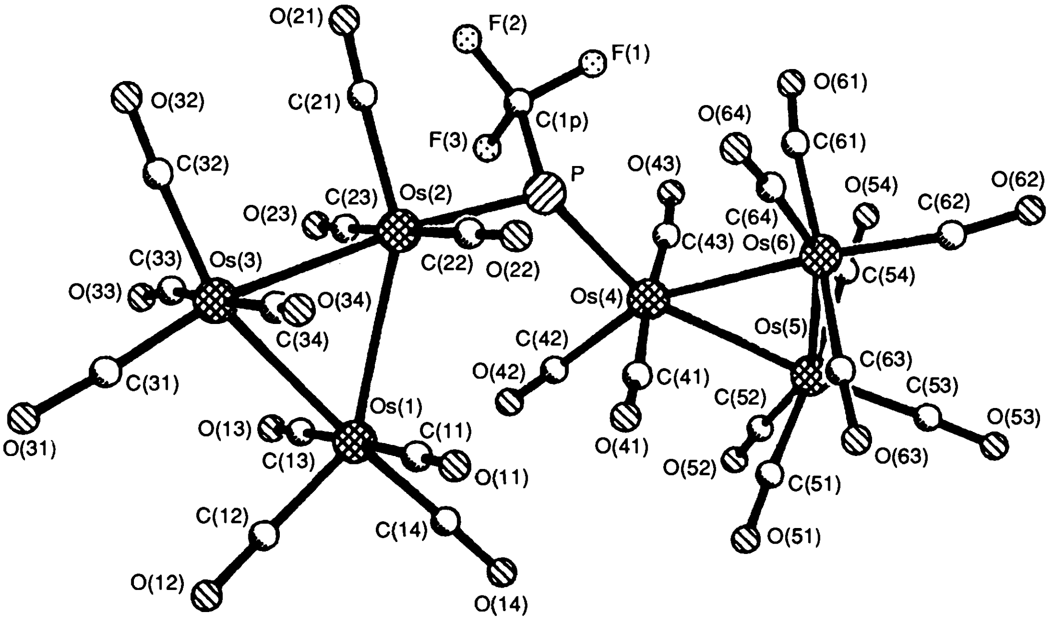


Fig. 2 Molecular structure of $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$ **2**

edge as does the phosphido group. The doubly bridged edge of the Os_3 triangle is the longest [2.929(3) Å] among the three Os–Os bonds, and the non-bridging edges Os(1)–Os(2) 2.878(3) and Os(2)–Os(3) 2.872(3) Å are in good agreement with the average Os–Os distance of 2.877 Å in the parent triosmium carbonyl cluster $[Os_3(CO)_{12}]$.[23]

The Os(1)–Os(2)–Os(3) plane makes a dihedral angle of 75.4° with the Os(1)–P–Os(3) plane, which is similar to the corresponding angles in $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-PH}(C_6F_5)\}]$ **B**[12] and $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-PHPh}\}]$ **C**.[23,24] The phosphorus atom is approximately equidistant from Os(1) and Os(3), and the average Os–P distance of 2.327 Å is slightly shorter than those of **B** (2.365) and **C** (2.367 Å). The CF_3 group is pointing away from the triosmium plane and the bond parameters within the CF_3P group are similar to those for $[Fe(\eta\text{-}C_6H_5)(CO)_2\{P(CF_3)_2\}]$.[25]

Table 2 Fractional atomic coordinates for $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-PH}(CF_3)\}]$ **1** with standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	1865(1)	5644(1)	1907(1)
Os(2)	2879(1)	5679(1)	403(1)
Os(3)	1178(1)	6661(1)	584(1)
P	1984(4)	7044(4)	1753(4)
F(1)	435(13)	7472(13)	2594(12)
F(2)	1273(14)	8454(14)	2206(14)
F(3)	1768(17)	7773(16)	3138(16)
C(1P)	1306(20)	7700(19)	2447(20)
C(11)	1030(17)	5723(16)	2773(16)
C(12)	3004(20)	5484(18)	2523(20)
C(13)	1610(24)	4488(21)	1784(21)
C(21)	3700(16)	6539(15)	717(15)
C(22)	3880(17)	4937(16)	624(16)
C(23)	3107(16)	5891(15)	−725(17)
C(24)	2000(18)	4875(18)	119(18)
C(31)	−61(18)	7140(16)	878(17)
C(32)	679(17)	6100(17)	−365(17)
C(33)	1604(19)	7559(18)	−7(18)
O(11)	586(18)	5758(15)	3395(17)
O(12)	3730(17)	5399(15)	2828(15)
O(13)	1459(15)	3828(16)	1722(15)
O(21)	4207(14)	7079(13)	871(13)
O(22)	4446(16)	4414(13)	718(14)
O(23)	3280(15)	5996(14)	−1332(15)
O(24)	1489(15)	4340(13)	−103(14)
O(31)	−783(16)	7361(15)	999(15)
O(32)	413(15)	5766(13)	−901(14)
O(33)	1884(16)	8114(16)	−364(15)

The Os–C(carbonyl) distances range from 1.857(26) to 1.960(28) Å. The pair Os(1)–C(13) and Os(3)–C(32), *trans* to the phosphorus, have the longest average of 1.952 Å, due to competition with the phosphorus for back-bonding electrons. The pair Os(1)–C(12) and Os(3)–C(33), probably *trans* to the bridging hydride, have an average Os–C distance of 1.886 Å, which is significantly shorter than the average Os–C(equatorial) distance of 1.912 Å in $[Os_3(CO)_{12}]$.[23] A similar trend has also been observed in **B** and **C**. The Os–C–O angles range from 171.9(23) to 179.2(33)°, indicating that the carbonyl groups are essentially linear.

