Journal of Organometallic Chemistry, 219 (1981) 103—113
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE REACTION OF $H_2Os_3(CO)_{10}$ WITH TRIFLUOROACETONITRILE AND THE X-RAY CRYSTAL STRUCTURE OF $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HNCCF_3)$

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(Received April 2nd, 1981)

Summary

The reaction of $H_2Os_3(CO)_{10}$ with CF_3CN in hexane at 80°C leads to two isomeric products. The isomer constituting the major product contains a 1,1,1-trifluoroethylidenimido ligand which bridges one edge of the Os_3 triangle via the nitrogen atom and may be formulated as $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NC(H)CF_3)$ (I). The minor product, formulated as $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}HNCCF_3)$ (II), contains a 1,1,1-trifluoroacetimidoyl ligand which is also edge-bridging, being N-bonded to one Os atom and C-bonded to the other. Thermolysis of I and II in solution results in loss of a CO group in each case to give $(\mu\text{-}H)Os_3(CO)_9$-$(\mu_3\text{-}\eta^2\text{-}NC(H)CF_3)$ (III) and $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HNCCF_3)$ (IV), respectively, which, it is proposed, are structurally related to I and II, but with the C=N group coordinated also to the third Os atom in place of a CO group. In the case of IV this proposal has been confirmed by an X-ray crystallographic analysis. The compound crystallises in space group $C2/c$ with a = 14.258(7), b = 13.486(10), c = 18.193(8) Å, β = 92.68(4)°, and Z = 8. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least squares to R = 0.054 for 2489 unique observed diffractometer data. Reaction of I with Et_3P gives a 1 : 2 adduct which is formulated as $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}\bar{N}C(H)(CF_3)\overset{+}{P}Et_3]$ (V) on the basis of NMR evidence.

Introduction

We have recently reported that the rhenium complex, $H_2Re_2(CO)_6(dpm)$ (dpm = $Ph_2PCH_2PPh_2$), which has a double bond between the two rhenium atoms and can be regarded as an analogue of the well-studied $H_2Os_3(CO)_{10}$, reacts with RCN and RNC to give complexes containing C=N ligands which are formed by insertion of the CN triple bond into an M—H bond [1]. Such reactions are of interest in providing models for steps in the transition metal-cata-

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lysed reduction of small unsaturated molecules such as RCN, RNC and CO.

In some respects $H_2Re_2(CO)_6(dpm)$ is more reactive than $H_2Os_3(CO)_{10}$ in that, while both react with RNC under relatively mild conditions [1,2], only the former reacts with RCN (R = Me) to give insertion products [1]. In order to establish the nature of the reaction of RCN with $H_2Os_3(CO)_{10}$ for comparative purposes we have therefore treated the osmium complex with the activated nitrile CF_3CN, and the results of this study are now presented.

Results and discussion

(a) Reaction of $H_2Os_3(CO)_{10}$ with CF_3CN

The reaction was carried out in a sealed tube at 80° C and, after 16 h, a bright yellow solution was obtained. Separation of this reaction mixture by TLC showed the formation of two products in yields of 69% and 14%. The mass spectra of these complexes both contained parent ion peaks at *m/e* 953 (^{192}Os) which correspond to their formulation as the 1 : 1 adducts $[H_2Os_3(CO)_{10}(CF_3CN)]$ and suggests that they are isomeric.

The ^1H NMR spectrum of the major product (I) (Table 1) contains only one metal-hydride resonance, and the presence of a quartet at δ 7.75 ppm of relative intensity one, which may be assigned to NC*H*CF_3, suggests that proton transfer to the nitrile carbon atom has taken place. The infrared spectrum of I (Table 2) contains C—F absorptions confirming the presence of the organic ligand, and an electron count reveals that the donation of three electrons from the ligand is necessary in order for I to conform to the EAN (effective atomic number) rule. The most likely mode of attachment of the ligand, and one which has previously been observed for related complexes [1,3,4] involves the nitrogen atom acting as a bridging three-electron donor along the same edge of the osmium triangle as the remaining metal hydride ligand. The proposed structure is shown in Fig. 1 and this proposal has been confirmed by an X-ray crystal structure determination [5]. A subsequent neutron diffraction study has located both the hydrogen atoms in I in their expected positions [6].

