Reaction of the Unsaturated Triosmium Cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ with HBF_4 and $[Au(PPh_3)]PF_6$; Crystal Structure of $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$†

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Treatment of the unsaturated cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1** with $[Au(PPh_3)]PF_6$ gives the cationic cluster $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2**, while with HBF_4 it gives $[Os_3H_2(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]BF_4$ **3**. The crystal structure of **2**, obtained using synchrotron radiation, reveals that the $AuPPh_3$ moiety bridges the formally unsaturated Os–Os edge, while the hydride bridges the Os–Os edge which is also bridged by the P atoms of the metallated diphosphine ligand.

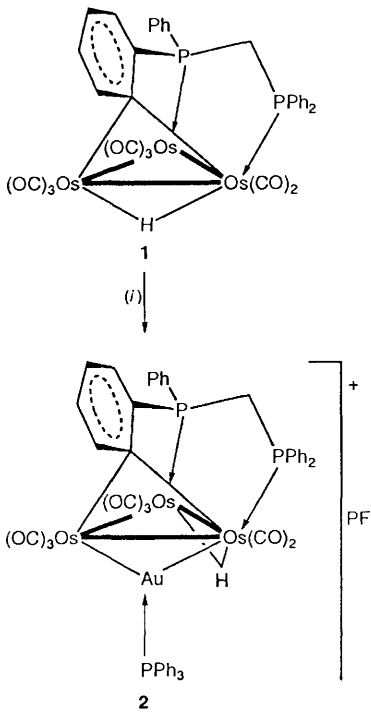
The complex $[Os_3(CO)_{12}]$ is protonated by treatment with strong acids such as sulfuric acid.[1–3] Protonation of the more electron-rich phosphine derivatives of $[Os_3(CO)_{12}]$ occurs on treatment with weaker acids.[2,4–7] In all cases the product formed is a cationic hydrido cluster in which the hydride adopts a bridging co-ordination site. The unsaturated triosmium clusters $[Os_3H_2(CO)_{10}]$ and $[Os_3H_2(CO)_9L]$ (L = PEt_3 or PPh_3) react with CF_3CO_2H to give the cationic clusters $[Os_3H_3(CO)_{10}]^+$ and $[Os_3H_3(CO)_9L]^+$, respectively, in which one hydride ligand is suggested to bridge each of the three Os–Os edges of the triosmium triangle.[8] The cyclometallated cluster $[Os_3H_2(CO)_9\{\mu_3\text{-}P(C_6H_4)Ph\}]$ reacts with Brønsted acids HX to give the addition products $[Os_3H_2(X)(CO)_9(\mu\text{-}PPh_2)]$ *via* a protonation reaction.[9] The protonated complex $[Os_3H_3(CO)_9\{\mu_3\text{-}P(C_6H_4)Ph\}]^+$ is obtained when $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ is treated with HBF_4.[9] In this case also, a hydride ligand bridges each of the three Os–Os edges.

We have previously reported that the reaction of the unsaturated triosmium cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1** with dihydrogen leads to demetallation of the phenyl group of the diphosphine ligand to give $[Os_3H_2(CO)_8(Ph_2PCH_2PPh_2)]$,[10] and that similar demetallation reactions occur on treatment of **1** with phosphines[11] or alkynes.[12] In the latter reactions the donor ligand induces migration of a hydride ligand from the metal core to the bridging, metallated carbon of the $Ph_2PCH_2PPh_2$ (dppm) ligand, thereby providing the co-ordination site to be occupied by the donor. By analogy, we first carried out reactions between **1** and nucleophilic carbonylmetalates [*e.g.* $(\eta\text{-}C_5H_5)Mo(CO)_3^-$, $Co(CO)_4^-$]. These reactions were anticipated to provide new access to dppm-stabilised heterometallic clusters of osmium. However, these attempts were unsuccessful. In contrast, reactions with electrophiles resulted in addition products and we report here on the reactions of the unsaturated cluster **1** with the electrophilic reagents $[Au(PPh_3)]PF_6$ and HBF_4.

