The Stepwise Hydrogenation of a Nitrile on an Osmium Cluster: *X*-Ray Crystal Structures of $[Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}]$, $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9]$, and $[Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ †

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The hydrogenation of $[Os_3(\mu\text{-}H)(\mu\text{-}NCHCF_3)(CO)_{10}]$ (1) and $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NHCCF_3)(CO)_{10}]$ (2) which are, respectively, the major and minor products of the reaction of CF_3CN with $[Os_3H_2(CO)_{10}]$ has been studied. Molecular hydrogen (49 atm, 140 °C, 16 h) reacts with (1) to give complexes $[Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}]$ (3), $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9]$ (4), and $[Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ (5), in comparable yields (25—30%). The reaction of hydrogen (23 atm, 120 °C, 16 h) with (2) gives (3) in *ca.* 80% yield together with at least two other unidentified complexes in low (<5%) yields. *X*-Ray diffraction studies of (3), (4), and (5) are reported. Crystals of (3) are monoclinic, space group *C*2/*c*, with a = 19.983(3), b = 15.562(3), c = 14.089(3) Å, β = 118.80(3)°, and Z = 8. 2 248 Reflections with $I \geqslant 3\sigma(I)$ [$3 \leqslant \theta \leqslant 25°$] refined to R = 0.042 and R' = 0.043. Complex (4) crystallises in space group $P2_1/c$, with a = 9.383(2), b = 12.388(2), c = 16.171(3) Å, β = 97.79(2)°, and Z = 4. 3 091 Unique data [$I \geqslant 3\sigma(I)$, $3 \leqslant \theta < 25°$] refined to R = 0.051 and R' = 0.053. Complex (5) is monoclinic, space group *C*2/*c*, with a = 17.387(3), b = 8.137(2), c = 26.142(3) Å, β = 99.15(4)°, and Z = 8. 1 944 Reflections with $I \geqslant 3\sigma(I)$ [$3 \leqslant \theta \leqslant 25°$] refined to R = 0.046 and R' = 0.046. A partial model for the hydrogenation of a nitrile on a cluster, based on the isolation of the complexes (1)—(5), is presented and discussed.

The hydrogenation of small molecules containing heteroatomic triple bonds such as CO, CN^-, RNC, and RCN is not, in general, an easy process. Solid-state catalysts are usually employed and elevated temperatures and pressures are needed.[1] The possibility of using metal clusters to effect these reductions has been studied.[1] For nitriles, the co-ordinatively unsaturated nickel cluster, $[Ni_4(CNCMe_3)_7]$ has been found to catalyse the hydrogenation of MeCN to $EtNH_2$ at 90 °C, albeit at a very slow rate.[2] It has also been reported that both $[RhH(PPr^i{}_3)_3]$ and $[Rh_2H_2(\mu\text{-}N_2)\{P(cyclo\text{-}C_6H_{11})_3\}_4]$ at 20 °C and 1 atm catalyse the hydrogenation of nitriles to give primary amines. Clusters may be involved in this reduction, the mechanism of which has not been established.[3]

The pathways which might be involved in the hydrogenation of a nitrile by a cluster have been discussed by Andrews and Kaesz,[4] who have outlined a partial model for the reduction of MeCN on the face of a tri-iron cluster. An important step in this model is the reaction of $[Fe_3H(\mu_3\text{-}\eta^2\text{-}N{=}CHMe)(CO)_9]$ with H_2 at 25 °C and 13 atm to give $[Fe_3H_2(\mu_3\text{-}NEt)(CO)_9]$, this latter complex representing the furthest stage reached in the reduction.

We have recently reported the reaction of CF_3CN with $[Os_3H_2(CO)_{10}]$ to give $[Os_3(\mu\text{-}H)(\mu\text{-}NCHCF_3)(CO)_{10}]$ (1) and $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NHCCF_3)(CO)_{10}]$ (2) in 69% and 14% yields respectively,[5] and this reaction was also investigated by Adams *et al.*[6] We now describe the reactions of (1) and (2) with molecular hydrogen, which provide additional information to that obtained by Andrews and Kaesz [4] and suggest alternative pathways which might be involved in the reduction of nitriles by clusters. We also present *X*-ray studies on three of the reaction products. Part of this work has been published as a preliminary communication.[7]