The ^1H NMR of the minor product (II) contains, in addition to a metal hydride singlet at δ —15.15 ppm, a broad singlet at δ 9.75 ppm. The position of

TABLE 1

^1H NMR DATA FOR NEW COMPLEXES

Complex	^1H NMR spectrum (ppm) [a]	Assignment
I	7.75 (q, 1 H), $^3J(HF) = 4.2$ Hz	CH
	—14.83 (s, 1 H)	OsH [b]
II	9.75 (s, 1 H)	NH
	—15.15 (s, 1 H)	OsH
IV	8.54 (s, 1 H)	NH
	—18.01 (s, 1H)	OsH
V	7.58 (m, 1 H)	CH
	—14.68 (d, 1 H), $J(HP) = 8.1$ Hz	OsH

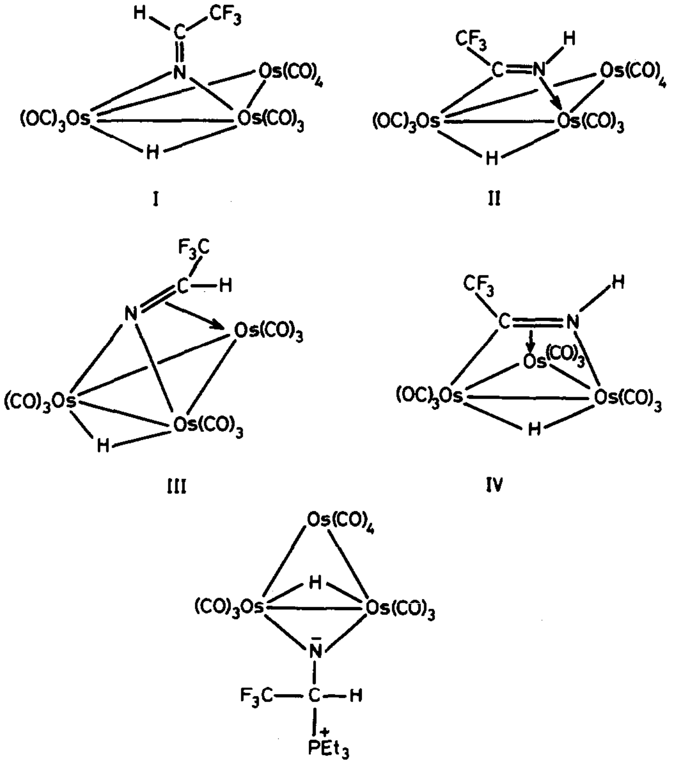
[a] s = singlet, d = doublet, q = quartet, m = multiplet. [b] Coupling of OsH to ^{19}F observed in ^{19}F NMR spectrum but nor resolved in ^1H spectrum.

TABLE 2

INFRARED AND MASS SPECTROSCOPIC DATA FOR NEW COMPLEXES

Complex	*m/e* (^{192}Os)	Solvent	Infrared absorption frequencies (cm^{-1})	Assignment
I	953	Hexane	2109m, 2071s, 2059s, 2023s, 2011s, 2001s, 1986m, 1967w	ν(CO)
			1370m, 1270s, 1156vs, 1140vs [b]	ν(C—F)
II	953	Hexane	2109m, 2072s, 2058s, 2023s, 2011s, 2001s, 1985m, 1967w	ν(CO)
			1255s, 1185m, 1160s [b]	ν(C—F)
			3320w [b]	ν(N—H)
III	925	Hexane	2119m, 2082s, 2056vs, 2035vs, 2010(sh), 2005vs 1992s, 1976m, 1953w	ν(CO)
IV	925	Hexane	2103m, 2077vs, 2051vs, 2023s, 2013(sh), 2005vs, 1995(sh), 1986m	ν(CO)
			1255m, 1242w, 1225w, 1212w, 1180m, 1165w, 1140w, 1125s [b]	ν(C—F)
			3320w [b]	ν(N—H)
V	1072	Hexane	2094s, 2055vs, 2014vs, 2006s, 2002s, 1992s, 1984s, 1974m, 1962w, 1941m	ν(CO)

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] Data from Nujol mull spectrum.



I

II

III

IV

V

Fig. 1. Proposed structures of new complexes.

this resonance, together with the presence of a weak band in the infrared at 3320 cm^{-1}, suggests that it is due to an N—H proton and that insertion has taken place to give an $HN{=}CCF_3$ ligand, also acting as a three-electron donor. As in related complexes [2] the ligand presumably bridges the same edge of the Os_3 triangle as the metal hydride ligand, being linked by an N → Os donor bond to one osmium atom and an C—Os σ-bond to the other (Fig. 1).