Results and Discussion

Treatment of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1** with $[Au(PPh_3)]PF_6$ leads to the formation of the orange, cationic cluster $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2** in good yield (Scheme 1). Cluster **2** has been characterised spectroscopically, and by a crystal structure determination. The hydride resonance in the ^1H NMR spectrum is a triplet of doublets at δ −13.76. Proton decoupling experiments (see Fig. 1) have established that the hydride is coupled equally to the two phosphorus atoms [*J*(PH) 12.7 Hz] and is also coupled to one of the hydrogen atoms on the CH_2 group of the diphosphine ligand [*J*(HH) 4.0 Hz].

Thus, when the CH_2 resonance at δ 4.54 is decoupled the



Scheme 1 (*i*) $[Au(PPh_3)]PF_6$, tetrahydrofuran (thf)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

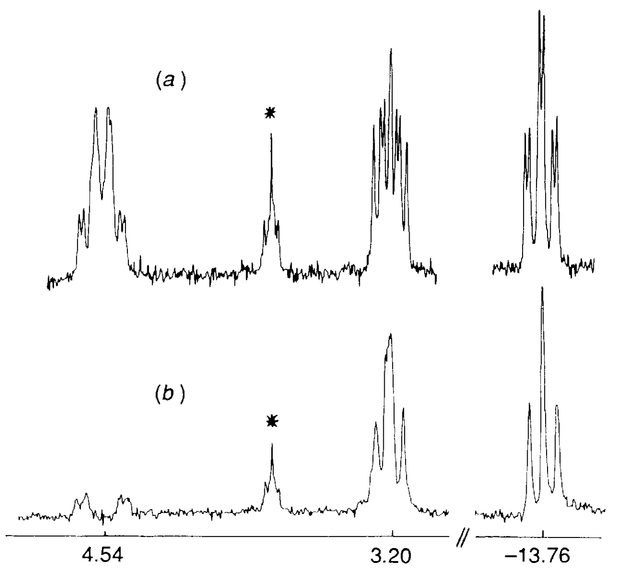

Fig. 1 Proton NMR spectrum of $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2** in $CDCl_3$, showing the CH_2 and hydride region only: (*a*) coupled spectrum; (*b*) spectrum with CH_2 proton at δ 4.54 decoupled. The resonance marked * at δ 3.59 is due to thf

hydride resonance becomes a triplet [Fig. 1(*b*)]. This four-bond coupling must arise from the all-*trans* W arrangement of the bridging hydride with one of the CH_2 protons. It suggests that the hydride is bridging the same Os–Os edge as the diphosphine ligand but on the opposite side of the Os_3 plane. Repeated attempts to grow crystals of compound **2** suitable for a crystal structure determination using a conventional X-ray source and detector were unsuccessful. However, a data set was obtained using the synchrotron radiation source at Daresbury and an area-detector diffractometer for a crystal of dimensions 50 × 20 × 20 μm. The structure is shown in Fig. 2 and selected bond lengths and angles are given in Table 1. The cation consists of a triangle of osmium atoms in which the shortest Os–Os edge [Os(2)–Os(3) 2.749(3) Å] is bridged by the $AuPPh_3$ moiety and the metallated phenyl ring. This short bond length is very similar to that in the parent compound **1**[13] [2.747(1) Å] and is indicative of the unsaturated, 46-electron character of these triosmium clusters. The Os–Os edge bridged by the diphosphine ligand [Os(1)–Os(2) 2.994(3) Å] is significantly longer than the equivalent edge in **1** [2.844(1) Å]. This suggests that the hydride ligand, which was not located from the electron-density map, is bridging this Os(1)–Os(2) edge in agreement with the spectroscopic data. This conclusion is further supported by the carbonyl ligand arrangement, in particular the large Os(2)–Os(1)–C(6) angle of 118.7(15)°, to accommodate the bridging hydride. The metallated phenyl group requires that the phosphorus atoms of the diphosphine ligand occupy axial co-ordination sites. It does not symmetrically bridge the Os(2)–Os(3) edge [Os(2)–C(46) 2.294(9), Os(3)–C(46) 2.381(8) Å], in contrast to the parent compound **1** in which there is no significant difference in the Os–C bond lengths for the bridging carbon atom of the metallated phenyl ring.[13]

