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**Preliminary communication**

**Synthesis and X-ray structural characterisation  
 of the phosphido-bridged triosmium carbonyl cluster  
 $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$ : cleavage of a P–C bond  
 of a secondary phosphine**

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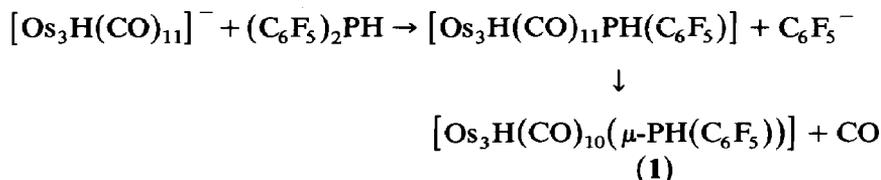
**Abstract**

The reaction of the anion  $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$  with bis(pentafluorophenyl)phosphine,  $(\text{C}_6\text{F}_5)_2\text{PH}$ , results in the cleavage of a P–C bond and the formation of the bridged phosphido cluster  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$ . The structure of this product has been confirmed by a single-crystal X-ray diffraction study which shows that the  $\text{P}(\text{C}_6\text{F}_5)_2\text{H}$  ligand and the hydrido bridge the long edge (2.916(1) Å) of the isosceles osmium triangle.

The importance of reactions involving P–C bond cleavage of coordinated phosphines in catalytic systems has long been recognised, and there have been many studies on model bi- and polynuclear organometallic complexes containing alkyl- and aryl-phosphines [1]. However, there have been relatively few studies of P–C bond cleavage reactions for phosphines which contain fluorophenyl substituents, although the electron-withdrawing nature of this substituent might be expected to modify the reactivity of the ligand. We now report the synthesis and characterisation of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$  (**1**) prepared by the reaction of the  $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$  anion with the tertiary phosphine  $(\text{C}_6\text{F}_5)_2\text{PH}$ .

The cluster  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$  (**1**) was obtained as a yellow solid from the reaction of  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_3\text{H}(\text{CO})_{11}]$  with bis(pentafluorophenyl)phosphine, in  $\text{CH}_3\text{OH}$ , at room temperature. The yellow crystalline product was ob-

tained upon separation by TLC on silica using 1:1 CH<sub>2</sub>Cl<sub>2</sub>/n-hexane as eluant, followed by recrystallisation from hexane.



Complex **1** was identified initially on the basis of spectroscopic and microanalytical data (MS  $m/e = 1056$ ; IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  2111m, 2071vs, 2061s, 2029s, 2013s, 2001sh, 1985sh,  $\nu(\text{C}_6\text{F}_5)$  1641vw, 1517w, 1481m, 1388vw, 1296vw, 1095w, 962w, 606w; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.37dd ( $J(\text{PH}) = 445$  Hz,  $J(\text{HH}) = 4.39$  Hz), -19.40dd ( $J(\text{PH}) = 18.31$  Hz,  $J(\text{HF}) = 2.2$  Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): -103.45dd; <sup>19</sup>F NMR (CDCl<sub>3</sub>,  $\delta$ ): -52.8m(*o*-F), -72.4m(*p*-F), -83.3m(*m*-F). The nature of the product suggests that cleavage of a C<sub>6</sub>F<sub>5</sub> moiety from the phosphine has occurred during the course of the reaction. The <sup>1</sup>H NMR spectrum shows signals characteristic of a hydride ( $\delta$  -19.40dd) and of the phosphine proton ( $\delta$  7.37dd). These signals and the corresponding coupling constants are similar to those of the related hydrido-phosphido osmium cluster [Os<sub>3</sub>( $\mu$ -H)(CO)<sub>10</sub>( $\mu$ -P(C<sub>6</sub>F<sub>5</sub>)H)] (**2**) [2]. Also, the IR data for the two complexes in the carbonyl stretching region are very similar.