The structure of II could not be confirmed by an X-ray determination due to the unavailability of suitable crystals, but an X-ray analysis of its thermolysis product IV (vide infra) provides supporting evidence for the structure proposed. Thus the reaction of CF_3CN with $H_2Os_3(CO)_{10}$ gives insertion products which are analogous to those obtained in the reaction of CH_3CN with $H_2Re_2(CO)_6(dpm)$ and provides further evidence for the parallel we have drawn between these two complexes [1]. It is interesting that in both cases the major product of the reaction is the isomer containing the 1,1,N-bonded ligand, $N{=}CHCH_3$, whereas in the reaction of $[HFe_3(CO)_{11}]^-$ with CH_3CN an anionic complex, $[(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-HN{=}CCH}_3)]^-$, is obtained as the major product with the $HN{=}CCH_3$ ligand bonded to all three metal atoms and acting as a five-electron donor. The corresponding complex containing a five-electron donor $N{=}CHCH_3$ ligand is also formed but in lower yield [7].

(b) Thermolysis of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NC(H)CF}_3)$ (I) and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-HNCCF}_3)$ (II)

Complex I was found to be extremely resistant towards thermal ejection of a carbonyl ligand and is unchanged after several hours in refluxing octane (125° C). When the temperature is raised to that of refluxing nonane (151° C) considerable decomposition has taken place after 20 h, but an amber complex

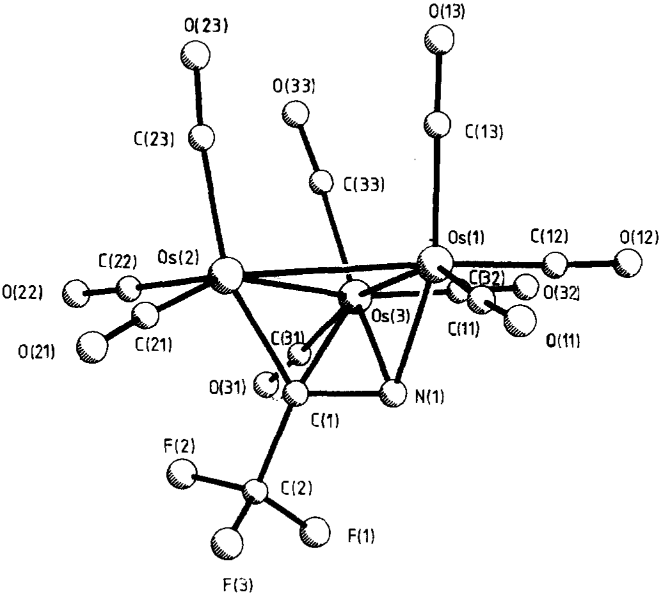


Fig. 2. The molecular structure of $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-HNCCF}_3)$.

may be isolated by TLC in very low yield. This complex (III) exhibits a mass spectrum indicative of the formula $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-NC(H)CF}_3)$ (*m/e* 925, ^{192}Os) which corresponds to the loss of one carbonyl ligand from I. Although the infrared spectrum of III shows a pattern of carbonyl bands considerably different from that of I, sufficient material for an ^{1}H NMR spectrum was not available. The suggested structure for III, shown in Fig. 1, is based on that of the analogous iron complex, $(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-NC(H)CH}_3)$ [7] which has been determined by X-ray crystallography [8].

Complex II thermolyses more readily than I and, when an octane solution is refluxed for three days, approximately 50% conversion to a single complex takes place. The mass spectrum of this product (IV) shows a parent ion at *m/e* 925 (^{192}Os) indicating that it is isomeric with III and its ^{1}H NMR spectrum shows peaks at δ 8.54 ppm and −18.01 ppm which may be assigned respectively to an N—H proton and a metal hydride ligand. IV is therefore formulated as $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-HNCCF}_3)$ and this formulation has been confirmed by an X-ray diffraction study.

The structure of IV is shown in Fig. 2 and includes the atom numbering scheme adopted. The corresponding bond lengths and interbond angles are given in Tables 3 and 4, respectively. The three Os atoms define a slightly distorted isosceles triangle. The two shorter edges, Os(1)—Os(3) and Os(2)—Os(3), are significantly shorter than the average metal—metal distance of 2.877(1) Å in the parent binary carbonyl, $Os_3(CO)_{12}$ [9], and are similar to the distance of 2.78(1) Å for the shortest such bond in $(\mu\text{-H})Os_3(CO)_{10}(CF_3CCHCF_3)$ [10]. The third Os—Os edge in IV is longer, and is similar to the value for the hydride bridged Os—Os bond of 2.918(1) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-C}_6H_5CNCH_3)$ [11]. The carbonyl groups C(11)O(11) and C(21)O(21) bend away from this long Os(1)—Os(2) edge with an average *cis* Os—Os—C angle of 114(2)°, compared to the value of 98(3)° for the other carbonyl groups. This indicates that the hydride in IV bridges the Os(1)—Os(2) edge.