Results and Discussion

Reaction of (1) *with* H_2.—When a hexane solution of (1) is treated with hydrogen gas (49 atm, 140 °C, 16 h) three complexes are formed in approximately equal yields (25—30%). These have been characterised by their spectroscopic properties (Table 1) and by *X*-ray diffraction studies (see below) as $[Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}]$ (3), $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9]$ (4), and $[Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ (5). The metal-bound hydride ligands were not located in the *X*-ray studies of (3) and (5) but gave rise to characteristic resonances in the ^1H n.m.r. spectra of the complexes (Table 1). Thus four Os–H resonances were observed in the ^1H n.m.r. spectra of (5) with intensity ratio 1 : 1 : 1 : 1, at δ −12.29 [d, J(HH) = 9.81], −16.11 [d, J(HH) = 10.99 Hz], −17.85 (s), and −19.01 (s).

Complexes of the type $[Os_3H(\mu\text{-}H)(CO)_{10}L]$ give rise to ^1H n.m.r. signals in the region δ −9 to −10 for the terminal H and δ −17 to −20 for the bridging H, and these signals are usually spin-coupled. For example, $[Os_3H(\mu\text{-}H)(CO)_{11}]$ gives signals at δ −10.25 (d) and −19.96 [d, J(HH) = 3.8 Hz] [8] and the ^1H n.m.r. spectrum of (5) is therefore in accord with the presence of one terminal (δ −12.29) and three bridging hydride ligands. Four Os–H ligands are, of course, required in order to satisfy the effective atomic number rule, since there is no evidence from the *X*-ray study of (5) for short Os–Os distances indicative of co-ordinative unsaturation and a formal M–M bond order of >1, as in $[Os_3H_2(CO)_{10}]$.[9]

The ^1H n.m.r. spectrum of complex (3) contains, in addition to the Os–H and CH_2CF_3 resonances, a broad peak at δ 7.65 which may be assigned to the N–H proton. The presence of this proton is also revealed by the i.r. spectrum of a Nujol mull of (3) which shows a weak absorption at 3 375 cm^{-1}.

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† 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ-(2′,2′,2′-trifluoroethylamido)-, 1,1,1,2,2,2,3,3,3-nonacarbonyl-1,2;1,3-di-μ-hydrido-μ$_3$-(2′,2′,2′-trifluoroethylimido)-, and 1,1,2,2,2,3,3,3-octacarbonyl-1,2;1,3;2,3-tri-μ-hydrido-1-hydrido-μ$_3$-(2′,2′,2′-trifluoroethylimido)-*triangulo*-triosmium.

Supplementary data available (No. SUP 23796, 60 pp.): least-squares planes, thermal parameters, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Non-S.I. unit employed: 1 atm = 101 325 N m^{-2}.

Table 1. Infrared, mass spectroscopic, and ^1H n.m.r. data for compounds (3)—(5)

Compound	ν(CO)/cm^{-1} (hexane)	m/z (^{192}Os)	^1H N.m.r.[a] δ (p.p.m.)	assignment	J/Hz
(3) $[Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}]$ [b]	2 106w, 2 069vs, 2 054s, 2 033m, 2 023s, 2 008 (sh), 2 005s, 1 997 (sh), 1 993s, 1 981m	955	7.65 (s) 4.18 (m) – 14.84 (s)	NH CH_2 Os–H	
(4) $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9]$ [c]	2 118m, 2 082s, 2 056vs, 2 039 (sh), 2 034s, 2 010 (sh), 2 005s, 1 992s, 1 976m	927	4.48 (q) – 18.57 (s)	CH_2 Os–H	J(HF) = 8.56
(5) $[Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ [d]	2 122w, 2 104s, 2 045m, 2 043m, 2 034vs, 2 026 (sh), 2 022m, 1 964w, 1 957m	899	4.77 (q) – 12.29 (d) – 16.11 (d) – 17.85 (s) – 19.01 (s)	CH_2 Os–H Os–H Os–H Os–H	J(HF) = 7.36 J(HH) = 9.81 J(HH) = 10.99

[a] Recorded at 298 K in CD_2Cl_2 solution; s = singlet, d = doublet, q = quartet, m = multiplet. [b] I.r. (Nujol): ν(C–F), 1 288m, 1 280s, 1 269m, 1 260s, 1 165vs, and 1 156vs cm^{-1}; ν(N–H) 3 375w cm^{-1}. [c] I.r. (Nujol): ν(C–F), 1 297w, 1 271m, 1 160s, and 1 145vs cm^{-1}. [d] I.r. (Nujol): ν(C–F), 1 250s br, 1 145 (sh), 1 120s, 1 070w, and 1 050w br cm^{-1}.