The structure of compound **2** comprises two discrete triosmium triangles linked by the CF_3PH group, with the phosphorus at an equatorial site with respect to each Os_3 unit. The atoms Os(1), Os(4), P and C(1P) lie on a plane and this plane makes dihedral angles of 29.9 and 60.2° with the Os(1)–Os(2)–Os(3) and Os(4)–Os(5)–Os(6) planes respectively. The two triosmium triangles are almost perpendicular to each other (88.8°).

In the Os(1)–Os(2)–Os(3) triangle the Os(1)–Os(2) bond is the longest edge. The metal hydride, though not located crystallographically, most probably bridges these two osmium atoms since it has been shown that the presence of a μ-H bridge on a triosmium cluster results in lengthening of the bridged Os–Os bond.[23] The lengthening effect is further enhanced by the co-ordination of the phosphido ligand to Os(2). Similarly, in the Os(4)–Os(5)–Os(6) triangle the longest edge is Os(4)–Os(6). These findings are consistent with the observation that the substitution of a CO group by a σ-donating ligand at the equatorial position usually results in the lengthening of the Os–Os bond *cis* to it.[16] Each of the Os_3 units has eleven terminally bonded carbonyl groups.

Table 3 Fractional atomic coordinates for $[\{Os_3(\mu\text{-H})(CO)_{11}\}\{\mu\text{-PH}(CF_3)\}\{Os_3(CO)_{11}\}]$ **2** with standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	4 392(1)	7 120(2)	626(1)
Os(2)	3 453(1)	6 531(2)	−105(1)
Os(3)	3 719(1)	6 496(2)	1 043(1)
Os(4)	3 829(1)	7 164(2)	−1 418(1)
Os(5)	4 204(1)	8 249(2)	−2 151(1)
Os(6)	3 458(1)	9 704(2)	−2 066(1)
P	3 306(3)	6 618(11)	−1 044(3)
F(1)	2 786(8)	5 108(29)	−1 876(9)
F(2)	2 674(10)	4 718(32)	−1 176(9)
F(3)	3 274(11)	3 757(27)	−1 280(12)
C(1P)	2 976(11)	4 987(51)	−1 342(14)
C(11)	4 261(10)	9 258(31)	618(13)
C(12)	4 773(11)	7 343(35)	1 342(19)
C(13)	4 545(11)	4 967(39)	630(16)
C(14)	4 798(10)	7 560(32)	319(12)
C(21)	2 845(14)	6 136(43)	−197(13)
C(22)	3 318(11)	8 646(38)	−161(13)
C(23)	3 583(11)	4 470(52)	−110(15)
C(31)	3 996(12)	6 588(44)	1 771(14)
C(32)	3 167(15)	5 943(53)	1 052(14)
C(33)	3 835(14)	4 379(40)	1 012(15)
C(34)	3 588(12)	8 583(49)	1 006(12)
C(41)	4 039(11)	8 841(32)	−887(13)
C(42)	4 281(15)	5 759(40)	−947(22)
C(43)	3 632(14)	5 703(44)	−1 948(14)
C(51)	4 593(11)	9 128(48)	−1 499(19)
C(52)	4 631(12)	6 658(48)	−2 049(14)
C(53)	4 360(15)	9 477(48)	−2 631(16)
C(54)	3 751(19)	7 420(50)	−2 773(14)
C(61)	3 031(14)	8 091(50)	−2 450(17)
C(62)	3 293(13)	11 007(44)	−2 662(14)
C(63)	3 882(14)	11 184(45)	−1 674(17)
C(64)	3 073(13)	10 227(53)	−1 713(15)
O(11)	4 194(8)	10 441(25)	607(11)
O(12)	5 012(9)	7 461(27)	1 778(10)
O(13)	4 630(9)	3 844(29)	649(11)
O(14)	5 061(8)	7 893(26)	131(11)
O(21)	2 512(8)	5 975(30)	−253(10)
O(22)	3 245(10)	9 852(27)	−210(11)
O(23)	3 659(11)	3 193(31)	−123(13)
O(31)	4 177(11)	6 544(39)	2 267(11)
O(32)	2 838(11)	5 814(37)	1 063(13)
O(33)	3 961(11)	3 181(29)	1 061(14)
O(34)	3 506(9)	9 722(32)	1 050(11)
O(41)	4 144(9)	9 672(27)	−584(9)
O(42)	4 504(10)	5 018(28)	−720(14)
O(43)	3 489(12)	4 720(33)	−2 260(13)
O(51)	4 846(9)	9 684(38)	−1 109(14)
O(52)	4 883(16)	5 864(36)	−1 976(15)
O(53)	4 478(11)	10 145(38)	−2 891(11)
O(54)	3 515(14)	6 839(37)	−3 159(12)
O(61)	2 790(12)	7 331(34)	−2 695(14)
O(62)	3 144(13)	11 677(39)	−3 046(14)
O(63)	4 120(10)	12 097(31)	−1 453(12)
O(64)	2 865(13)	10 582(35)	−1 466(13)

The two Os–P distances are not equal: Os(2)–P [2.396(9) Å] is about 0.04 Å longer than Os(4)–P [2.350(11) Å]. The CF_3 group is pointing away from the two triosmium triangles, and the bond parameters within the CF_3P group are similar to those of complex **1**. The angle Os(2)–P–Os(4) is wide [124.4(3)°], compared to Os(1)–P–Os(3) in **1** [78.0(2)°].

