Protonation *versus* Oxidation in the Reactions of Trifluoroacetic Acid with Dinuclear Osmium(I) Complexes: Molecular Structure of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2][PF_6]$†

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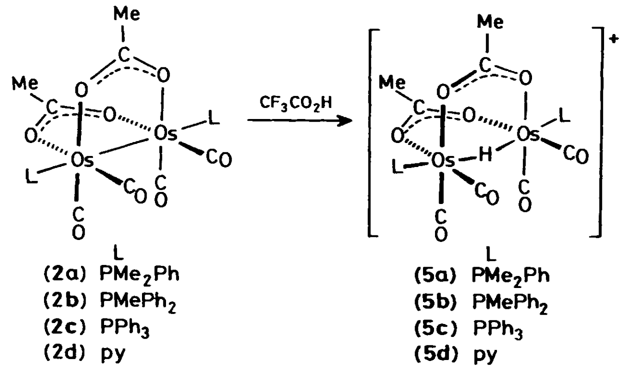
The room temperature reaction between trifluoroacetic acid and the osmium(I) dimer $[Os_2(MeCO_2)_2(CO)_6]$ gives the osmium(II) compound $[Os(CF_3CO_2)_2(CO)_3]$ as a single osmium product, which is also very easily prepared by the direction reaction of CF_3CO_2H with $[Os_3(CO)_{12}]$ at above 160 °C. However, this acid protonates the more basic derivatives $[Os_2(MeCO_2)_2(CO)_4L_2]$ (L = PMe_2Ph, $PMePh_2$, PPh_3, or pyridine), to give the hydrido complexes $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4L_2]^+$, isolated as the $[(CF_3CO_2)_2H]^-$ or $[PF_6]^-$ salts, which are stable to an excess of CF_3CO_2H. The *X*-ray structure of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2][PF_6]$ indicates that the overall geometry of the molecule is preserved on protonation although the Os • • • Os distance is increased to 3.075(1) Å. Protonation of $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)(PPh_3)]$ leads to only a small reduction of the phosphorus–phosphorus nuclear spin–spin coupling constant from ^3J = 59.3 to ^4J = 46.0 Hz. The direct Os–Os bond is replaced by an interaction *via* a bridging hydride which substantially preserves the P–P coupling.

Lewis and co-workers[1] reported a series of dinuclear osmium(I) complexes $[Os_2(MeCO_2)_2(CO)_4L_2]$ (**2**) derived from $[Os_2(MeCO_2)_2(CO)_6]$ (**1**) by replacement of the two CO ligands *trans* to the metal–metal bond by various monodentate ligands L (L = PPh_3, pyridine *etc.*) and recently we extended this series for L = $PMePh_2$, PMe_2Ph, MeCN, and MeNC.[2] We also described the monosubstituted compounds $[Os_2(MeCO_2)_2(CO)_5L]$ (**3**) and mixed compounds such as $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)(PPh_3)]$ (**4**). The introduction of ligands such as tertiary phosphines into metal carbonyl clusters increases their basicity. For example, the triosmium clusters $[Os_3(CO)_{12}]$ and $[Os_3(CO)_9L_3]$ (L = PMe_2Ph, PEt_3 *etc.*) are protonated in concentrated sulphuric acid solution to give $[Os_3(\mu\text{-}H)(CO)_{12}]^+$ and $[Os_3(\mu\text{-}H)_2(CO)_9L_3]^{2+}$ respectively.[3–6] In this paper we have compared the reaction of the osmium(I) dimers $[Os_2(MeCO_2)_2(CO)_6]$ (**1**) and $[Os_2(MeCO_2)_2(CO)_4L_2]$ (**2**; L = tertiary phosphine or pyridine) with trifluoroacetic acid and find that different reactions occur. Simple cationic hydrido complexes are formed from the tertiary phosphine complexes but the hexacarbonyl is cleanly oxidised to the mononuclear osmium(II) complex $[Os(CF_3CO_2)_2(CO)_3]$.

Results and Discussion

Reactions of Dinuclear Osmium(I) *Compounds with Trifluoroacetic Acid.*—The pale yellow complex $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)_2]$[2] (**2a**) reacts with a five-fold excess of CF_3CO_2H in chloroform solution at room temperature to give the colourless product $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2]X$ [**5a**; X = $(CF_3CO_2)_2H$] (84%) (Scheme 1). Immediately on adding the acid the solution became pink but faded to colourless over 2 h. I.r. and ^1H n.m.r. spectra recorded during the course of the protonation showed only signals assignable to the starting material (**2a**) and product (**5a**). Hence it seems that only very small amounts of an intensely coloured pink complex are formed as an intermediate and we have been unable to identify it. The cation of (**5a**), also isolated as the hexafluorophosphate salt (**5a**; X = PF_6), is stable to an excess of acid and shows no change in neat trifluoroacetic acid solution over 48 h.