The $HNCCF_3$ ligand in IV is σ-bonded to Os(1) via N(1) and to Os(2) via C(1), and π-bonded to Os(3). The two σ-bonds are similar in length to the Os—N distance of 2.111(6) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-C}_6H_5CNCH_3)$ [11] and to the Os—C distance of 2.032(10) Å in $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-HCNC}_6H_5)$ [2]. The π-bond to Os(3) is symmetric and the Os—N and Os—C bonds are slightly shorter than the corresponding Os—N of 2.121(9) and 2.219(9) Å and the Os—C distance of 2.266(10) Å in $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-HCNC}_6H_5)$ [2] where there is a similar mode of ligand coordination. The C—N distance is also similar to the value of 1.415(11) Å in $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-HCNC}_6H_5)$ [2], and shows a reduction in the multiple bond order when compared to the distance of 1.278(10) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-C}_6H_5CNCH_3)$ [11] where the organic ligand bridges only two metal atoms.

The nine carbonyl groups are all terminal and linear. The equatorial Os—C bonds are shorter (mean 1.91(4) Å) than those *trans* to the capping organic ligand (mean 1.93(2) Å). The dimensions of the CCF_3 fragment are similar to those in $(\mu\text{-H})Os_3(CO)_{10}(CF_3CCHCF_3)$ [10].

The results of the thermolysis experiments described above are in marked contrast to what is observed for analogous iron complexes. Thus the neutral iron complex $(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-HNCCH}_3)$, obtained by protonation of the

TABLE 3

BOND LENGTHS (Å)

Os(2)—Os(1)	2.925(2)	C(11)—Os(1)	1.932(25)
Os(3)—Os(1)	2.750(2)	C(12)—Os(1)	1.880(23)
Os(3)—Os(2)	2.789(2)	C(13)—Os(1)	1.933(25)
N(1)—Os(1)	2.072(16)	C(21)—Os(2)	1.919(26)
C(1)—Os(2)	2.041(20)	C(22)—Os(2)	1.891(29)
N(1)—Os(3)	2.186(18)	C(23)—Os(2)	1.949(24)
C(1)—Os(3)	2.178(22)	C(31)—Os(3)	1.943(28)
C(1)—N(1)	1.403(23)	C(32)—Os(3)	1.862(25)
C(2)—C(1)	1.550(32)	C(33)—Os(3)	1.896(31)
F(1)—C(2)	1.340(26)	O(11)—C(11)	1.111(29)
F(2)—C(2)	1.324(26)	O(12)—C(12)	1.156(28)
F(3)—C(2)	1.306(34)	O(13)—C(13)	1.134(27)
O(21)—C(21)	1.145(29)	O(31)—C(31)	1.112(30)
O(22)—C(22)	1.155(31)	O(32)—C(32)	1.197(28)
O(23)—C(23)	1.117(27)	O(33)—C(33)	1.104(31)

TABLE 4

BOND ANGLES (deg)