Among the linked triosmium clusters reported,[26–30] the linkage has been noted to be mostly effected through ligands having multi-co-ordinating sites, such as diphosphines, dienes and sulfides. In the case of $[Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)]$[29] it was shown from X-ray structural analysis that a diphenylphosphido group linked two triosmium moieties and in addition being supported by a μ_4-sulfido ligand. In each of the Os_3 units one of the Os–Os bonds was broken. On the other hand, the phosphorus atom in $[Os_6(CO)_{18}(\mu_4\text{-}P)]^-$ occupies an interstitial site in a trigonal-prismatic hexaosmium framework and co-ordinates to all six metal atoms with an average Os–P distance of 2.31(1) Å.[30] Thus cluster **2** represents the first of its structural type, where two intact triosmium triangles are supported by a single PR_2 phosphido group.

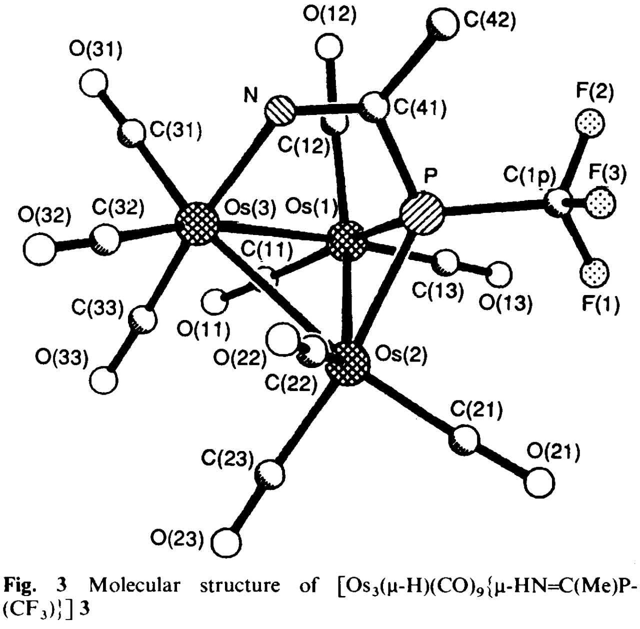


Fig. 3 Molecular structure of $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ **3**

Table 4 Relevant bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ **1**

Os(1)–Os(2)	2.878(3)	P–C(1P)	1.841(32)
Os(1)–Os(3)	2.929(3)	Mean C–F	1.305
Os(2)–Os(3)	2.872(3)	Mean Os–CO	1.905
Os(1)–P	2.320(7)	Mean C–O	1.14
Os(3)–P	2.334(7)		
Os(1)–Os(2)–Os(3)	61.2(1)	Os(3)–Os(1)–P	51.2(2)
Os(1)–Os(3)–Os(2)	59.5(1)	Os(1)–Os(3)–P	50.8(2)
Os(2)–Os(1)–Os(3)	59.3(1)	Os(1)–P–C(1P)	118.3(10)
Os(2)–Os(1)–P	81.3(2)	Os(3)–P–C(1P)	116.2(10)
Os(2)–Os(3)–P	81.2(2)	Mean Os–C–O	176.3

Structure of $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ **3**.—The molecular structure of cluster **3** is shown in Fig. 3, the atomic coordinates are given in Table 6 and selected bond lengths and angles in Table 7. The triosmium cluster contains nine terminally bonded carbonyl ligands, a $HN{=}C(Me)P(CF_3)$ moiety and a μ-hydride.

The $HN{=}C(Me)P(CF_3)$ moiety is co-ordinated to the triosmium framework *via* the N and P atoms. The former is bonded to Os(3), while the latter bridges the Os(1)–Os(2) edge. The average Os–P distance of 2.320 Å is similar to that in the phosphido-bridged cluster **1**. However, the dihedral angle between the Os_3 plane and the Os(1)–Os(2)–P plane in **3** has been reduced to 87.7°, as compared to the equivalent angle of 104.6° in **1**. The atoms Os(3), N(1), C(41), C(42), P, C(1P) and F(1) are planar, and this plane bisects both the Os_3 plane (dihedral angle 89.3°) and the Os(1)–Os(2)–P(1) plane (dihedral angle 89.1°). The Os(3)–N distance [2.122(17) Å] in **3** is similar to the average Os–N distance of 2.128 Å in the parent cluster $[Os_3(CO)_{10}(MeCN)_2]$.[31] The N–C(41) distance of 1.284(24) Å is significantly longer than the N–C triple bond in both $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$, and is close to the value of 1.274(14) Å in $[Os_3H_3(CO)_8(\mu\text{-}C_6H_4)(\mu\text{-}HC{=}NPh)]$,[32] thus indicative of a N–C double bond. The P–C(41) distance of 1.810(19) Å is also typical of a P–C single bond.