Scheme 1.

Coloured solutions are also generated by treating each compound (**2**) with CF_3CO_2H [L = PMe_2Ph (pink), $PMePh_2$ (pink), PPh_3 (pink), pyridine (py) (orange)] while $[Os_2(CF_3CO_2)_2(CO)_4(PPh_3)_2]$ gives a purple solution. However, from each solution a colourless hydrido product was isolated (see Experimental section for details and Table 1 for characterising spectroscopic data). The rate of protonation is quite sensitive to the nature of L and also successively higher acid concentrations are required to protonate $[Os_2(MeCO_2)_2(CO)_4L_2]$ (**2**) along the series L = PMe_2Ph, $PMePh_2$, or PPh_3. The PMe_2Ph complex (**2a**) is the most basic. Protonation of $[Os_2(CF_3CO_2)_2(CO)_4(PPh_3)_2]$ to give $[Os_2(CF_3CO_2)_2(\mu\text{-}H)(CO)_4(PPh_3)_2][PF_6]$ may be carried out similarly.

The ^1H n.m.r. spectra of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4L_2]^+$

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† Di-μ-(acetato-*O,O'*)-μ-hydrido-bis[dicarbonyl(dimethylphenylphosphine)osmium(II)] hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. I.r. and ^{1}H n.m.r. spectroscopic data for cationic hydrides of the type $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4L_2]X$

Complex	L	X	$\nu(CO)^a/cm^{-1}$	$\nu(CO_2)^a/cm^{-1}$	$\delta(^1H)^b$
(5a)	PMe_2Ph	$[(CF_3CO_2)_2H]$	2 064vs, 2 044m, 1 992vs, 1 956w	1 776m, 1 686m, 1 571s, 1 450s	
(5a)^c	PMe_2Ph	PF_6	2 061vs, 2 041m, 1 989vs, 1 953w	1 571s, 1 450s	2.09 (t,^{d} PMe), J 10.5^d 2.04 (s, $MeCO_2$) −12.28 (t, OsH), J 31.2
(5b)	$PMePh_2$	PF_6	2 065vs, 2 046m, 1 996vs, 1 956w	1 570s, 1 450s	2.28 (t,^{d} PMe), J 10.3^d 2.00 (s, $MeCO_2$) −12.85 (t, OsH), J 31.8
(5c)^e	PPh_3	PF_6	2 066vs, 2 048m, 1 997vs, 1 970w	1 567s, 1 447ms	1.74 (s, $MeCO_2$) −13.47 (t, OsH), J 32.4
(5d)	py	PF_6	2 067vs, 2 042m, 1 992vs, 1 969w	1 575ms, 1 454ms	8.71 (m, py) 8.21 (m, py) 7.66 (m, py) 2.15 (s, $MeCO_2$) −23.96 (s, OsH)
(6)^f	PPh_3 PMe_2Ph	PF_6	2 062vs, 2 042m, 1 992vs, 1 958w	1 567s, 1 450ms	2.13 (d, PMe), J 11.3 1.94 (s, $MeCO_2$) −13.00 (dd, OsH), J 37.0, 27.0

[a] In $CHCl_3$. [b] Recorded in $CDCl_3$ at 200 MHz; J in Hz; phenyl resonances omitted. [c] ^{31}P N.m.r.: δ −149.4 (s) in $CHCl_3$–$CDCl_3$ relative to $P(OMe)_3$. [d] Virtual triplet, $J = |^2J_{PH} + {}^6J_{PH}|$. [e] Data for the corresponding CF_3CO_2 complex: ν(CO) 2 080vs, 2 055m, 2 015vs, and 1 984w cm^{-1}; $\delta(^1H)$ −13.27 (t, OsH), J_{PH} = 30.3 Hz. [f] ^{31}P N.m.r.: δ −129.5 (d), −149.7 (d), J_{PP} = 46.0 Hz.

