Reactions of the Cyclometallated Triosmium Cluster $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ with Brønsted Acids and Dihydrogen: Synthesis and *X*-Ray Crystal Structure of $[Os_3H_2(CF_3CO_2)(CO)_9(\mu\text{-}PPh_2)]$†

Stephen B. Colbran, Patricia T. Irele, Brian F. G. Johnson, Perry T. Kaye, Jack Lewis,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The cyclometallated cluster $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**1**) reacts with Brønsted acids HX *via* a protonation then anion co-ordination sequence to give the addition products $[Os_3H_2(X)(CO)_9(PPh_2)]$ [X = Cl (**2**), Br (**3**), CF_3CO_2 (**4**), or $MeCO_2$ (**6**)]. An *X*-ray analysis of (**4**) shows that the triangular metal framework of (**1**) is retained, and the oxygen-bound CF_3CO_2 ligand occupies a terminal axial site on the Os atom which is not bridged by the μ-PPh_2 group. With $HBF_4{\cdot}Et_2O$ the cationic cluster $[Os_3H_3(CO)_9\{P(C_6H_4)Ph\}]^+$ (**5**) is obtained, and this reaction may be thought of as involving the isolation of an intermediate in the above reactions. With HBr, addition of excess of acid to (**1**) leads to metal bond cleavage and cluster fragmentation, providing a novel route to new dimeric phosphido-bridged complexes $[Os_2H_3(CO)_6(PPh_2)]$ (**7**), $[Os_2H_2(Br)(CO)_6(PPh_2)]$ (**8**), and $[Os_2H(Br)_2(CO)_6(PPh_2)]$ (**9**). In contrast, reaction of (**1**) with H_2 leads to carbon–phosphorus bond cleavage to give the phosphinidene-capped cluster $[Os_3H_2(CO)_9(\mu_3\text{-}PPh)]$ (**10**).

In the preceding paper[1] we reported the use of the cyclometallated cluster $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**1**) as a convenient starting material for the formation of substituted clusters with a diphenylphosphido group {*i.e.* substituted clusters of the type $[Os_3H(CO)_9L(PPh_2)]$}, and some reactions of these clusters.[1] Here we extend the study of the reactions of (**1**) to include protic acids and dihydrogen. Fluxional processes in the new products are observed.

Results and Discussion

Reactions of $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**1**) with anhydrous acids HX in CH_2Cl_2 or $(CH_2Cl)_2$ give high yields of light yellow air-stable cluster products $[Os_3H_2(X)(CO)_9(PPh_2)]$ [X = Cl (**2**), Br (**3**), or CF_3CO_2 (**4**)] that all exhibit similar i.r. profiles (Table 1). In their ^1H n.m.r. spectra at ambient temperature (**2**)—(**4**) show resonances attributable to the diphenylphosphido moiety as well as two very broad featureless peaks in the hydride region. As the temperature is lowered both of these latter peaks sharpen to give two equal-intensity doublet of doublets as expected for two inequivalent metal hydrides which couple to each other and to the phosphorus atom of the PPh_2 group (Table 2). A 'merry-go-round' dynamic process, as has been previously described for other triosmium cluster systems with two inequivalent hydrides,[1,2] is a likely mechanism for the fluxional behaviour of the hydrides in complexes (**2**)—(**4**). Mass spectroscopic evidence for (**2**)—(**4**) suggested their formation as $[Os_3H_2(X)(CO)_9(PPh_2)]$ in which the ligand X acts as a three-electron donor. However, in attempting to cyclometallate (**4**) by heating it was found that (**1**) is regenerated in good yield. Loss of a bridging X ligand in thermal reactions is unusual (but not unprecedented)[3] in osmium cluster systems and thus the regeneration of (**1**) from (**4**) threw doubt on the above formulations for (**2**)—(**4**). A single-crystal *X*-ray analysis was, therefore, undertaken on light yellow rhombs of complex (**4**) grown from dichloromethane–hexane solution.