In the triosmium framework of compound **3** the edge associated with the phosphido bridge, *i.e.* Os(1)–Os(2), is long [2.935(1) Å] while the other two edges, Os(1)–Os(3) [2.847(1) Å] and Os(2)–Os(3) [2.840(1) Å], are significantly shorter than the average Os–Os distance of 2.877 Å in $[Os_3(CO)_{12}]$.[23] These two short edges are associated with the metal atom [Os(3)] which is bonded to the nitrogen atom.

Each of the three osmium atoms has three carbonyl groups, one axial and two equatorial. An examination of the Os–CO distances shows that the axial carbonyls that are *trans* to the phosphorus have a longer Os–CO bond length compared to the equatorial carbonyls attached to the same osmium atom. However, the Os–CO distance for the axial carbonyl that is *trans* to the nitrogen is the shortest among the three carbonyls attached to Os(3). The observed trend is attributed to the fact that the nitrogen atom is a good σ donor but a poor π acceptor. Therefore, the CO group *trans* to it receives most of the back-donated electron density from the metal orbital and this results in a short Os–CO bond. The other two axial carbonyls have to compete with the phosphorus atom, which is a good π acceptor, for the back-bonding electron density; this results in a longer Os–CO distance. The Os–CO angles range from 174.7(21) to

Table 5 Relevant bond lengths (Å) and angles (°) for $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$ **2**

Os(1)–Os(2)	3.050(2)	Os(4)–Os(5)	2.862(3)	Mean C(1P)–F	1.345
Os(1)–Os(3)	2.892(2)	Os(4)–Os(6)	2.883(2)	Mean Os–CO[a]	1.932
Os(2)–Os(3)	2.889(2)	Os(5)–Os(6)	2.877(3)	Mean Os–CO[b]	1.953
Os(2)–P	2.396(9)	Os(4)–P	2.350(11)	Mean C–O	1.14
P–C(1P)	1.841(43)				
Os(1)–Os(2)–Os(3)	58.2(1)	Os(5)–Os(4)–Os(6)	60.1(1)	Os(2)–P–Os(4)	124.4(3)
Os(1)–Os(3)–Os(2)	63.7(1)	Os(4)–Os(6)–Os(5)	60.3(1)	Os(2)–P–C(1P)	106.9(13)
Os(2)–Os(1)–Os(3)	58.1(1)	Os(4)–Os(6)–Os(5)	59.6(1)		
Os(1)–Os(2)–P	116.1(2)	Os(6)–Os(4)–P	102.3(2)		
Os(3)–Os(2)–P	174.3(2)	Os(5)–Os(4)–P	160.1(2)		
Os(2)–Os(1)–C(14)	118.6(8)	Os(4)–P–C(1P)	113.2(14)		

[a] These are from the Os(1), Os(2), Os(3). [b] These are from the Os(4), Os(5), Os(6).

Table 6 Fractional atomic coordinates for $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ **3** with standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	609(1)	6 573(1)	7 958(1)
Os(2)	−442(1)	8 595(1)	7 660(1)
Os(3)	2 024(1)	8 168(1)	8 971(1)
P	−1 027(5)	7 391(3)	8 587(3)
F(1)	−3 412(14)	6 769(12)	7 563(10)
F(2)	−3 038(15)	6 122(10)	8 865(11)
F(3)	−3 738(13)	7 598(11)	8 667(11)
C(1P)	−2 881(20)	6 947(14)	8 418(14)
C(11)	2 215(24)	6 341(15)	7 442(12)
C(12)	1 226(21)	5 724(16)	8 928(12)
C(13)	−561(24)	5 652(19)	7 211(14)
C(21)	−2 232(22)	8 712(15)	6 881(14)
C(22)	−538(19)	9 656(13)	8 373(12)
C(23)	469(21)	9 284(14)	6 849(12)
C(31)	3 520(22)	7 409(18)	9 648(13)
C(32)	2 574(24)	9 440(14)	9 439(13)
C(33)	2 975(19)	8 376(14)	8 069(12)
O(11)	3 206(18)	6 232(11)	7 152(12)
O(12)	1 550(20)	5 212(11)	9 543(10)
O(13)	−1 173(20)	5 059(11)	6 755(12)
O(21)	−3 362(20)	8 763(13)	6 449(10)
O(22)	−570(15)	10 363(11)	8 868(10)
O(23)	954(19)	9 663(14)	6 323(11)
O(31)	4 422(21)	6 990(16)	10 046(13)
O(32)	2 944(24)	10 183(11)	9 735(10)
O(33)	3 597(16)	8 560(12)	7 502(11)
N	791(17)	7 933(11)	9 934(10)
C(41)	−484(20)	7 618(12)	9 771(13)
C(42)	−1 400(26)	7 461(16)	10 424(13)

Table 7 Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)(CO)_9\text{-}\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ **3**

Os(1)–Os(2)	2.935(1)	N–C(41)	1.284(24)
Os(1)–Os(3)	2.847(1)	P–C(41)	1.810(19)
Os(2)–Os(3)	2.840(1)	P–C(1P)	1.865(20)
Os(1)–P	2.317(5)	C(41)–C(42)	1.495(33)
Os(2)–P	2.323(5)	Mean C(1P)–F	1.334
Os(3)–N	2.122(17)	Mean Os–CO	1.889
Os(1)–Os(2)–Os(3)	59.0(1)	Os(1)–Os(3)–N	89.4(4)
Os(1)–Os(3)–Os(2)	62.1(1)	Os(2)–Os(3)–N	90.6(4)
Os(2)–Os(1)–Os(3)	58.8(1)	Os(3)–N–C(41)	125.5(13)
Os(2)–Os(1)–P	50.8(1)	N–C(41)–P	108.3(15)
Os(1)–Os(2)–P	50.7(1)	P–C(41)–C(42)	124.4(14)
Os(3)–Os(1)–P	72.5(1)	N–C(41)–C(42)	127.3(17)
Os(3)–Os(2)–P	72.5(1)	Os(1)–P–C(1P)	121.1(7)
C(41)–P–C(1P)	105.0(10)	Os(2)–P–C(1P)	120.0(6)

178.3(15)°, indicating that the carbonyl groups are essentially linear.