Table 2. Crystal data and selected details of structure determinations *

	(3)	(4)	(5)
Molecular formula	$C_{12}H_4F_3NO_{10}Os_3$	$C_{11}H_4F_3NO_9Os_3$	$C_{10}H_6F_3NO_8Os_3$
Molecular weight, M	947.75	921.76	895.76
Colour	Yellow	Pale yellow	Colourless
Crystal dimensions (mm)	0.24 × 0.27 × 0.14	0.31 × 0.12 × 0.14	0.16 × 0.12 × 0.09
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$
a/Å	19.983(3)	9.383(2)	17.387(3)
b/Å	15.562(3)	12.388(2)	8.137(2)
c/Å	14.089(3)	16.171(3)	26.142(3)
β/°	118.80(3)	97.79(2)	99.15(4)
U/Å^3	3 839.54	1 862.32	3 651.47
D_c/g cm^{-3}	3.278	3.279	3.258
F(000)	3 296	1 612	3 136
Z	8	4	8
μ(Mo-K_α)/cm^{-1}	191.02	196.87	200.75
θ range (min, max)	3, 25°	3, 25°	3, 25°
No. unique observed reflections, $I > 3\sigma(I)$	2 248	3 091	1 944
No. parameters in refinement	263	245	151
R	0.042	0.051	0.046
R' [$w = 1/\sigma^2(F)$]	0.043	0.053	0.046

* Intensity measurements were made on a Philips PW1100 diffractometer using Mo-K_α radiation.

Molecular ion peaks were observed in the mass spectra of (3) and (4) but, for (5), the highest peak observed was the fragment ion corresponding to $[P - H_2]^+$.

Reaction of (2) *with* H_2.—The treatment of a hexane solution of (2) with hydrogen (23 atm, 120 °C, 16 h) gives rise to the formation of one major and at least two minor products. Conversion is complete and no starting material was detected in the reaction mixture at the conclusion of the reaction. The major product (*ca.* 80% yield) was separated by t.l.c. as a bright yellow complex for which the highest peak in the mass spectrum was at m/z 955 (^{192}Os). This complex was identified by its mass, i.r., and ^1H n.m.r. spectra as being identical to (3), obtained in the reaction of (1) with H_2. The minor products of the reaction of (2) with H_2 could not be obtained free from impurities and they were not characterised.

X-*Ray Crystal Structures of Compounds* (3), (4), *and* (5).—Crystal data for these three compounds are given in Table 2. Selected interatomic distances and angles for compound (3) are presented in Tables 3 and 4. Interatomic distances (Table 5) and intramolecular angles (Table 6) for compounds (4) and (5) are tabulated together for comparison. The molecular structures are shown in Figures 1, 2, and 3 respectively.

The structure of (3) comprises a triangle of osmium atoms with ten terminal carbonyl groups. The organic ligand is attached to the cluster *via* the nitrogen atom, which bridges Os(1) and Os(3) and acts as a three-electron donor. The approximately tetrahedral geometry of both the nitrogen atom and C(1) indicates that the ligand is saturated, with a C(1)–N distance of 1.460 Å consistent with a single C–N bond. The NH, CH_2, and hydride hydrogen atoms were not located. The bridged Os(1)–Os(3) distance (2.792 Å) is less than the non-bridged ones (2.848 and 2.851 Å) by approximately the same amount as found for the large number of related clusters of the type $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ where X is a ligand which bridges by a single N or C atom (see Table 7). For this class of compound the bridged Os–Os distances vary from 2.785 to 2.814 Å (mean 2.802 Å) with the non-bridged distances varying from 2.828 to 2.873 Å (mean 2.859 Å) for the selected examples presented in Table 7. For triangular osmium clusters containing an $Os_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C{=}C)$ or Os_2-