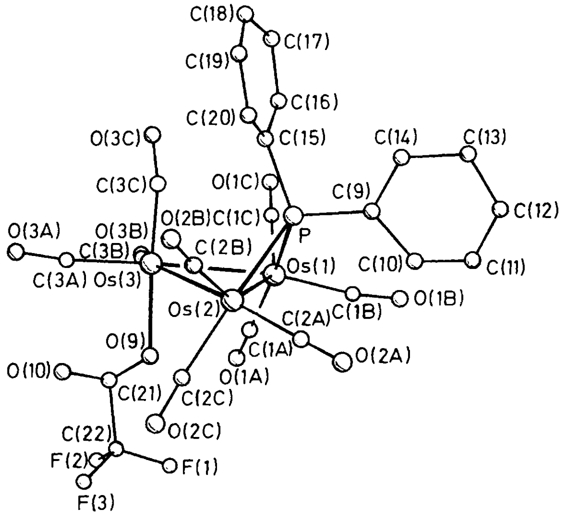

Figure. Molecular structure of $[Os_3H_2(CF_3CO_2)(CO)_9(PPh_2)]$ showing the atom labelling scheme

The molecular structure of $[Os_3(\mu\text{-}H)_2(CF_3CO_2)(CO)_9(\mu\text{-}PPh_2)]$ (**4**) is shown in the Figure. Selected bond lengths and angles are listed in Table 3. There are no abnormally short intermolecular contacts between the molecules in the crystal. The structure consists of a triangle of Os atoms two of which are bridged by the diphenylphosphido group. Each Os atom binds three terminal carbonyl ligands giving a carbonyl arrangement not unlike that found in the simpler $[Os_3H(X)(CO)_{10}]$ systems[4] but with the axial carbonyl of the unique non-bridgehead Os atom on the side opposite the PPh_2 group replaced by a terminal trifluoroacetate ligand.[5] Lengthening of the Os–Os edges and the packing of the carbonyl ligands are consistent with the two hydrides, which were not directly located in this analysis, bridging the Os(1)–Os(2) and Os(2)–Os(3) edges.

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† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-diphenylphosphido-1,2;1,3-di-μ-hydrido-3-trifluoroacetato-*triangulo*-triosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Infrared data [ν(CO), cm^{-1}]

Compound	
(**2**) $[Os_3H_2(Cl)(CO)_9(PPh_2)]^a$	2 116m, 2 092vs, 2 065vs, 2 056m, 2 021s, 2 015s, 1 991m, 1 982mw
(**3**) $[Os_3H_2(Br)(CO)_9(PPh_2)]^a$	2 115m, 2 091vs, 2 065vs, 2 055m, 2 023s, 2 016s, 1 992m, 1 983mw
(**4**) $[Os_3H_2(CF_3CO_2)(CO)_9(PPh_2)]^b$	2 123m, 2 095vs, 2 064vs, 2 031m, 2 012ms, 1 997m
(**6**) $[Os_3H_2(MeCO_2)(CO)_9(PPh_2)]^b$	2 122m, 2 100vs, 2 067vs, 2 036m, 2 015ms, 2 004(sh)
(**5**) $[Os_3H_3(CO)_9\{P(C_6H_4)Ph\}]BF_4{}^b$	2 143m, 2 121vs, 2 106m, 2 081s, 2 062s
(**7**) $[Os_2H_3(CO)_6(PPh_2)]^a$	2 104m, 2 095s, 2 046vs, 2 011vs, 1 986vw, 1 963vw
(**8**) $[Os_2H_2(Br)(CO)_6(PPh_2)]^a$	2 117m, 2 100s, 2 050vs, 2 018ms, 1 985vw
(**9**) $[Os_2H(Br)_2(CO)_6(PPh_2)]^a$	2 114m, 2 101s, 2 050vs, 2 017vs, 1 992vw, 1 981vw

[a] Recorded in hexane. [b] Recorded in dichloromethane.

Table 2. Proton n.m.r. data[a]