It is interesting that the gold cation $[Au(PPh_3)]^+$ simply adds to the cluster and thus behaves towards compound **1** very much like H^+ does towards the clusters mentioned in the Introduction. Replacement of a hydride ligand by $[Au(PPh_3)]^+$ has been observed with platinum and resulted in the first platinum–gold cluster.[14]

Treatment of the unsaturated cluster **1** with HBF_4 leads to the formation of a single product which has been formulated as $[Os_3H_2(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]BF_4$ **3** on the basis of infrared and NMR spectroscopy. There are two hydride resonances in the ^1H NMR spectrum, a doublet of doublets at δ −13.82 [*J*(PH) 28.1, *J*(P′H) 8.0 Hz] and a triplet of doublets at δ −14.17 [*J*(PH) = *J*(P′H) = 13.3, *J*(HH) 4.2 Hz]. This clearly indicates that **3** has a similar structure to that of **2** with the $AuPPh_3$ group in **2** being replaced by H. The hydride bridging the same Os–Os edge as the diphosphine ligand has the same triplet of doublets resonance, with the same coupling constants, in the two clusters. Thus, once again, coupling between the hydride and a methylene hydrogen of the diphosphine ligand is observed.

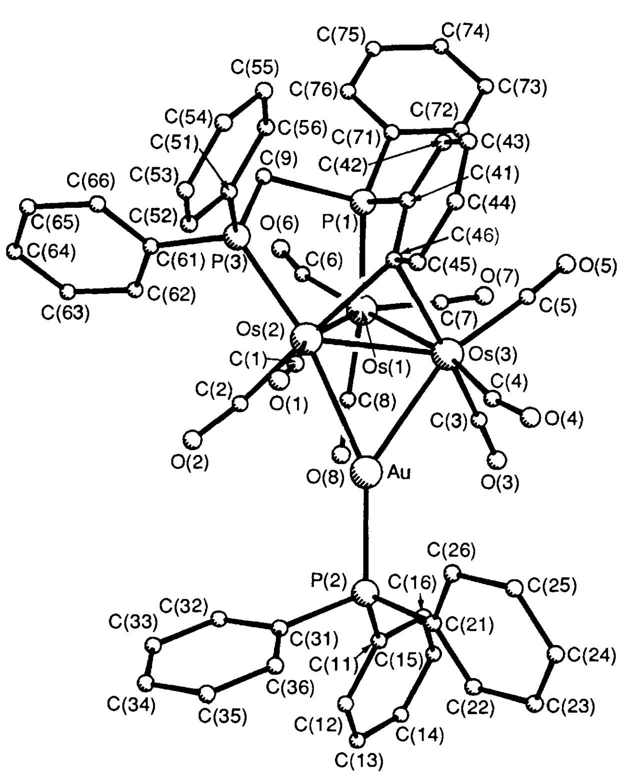

Fig. 2 The molecular structure of $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]^+$ **2**, with hydrogen atoms omitted

Table 1 Selected bond lengths (Å) and angles (°) for $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2**

Os(1)–Os(2)	2.994(3)	C(46)–Os(2)	2.294(9)
Os(1)–Os(3)	2.856(3)	C(46)–Os(3)	2.381(8)
Os(2)–Os(3)	2.749(3)	Os(1)–P(1)	2.362(10)
Au–Os(2)	2.784(2)	Os(2)–P(3)	2.360(10)
Au–Os(3)	2.793(2)	Au–P(2)	2.311(9)
Os(2)–Os(1)–Os(3)	56.0(1)	Os(2)–Os(1)–C(6)	118.7(15)
Os(1)–Os(2)–Os(3)	59.5(1)	Os(3)–Os(1)–C(7)	86.0(23)
Os(1)–Os(3)–Os(2)	64.5(1)	Os(2)–Os(1)–P(1)	75.7(3)
Os(2)–C(46)–Os(3)	72.0(2)	Os(1)–Os(2)–P(3)	92.9(3)
Os(2)–Au–Os(3)	59.1(1)	P(1)–Os(1)–C(8)	166.3(16)
P(1)–C(9)–P(3)	103.8(6)		

Experimental

All reactions were carried out under nitrogen using dried, degassed solvents. Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer, mass spectra on a VG 7070E instrument, and NMR spectra in $CDCl_3$ using a Bruker WM250 instrument with chemical shifts relative to 85% H_3PO_4 (^{31}P) or $SiMe_4$ (^1H). The compounds $[AuCl(PPh_3)]$[15] and $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1**[13] were prepared as previously described.