Os(3)—Os(1)—Os(2)	58.8(1)	C(11)—Os(1)—Os(2)	112.4(7)
Os(3)—Os(2)—Os(1)	57.5(1)	C(11)—Os(1)—Os(3)	154.8(8)
Os(2)—Os(3)—Os(1)	63.7(1)	C(12)—Os(1)—Os(2)	150.7(7)
N(1)—Os(1)—Os(2)	68.8(4)	C(12)—Os(1)—Os(3)	92.0(7)
N(1)—Os(1)—Os(3)	51.6(5)	C(13)—Os(1)—Os(2)	94.4(7)
C(1)—Os(2)—Os(1)	67.8(5)	C(13)—Os(1)—Os(3)	106.6(7)
C(1)—Os(2)—Os(3)	50.8(6)	C(21)—Os(2)—Os(1)	115.8(7)
N(1)—Os(3)—Os(1)	48.0(4)	C(21)—Os(2)—Os(3)	155.6(8)
N(1)—Os(3)—Os(2)	70.3(4)	C(22)—Os(2)—Os(1)	149.3(7)
C(1)—Os(3)—Os(1)	70.0(5)	C(22)—Os(2)—Os(3)	91.9(7)
C(1)—Os(3)—Os(2)	46.5(5)	C(23)—Os(2)—Os(1)	95.9(6)
C(1)—Os(3)—N(1)	37.5(6)	C(23)—Os(2)—Os(3)	107.8(7)
C(11)—Os(1)—N(1)	103.5(10)	C(31)—Os(3)—Os(1)	160.9(9)
C(12)—Os(1)—N(1)	96.1(9)	C(31)—Os(3)—Os(2)	108.5(8)
C(13)—Os(1)—N(1)	157.0(8)	C(32)—Os(3)—Os(1)	95.0(8)
C(21)—Os(2)—C(1)	104.9(10)	C(32)—Os(3)—Os(2)	157.7(8)
C(22)—Os(2)—C(1)	95.8(9)	C(33)—Os(3)—Os(1)	100.8(7)
C(23)—Os(2)—C(1)	157.6(9)	C(33)—Os(3)—Os(2)	85.3(8)
C(31)—Os(3)—N(1)	113.6(10)	C(12)—Os(1)—C(11)	95.1(10)
C(31)—Os(3)—C(1)	92.0(9)	C(13)—Os(1)—C(11)	97.3(11)
C(32)—Os(3)—N(1)	101.0(10)	C(13)—Os(1)—C(12)	91.6(10)
C(32)—Os(3)—C(1)	135.1(10)	C(22)—Os(2)—C(21)	93.0(11)
C(33)—Os(3)—N(1)	146.4(8)	C(23)—Os(2)—C(21)	95.9(11)
C(33)—Os(3)—C(1)	130.8(9)	C(23)—Os(2)—C(22)	91.3(11)
Os(3)—N(1)—Os(1)	80.4(6)	C(32)—Os(3)—C(31)	93.8(11)
C(1)—N(1)—Os(1)	109.5(12)	C(33)—Os(3)—C(31)	95.6(12)
C(1)—N(1)—Os(3)	71.0(11)	C(33)—Os(3)—C(32)	92.9(11)
Os(3)—C(1)—Os(2)	82.7(8)	F(1)—C(2)—C(1)	110.3(20)
N(1)—C(1)—Os(2)	113.9(13)	F(2)—C(2)—C(1)	111.6(23)
N(1)—C(1)—Os(3)	71.5(11)	F(3)—C(2)—C(1)	113.3(19)
C(2)—C(1)—Os(2)	128.0(14)	F(2)—C(2)—F(1)	107.4(19)
C(2)—C(1)—Os(3)	125.1(16)	F(3)—C(2)—F(1)	107.8(27)
C(2)—C(1)—N(1)	116.4(17)	F(3)—C(2)—F(2)	106.2(21)
O(11)—C(11)—Os(1)	175.7(26)	O(21)—C(21)—Os(2)	175.2(24)
O(12)—C(12)—Os(1)	178.1(23)	O(22)—C(22)—Os(2)	177.3(26)
O(13)—C(13)—Os(1)	177.9(21)	O(23)—C(23)—Os(2)	174.5(20)
O(31)—C(31)—Os(3)	178.8(33)	O(33)—C(33)—Os(3)	175.2(25)
O(32)—C(32)—Os(3)	177.2(25)		

corresponding anion, isomerises irreversibly at 65° C to give (μ-H)$Fe_3(CO)_9$-(μ_3-η^2-NC(H)CH_3), indicating that this latter complex is thermodynamically the more stable [7]. For osmium, isomer interconversion, in this particular case at least, obviously requires a higher activation energy and it is not possible to determine whether III or IV is thermodynamically the more stable. Adams has also noted that the related isomeric complexes (μ-H)$Os_3(CO)_{10}$(μ-CN(H)R) and (μ-H)$Os_3(CO)_{10}$(μ-η^2-HCNR) do not interconvert, even under prolonged and forcing thermolytic treatment [2].

(c) Reaction of (μ-H)$Os_3(CO)_{10}$(μ-NC(H)CF_3) (I) with Et_3P

Trinuclear osmium complexes containing ligands which possess multiple bonds generally undergo nucleophilic attack on reaction with phosphorus donor molecules. Such nucleophilic attack most commonly leads to the phosphorus atom becoming attached to the organic ligand [12]. When fluorocarbon groups are present, however, attachment of the phosphine to the metal, with transfer of a metal-bound H atom to the organic ligand [13] or cleavage of a metal—metal bond [14] have also been reported as alternative processes. It therefore seemed of interest to study the reaction of I and II with phosphorus donor molecules, but only I was obtained in sufficient amount for this to be possible.