All the hydrogen atoms in compound **3** are not observed crystallographically but these have been established from the ^1H NMR spectrum. The metal hydride is expected to bridge Os(1) and Os(2), based on electron count, the long Os(1)–Os(2) distance and the distribution of the carbonyl groups on Os(1) and Os(2). The hydrogen on the nitrogen atom is required for bonding considerations. Moreover, the short intermolecular distance (2.999 Å) between N(1) and O(3) of another molecule suggests the possibility of hydrogen bonding between these two atoms.

Structure of $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$ **4**.—The molecular structure of compound **4** is shown in Fig. 4, the atomic coordinates are given in Table 8 and selected bond lengths and angles in Table 9. The triosmium cluster comprises ten terminally bonded carbonyl ligands, with the two $P(CF_3)_3$ groups being diequatorially substituted at Os(2) and Os(3). The Os(2)–P(1) and Os(3)–P(2) bond lengths of 2.257(7) and 2.236(9) Å respectively are shorter than those in $[Os_3(CO)_{11}\{P(C_6F_5)_3\}]$ [2.337(2) Å][15] and $[Os_3(CO)_{11}(PPh_3)]$ [2.370(2) Å].[16] This presumably is due to greater steric bulkiness of the phenyl substituents in the last two cases.

The three osmium atoms form an isosceles triangle [Os(1)–Os(2) 2.892(1), Os(1)–Os(3) 2.896(1) and Os(2)–Os(3) 2.884(1) Å]. The somewhat longer Os(1)–Os(2) and Os(1)–Os(3) bond distances are probably due to the proximity of the $P(CF_3)_3$ substituents as has been observed in $[Os_3(CO)_{11}\{P(C_6F_5)_3\}]$.[15] Around each P, the CF_3 groups are being pushed back so that the average C–P–C angle is 98.7° while Os–P–C assumes an average of 119.0°.

The average Os–CO distances are 1.964, 1.992 and 1.938 Å for Os(1), Os(2) and Os(3) respectively. The large estimated standard deviations (e.s.d.s) associated with these parameters preclude an accurate assessment of the bonding effect due to the $P(CF_3)_3$ substituents. The average C–O distance (1.13 Å) is close to that [1.14(11) Å] reported for $[Os_3(CO)_{12}]$.[23]

Conclusion

The primary perfluoroalkyl phosphines as well as the secondary perfluoroalkyl phosphines undergo P–C bond cleavage upon reactions with the anionic cluster $[Os_3H(CO)_{10}]^-$ to afford $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ and $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ respectively. In addition $(CF_3)_2C(OH)PH$ similarly displays P–C bond cleavage in its reaction with $[Os_3(CO)_{11}(MeCN)]$ to give the phosphido-bridged cluster $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ and the linked cluster $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$. Moreover reaction of this phosphine with $[Os_3(CO)_{10}(MeCN)_2]$ afforded the novel molecule $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$. However, reactions of $(CF_3)_2C(OH)PH_2$ and the tertiary phosphine $P(CF_3)_3$ with the mono- and bis-acetonitrile derivatives afforded only substitution products.

Experimental

Infrared spectra were recorded on a Perkin Elmer 983G spectrophotometer and NMR spectra (in $CDCl_3$) on a JEOL FX 90Q Fourier-transform spectrometer. Solvents were distilled from calcium hydride and used fresh. Thin-layer chromatography was done on 20 × 20 × 0.1 cm plates coated with Merck Kieselgel 60 F254 silica gel. The compound $[Os_3(CO)_{11}(MeCN)]$ was prepared as described.[33]

Reactions.—$[Os_3(CO)_{11}(MeCN)]$ *with* $(CF_3)_2C(OH)PH(CF_3)$. The compound $(CF_3)_2C(OH)PH(CF_3)$ (20.3 mg, 85.3 μmol) was condensed at liquid-nitrogen temperature into a degassed solution of $[Os_3(CO)_{11}(MeCN)]$ (56.8 mg, 61.8 μmol) in dichloromethane. The mixture was warmed to room temperature and stirred for 24 h. Work-up (TLC) gave as a first fraction a yellow solid which was recrystallised from chloroform solution affording yellow crystals of compound **1** (13%), and **2** (36%) as a second fraction giving deep yellow blocks on crystallisation from dichloromethane (Found: C, 14.8; H, 0.15; F, 3.60; P, 1.55. Calc. for $C_{23}H_2F_3O_{22}Os_6P$: C, 14.85; H, 0.10; F, 3.05; P, 1.65%).