Compound	T^b/K	
(**2**) $[Os_3H_2(Cl)(CO)_9(PPh_2)]$	250	7.84—7.24 (m, PPh_2), −15.42 [dd, *J*(PH) 10.0, *J*(HH′) 1.5, OsH], −17.43 [dd, *J*(PH′) 5.0, *J*(HH′) 1.5, OsH]
(**3**) $[Os_3H_2(Br)(CO)_9(PPh_2)]$	250	7.69—7.27 (m, PPh_2), −15.50 [dd, *J*(PH) 9.0, *J*(HH′) 1.4, OsH], −18.21 [dd, *J*(PH′) 5.1, *J*(HH) 1.4, OsH]
(**4**) $[Os_3H_2(CF_3CO_2)(CO)_9(PPh_2)]$	290	7.85—7.26 (m, PPh_2), −15.95 [dd, *J*(PH) 10.9, *J*(HH′) 1.1, OsH], −17.09 [dd, *J*(PH′) 5.1, *J*(HH′) 1.1, OsH]
(**5**) $[Os_3H_3(CO)_9\{P(C_6H_4)Ph\}]BF_4$	—	7.76, 7.06, 6.89, 6.48 (complex multiplets, PC_6H_4), 7.71—7.16 (m, PPh), −15.65 [dd, *J*(PH) 8.1, *J*(HH′) 0.8, OsH], −19.08 [dd, *J*(PH′) 6.5, *J*(HH′) 0.8, 2 OsH]
(**7**) $[Os_2H_3(CO)_6(PPh_2)]$	240	7.75—7.32 (m, PPh_2), −9.86 [dd, *J*(PH) 18.5, *J*(HH′) 4.0, 2 OsH], −18.36 [dt, *J*(PH) 11.9, *J*(HH) 4.0, OsH]
(**8**) $[Os_2H_2(Br)(CO)_6(PPh_2)]$	—	7.92—7.23 (m, PPh_2), −9.85 [dd, *J*(PH) 19.3, *J*(HH′) 3.9, OsH], −16.10 [dd, *J*(PH′) 12.6, *J*(HH′) 3.9, OsH]
(**9**) $[Os_2H(Br)_2(CO)_6(PPh_2)]$	—	7.83—7.22 (m, PPh_2), −17.05 [d, *J*(PH) 7.7, OsH]

[a] δ referenced to $SiMe_4$ in CD_2Cl_2, *J* values in Hz. [b] For compounds where dynamic behaviour was observed, *T* is the temperature required to obtain a limiting low-temperature spectrum at 400.0013 MHz.

Table 3. Selected bond lengths (Å) and angles (°) for $[Os_3H_2(CF_3CO_2)(CO)_9(\mu\text{-}PPh_2)]$ (**4**)