(5a)—**(5d)** (Scheme 1) show the expected low-frequency hydride signals; for the phosphine compounds these are simple triplets even down to −90 °C in CD_2Cl_2 indicating that the hydride ligands are symmetrically bridging (Table 1). The cations of **(5a)** (L = PMe_2Ph) and **(5b)** (L = $PMePh_2$) each show methyl triplets with the central peak broader than the outer ones as characteristically observed when there is virtual coupling. These signals are not unlike those observed for the parent compounds and indicate that coupling between the phosphorus nuclei, much greater than $^2J_{PH}$ coupling within each ligand, is maintained on protonation. This is confirmed by observations on the mixed phosphine compound $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)(PPh_3)]$ **(4)**. Compound **(4)** and its protonated form **(6)** each show two ^{31}P n.m.r. doublets with $^3J_{PP}$ = 59.3 Hz for **(4)**, only dropping to $^4J_{PP}$ = 46.0 Hz for **(6)**. The latter is a very large value for a four-bond coupling and there is only 22% reduction in the phosphorus–phosphorus coupling on protonation. The direct metal–metal bond is replaced by an Os–H–Os arrangement without substantial loss of P–P coupling.

The single-crystal *X*-ray structure of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2]X$ (**5a**; X = PF_6) confirms the above observations on these cationic hydrides. The structure is shown in the Figure and selected bond lengths and angles are in Table 2. Although the hydride ligand was not located in this study, it appears to be symmetrically bridging the osmium atoms since the two sides of the cation are essentially equivalent apart from the different conformations of the PMe_2Ph ligands. The osmium–osmium distance of 3.075(1) Å is *ca.* 0.35 Å longer than those in corresponding non-hydrido analogues: 2.731(2) Å in $[Os_2(MeCO_2)_2(CO)_6]$ **(1)**[7] and 2.714(4) Å in $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$.[2] This increase is consistent with a hydride-bridged osmium–osmium contact with no direct metal–metal bond. Another feature is that the axial phosphine ligands are displaced towards the acetate bridges [P(1)–Os(1)–Os(2) = 157.5(1) and P(2)–Os(2)–Os(1) = 155.9(1)°]. Even in the non-hydrido analogues **(1)** and $[N(PPh_3)_2][Os_2(MeCO_2)_2Cl(CO)_5]$ the axial ligands are displaced in this way to a much smaller extent. The corresponding angles in **(1)** are 170.5°. Positioning the hydride ligand at the intersection of the P–Os directions would maintain closely octahedral geometries at the metal atoms and give an Os–H–Os angle of *ca.* 133°.

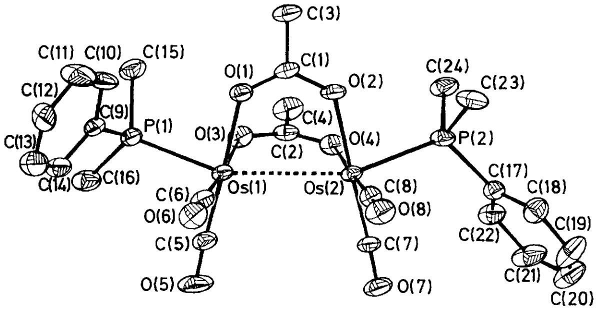


Figure. Molecular structure of the cation of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2]X$ (**5a**; X = PF_6) (hydride ligand not located)

The unsubstituted compound **(1)** should be even less basic than **(2c)** and in an attempt to protonate it we examined a solution of **(1)** in neat trifluoroacetic acid. Reaction occurs at room temperature and there is a similar shift in ν(CO) to higher wavenumbers as expected for protonation. However, there is no hydride signal in the ^{1}H n.m.r. spectrum and the isolated product is the new osmium(II) complex $[Os(CF_3CO_2)_2(CO)_3]$ **(7)**. Although the more basic compounds **(2)** might be expected to be more easily oxidised, they show no tendency to be oxidised to $[Os(CF_3CO_2)_2(CO)_2L]$ at room temperature.

Treatment of $[Os_3(CO)_{12}]$ *and Substituted Derivatives with Trifluoroacetic Acid.*—In view of the formation of **(7)** from **(1)** and trifluoroacetic acid, we examined the reaction of $[Os_3(CO)_{12}]$ with this acid as solvent at 185 °C. The colourless solution formed deposited white needles on addition of water which we characterised as $[Os(CF_3CO_2)_2(CO)_4]$ **(8)** (Scheme 2). This compound is unstable towards decarbonylation and at room temperature in solution converts to $[Os(CF_3CO_2)_2(CO)_3]$ **(7)**. Compound **(8)** is only formed at all because its synthesis was carried out in a Carius tube and no CO could be lost under these conditions. Under milder conditions (120 °C) $[Os_3(CO)_{12}]$ reacts with neat CF_3CO_2H to give $[Os_2(CF_3CO_2)_2(CO)_6]$ (50%) which therefore reacts with trifluoroacetic acid at higher temperatures to give complex **(8)** if the CO lost is contained in the reaction vessel. The osmium(II) complexes (**7**) and (**8**) are easily formed in high yield and are excellent starting materials for the synthesis of osmium(II) carbonyl complexes. We will describe this chemistry later.