$[Os_3(CO)_{11}(MeCN)]$ *with* $(CF_3)_2C(OH)PH_2$. The compound $(CF_3)_2C(OH)PH_2$ (13.3 mg, 66.5 μmol) was condensed into a CH_2Cl_2 solution containing $[Os_3(CO)_{11}(MeCN)]$ (50.5 mg, 54.9 μmol). The mixture was warmed to room temperature and allowed to stir overnight. The yellow solid obtained after removal of solvent was purified by TLC on silica plates using CH_2Cl_2–hexane (90%:10%) as eluent. The monosubstituted cluster $[Os_3(CO)_{11}\{(CF_3)_2C(OH)PH_2\}]$ was obtained in 82.2% yield (48.7 mg, 45.2 μmol) (Found: C, 15.10; H, 0.25; F, 10.7; P, 2.95. Calc. for $C_{14}H_3F_6O_{12}Os_3P$: C, 15.60; H, 0.30; F, 10.55; P, 2.85%).

$[Os_3(CO)_{10}(MeCN)_2]$ *with* $(CF_3)_2C(OH)PH_2$. The com-

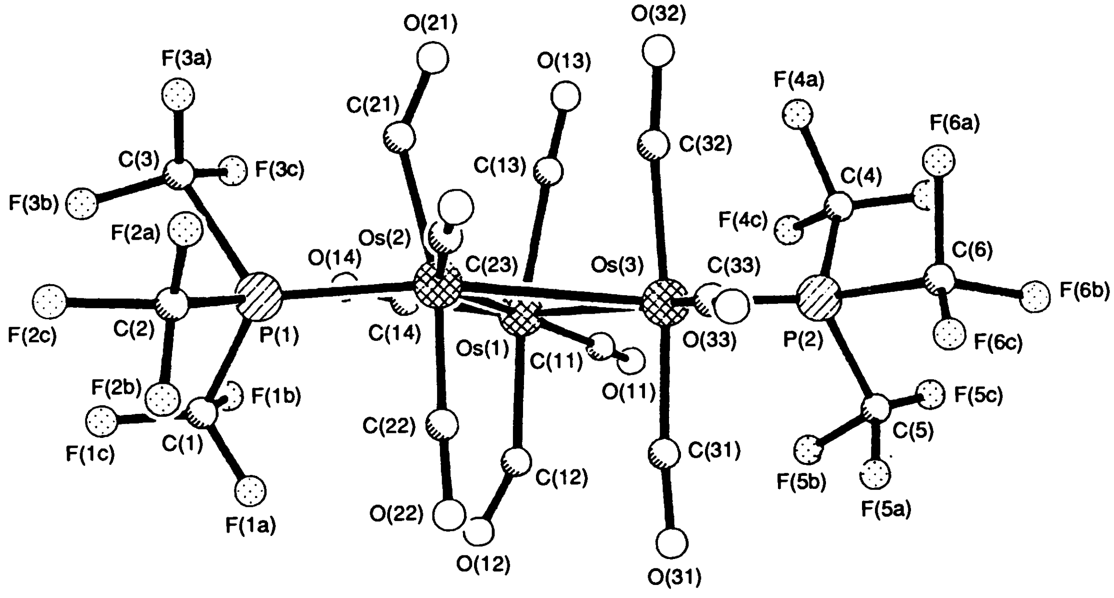


Fig. 4 Molecular structure of $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$ **4**

Table 8 Fractional atomic coordinates for $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$ **4** with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Os(1)	2950(1)	4960	3592(1)	C(1)	6071(45)	6765	2154(29)
Os(2)	2824(1)	4911	1681(1)	C(2)	4526(56)	6635	409(35)
Os(3)	1592(1)	2822	2441(1)	C(3)	3373(52)	8447(47)	1402(35)
P(1)	4158(11)	6590	1461(6)	C(4)	−622(40)	2393	3887(26)
P(2)	585(10)	1651	3313(6)	C(5)	1620(60)	572	4229(39)
C(11)	2962(37)	4437	4759(20)	C(6)	−503(64)	233(62)	2650(39)
C(12)	4823(30)	3944	3850(20)	F(1a)	6668(44)	5780	2421(26)
C(13)	988(37)	5689	3346(25)	F(1b)	5980(31)	7241	3014(21)
C(14)	3751(39)	6677	3992(22)	F(1c)	6821(29)	7628	1946(18)
C(21)	1427(56)	6362	1483(38)	F(2a)	3484(39)	6478	−325(25)
C(22)	4390(42)	3892	1863(19)	F(2b)	5532(43)	5908	317(27)
C(23)	2047(31)	4377	462(19)	F(2c)	5252(30)	7732	194(19)
C(31)	3435(37)	1975	2980(21)	F(3a)	2340(40)	8485(37)	663(25)
C(32)	−166(42)	3882	1953(23)	F(3b)	4396(50)	9254(46)	1372(31)
C(33)	1135(43)	1834	1392(20)	F(3c)	3127(37)	8551(37)	2229(25)
O(11)	3051(30)	4347	5510(20)	F(4a)	−1487(33)	3327	3335(21)
O(12)	5960(26)	3837	3945(15)	F(4b)	−1412(35)	1630	4194(22)
O(13)	−86(32)	6094	3295(18)	F(4c)	65(29)	3143	4634(17)
O(14)	4101(35)	7670	4195(22)	F(5a)	2365(45)	0	3954(27)
O(21)	286(35)	6591	1431(22)	F(5b)	2707(37)	1221	4756(23)
O(22)	5313(28)	3155	1891(17)	F(5c)	1108(29)	317	4869(19)
O(23)	1572(29)	4013	−243(20)	F(6a)	−1859(42)	880(38)	2170(25)
O(31)	4471(36)	1353	3277(22)	F(6b)	−934(38)	−612(37)	3343(25)
O(32)	−1295(29)	4330	1611(18)	F(6c)	31(36)	−402(33)	2236(23)
O(33)	1004(29)	1272	757(19)				