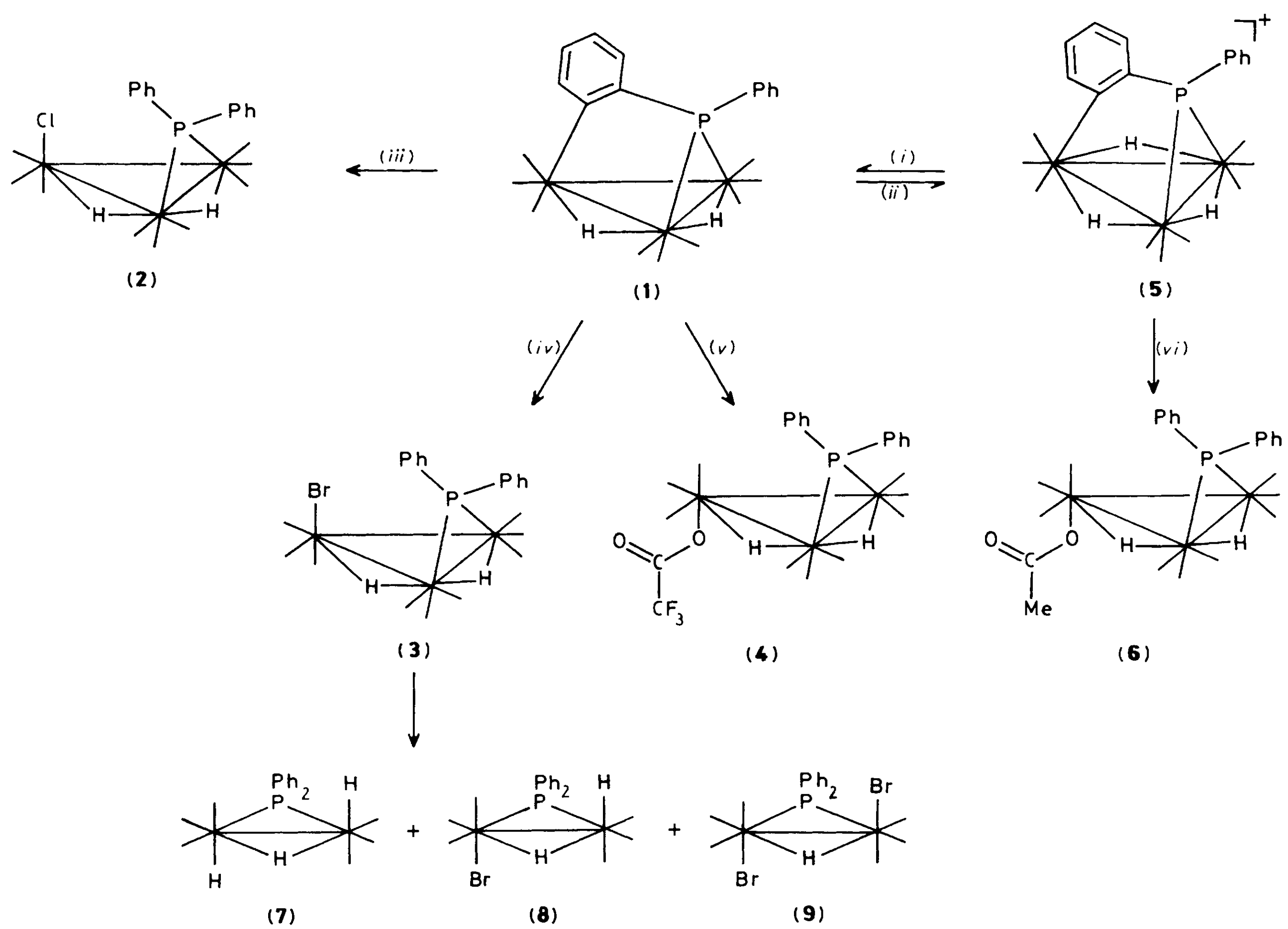
Os(2)–Os(1)	2.947(2)	C(1A)–Os(1)	1.96(4)
Os(3)–Os(1)	2.859(2)	C(1B)–Os(1)	1.94(4)
Os(3)–Os(2)	3.083(2)	C(1C)–Os(1)	1.88(4)
P–Os(1)	2.379(7)	C(2A)–Os(2)	1.92(3)
P–Os(2)	2.412(7)	C(2B)–Os(2)	1.90(3)
O(9)–Os(3)	2.149(21)	C(2C)–Os(2)	2.00(4)
C(9)–P	1.81(3)	C(3A)–Os(3)	1.96(4)
C(15)–P	1.81(3)	C(3B)–Os(3)	1.90(4)
C(21)–O(9)	1.21(5)	C(3C)–Os(3)	1.84(4)
C(21)–O(10)	1.21(8)	F(1)–C(22)	1.29(4)
C(21)–C(22)	1.60(6)	F(2)–C(22)	1.36(5)
		F(3)–C(22)	1.29(5)
Os(3)–Os(1)–Os(2)	64.1(1)	P–Os(1)–Os(2)	52.5(2)
Os(3)–Os(2)–Os(1)	56.5(1)	P–Os(1)–Os(3)	89.3(2)
Os(2)–Os(3)–Os(1)	59.3(1)	P–Os(2)–Os(1)	51.5(2)
O(9)–Os(3)–Os(1)	85.7(6)	P–Os(2)–Os(3)	83.6(2)
O(9)–Os(3)–Os(2)	76.6(6)	Os(2)–P–Os(1)	75.9(2)
O(9)–Os(3)–C(3C)	175.5(13)	C(21)–O(9)–Os(3)	121(3)
O(10)–C(21)–O(9)	113(4)	F(1)–C(22)–C(21)	114(3)
C(22)–C(21)–O(9)	111(3)	F(2)–C(22)–C(21)	98(3)
C(22)–C(21)–O(10)	103(5)	F(3)–C(22)–C(21)	122(3)
F(2)–C(22)–F(1)	106(3)	F(3)–C(22)–F(2)	104(3)
F(3)–C(22)–F(1)	110(4)		

From this *X*-ray analysis it can be seen that (**2**)—(**4**) appear to be the products of simple addition of HX to (**1**) and should be correctly formulated as $[Os_3(\mu\text{-}H)_2(X)(CO)_9(\mu\text{-}PPh_2)]$ (Scheme 1). The ease of formation of these products follows the acid strength of HX.[6] Thus no reaction is observed between an excess of the weak acid CH_3CO_2H and complex (**1**) on prolonged reflux in $(CH_2Cl)_2$, reaction of (**1**) with CF_3CO_2H goes only at reflux in $(CH_2Cl)_2$, whereas the reactions of both HCl(g) and HBr(g) go at room temperature. These results indicate that complexes (**2**)—(**4**) are formed by a mechanism involving protonation of (**1**) rather than by direct oxidative addition of HX.