Since CF_3CO_2H oxidises $[Os_3(CO)_{12}]$ to osmium(II), whereas CH_3CO_2H gives only osmium(I), we have examined the effect of substituting CO of the dodecacarbonyl by tertiary phosphine on the oxidation state achieved on reaction with these acids. It was expected that substitution would favour oxidation. $[Os_3(CO)_9(PMePh_2)_3]$ reacts with acetic acid at 185 °C to give some osmium(I) as $[Os_2(MeCO_2)_2(CO)_5(PMePh_2)]$ but mainly osmium(II) as a mixture of $[Os(MeCO_2)_2(CO)_2(PMePh_2)_2]$ and $[Os(MeCO_2)_2(CO)_3(PMePh_2)]$. The corresponding reaction with trifluoroacetic acid gave only the osmium(II) products $[Os(CF_3CO_2)_2(CO)_2(PMePh_2)_2]$ and $[Os(CF_3CO_2)_2(CO)_3(PMePh_2)]$. These reactions are not simple since phosphine transfer between osmium atoms is involved. Characterising data for these osmium(II) products are in Table 3.

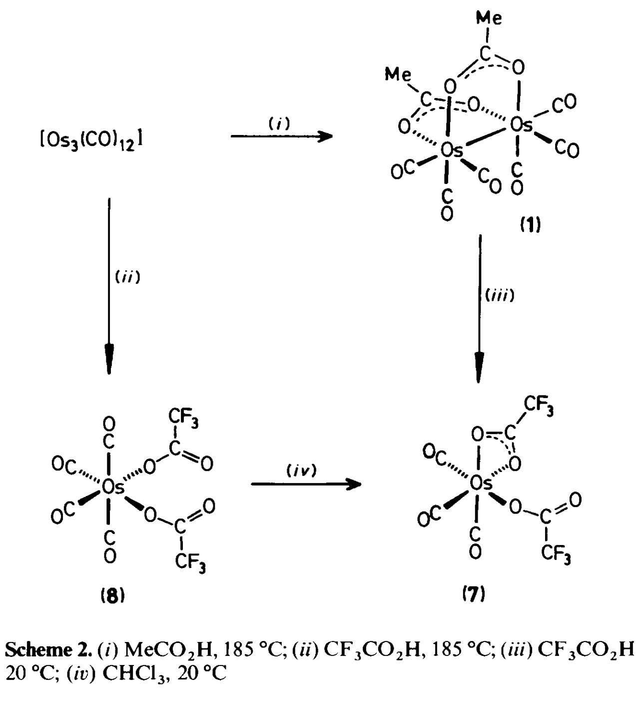
Experimental

The dinuclear osmium(I) complexes $[Os_2(MeCO_2)_2(CO)_4L_2]$ (L = CO, PMe_2Ph, $PMePh_2$, PPh_3, MeCN, or MeNC) were prepared as described.[1,2]

Protonation of $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)_2]$ (**2a**) *with Trifluoroacetic Acid.*—A yellow solution of the osmium(I) compound (0.030 g) in chloroform (10 cm^3) turned pink

Table 2. Selected bond lengths (Å) and angles (°) for $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph_2)_2]X$ (**5a**; X = PF_6)

O(1)–Os(1)	2.105(7)	P(1)–Os(1)	2.361(4)
C(5)–Os(1)	1.845(10)	O(3)–Os(1)	2.112(6)
P(2)–Os(2)	2.362(4)	C(6)–Os(1)	1.864(9)
O(4)–Os(2)	2.100(7)	O(2)–Os(2)	2.107(7)
C(8)–O(2)	1.875(9)	C(7)–Os(2)	1.873(10)
C(1)–O(2)	1.246(10)	C(1)–O(1)	1.234(10)
C(2)–O(4)	1.256(10)	C(2)–O(3)	1.231(10)
C(6)–O(6)	1.106(10)	C(5)–O(5)	1.164(11)
C(8)–O(8)	1.126(9)	C(7)–O(7)	1.127(10)
Os(2) ··· Os(1)	3.075(1)		
P(1)–Os(1)–Os(2)	157.5(1)	O(1)–Os(1)–Os(2)	78.1(2)
O(1)–Os(1)–P(1)	85.2(2)	O(3)–Os(1)–Os(2)	78.5(2)
O(3)–Os(1)–P(1)	85.0(3)	O(3)–Os(1)–O(1)	85.0(3)
C(5)–Os(1)–Os(2)	103.0(4)	C(5)–Os(1)–P(1)	93.0(4)
C(5)–Os(1)–O(1)	177.4(3)	C(5)–Os(1)–O(3)	92.9(4)
C(6)–Os(1)–Os(2)	104.6(3)	C(6)–Os(1)–P(1)	91.1(3)
C(6)–Os(1)–O(1)	92.6(4)	C(6)–Os(1)–O(3)	175.6(3)
C(6)–Os(1)–C(5)	89.3(5)	P(2)–Os(2)–Os(1)	155.9(1)
O(2)–Os(2)–Os(1)	77.9(3)	O(2)–Os(2)–P(2)	84.4(3)
O(4)–Os(2)–Os(1)	77.7(2)	O(4)–Os(2)–P(2)	85.1(2)
O(4)–Os(2)–O(2)	86.6(3)	C(7)–Os(2)–Os(1)	103.0(3)
C(7)–Os(2)–P(2)	94.0(3)	C(7)–Os(2)–O(2)	177.1(3)
C(7)–Os(2)–O(4)	90.9(4)	C(8)–Os(2)–Os(1)	104.0(3)
C(8)–Os(2)–P(2)	92.5(3)	C(8)–Os(2)–O(2)	91.7(4)
C(8)–Os(2)–O(4)	177.2(3)	C(8)–Os(2)–C(7)	90.8(4)