Preparation of $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2**.—An excess of $TlPF_6$ (0.025 g, 7.22×10^{-5} mol) was added to a thf solution (30 cm^3) of $[AuCl(PPh_3)]$ (0.028 g, 5.66×10^{5} mol). The solution was stirred at room temperature for 3 h, and then filtered through Celite to remove the TlCl formed. To the resulting solution was added $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1** (0.061 g, 5.17×10^{-5} mol). After stirring for 1 h at room temperature the resulting orange solution was evaporated to dryness, and the residue recrystallised from dichloromethane–heptane to give orange needles of $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2** (0.046 g, 49.9%) (Found: C, 34.9; H, 2.7%; *M* 1639. $C_{51}H_{37}AuF_6O_8Os_3P_4$ requires C, 34.4; H, 2.1%; *M* − PF_6 1639); ν(CO)(thf) 2077s, 2024vs and 1972s cm^{-1}. NMR: $^{31}P-\{^1H\}$, δ 71.63 [d, *J*(PP) 32.5, PPh_3], −1.41 [d, *J*(PP) 58.9, $PPhC_6H_4$], −14.84 [dd, *J*(PP) 58.9 and 32.5, PPh_2] and −143.0 [spt, *J*(PF) 713, PF_6]; ^1H, δ 4.54 (m, CH_2), 3.20 (m, CH_2) and −13.76 [t of d, *J*(PH) = *J*(P′H) 12.7, *J*(HH) 4.0 Hz, OsHOs].

Preparation of $[Os_3H_2(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]BF_4$ **3**.—A diethyl ether solution containing HBF_4 (7.44 mg, 8.5×10^{5} mol) was added to a toluene solution (10 cm^3) of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1** (0.100 g, 8.5×10^{-5} mol), and the resulting mixture was stirred at room temperature for 1 h. The resulting yellow solution was evaporated to dryness and the residue recrystallised from dichloromethane–heptane to give $[Os_3H_2(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]BF_4$ **3** as an orange crystalline solid (0.056 g, 52%) (Found: C, 31.2; H, 1.9%; *M* 1181. $C_{23}H_{33}BF_4Os_3O_8P_2$ requires C, 31.3; H, 1.8%; *M* − BF_4 1181); ν(CO)(CH_2Cl_2) 2100s, 2070s, 2060s, 2030m and 2000s cm^{-1}. NMR: $^{31}P-\{^1H\}$, δ −9.07 (d) and −18.48 (d) [*J*(PP) 40.9]; ^1H, δ −13.82 [dd, *J*(PH) 28.1, *J*(P′H) 8.0] and −14.17 [t of d, *J*(PH) = *J*(P′H) 13.3, *J*(HH) 4.2 Hz].

Crystal Structure Determination of $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6$ **2**.—Crystals of complex **2** were grown from a chlorobenzene solution and a suitable crystal of dimensions 50 × 20 × 20 μm was mounted on a glass fibre.

Crystal data. $C_{51}H_{37}AuF_6O_8Os_3P_4{\cdot}0.5C_6H_5Cl$, *M* = 1839.5, monoclinic, space group *C*2/*c*, *a* = 37.667(5), *b* = 9.693(2), *c* = 34.958(11) Å, β = 104.50(1)°, *U* = 12 357.6 $Å^3$ (by least-squares refinement on a TV area-detector diffractometer of coordinates for 250 reflections), Daresbury synchrotron radiation source, λ = 0.895(5) Å, *Z* = 8, D_c = 1.96 g cm^{-3}, *F*(000) = 6856, μ = 147.16 cm^{-1}.