This conclusion is substantiated by observations on the reactivity of complex (**1**) with $HBF_4\cdot Et_2O$ (*i.e.* a protic acid with a non-co-ordinating conjugate base). Following addition of excess of $HBF_4\cdot Et_2O$ to a dichloromethane solution of (**1**) there ensues smooth reaction to a cation (**5**) as evidenced by a change in the pattern of the ν(CO) bands in the i.r. spectrum and a general shift of these bands to higher frequency by 50 cm^{-1} (Table 1). Pure (**5**) may be isolated as a very moisture-sensitive pale yellow powder by trituration of the dichloromethane solution with diethyl ether. The ^1H n.m.r. spectrum of (**5**) shows peaks in the region δ 8—6 typical of the cyclometallated $P(C_6H_4)Ph$ moiety[1] as well as two coupled hydride resonances in the ratio of 1:2 at −15.65 and −19.08, respectively (Table 2), as is consistent with simple proton addition to the Os–Os edge of (**1**) not bridged by a hydride ligand (Scheme 1). Shaking a solution of (**5**) with water cleanly reforms (**1**) whereas reaction with $[N(PPh_3)_2]Cl$ (*ca.* 1 equivalent) gives (**2**) in good yield. Thus (**5**) is implicated as the intermediate in the reactions of (**1**) with acids, transfer of the metal hydride to the cyclometallated carbon atom occurring under the influence of the entering co-ordination anion.

Indeed, although acetic acid has insufficient strength to react with complex (**1**) alone, addition of it to (**5**) initiates a clean transformation to a new product (**6**) which has the same ν(CO) i.r. profile (Table 1) as the clusters (**2**)—(**4**). Although this reaction is quantitative according to i.r. spectroscopy it has not been possible to isolate the product due to its instability to hydrolysis to give (**1**). Adding further $HBF_4\cdot Et_2O$ to (**6**) gives back (**5**). On the basis of these results alone we tentatively suggest (**6**) is the addend cluster $[Os_3H_2(MeCO_2)(CO)_9(PPh_2)]$ (Scheme 1).

Unless care is taken in the reactions of (**1**) with HBr(g) to give



Scheme 1. (*i*) Water; (*ii*) $HBF_4 \cdot OEt_2$; (*iii*) HCl; (*iv*) HBr; (*v*) CF_3CO_2H; (*vi*) $MeCO_2H$

(3) further products are obtained. In detail, three new very pale yellow air-stable compounds (7)—(9) [along with some (3)] may be separated by thin-layer chromatography from the residue of the prolonged reaction of excess of HBr(g) with (**1**). Analytical and mass spectroscopic data suggest formulation of (7) as $[Os_2H_3(CO)_6(PPh_2)]$, of (**8**) as $[Os_2H_2(Br)(CO)_6(PPh_2)]$, and of (**9**) as $[Os_2H(Br)_2(CO)_6(PPh_2)]$. The i.r. patterns of (7)—(**9**) are similar (Table 1) indicating that they have related structures. All three compounds show in their ^1H n.m.r. spectrum resonances appropriate for a bridging diphenylphosphido group (Table 2).

The molecule (7) exhibits dynamic behaviour as evidenced by the ^1H n.m.r. spectrum in the hydride region which shows, at room temperature, two very broad featureless peaks centred at -9.86 and -18.36. On cooling these signals sharpen until, in the limiting spectrum at 240 K, a doublet of doublets (relative intensity 2) is observed for the signal at -9.86 and a doublet of triplets (relative intensity 1) for the peak at -18.36 (Table 2). The coupling constant between these two sets of hydride peaks is $^2J(HH') = 4.0$ Hz. The remaining coupling in each case is to the phosphorus atom of the PPh_2 group. Thus it is proposed that (7) is a PPh_2-bridged dimer with each Os atom having three terminal carbonyl ligands, a single terminal hydride ligand (-9.86), and sharing a third bridging hydride ligand (-18.36). These conclusions are conveniently summarised by the structure shown in Scheme 1.