Scheme 2. (*i*) $MeCO_2H$, 185 °C; (*ii*) CF_3CO_2H, 185 °C; (*iii*) CF_3CO_2H, 20 °C; (*iv*) $CHCl_3$, 20 °C

Table 3. Selected i.r. and n.m.r. spectroscopic data for osmium(II) complexes

			δ	
Compound[a]	ν(CO)[b]/cm^{-1}	$\nu(CO_2)$[b]/cm^{-1}	^{19}F[c]	^{13}C or ^{1}H[d]
(**7**) $[Os(CF_3CO_2)_2(CO)_3]$	2 133vs, 2 054vs, 2 041vs	1 698s, 1 653m, 1 434m, 1 410m	−73.66 −76.18	169.2[e] 167.6[f]
(**8**) $[Os(CF_3CO_2)_2(CO)_4]$	2 190w, 2 125vs, 2 106s, 2 068s	1 694vs, 1 408m	−73.64	
$[Os(CF_3CO_2)_2(CO)_3L]$	2 133vs, 2 066vs, 2 026vs	1 697s, 1 410m	−74.61	2.17 (d, PMe) (J_{PH} 11.3)
$[Os(CF_3CO_2)_2(CO)_2L_2]$	2 051vs, 1 984vs	1 688vs, 1 412m	−74.87	2.17 (t, PMe)[g] (J_{PH} 7.8)
$[Os(MeCO_2)_2(CO)_3L]$	2 120vs, 2 051vs, 2 011vs	1 618s, 1 333m		1.99 (d, PMe) (J_{PH} 6.0) 1.65 (s, $MeCO_2$)
$[Os(MeCO_2)_2(CO)_2L_2]$	2 037vs, 1 967vs	1 610s, 1 334m		2.14 (t, PMe)[g] (J_{PH} 6.6) 1.65 (s, $MeCO_2$)

[a] L = $PMePh_2$. [b] Recorded in chloroform solution. [c] In $CDCl_3$–$CFCl_3$ mixed solvent with chemical shifts relative to $CFCl_3$. [d] In $CDCl_3$ relative to $SiMe_4$. [e] CO *trans* to bidentate CF_3CO_2. [f] CO *trans* to monodentate CF_3CO_2. [g] Virtual triplet, $J = |^2J_{PH} + {}^4J_{PH}|$, *trans* phosphines, *cis* carbonyls, and *cis* monodentate carboxylate ligands.

immediately on addition of CF_3CO_2H (0.025 cm^3, 5 mol per mol Os_2) and then colourless over 2 h. Removal of the solvent under reduced pressure gave a white solid which was recrystallised by dissolving in a minimum of dichloromethane and precipitating with diethyl ether to give $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2]X$ [**5a**; X = $(CF_3CO_2)_2H$] as white crystals (0.031 g, 84%) (Found: C, 30.25; H, 2.75; P, 5.5. $C_{28}H_{30}F_6O_{12}Os_2P_2$ requires C, 30.15; H, 2.7; P, 5.55%).

Synthesis of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2]X$ (**5a**; X = PF_6).—The hydrido species [**5a**; X = $(CF_3CO_2)_2H$] as prepared above (0.030 g) in methanol (5 cm^3) was treated with a solution of NH_4PF_6 (0.005 g, 1 mol per mol Os_2) in methanol (2 cm^3). The white precipitate (0.025 g, 90%) was recrystallised by dissolving in a minimum of dichloromethane and, by careful addition of diethyl ether, well-formed colourless crystals suitable for *X*-ray studies were deposited.