Data collection and processing. As described previously.[16,17] Synchrotron radiation source (SRS) at SERC Daresbury Laboratory, Enraf-Nonius FAST area-detector diffractometer; SRS at 2 GeV (*ca.* 3.2×10^{-10} J), 92 mA, collimator 0.2 mm, θ range = 0–245°, frame size 0.2°, frame time 11 s. A total of 27 741 reflections were measured, including absences; 2212 unique with $F \geqslant 3\sigma(F)$, merging *R* = 0.056.

Structure analysis and refinement. The structure was solved by

Table 2 Atomic coordinates for $[Os_3AuH(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]PF_6{\cdot}0.5$ PhCl **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.176 89(4)	0.179 21(24)	0.194 38(5)	C(34)	0.287 5(2)	−0.010 6(11)	−0.013 0(3)
Os(2)	0.163 05(4)	0.029 02(22)	0.117 22(5)	C(35)	0.291 2(2)	−0.148 6(11)	−0.001 4(3)
Os(3)	0.192 00(4)	−0.106 93(24)	0.187 07(6)	C(36)	0.291 4(2)	−0.184 8(11)	0.037 3(3)
Au	0.234 50(5)	−0.071 15(25)	0.132 81(6)	C(41)	0.108 7(2)	−0.065 6(11)	0.171 3(3)
P(1)	0.114 8(3)	0.110 9(15)	0.181 7(3)	C(42)	0.080 6(2)	−0.146 9(11)	0.178 7(3)
P(2)	0.288 4(3)	−0.125 2(15)	0.116 0(3)	C(43)	0.074 4(2)	−0.279 0(11)	0.162 5(3)
P(3)	0.104 8(3)	0.130 8(13)	0.093 5(3)	C(44)	0.096 3(2)	−0.329 6(11)	0.138 9(3)
P(4)	0.012 8(4)	0.417 8(22)	0.390 8(5)	C(45)	0.124 4(2)	−0.248 3(11)	0.131 4(3)
O(1)	0.156 4(8)	−0.171 1(41)	0.051 1(10)	C(46)	0.130 5(2)	−0.116 2(11)	0.147 6(3)
O(2)	0.204 6(8)	0.212 9(42)	0.073 3(10)	C(51)	0.071 4(2)	0.010 1(11)	0.062 7(3)
O(3)	0.267 6(9)	−0.044 7(41)	0.237 9(10)	C(52)	0.075 2(2)	−0.031 1(11)	0.025 7(3)
O(4)	0.210 6(10)	−0.401 1(56)	0.168 6(12)	C(53)	0.051 1(2)	−0.127 7(11)	0.003 6(3)
O(5)	0.167 9(9)	−0.181 7(44)	0.259 3(11)	C(54)	0.023 1(2)	−0.183 0(11)	0.018 6(3)
O(6)	0.150 7(10)	0.469 6(50)	0.201 7(11)	C(55)	0.019 3(2)	−0.141 8(11)	0.055 6(3)
O(7)	0.198 2(8)	0.147 9(40)	0.282 7(10)	C(56)	0.043 4(2)	−0.045 2(11)	0.077 6(3)
O(8)	0.256 1(8)	0.249 9(40)	0.191 1(10)	C(61)	0.102 9(2)	0.283 3(11)	0.064 8(3)
C(1)	0.159 6(11)	−0.100 6(60)	0.078 9(14)	C(62)	0.129 9(2)	0.385 3(11)	0.073 3(3)
C(2)	0.190 7(10)	0.139 0(51)	0.092 7(12)	C(63)	0.125 8(2)	0.505 5(11)	0.050 7(3)
C(3)	0.239 7(14)	−0.059 2(67)	0.221 4(16)	C(64)	0.094 8(2)	0.523 7(11)	0.019 5(3)
C(4)	0.205 2(14)	−0.288 2(76)	0.171 8(16)	C(65)	0.067 8(2)	0.421 7(11)	0.011 0(3)
C(5)	0.175 2(16)	−0.177 6(78)	0.229 4(20)	C(66)	0.071 9(2)	0.301 5(11)	0.033 6(3)
C(6)	0.160 8(13)	0.368 7(66)	0.194 5(15)	C(71)	0.089 0(2)	0.160 1(11)	0.217 3(3)