The molecular structure of **1** has been confirmed by a single-crystal X-ray analysis. The structure \* is shown in Fig. 1, which includes some important bond parameters. In agreement with the spectroscopic data, the complex contains an isosceles triangle of osmium atoms, the longest edge of which is bridged symmetrically by the P(C<sub>6</sub>F<sub>5</sub>)H ligand and by a hydride. The ten carbonyl ligands are all essentially linear, and are terminally bound to the metal framework. The hydride and the phosphine hydrogen were not located directly in the X-ray analysis but their positions were determined from potential energy calculations [3].

The cleavage of one of the C<sub>6</sub>F<sub>5</sub> rings from the P(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>H group is unequivocally established by the structure determination, and as indicated from the solution spectroscopic data, only one of the two possible isomers, the one with the C<sub>6</sub>F<sub>5</sub> ring lying perpendicular to and away from the Os<sub>3</sub> plane, is found in the solid state. Spectroscopic data indicates that only one isomer is observed in a number of other hydrido-phosphido osmium clusters [4–6], and where crystal structures as available these show that the same isomer as found in **1** is present [7]. The planar C<sub>6</sub>F<sub>5</sub> ring in **1** makes angles of 92.7° and 87.4° with the Os<sub>3</sub> triangle and the Os(1)–Os(2)–P(1) triangle, respectively, which are similar to the equivalent angles of 99.5° and 85.6° found in [Os<sub>3</sub>( $\mu$ -H)(CO)<sub>10</sub>( $\mu$ -P(C<sub>6</sub>H<sub>5</sub>)H)] (**2**) [7,8]. The dihedral angle between the

\* **1**: C<sub>16</sub>H<sub>2</sub>F<sub>5</sub>O<sub>10</sub>Os<sub>3</sub>P,  $M = 1050.75$ , monoclinic, space group  $P2_1/c$  (No. 14),  $a$  9.359(2),  $b$  13.177(4),  $c$  18.647(4) Å,  $\beta$  96.30(2)°,  $V$  2285.7 Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  3.05 g cm<sup>-3</sup>,  $F(000) = 1900$ ,  $\mu(\text{Mo-K}\alpha)$  167.73 cm<sup>-1</sup>. 3239 reflections measured on a Stoe diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  0.71069 Å), and  $2\theta_{\text{max}}$  45°, give 2565 unique, observed, absorption corrected data [ $F > 4\sigma(F)$ ]. Structure solved by direct methods (Os atoms) and Fourier difference techniques, and refined by full-matrix least squares (all non-hydrogen atoms anisotropic) to  $R = 0.049$  and  $R_w = 0.053$ . Tables of atomic coordinates, thermal parameters, bond parameters and structure factors have been deposited with the Cambridge Crystallographic Data Centre.