The formulations for complexes (**8**) and (**9**) (given above) suggest that they are formed from (7) by successive replacement of a terminal hydride by a terminal bromine ligand (Scheme 1). This is confirmed by the observed resonances in the hydride region of their ^1H n.m.r. spectra. Thus (**8**) has only two equal-intensity multiplets at -9.85 and -16.10 assigned to a terminal and to a bridging hydride ligand, respectively (Table 2), whereas (**9**) has a single doublet at -17.05 from its remaining bridging hydride ligand. It is worth noting that neither (**8**) nor (**9**) showed any of the fluxional processes found for (7).

Finally, when complex (**1**) is heated in an inert solvent under an atmosphere of H_2 no appreciable reaction is observed until temperatures of the order of 120 °C are reached. Then there ensues smooth reaction to give moderate yields of the known phosphinidene-capped cluster $[Os_3H_2(CO)_9(\mu_3\text{-}PPh)]$ (**10**).[7] Presumably, formation of (**10**) occurs *via* oxidative addition of H_2 to (**1**) followed by carbon–phosphorus bond cleavage and elimination as indicated in Scheme 2. This reaction represents an alternative route of comparable yield to those already published to (**10**).[7]

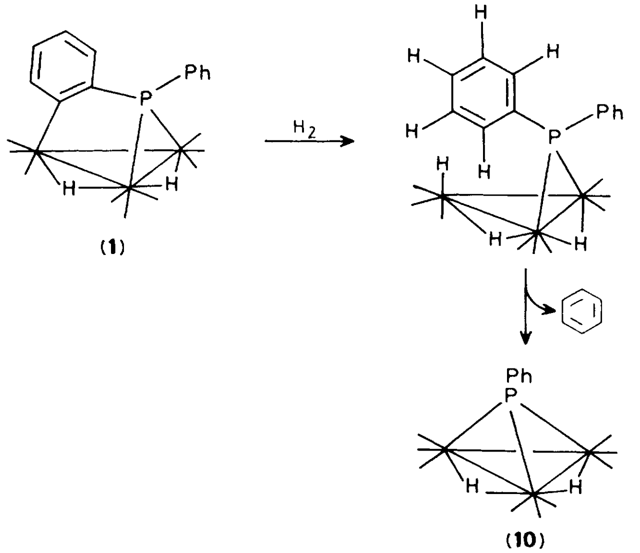
Experimental

Experimental techniques and spectroscopic equipment have been described previously. The complex $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**1**) was prepared by the method detailed in the preceding paper.[1] All other reagents were commercial and used as supplied.

Preparation of $[Os_3H_2(CF_3CO_2)(CO)_9(PPh_2)]$ (**4**).—Complex (**1**) (41 mg) was refluxed in 1,2-dichloromethane (15 cm^3) with a large excess of CF_3CO_2H (*ca.* 0.25 cm^3) for 3 h. Removal of the solvent *in vacuo* and t.l.c. eluting with 20% CH_2Cl_2–

Table 4. Atomic co-ordinates (× 10^4) for $[Os_3H_2(CF_3CO)_2(CO)_9(\mu\text{-}PPh_2)]$ (**4**)

Atom	*x*	*y*	*z*
Os(1)	8 004(1)	−357(1)	3 382(1)
Os(2)	6 217(1)	1 375(1)	3 759(1)
Os(3)	7 892(1)	2 442(1)	2 900(1)
C(1A)	7 916(27)	−926(35)	2 558(17)
O(1A)	7 895(25)	−1 225(26)	2 107(12)
C(1B)	7 952(29)	−2 347(40)	3 595(17)
O(1B)	8 044(21)	−3 522(23)	3 755(9)
C(1C)	9 462(31)	−255(39)	3 394(17)
O(1C)	10 346(21)	−224(26)	3 391(12)
C(2A)	5 242(23)	184(28)	4 167(13)
O(2A)	4 692(20)	−514(29)	4 405(12)
C(2B)	5 813(25)	3 021(33)	4 186(14)
O(2B)	5 622(22)	3 986(27)	4 465(12)
C(2C)	5 166(29)	1 756(35)	3 135(16)
O(2C)	4 537(23)	1 924(37)	2 796(15)
P	7 694(5)	615(8)	4 327(3)
C(9)	7 400(21)	−592(28)	4 921(13)
C(10)	6 895(28)	−1 950(37)	4 821(16)
C(11)	6 688(24)	−2 853(38)	5 222(18)
C(12)	7 025(23)	−2 666(34)	5 760(18)
C(13)	7 549(27)	−1 470(34)	5 948(16)
C(14)	7 736(26)	−431(33)	5 502(15)
C(15)	8 508(21)	1 934(27)	4 679(12)
C(16)	9 557(22)	1 650(27)	4 732(12)
C(17)	10 178(27)	2 486(31)	5 134(18)
C(18)	9 702(37)	3 661(29)	5 426(20)
C(19)	8 667(26)	3 757(38)	5 390(17)
C(20)	8 004(38)	2 993(46)	5 062(14)
C(3A)	7 636(28)	4 382(39)	2 621(16)
O(3A)	7 579(25)	5 561(21)	2 480(12)
C(3B)	8 965(30)	2 018(37)	2 354(16)
O(3B)	9 619(24)	1 675(36)	2 047(15)
C(3C)	8 858(31)	3 083(39)	3 429(16)
O(3C)	9 580(20)	3 603(27)	3 648(10)
O(9)	6 714(18)	1 590(25)	2 334(9)
O(10)	6 404(71)	3 303(85)	1 828(22)
C(21)	6 599(32)	2 043(46)	1 841(19)
C(22)	5 606(35)	1 340(39)	1 537(16)
F(1)	5 414(28)	71(25)	1 718(11)
F(2)	5 999(29)	1 194(25)	986(9)
F(3)	4 753(23)	2 030(22)	1 464(14)