C(7)	0.190 5(17)	0.149 6(79)	0.248 7(21)	C(72)	0.097 8(2)	0.087 3(11)	0.252 8(3)
C(8)	0.225 5(13)	0.223 2(63)	0.191 7(15)	C(73)	0.084 0(2)	0.130 8(11)	0.284 4(3)
C(9)	0.086 8(2)	0.207 2(11)	0.131 6(3)	C(74)	0.061 5(2)	0.246 9(11)	0.280 3(3)
C(11)	0.329 2(2)	−0.037 0(11)	0.146 0(3)	C(75)	0.052 7(2)	0.319 6(11)	0.244 7(3)
C(12)	0.357 1(2)	−0.000 8(11)	0.128 1(3)	C(76)	0.066 5(2)	0.276 2(11)	0.213 2(3)
C(13)	0.389 1(2)	0.060 5(11)	0.150 4(3)	F(1)	0.017 3(15)	0.427 2(85)	0.351 9(19)
C(14)	0.393 3(2)	0.085 4(11)	0.190 5(3)	F(2)	0.023 1(14)	0.577 6(60)	0.394 0(19)
C(15)	0.365 5(2)	0.049 2(11)	0.208 5(3)	F(3)	−0.025 7(11)	0.437 0(44)	0.372 5(16)
C(16)	0.333 4(2)	−0.012 1(11)	0.186 2(3)	F(4)	0.006 8(15)	0.266 8(97)	0.386 0(35)
C(21)	0.298 7(2)	−0.301 5(11)	0.120 5(3)	F(5)	0.016 7(23)	0.433 4(131)	0.431 6(17)
C(22)	0.333 6(2)	−0.359 2(11)	0.133 1(3)	F(6)	0.054 3(16)	0.405 8(84)	0.405 6(25)
C(23)	0.337 6(2)	−0.501 3(11)	0.138 8(3)	Cl*	0.316 7(7)	0.470 6(29)	0.011 7(7)
C(24)	0.306 6(2)	−0.585 8(11)	0.132 1(3)	C(81)*	0.357 2(7)	0.437 2(29)	0.035 2(7)
C(25)	0.271 7(2)	−0.528 1(11)	0.119 5(3)	C(82)*	0.378 0(7)	0.543 3(29)	0.056 8(7)
C(26)	0.267 7(2)	−0.386 0(11)	0.113 8(3)	C(83)*	0.410 8(7)	0.513 0(29)	0.084 5(7)
C(31)	0.287 9(2)	−0.830 0(11)	0.064 4(3)	C(84)*	0.422 7(7)	0.376 7(29)	0.090 5(7)
C(32)	0.284 2(2)	0.055 0(11)	0.052 7(3)	C(85)*	0.401 9(7)	0.270 6(29)	0.068 9(7)
C(33)	0.284 0(2)	0.091 2(11)	0.014 0(3)	C(86)*	0.369 2(7)	0.300 9(29)	0.041 3(7)

* Atom refined with site occupancy factor = 0.5.

direct methods[18] (Au, Os, P atoms) followed by Fourier difference techniques. It was refined by full-matrix least squares[19] with Au, Os, P, F and Cl atoms assigned anisotropic thermal parameters. The phenyl rings were refined as regular hexagons (C–C 1.395 Å). Hydrogen atoms were placed in calculated positions with U_{iso} fixed at 0.12 Å^2. A disordered chlorobenzene molecule was present; this was refined with 0.5 occupancy. The weighting scheme $w = 1/[\sigma^2(F) + 0.0069F^2]$ gave satisfactory agreement analyses. Final R and R' values were both 0.063. Atom scattering factors were taken from ref. 20 with corrections for anomalous dispersion calculated using ref. 21. A list of fractional atomic coordinates is given in Table 2. The uncertainty in the wavelength was not included in the bond-length calculations.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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