Table 3. Selected interatomic distances (Å) for (3)

(*a*) Metal–metal bonds	
Os(1)–Os(2)	2.851(1)
Os(1)–Os(3)	2.792(1)
Os(2)–Os(3)	2.848(1)
(*b*) Metal–nitrogen bonds	
Os(1)–N	2.166(14)
Os(3)–N	2.150(15)
(*c*) Metal–C(carbonyl)	
Range	1.86—1.95(2)
Mean	1.903
(*d*) Ligand distances	
N–C(1)	1.460(25)
C(1)–C(2)	1.50(2)
C(2)–F(1)	1.35(2)
C(2)–F(2)	1.37(3)
C(2)–F(3)	1.28(2)
(*e*) C–O (carbonyl)	
Range	1.05—1.19(2)
Mean	1.155

Table 4. Selected intramolecular angles (°) for (3)

(*a*) Angles at osmium			
Os(2)–Os(1)–Os(3)	60.6(1)	N–Os(1)–Os(2)	83.7(4)
Os(3)–Os(2)–Os(1)	58.6(1)	N–Os(1)–Os(3)	49.4(4)
Os(2)–Os(3)–Os(1)	60.7(1)	N–Os(3)–Os(1)	50.0(4)
		N–Os(3)–Os(2)	84.1(4)
Os(2)–Os(1)–C(11)	87.7(6)	N–Os(1)–C(11)	99(1)
Os(3)–Os(1)–C(11)	134.5(6)	N–Os(1)–C(12)	94(1)
Os(2)–Os(1)–C(12)	177.4(6)	N–Os(1)–C(13)	167(1)
Os(3)–Os(1)–C(12)	116.8(5)	N–Os(3)–C(31)	170(1)
Os(2)–Os(1)–C(13)	90.4(6)	N–Os(3)–C(32)	95(1)
Os(3)–Os(1)–C(13)	117.7(6)	N–Os(3)–C(33)	95(1)
Os(1)–Os(2)–C(21)	100.6(7)	C(11)–Os(1)–C(12)	94(1)
Os(3)–Os(2)–C(21)	159.2(7)	C(11)–Os(1)–C(13)	92(1)
Os(1)–Os(2)–C(22)	157.9(8)	C(12)–Os(1)–C(13)	91(1)
Os(3)–Os(2)–C(22)	99.3(8)	C(21)–Os(2)–C(22)	101(1)
Os(1)–Os(2)–C(23)	87.9(6)	C(21)–Os(2)–C(23)	92(1)
Os(3)–Os(2)–C(23)	87.0(6)	C(21)–Os(2)–C(24)	92(1)
Os(1)–Os(3)–C(31)	120.3(6)	C(22)–Os(2)–C(23)	93(1)
Os(2)–Os(3)–C(31)	89.1(6)	C(22)–Os(2)–C(24)	90(1)
Os(1)–Os(3)–C(32)	112.8(7)	C(23)–Os(2)–C(24)	174(1)
Os(2)–Os(3)–C(32)	172.0(7)	C(31)–Os(3)–C(32)	90(1)
Os(1)–Os(3)–C(33)	134.9(6)	C(31)–Os(3)–C(33)	92(1)
Os(2)–Os(3)–C(33)	92.8(7)	C(32)–Os(3)–C(33)	95(1)
Os(1)–Os(2)–C(24)	87.1(7)		
Os(3)–Os(2)–C(24)	87.9(7)		
(*b*) Ligand geometry			
Os(1)–N–Os(3)	80.6(5)	C(1)–C(2)–F	
		Range	112—114(2)
C(1)–N–Os(1)	117(1)	Mean	113
C(1)–N–Os(3)	120(1)		
N–C(1)–C(2)	112(1)	F–C(2)–F	
		Range	103—107(2)
		Mean	104.7
(*c*) Os–C–O (carbonyl)			
Range	170—179(2)		
Mean	175.8		

Table 5. Selected interatomic distances (Å) for (4) and (5)