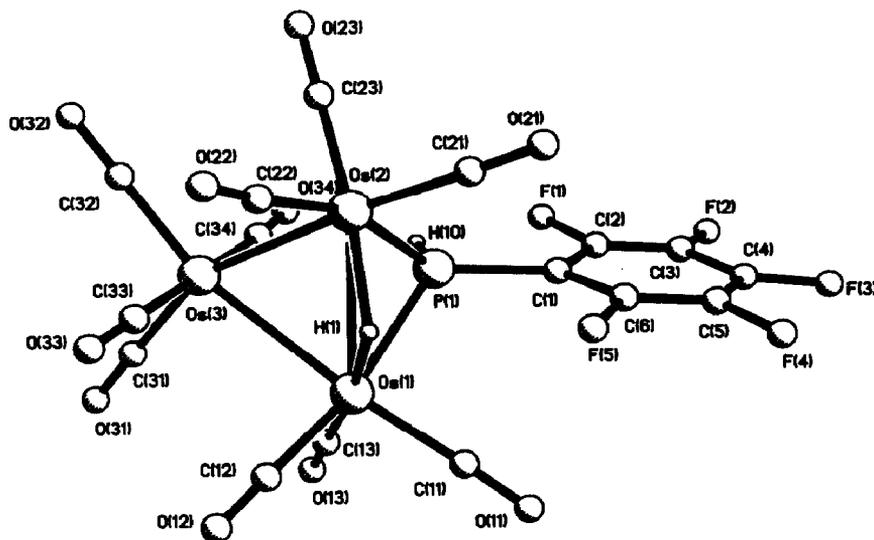


Fig. 1. The molecular structure of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$  (1) showing the atom labelling. Bond lengths: Os(1)–Os(2), 2.916(1); Os(1)–Os(3), 2.885(1); Os(2)–Os(3), 2.881(1); Os(1)–P(1), 2.368(5); Os(2)–P(1), 2.361(4); P(1)–C(1), 1.827(19) Å. Bond angles: Os(3)–Os(1)–Os(2), 59.6(1); Os(3)–Os(2)–Os(1), 59.7(1); Os(2)–Os(3)–Os(1), 60.8(1); P(1)–Os(1)–Os(2), 51.8(1); P(1)–Os(1)–Os(3), 80.1(1); P(1)–Os(2)–Os(1), 52.0(1); P(1)–Os(2)–Os(3), 80.3(1); Os(2)–P(1)–Os(1), 76.1(1); C(1)–P(1)–Os(1), 120.2(7); C(1)–P(1)–Os(2), 123.9(7)°.

Os(1)–Os(2)–Os(3) plane and the Os(1)–Os(2)–P(1) plane in  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$  (1) at 102.1° is also similar to the value of 107.1 for the equivalent dihedral angle in **2**, which suggests that the replacement of the  $\text{C}_6\text{H}_5$  group in **2** by the bulkier  $\text{C}_6\text{F}_5$  group in **1** has little effect on the geometry around the cluster core.

The overall molecular structure of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$  (1) is similar to that of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{H}_5)\text{H})]$  (2). The dibridged Os–Os edge in **1** is similar in length to the value of 2.917(4) Å in **2**, while the two unbridged Os–Os edges show less deviation than the range of distances 2.868(4)–2.896(4) Å, in **2**. All these metal–metal distances are somewhat longer than the average Os–Os length of 2.877(3) Å found in the parent carbonyl,  $[\text{Os}_3(\text{CO})_{12}]$  [9]. The phosphorus atom of the  $\text{P}(\text{C}_6\text{F}_5)\text{H}$  ligand symmetrically bridges the long Os(1)–Os(2) edge, with Os–P distances very similar to the two lengths 2.361(7) and 2.372(7) Å found in **2** [8]; the angles at P(1) are also very similar in the two complexes. The bond parameters within the  $\text{C}_6\text{F}_5$  group are similar to those reported for the  $\mu\text{-P}(\text{C}_6\text{F}_5)_2$  ligand in the complex  $[\text{Fe}_2(\text{CO})_6\{(\text{C}_6\text{F}_5)_2\text{PC}_4(\text{Ph})_2\}\text{P}(\text{C}_6\text{F}_4)_2]$  [10], which is another rare example of a polynuclear complex containing a bridging fluorophosphine.

The Os–C(carbonyl) distances in  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{F}_5)\text{H})]$  (1) lie in the range 1.87(2)–1.99(2) Å (average 1.93 Å) while the C–O distances average 1.12 Å. Of the ten Os–C (carbonyl) distances, the pair Os(1)–C(13) and Os(2)–C(23), *trans* to the bridging hydride, have smallest average of 1.89 Å, while the pair, Os(1)–C(12) and Os(2)–C(22), *trans* to the bridging phosphorus have an average length of 1.96 Å. A similar trend is observed in  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-P}(\text{C}_6\text{H}_5)\text{H})]$  (2) [8], and the replacement of a  $\text{C}_6\text{H}_5$  group in **2** by a  $\text{C}_6\text{F}_5$  in **1** appears to have little effect on the bonding within the rest of the cluster.

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