Table 9 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$ **4**

Os(1)–Os(2)	2.892(2)	Mean P–C	1.878
Os(1)–Os(3)	2.896(1)	Mean C–F	1.315
Os(2)–Os(3)	2.884(1)	Mean Os–CO	1.931
Os(2)–P(1)	2.257(7)	Mean C–O	1.12
Os(3)–P(2)	2.236(9)		
Os(1)–Os(2)–Os(3)	60.2(1)	Os(3)–Os(2)–P(1)	165.2(2)
Os(1)–Os(3)–Os(2)	60.0(1)	Os(1)–Os(2)–P(1)	106.5(2)
Os(2)–Os(1)–Os(3)	59.8(1)	Mean Os(2)–P(1)–C	119.1
Os(2)–Os(1)–P(2)	163.3(1)	Mean Os(3)–P(2)–C	118.7
Os(1)–Os(3)–P(2)	104.8(2)	Mean Os–C–O	167.7

pound $(CF_3)_2C(OH)PH_2$ (28.0 mg, 140 μmol) was condensed *in vacuo* into a degassed solution of $[Os_3(CO)_{10}(MeCN)_2]$ (49.9 mg, 53.5 μmol) in CH_2Cl_2. After stirring at room temperature for 2 h, the solvent was removed under vacuum. Thin-layer chromatography of the residue using CH_2Cl_2 as eluent gave three bands from which $[Os_3(CO)_{11}\{(CF_3)_2C(OH)PH_2\}]$ (7.3 mg, 6.8 μmol, 12.7%) was isolated in band 2 as a yellow solid and $[Os_3(CO)_{10}\{(CF_3)_2C(OH)PH_2\}_2]$ (34.9 mg, 27.9 μmol, 52.2%) from band 3.

$[N(PPh_3)_2][Os_3H(CO)_{11}]$ *with* $(CF_3)_2C(OH)PH_2$. To a CH_2Cl_2 solution of $[N(PPh_3)_2][Os_3H(CO)_{11}]$ (61.5 mg, 43.4 μmol) was added $(CF_3)_2(OH)PH_2$ (8.6 mg, 43.0 μmol) at liquid-nitrogen temperature. The mixture was allowed to stir at room temperature for 1 h, during which time the colour changed from red to yellow. The solvent was removed under vacuum and TLC of the residue using CH_2Cl_2–hexane afforded $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (16.5 mg, 43.0%) (Found: C, 14.30; H, 0.35; P, 3.70. Calc. for $C_{10}H_3O_{10}Os_3P$: C, 13.55; H, 0.30; P, 3.50%). The reaction was completed after stirring at room tempera-

Table 10 Crystal data and details of measurements for compounds **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{11}H_2F_3O_{10}Os_3P$	$C_{23}H_2F_3O_{22}Os_3P$	$C_{12}H_5F_3NO_9Os_3P$	$C_{16}F_{18}O_{10}Os_3P_2$
M_r	950.7	1857.4	960.7	1326.7
Crystal size(mm)	0.40 × 0.30 × 0.25	0.20 × 0.25 × 0.35	0.25 × 0.35 × 0.35	0.20 × 0.30 × 0.35
Crystal symmetry	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	*C2/c*	$P2_1/n$	$P2_1$
a/Å	13.848(11)	33.012(7)	9.720(3)	9.743(2)
b/Å	16.433(8)	9.089(2)	13.597(3)	10.373(2)
c/Å	16.703(15)	26.943(6)	15.389(3)	15.305(3)
β/°		111.550(6)	102.460	107.26(2)
U/Å^3	3801(5)	7519(3)	1985.9(8)	1477.1(4)
Z	8	8	4	2
F(000)	3328	6496	1684	1192
D_c/g cm^{-3}	3.328	3.281	3.213	2.983
μ(Mo-Kα)/cm^{-1}	202.0	203.7	193.3	131.4
ω scan width/°	2.00	2.00	2.00	1.30
Measured reflections	3707	13 062	3880	6010
Independent reflections	3306	6025	3492	2765
Observed reflections[a]	2347	3202	2453	2167
Absorption correction (minimum, maximum)	0.0415, 0.0946	0.2521, 0.8907	0.0465, 0.0840	0.1438, 0.1918
R	6.32	5.35	4.19	4.62
R'[b]	7.83	6.79	6.20	5.72
g	0.002	0.0017	0.0101	0.0012
Goodness of fit	1.28	1.23	0.58	1.22

[a] $F > 6.0\sigma(F)$. [b] Weighting scheme $w^{-1} = \sigma^2(F) + |g|F^2$.

ture for 24 h. The solvent was removed *in vacuo* and TLC of the residue using CH_2Cl_2–hexane (50%:50%) as eluent afforded three bands: $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ was obtained from band 1 as yellow crystals (7.8 mg, 13.3%), and $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$ (36.2%) was isolated from band 3 as orange crystals.