Scheme 2.

hexane afforded (**4**) (40 mg, 90%) as a fine yellow powder (Found: C, 24.65; H, 1.1; P, 2.9%; M^+ at m/z 1 100. Calc. for $C_{23}H_{12}F_3O_{11}Os_3P$: C, 24.5; H, 1.1; P, 2.75%).

Preparation of $[Os_3H_2(Cl)(CO)_9(PPh_2)]$ (**2**).—Hydrogen chloride was bubbled through dichloromethane (20 cm^3) for 1 min. This solution was added dropwise to complex (**1**) (53 mg) in dichloromethane (20 cm^3) until the carbonyl i.r. bands of the reactant had disappeared. Removal of the solvent and t.l.c. gave yellow (**2**) (50 mg, 93%) (Found: C, 24.5; H, 1.3; P, 3.0%; M^+ at m/z 1 011. Calc. for $C_{21}H_{12}ClO_9Os_3P$: C, 24.0; H, 1.1; P, 2.95%).

Reaction of Complex (**1**) *with* HBr(g).—Using the same procedure as above, the residue of the reaction of (**1**) (82 mg) with HBr(g) gave four pale yellow bands on t.l.c. (in order of elution with 10% CH_2Cl_2–hexane): (*i*) $[Os_2H_3(CO)_6(PPh_2)]$ (**7**) (18 mg, 30%) (Found: C, 30.3; H, 1.9; P, 4.05; M^+ at m/z 738. Calc. for $C_{18}H_{13}O_6Os_2P$: C, 29.7; H, 1.8; P, 4.25%); (*ii*) $[Os_2H_2(Br)(CO)_6(PPh_2)]$ (**8**) (7 mg, 10%) (M^+ at m/z 820); (*iii*) $[Os_2H(Br)_2(CO)_6(PPh_2)]$ (**9**) (6 mg, 8%) (M^+ at m/z 900); (*iv*) $[Os_3H_2(Br)(CO)_9(PPh_2)]$ (**3**) (40 mg, 45%) (Found: C, 22.9; H, 1.1; P, 3.2; M^+ at m/z 1 066. Calc. for $C_{21}H_{12}BrO_9Os_3P$: C, 23.0; H, 1.1; P, 2.8%).

If the reaction is allowed to continue for longer periods increased yields of the dinuclear products (**7**)—(**9**) are obtained.

Preparation of $[Os_3H_3(CO)_9\{P(C_6H_4)Ph\}]BF_4$ (**5**).—Complex (**1**) (40 mg) in dichloromethane (20 cm^3) was stirred with excess of $HBF_4 \cdot Et_2O$ (*ca.* 0.5 cm^3). The reaction was allowed to continue until i.r. spectroscopy showed complete conversion of the reactant cluster (typically 0.5 h). The solution was then concentrated to 2 cm^3 and triturated with excess of diethyl ether. The resulting fine yellow precipitate was filtered off, washed with excess of diethyl ether, and dried *in vacuo*. Yield 38 mg, 95%.