When I is treated with an excess of Et_3P in refluxing hexane no starting material remains after 4 h. Separation of the reaction mixture on TLC plates reveals the formation of a single product in good yield in addition to a trace of decomposition. A mass spectrum of this product contains a parent ion at *m/e* 1072 (^{192}Os), indicative of the formation of a 1 : 1 adduct rather than a substituted derivative with Et_3P replacing CO. The most likely point of attack by a nucleophile on I is probably the nitrile carbon atom, at which the δ+ charge conferred by the polarity in the $\overset{\delta-}{N}=\overset{\delta+}{C}$ system would be expected to be enhanced somewhat by the electronegative character of the attached CF_3 group. Addition of the phosphine at this carbon atom would give the species (μ-H)$Os_3(CO)_{10}$[μ-$\overset{-}{N}CH(CF_3)\overset{+}{P}Et_3$] (V) with the structure shown in Fig. 1, and this is believed to be the identity of the adduct. The proposed structure is related to that of (μ-H)$Os_3(CO)_{10}$(μ-$\overset{-}{C}HCH_2P^+Me_2Ph$) which is formed by the

TABLE 5

^{19}F NMR DATA FOR NEW COMPLEXES

Complex	^{19}F NMR spectrum (δ, ppm) [a]
I	64.98 (d of d), ^3J(FC*H*) = 4.5 Hz ^5J(FOs*H*) = 0.7 Hz 70.0(s) [b]
II	77.29(d), ^4J(FH) = 2 Hz
III	68.1(s)
V	70.61 (d of d of d), ^3J(FP) = 2.9 Hz ^3J(FC*H*) = 4.8 Hz, ^5J(FOs*H*) = 0.7 Hz 71.4(d), ^3J(FP) = 3.0 Hz [b]

[a] At high field relative to CCl_3F; s = singlet, d = doublet. [b] ^{1}H-decoupled spectrum.

treatment of $HOs_3(CO)_{10}(CH{=}CH_2)$ with PMe_2Ph [12], and it is supported by NMR evidence. Thus the ^1H NMR shows a doublet resonance at δ −14.68 ppm (J = 8.1 Hz) due to Os*H* with the coupling presumably being to the phosphorus nucleus. A further broad multiplet signal at δ 7.58 ppm can be assigned to the $\bar{N}CH(CF_3)\overset{+}{P}Et_3$ proton for which the eight-line coupling expected to be produced by the phosphorus and fluorine nuclei is only partially resolved. The ^{19}F spectrum of V shows a resonance at δ 70.61 ppm consisting of a doublet of doublets of doublets, and comparison with the ^{19}F NMR spectrum of I (Table 5) enables the couplings to be assigned as $^3J(F{-}P)$ = 2.9 Hz. $^3J(F{-}HC)$ = 4.8 Hz and $^5J(F{-}HOs)$ = 0.7 Hz. The ^1H-decoupled ^{19}F NMR spectrum of V comprises a doublet signal (δ 71.4 ppm, $^3J(F{-}P)$ = 3.0 Hz) due to splitting of the fluorine resonance by phosphorus only, providing confirmation of the above assignments. Thus nucleophilic attack of Et_3P on I leads to the expected attachment of the nucleophile to the organic ligand [12] rather than to transfer of the remaining metal hydride to the organic ligand [13] or to metal—metal bond cleavage [14] as in certain related fluorocarbon-containing complexes.

Experimental

All experiments were carried out in an atmosphere of dry nitrogen using freshly redistilled degassed solvents. Infrared spectra were recorded on Perkin-Elmer 257 or 577 spectrophotometers for dichloromethane or hexane solutions in 0.5 mm sodium chloride cells or, for Nujol mulls, between caesium bromide plates, and were calibrated with CO gas or polystyrene. Mass spectra were recorded on an AEI MS12 spectrometer using perfluoroheptyl-s-triazine introduced indirectly as calibrant. ^1H NMR spectra were recorded for CD_2Cl_2 solutions on Varian XL-100-12 and XL-100-15 instruments in the Fourier Transform mode, and solvent resonances were used as secondary standards to calibrate spectra. ^{19}F NMR spectra were recorded for CD_2Cl_2 solutions on a Varian XL-100-12 instrument in the continuous wave mode with CCl_3F as internal standard. All chromatography was carried out on commercial Merck TLC plates coated with a 0.25 mm layer of silica.