$[Os_3(CO)_{10}(MeCN)_2]$ *with* $(CF_3)_2C(OH)PH(CF_3)$. The compound $(CF_3)_2C(OH)PH(CF_3)$ (37.8 mg, 141 μmol) was condensed at liquid-nitrogen temperature onto a CH_2Cl_2 solution of $[Os_3(CO)_{10}(MeCN)_2]$ (63.8 mg, 68.4 μmol). The solution turned from yellow to orange after stirring at room temperature for 1 h. The solvent was removed *in vacuo* and the residual solid gave four bands when chromatographed on silica plates, using CH_2Cl_2–hexane (50%:50%) as eluent. The compound $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}]$ (6.8 mg) was obtained as reddish orange crystals from band 2.

$[Os_3(CO)_{11}(MeCN)]$ *with* $P(CF_3)_3$. Into a CH_2Cl_2 solution (5 cm^3) containing $[Os_3(CO)_{11}(MeCN)]$ (72.7 mg, 79.0 μmol) was condensed $P(CF_3)_3$ (89.0 μmol) and the reaction mixture allowed to stir at 72 °C for 16 h. Thin-layer chromatography of the solution (CH_2Cl_2–hexane, 10%:90%) gave one major yellow band which afforded $[Os_3(CO)_{11}\{P(CF_3)_3\}]$ as a yellow solid (Found: C, 15.0; F, 15.1; P, 2.6. Calc. for $C_{14}F_9O_{11}Os_3P$: C, 15.0; F, 15.3; P, 2.8%).

$[Os_3(CO)_{10}(MeCN)_2]$ *with* $P(CF_3)_3$. The compound $[Os_3(CO)_{10}(MeCN)_2]$ (100.8 mg, 108.1 μmol) in hexane (10 cm^3) and $P(CF_3)_3$ (49.0 mg, 205.9 μmol) were heated with stirring at about 58 °C for 4.5 h. Removal of the solvent and volatiles by rotary evaporation, followed by TLC (CH_2Cl_2–hexane, 10%:90%) gave three major yellow bands: $[Os_3(CO)_{10}\{P(CF_3)_3\}_2]$ (72.3 mg, 63%) was isolated as orange crystals from band 1.

$[Os_3(\mu\text{-}H)_2(CO)_{10}]$ *with* $P(CF_3)_3$. The compounds $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (30 mg, 35 μmol) and $P(CF_3)_3$ (10 mg, 42 μmol) were stirred in degassed hexane (10 cm^3) at 50 °C in an evacuated ampoule. Initially, some yellow precipitate was observed, which redissolved to yield a final purplish brown solution. After the solvent was removed, careful chromatography on silica gel with dichloromethane–hexane (1:9) as eluent afforded a major band (*ca.* 20 mg) which was identified as $[Os_3(\mu\text{-}H)_2(CO)_9\{P(CF_3)_3\}]$ (Found: C, 13.85; H, 0.20; F, 15.9; P, 2.8. $C_{12}H_2F_9O_9Os_3P$ requires C, 13.55; H, 0.20; F, 16.1; P, 2.9%).

$[Os_3(CO)_{10}(MeCN)_2]$ *with* $PH_2(CF_3)$. A CH_2Cl_2 solution (15 cm^3) containing $PH_2(CF_3)$ (111.2 μmol) was condensed onto $[Os_3(CO)_{10}(MeCN)_2]$ (41.6 mg, 44.6 μmol). The mixture was allowed to stir at 58 °C overnight. Evaporation of the solvent under N_2 followed by TLC using CH_2Cl_2–hexane (30%:70%) afforded one major yellow band from which $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}]$ (22.2 mg, 52%) was obtained.

$[N(PPh_3)_2][Os_3H(CO)_{11}]$ *with* $PH_2(CF_3)$. A CH_2Cl_2 (10 cm^3) solution containing $PH_2(CF_3)$ (88.0 μmol) was condensed onto $[N(PPh_3)_2][Os_3H(CO)_{11}]$ (124.5 mg, 87.8 μmol). The reaction mixture was allowed to stir overnight at room temperature. The yellow solution was then concentrated and chromatographed using CH_2Cl_2–hexane (70%:30%) to give two major bands. The cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OH)]$ was obtained from band 2 as a yellow solid. The first band was rechromatographed using CH_2Cl_2–hexane (10%:90%) to give two yellow bands which afforded $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (6.7 mg, 9%) from band 1 and $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CH_2Cl)\}]$ (4.1 mg, 5%) from band 2.

X-Ray Structural Determinations.—Crystal data and details of measurements for complexes **1**–**4** are reported in Table 10. Diffraction intensities were collected at 298 K on a Siemens R3m/V diffractometer, using the ω–2θ scan mode with graphite-monochromatised Mo-Kα radiation (λ = 0.710 69 Å), scan speed 3.5–15° min^{-1} and $3.0 < 2\theta < 50.0°$, $+h$, $+k$, $\pm l$ for **2**–**4** and $+h$, $+k$, $+l$ for **1**. All computations were carried out on a MicroVAX 2000 computer using the SHELXTL PLUS program package.[34] The structures were solved by direct methods for the osmium atoms and Fourier difference techniques for the remaining non-hydrogen atoms. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic except for that of **1**. An empirical (ψ-scan) correction was performed in each case.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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