Synthesis of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMePh_2)_2][PF_6]$ (**5b**).—This compound was prepared similarly from CF_3CO_2H (0.050 cm^3) and $[Os_2(MeCO_2)_2(CO)_4(PMePh_2)_2]$ (**2b**) (0.030 g) followed by treatment with NH_4PF_6 to give white crystals (0.029 g, 85%).

Synthesis of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PPh_3)_2][PF_6]$ (**5c**).—Addition of CF_3CO_2H (0.205 cm^3, 100 mol per mol Os_2) to a solution of $[Os_2(MeCO_2)_2(CO)_4(PPh_3)_2]$ (**2c**) (0.030 g) in chloroform (5 cm^3) gave a pink solution which paled to colourless over 24 h. The solvent was removed and the colourless solid in methanol solution (5 cm^3) was treated with a solution of NH_4PF_6 (0.005 g, 1 mol per mol Os_2) in methanol (2 cm^3) and a few drops of water to give a white solid. Recrystallisation by dissolving in dichloromethane and precipitation with hexane gave the product as white crystals (0.031 g, 90%) (Found: C, 42.75; H, 3.35; P, 7.15. $C_{44}H_{37}F_6O_8Os_2P_3$ requires C, 42.25; H, 2.9; P, 7.25%).

Synthesis of $[Os_2(CF_3CO_2)_2(\mu\text{-}H)(CO)_4(PPh_3)_2][PF_6]$.—This compound was prepared similarly from $[Os_2(CF_3CO_2)_2(CO)_4(PPh_3)_2]$ (0.030 g) as white crystals (0.029 g, 86%).

Synthesis of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)(PPh_3)][PF_6]$ (**6**).—Addition of CF_3CO_2H (0.050 g, 5 mol per mol Os_2) to a colourless solution of $[Os_2(MeCO_2)_2(CO)_4(PMe_2Ph)(PPh_3)]$ (**4**) (0.090 g) in chloroform (10 cm^3) gave an immediate pink colour which paled to colourless over 2 h. The colourless oil after removal of solvent was dissolved in methanol (10 cm^3) and treated with NH_4PF_6 as above to give the product as white crystals (0.087 g, 87%) (Found: C, 35.0; H, 2.9; P, 7.8. $C_{34}H_{33}F_6O_8Os_2P_3$ requires C, 35.3; H, 2.9; P, 8.0%).

Synthesis of $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(py)_2][PF_6]$ (**5d**).—CF_3CO_2H (0.050 cm^3, 5 mol per mol Os_2) was added to a suspension of $[Os_2(MeCO_2)_2(CO)_4(py)_2]$ (**2d**) (0.100 g) in chloroform (20 cm^3) to give a clear orange solution which became colourless over 16 h. Removal of the solvent and treatment of the residue with NH_4PF_6 as above gave a white solid which was recrystallised by dissolving in dichloromethane and precipitating with hexane to give the product as white crystals (0.091 g, 79%) (Found: C, 23.75; H, 1.9; N, 3.05; P, 2.9. $C_{18}H_{17}F_6N_2O_8Os_2P$ requires C, 23.65; H, 1.85; N, 3.05; P, 3.4%).

Treatment of $[Os_2(MeCO_2)_2(CO)_6]$ (**1**) *with Trifluoroacetic Acid*.—The acetato compound (0.100 g) was dissolved in neat CF_3CO_2H (20 cm^3) to give an almost colourless solution. The solvent was removed under reduced pressure after 3 h to give a white solid which was washed with diethyl ether and pentane to give $[Os(CF_3CO_2)_2(CO)_3]\cdot H_2O$ (**7**) (0.122 g, 81%) (Found: C, 16.85; H, 0.3; O, 25.7. $C_7H_2F_6O_8Os$ requires C, 16.4; H, 0.3; O, 24.7%) (the alternative formulation without H_2O requires C, 16.8; H, 0.00; O, 22.8%).