(i) Reaction between $H_2Os_3(CO)_{10}$ and trifluoroacetonitrile

Typically, a large excess of CF_3CN gas (188 cm^3, 10 cm Hg) was sealed into a glass tube containing a solution of $H_2Os_3(CO)_{10}$ (0.50 g, 0.59 mmol) in hexane (25 cm^3). The tube was then heated in an oven at 80° C for 16 h, during which time the solution changed from an intense purple colour to bright yellow. It was then evaporated to dryness and the residue placed on TLC plates. A single elution with dichloromethane/hexane (5/95) gave two well separated yellow bands. These were extracted and crystallised from saturated warm hexane solutions to give yellow blocks of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NC(H)CF_3)$ (I) (0.382 g, 69%) and yellow needles of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}HNCCF_3)$ (II) (0.080 g, 14%), respectively.

(ii) Thermolysis of I

A solution of I (0.10 g, 0.11 mmol) in nonane (15 cm^3) was refluxed for 20 h. The yellow solution had turned yellow-brown after this time and the solvent was then distilled off under reduced pressure. The residue was placed on TLC plates and elution with dichloromethane/hexane (10/90) gave, in addition to considerable amounts of a yellow band due to the starting complex, an amber band which eluted more slowly. On removing the solvent a low yield of a yellow-brown complex, identified spectroscopically as $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-NC(H)CF}_3)$ (III) remained.

(iii) Thermolysis of II

A solution of II (0.02 g, 0.02 mmol) in n-octane (10 cm^3) was refluxed for 3 days after which the solvent was distilled off under reduced pressure. The residue was placed on TLC plates and several elutions with dichloromethane/hexane (10/90) gave, in addition to starting material (50%), a single yellow band. This was extracted and crystallised by slow evaporation of a hexane solution to give pale yellow blocks of $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-HNCCF}_3)$ (IV) (50%).

(iv) Reaction between I and triethylphosphine

To a solution of I (0.038 g, 0.04 mmol) in hexane (15 cm^3) was added a slight excess of PEt_3 (0.008 cm^3, 0.05 mmol). The mixture was refluxed for 4 h, taken to dryness under reduced pressure and the residue placed on TLC plates. Several elutions with hexane gave a single yellow band which was taken to dryness to give a yellow powder in ca. 80% yield. This was identified spectroscopically as $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\overset{-}{N}CH(CF_3)\overset{+}{P}Et_3)$ (V).

(v) The molecular and crystal structure of $HOs(CO)_9(\mu_3\text{-}\eta^2\text{-HNCCF}_3)$ (IV)

Crystal data: $C_{11}H_2F_3NO_9Os_3$, mol wt. 919.73, monoclinic $a = 14.258(7)$, $b = 13.486(10)$, $c = 18.193(8)$ Å, $\beta = 92.68(4)°$, $U = 3587.6$ Å, $D_c = 3.40$ g cm^{-3}, $Z = 8$. Space group $C2/c$ from systematic absences and structure solution. Graphite-monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 212.62$ cm^{-1}. Intensity data was recorded from a crystal of dimensions $0.157 \times 0.120 \times 0.258$ mm.

Yellow blocks of IV were obtained by slow crystallisation from hexane solution, and mounted on glass fibres. A single crystal was transferred to a Syntex $P2_1$ four-circle diffractometer and accurate cell parameters determined by the angular measurement of 15 reflections in the range $15 < 2\theta < 25°$. 4685 intensities were recorded ($3.0 < 2\theta < 50.0°$) using graphite-monochromated Mo-K_α radiation, and a 96-step $\omega/2\theta$ scan technique. Lp corrections, and semi-empirical absorption corrections, based on a pseudo-ellipsoid model and 429 azimuthal scan data from 12 independent reflections were applied. This gave transmission coefficients which ranged from 0.533 to 0.998 for the full data set. The data were averaged to give 2489 unique observed reflections $|F > 5\sigma(F)|$.

The three Os atoms were located by multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms from a subsequent Fourier difference synthesis; the H atoms were not located. The structure was refined by full-matrix least squares with all the atoms assigned anisotropic thermal parameters and using complex neutral-atom scattering factors [15]. In the last cycles of least squares a weighting scheme of the form $w = 0.9449/|\sigma^2(F) + 0.002|F|^2|$ was introduced. The refinement converged to $R = 0.054$ and $R' = \Sigma w^{1/2}\ \Delta/\Sigma w^{1/2}$-