Reactions of Complex (**5**).—(*a*) *With Water.* Complex (**5**) (10 mg) in dichloromethane (10 cm^3) was shaken with water (1 cm^3). Infrared spectroscopy showed quantitative conversion into (**1**) and t.l.c. of the residue of the dichloromethane fraction gave this product (8 mg, 85%).

(*b*) *With* $[N(PPh_3)_2]Cl$. Complex (**5**) (20 mg) in dichloromethane (20 cm^3) was stirred with $[N(PPh_3)_2]Cl$ (10 mg) for 1 h. T.l.c. of the residue gave (**1**) (8 mg, 40%) and (**2**) (9 mg, 46%).

(*c*) *With acetic acid.* To complex (**5**) (20 mg) in dichloromethane (20 cm^3) was added excess of acetic acid (*ca.* 0.2 cm^3). There was an immediate reaction to a single product as evidenced by the i.r. spectrum: ν(CO), 2 122m, 2 100vs, 2 067vs, 2 036m, 2 015ms, and 2 004 (sh) cm^{-1}. Despite considerable effort it has not been possible to isolate the product of this reaction and we have only obtained (**1**) from work up of the reaction residues.

Reaction of Complex (**1**) *with Dihydrogen.*—Dihydrogen was slowly bubbled through complex (**1**) (50 mg) in decane (40 cm^3) at reflux for 4 h. Removal of the solvent and t.l.c. (20% CH_2Cl_2–hexane as eluant) gave three bands (in order of decreasing R_f): (*i*) pale yellow $[Os_3H_2(CO)_9(PPh)]$ (**10**) (36 mg, 78%) identified by comparison of its properties with those of an authentic sample; (*ii*) brown, not identified (6 mg), ν(CO) (C_6H_{14}) 2 100m, 2 077vs, 2 057vs, 2 035vs, 2 018s, 2 010s, 2 000m, 1 990w, 1 974w, and 1 950m cm^{-1}; (*iii*) orange, not identified (2 mg), ν(CO) (C_6H_{14}) 2 084ms, 2 069w, 2 040m, 2 019vs, 2 010m (sh), and 1 939w cm^{-1}.

No reaction occurred on heating (**1**) under H_2 in octane at 85 °C for 4 h.

X-Ray Analysis of $[Os_3H_2(CF_3CO_2)(CO)_9(PPh_2)]$ (**4**).—Single crystals of complex (**4**) were obtained by recrystallisation from CH_2Cl_2–hexane solution.

Crystal data. $C_{23}H_{12}F_3O_{11}Os_3P$, M = 1 399.13, monoclinic, a = 12.876(5), b = 9.408(3), c = 22.854(12) Å, β = 89.97(4)°, U = 2 768.5 Å^3 (by least-squares refinement of diffractometer angles for 52 automatically centred reflections in the range $15 < 2\theta < 25°$, λ = 0.710 69Å), space group $P2_1/c$ (no. 14), Z = 4, D_m not measured, D_c = 3.356 g cm^{-3}, $F(000)$ = 2 032. Pale yellow, rectangular blocks. Crystal dimensions (distance to faces from centre): 0.110 (100, $\bar{1}00$) × 0.144 (012, $0\bar{1}\bar{2}$) × 0.179 ($0\bar{1}2$, $01\bar{2}$) mm, μ(Mo-K_α) = 138.37 cm^{-1}.

Data collection and processing.[8] Stoe-Siemens four-circle diffractometer, 24-step ω—θ scan mode with scan width = 0.04°, scan speed 0.0133—0.0533° s^{-1}, graphite-monochromated Mo-K_α radiation; 4 191 reflections measured ($5.0 < 2\theta < 45.0°$, $+h, +k, \pm l$), 4 049 unique [merging R = 0.018 after absorption correction (maximum, minimum transmission factors 0.109, 0.025)], giving 2 797 with $F > 4\sigma(F)$. No significant crystal decay was observed during data collection.

Structure analysis and refinement. Direct methods (Os atoms) followed by Fourier difference techniques. Full-matrix least-squares refinement with Os, P, F, O, and phenyl C atoms anisotropic, and hydrogens in calculated positions with one, overall, refined U_{iso}[= 0.086(38) Å^2]. The weighting scheme $w = 2.083/[\sigma^2(F_o) + 0.040F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values were 0.078 and 0.088. Final atomic co-ordinates are presented in Table 4. Programs and computers used and sources of scattering factor data are given in ref. 8.

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

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