Reaction of $[Os_3(CO)_{12}]$ *with Trifluoroacetic Acid*.—(*a*) $[Os_3(CO)_{12}]$ (1.00 g) and trifluoroacetic acid (30 cm^3) in a 100-cm^3 Carius tube were degassed and the tube sealed under vacuum and heated at 185 °C for 5 h. The tube was cooled and opened. A similar treatment, but with acetic acid, gave the osmium(I) dimer $[Os_2(MeCO_2)_2(CO)_6]$ (**1**), but addition of water to the trifluoroacetic acid solution gave white needles (0.92 g, 75%) of the osmium(II) compound $[Os(CF_3CO_2)_2(CO)_4]$ (**8**) (Found: C, 17.85; H, 0.25; O, 24.8. $C_8F_6O_8Os$ requires C, 18.15; H, 0.00; O, 24.35%). Recrystallisation of this tetracarbonyl complex was not possible because spontaneous and quantitative decarbonylation to $[Os(CF_3CO_2)_2(CO)_3]$ (**7**) occurs in solution in the absence of an atmosphere of CO.

(*b*) $[Os_3(CO)_{12}]$ (0.100 g) and trifluoroacetic acid (10 cm^3) were degassed and sealed in a 100-cm^3 Carius tube which was heated at 120 °C for 2 h. The tube was cooled, opened, and the solvent removed from the pale yellow solution to give a yellow-cream solid. Separation by preparative t.l.c. [SiO_2; eluant = light petroleum (b.p. 30—40 °C)–CH_2Cl_2, 7:3 v/v] gave $[Os_2(CF_3CO_2)_2(CO)_6]$ as colourless crystals (0.065 g, 50%) from a dichloromethane–methanol mixture (Found: C, 15.6; O, 20.5. $C_{10}F_6O_{10}Os_2$ requires C, 15.5; O, 20.65%). Small quantities of $[Os_3(CO)_{12}]$ (0.010 g, 10%) and the known complex $[Os_3(CF_3CO_2)(\mu\text{-}H)(CO)_{10}]$[8] (0.009 g, 8%) were also obtained.

Reaction of $[Os_3(CO)_9(PMePh_2)_3]$ *with Acetic Acid*.—The triosmium cluster (0.50 g) and acetic acid (30 cm^3) were degassed and sealed in a 100-cm^3 Carius tube under vacuum. The tube was heated at 185 °C for 24 h, cooled, opened, and the solvent removed under reduced pressure. T.l.c. separation [SiO_2; eluant = light petroleum (b.p. 30—40 °C)–CH_2Cl_2, 3:7 v/v] gave a minor yellow band identified as $[Os_2(MeCO_2)_2(CO)_5(PMePh_2)]$ (0.035 g, 8%) and another band containing a mixture of $[Os(MeCO_2)_2(CO)_2(PMePh_2)_2]$ and $[Os(MeCO_2)_2(CO)_3(PMePh_2)]$ which was characterised by ^1H n.m.r. and i.r. spectra. Since we could not separate this mixture by chromatography it was treated with $PMePh_2$ (0.1 cm^3) in refluxing chloroform (20 cm^3) for 4 h. Removal of the solvent and t.l.c. [SiO_2; eluant = light petroleum (b.p. 30—40 °C)–CH_2Cl_2, 3:7 v/v] gave $[Os(MeCO_2)_2(CO)_2(PMePh_2)_2]$ (0.40 g, 70%) as white crystals from dichloromethane–methanol mixtures (Found: C, 49.9; H, 4.25; P, 7.9. $C_{32}H_{32}O_6OsP_2$ requires C, 50.1; H, 4.2; P, 8.1%).

Reaction of $[Os_3(CO)_9(PMePh_2)_3]$ *with Trifluoroacetic Acid*.—A degassed mixture of the triosmium cluster (0.120 g) and trifluoroacetic acid (15 cm^3) in a sealed and evacuated 100-cm^3 Carius tube was heated at 170 °C for 8 h. The tube was opened, the solvent removed, and the residue separated by t.l.c. [SiO_2; eluant = light petroleum (b.p. 30—40 °C)–CH_2Cl_2, 4:6 v/v] to give $[Os(CF_3CO_2)_2(CO)_3(PMePh_2)]$ (0.076 g, 42%) (Found: C, 34.4; H, 1.95; P, 4.2. $C_{20}H_{13}F_6O_7OsP$ requires C, 34.3; H, 1.85; P, 4.4%) and $[Os(CF_3CO_2)_2(CO)_2(PMePh_2)_2]$ (0.041 g, 19%) (Found: C, 43.75; H, 3.05; P, 7.25. $C_{32}H_{26}F_6O_6OsP_2$ requires C, 44.05; H, 3.0; P, 7.1%). Both products gave white crystals from dichloromethane–hexane mixtures.