TABLE 6

ATOM COORDINATES ($\times 10^4$)

	x/a	y/b	z/c
Os(1)	2650(1)	4754(1)	5038(1)
Os(2)	1474(1)	4886(1)	3681(1)
Os(3)	3169(1)	5879(1)	3879(1)
N(1)	3386(12)	4350(13)	4133(9)
C(1)	2803(14)	4432(16)	2493(10)
C(2)	3163(16)	3955(25)	2789(12)
F(1)	4102(11)	3991(15)	2795(8)
F(2)	2839(11)	4405(13)	2187(7)
F(3)	2911(16)	3053(13)	2712(8)
C(11)	2476(21)	3551(20)	5553(12)
O(11)	2423(21)	2875(15)	5876(11)
C(12)	3705(18)	5143(19)	5624(11)
O(12)	4356(13)	5404(17)	5971(9)
C(13)	1824(18)	5534(19)	5607(12)
O(13)	1347(13)	5975(14)	5958(10)
C(21)	689(18)	3789(20)	3458(13)
O(21)	262(15)	3097(15)	3358(12)
C(22)	1238(15)	5440(24)	2740(14)
O(22)	1123(16)	5757(18)	2156(10)
C(23)	495(16)	5674(19)	4094(11)
O(23)	−23(14)	6127(16)	4381(10)
C(31)	3590(21)	6252(22)	2919(15)
O(31)	3815(18)	6471(20)	2367(11)
C(32)	4201(18)	6429(20)	4386(14)
O(32)	4886(15)	6750(16)	4703(12)
C(33)	2411(18)	6986(22)	4007(13)
O(33)	1930(15)	7607(14)	4043(13)

TABLE 7

ANISOTROPIC TEMPERATURE FACTORS (Å$^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	34(1)	36(1)	23(1)	−1(1)	3(1)	0(1)
Os(2)	27(1)	42(1)	28(1)	−1(1)	1(1)	−3(1)
Os(3)	32(1)	36(1)	32(1)	2(1)	5(1)	−5(1)
N(1)	28(9)	42(11)	30(8)	5(8)	5(7)	5(8)
C(1)	30(11)	38(12)	25(9)	11(8)	−4(8)	5(9)
C(2)	26(12)	115(27)	34(12)	13(14)	10(10)	−13(14)
F(1)	44(9)	138(17)	64(10)	−40(10)	13(7)	23(10)
F(2)	81(11)	91(12)	21(6)	5(7)	12(6)	1(10)
F(3)	141(17)	70(12)	44(9)	−24(8)	21(10)	−13(12)
C(11)	78(20)	59(17)	30(11)	11(11)	−2(12)	−30(15)
O(11)	194(28)	50(12)	47(11)	12(10)	33(14)	−17(15)
C(12)	50(14)	66(17)	22(9)	−1(10)	−7(10)	4(13)
O(12)	53(12)	123(18)	37(9)	−11(10)	−19(8)	17(12)
C(13)	52(15)	58(16)	30(11)	−3(10)	2(10)	13(13)
O(13)	59(12)	65(13)	68(11)	−13(10)	17(10)	−2(10)
C(21)	50(15)	49(15)	49(14)	−5(12)	−6(11)	−5(13)
O(21)	70(14)	64(14)	87(14)	−9(11)	16(11)	−29(12)
C(22)	18(11)	106(24)	58(15)	−16(16)	−14(10)	−15(3)
O(22)	95(17)	133(21)	40(10)	42(12)	−28(10)	−17(15)
C(23)	40(13)	54(15)	33(10)	−7(10)	8(10)	−1(11)
O(23)	62(12)	99(16)	50(10)	−17(11)	1(9)	28(12)
C(31)	73(20)	71(19)	64(17)	−16(15)	20(15)	−51(17)
O(31)	124(21)	142(24)	48(11)	21(13)	35(12)	−52(18)
C(32)	39(14)	67(19)	51(14)	−9(13)	−1(11)	−6(13)
O(32)	75(15)	72(14)	82(14)	−6(12)	−19(12)	−17(12)
C(33)	39(14)	73(20)	46(14)	10(12)	8(11)	−12(14)
O(33)	61(14)	53(13)	112(17)	−4(12)	−1(12)	26(11)

[a] The temperature factor exponent takes the form: $\exp - 2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

$|F_0|$ = 0.054. A final difference map showed ripples round the metal atoms but no other regions of significant electron density. The final atomic coordinates and associated thermal parameters are presented in Tables 6 and 7, respectively.

Calculations were performed with the University of Cambridge IBM 370/165 using the "SHELX" program [16]. Figure 2 was drawn using the PLUTO plotting program. Structure factor tables may be obtained from the authors.

Acknowledgements

We thank Johnson Matthey Ltd for a loan of OsO_4 and the SRC for financial support.

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