Crystallographic Studies.—*Crystal data*. $C_{24}H_{29}F_6O_8Os_2P_3$, M = 1 032.80, triclinic, space group $P\bar{1}$ (no. 2), a = 14.323(1), b = 14.844(1), c = 8.787(2) Å, α = 102.55(1), β = 107.25(1), γ = 102.49(1)°, U = 1 660.7(4) Å^3, Z = 2, D_c = 2.065 g cm^{-3}, λ = 0.710 69 Å, $F(000)$ = 976, $\mu(\text{Mo-}K_\alpha)$ = 78.7 cm^{-1}, crystal size 0.65 × 0.48 × 0.15 mm.

Table 4. Fractional atomic co-ordinates (× 10^4) for $[Os_2(MeCO_2)_2(\mu\text{-}H)(CO)_4(PMe_2Ph)_2]X$ (**5a**; X = PF_6)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	2 491.5(2)	−1 604.2(2)	331.2(3)	C(4)	397(7)	−83(7)	−1 973(12)
Os(2)	3 523.2(2)	597.5(2)	1 632.1(3)	C(5)	2 792(6)	−1 971(6)	−1 570(11)
P(1)	1 188(1)	−3 077(1)	−425(2)	C(6)	3 474(5)	−2 116(6)	1 440(10)
P(2)	3 625(1)	2 238(1)	2 661(2)	C(7)	4 159(6)	820(5)	111(10)
P(3)	1 294(2)	2 896(2)	6 232(3)	C(8)	4 790(5)	753(5)	3 251(10)
F(1)	735(11)	3 657(10)	6 441(16)	C(9)	1 545(6)	−3 804(6)	922(10)
F(2)	1 006(12)	2 801(14)	4 435(14)	C(10)	1 466(9)	−3 643(8)	2 471(12)
F(3)	1 845(13)	2 203(11)	5 999(19)	C(11)	1 786(11)	−4 134(9)	3 485(13)
F(4)	1 573(12)	3 010(14)	8 009(12)	C(12)	2 260(9)	−4 829(7)	3 078(13)
F(5)	2 234(12)	3 585(10)	6 495(31)	C(13)	2 349(9)	−5 015(7)	1 547(15)
F(6)	277(11)	2 278(12)	5 806(26)	C(14)	1 971(7)	−4 512(6)	463(12)
O(1)	2 078(4)	−1 206(4)	2 431(7)	C(15)	9(6)	−2 877(7)	−299(15)
O(2)	2 752(4)	378(4)	3 287(7)	C(16)	855(7)	−3 837(7)	−2 530(11)
O(3)	1 295(4)	−1 098(4)	−886(7)	C(17)	4 417(5)	3 044(5)	1 963(10)
O(4)	2 092(4)	474(4)	−96(7)	C(18)	5 413(7)	3 646(7)	2 997(14)
O(5)	2 995(7)	−2 169(6)	−2 764(10)	C(19)	6 000(8)	4 194(10)	2 385(19)
O(6)	4 082(5)	−2 376(5)	2 149(10)	C(20)	5 643(9)	4 225(9)	762(20)
O(7)	4 536(5)	933(5)	−819(9)	C(21)	4 689(10)	3 643(8)	−240(16)
O(8)	5 552(5)	813(5)	4 187(9)	C(22)	4 074(7)	3 057(7)	342(11)
C(1)	2 265(5)	−394(6)	3 395(9)	C(23)	4 087(9)	2 695(7)	4 896(11)
C(2)	1 334(5)	−265(6)	−912(8)	C(24)	2 381(6)	2 443(6)	2 027(13)
C(3)	1 887(6)	−339(7)	4 814(10)				

Data collection. Unit-cell parameters and intensity data were obtained by previously detailed procedures,[9] using a CAD4 diffractometer operating in the ω—2θ scan mode, with graphite monochromated Mo-K_α radiation. A total of 5 849 unique reflections were collected ($3 < 2\theta < 50°$). The segment of reciprocal space scanned was: (*h*) −17→17, (*k*) −17→17, (*l*) 0→10. The reflection intensities were corrected for absorption using the azimuthal scan method;[10] maximum transmission factor 1.00, minimum 0.57.

Structure solution and refinement. The structure was solved using routine heavy-atom methods (SHELX 86[11]) and refined by full-matrix least squares (SHELX 76[12]). All non-hydrogen atoms were refined anisotropically. Final stages of the refinement included all phenyl and methyl hydrogen atoms in calculated positions (C–H 0.96 Å, $U = 0.10$ Å^2). The final residuals R and R' were 0.035 and 0.040 respectively for the 406 variables and 4 694 data for which $F_o > 6\sigma(F_o)$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, *w*, being defined as $1/[\sigma^2(F_o) + 0.002F_o{}^2]$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 13 and 14 respectively. All computations were made on a DEC VAX-11/750 computer. Atomic co-ordinates are given in Table 4.

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

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