	(4)	(5)
(*a*) Metal–metal bonds		
Os(1)–Os(2)	2.863(1)	2.862(1)
Os(1)–Os(3)	2.717(1)	2.870(1)
Os(2)–Os(3)	2.856(1)	2.861(1)
(*b*) Metal–nitrogen bonds		
Os(1)–N	2.056(12)	2.067(16)
Os(2)–N	2.101(13)	2.050(16)
Os(3)–N	2.119(13)	2.072(15)
(*c*) Metal–C(carbonyl)		
Range	1.89—1.96(2)	1.82—1.96(2)
Mean	1.915	1.890
(*d*) Ligand distances		
N–C(1)	1.443(23)	1.48(2)
C(1)–C(2)	1.33(3)	1.36(4)
C(2)–F(1)	1.31(3)	1.31(4), 1.47(6) *
C(2)–F(2)	1.41(3)	1.44(4), 1.47(5) *
C(2)–F(3)	1.36(4)	1.44(4), 1.38(6) *
(*e*) C–O (carbonyl)		
Range	1.09—1.17(2)	1.11—1.28(3)
Mean	1.139	1.170

* Disorder in the CF_3 group for compound (5).

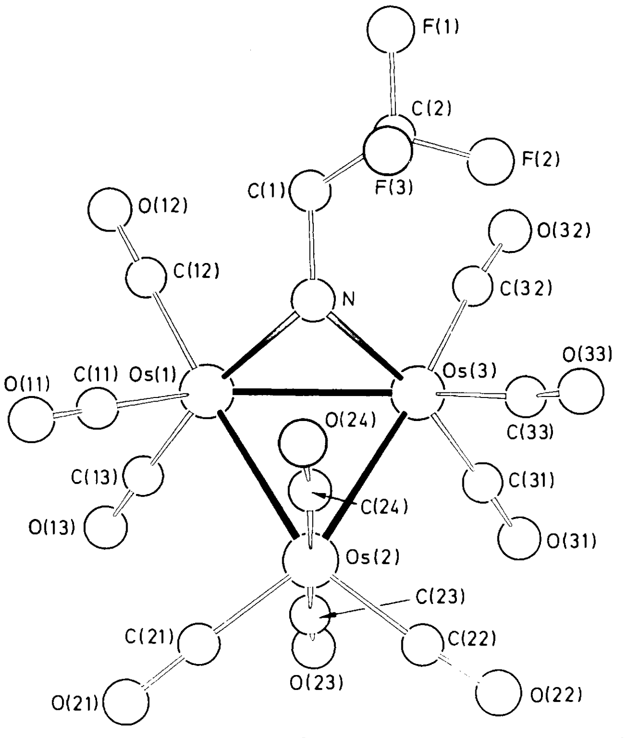


Figure 1. Molecular structure of $[Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}]$ (3) including the numbering scheme

$(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}N{=}C)$ moiety, the bridged Os–Os distance ranges from 2.918 to 2.987 Å (mean for eight compounds, 2.950 Å.[10–14]) and the non-bridged distances from 2.740 to 2.893 Å (mean 2.824 Å), indicating that for clusters of the type (3), *i.e.* $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ the shorter bridged Os–Os distance found for these clusters does not represent an increase in metal–metal bond order [compared to the $Os_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C{=}C)$ or $Os_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}N{=}C)$ four-membered-ring containing compounds] but is dictated by the presence of a three-

Table 6. Selected intramolecular angles (°) for (4) and (5)

	(4)	(5)
(*a*) Angles at osmium		
Os(2)-Os(1)-Os(3)	61.5(1)	59.9(1)
Os(3)-Os(2)-Os(1)	56.7(1)	60.2(1)
Os(2)-Os(3)-Os(1)	61.8(1)	59.9(1)
N-Os(1)-Os(2)	47.1(4)	45.7(4)
N-Os(1)-Os(3)	50.4(4)	46.2(4)
N-Os(2)-Os(1)	45.8(3)	46.2(5)
N-Os(2)-Os(3)	47.7(4)	46.4(4)
N-Os(3)-Os(1)	48.4(3)	46.0(4)
N-Os(3)-Os(2)	47.1(4)	45.7(4)
Os(2)-Os(1)-C(11)	119.9(7)	123.6(7)
Os(3)-Os(1)-C(11)	104.4(8)	121.0(6)
Os(2)-Os(1)-C(12)	99.6(5)	92.9(9)
Os(3)-Os(1)-C(12)	155.3(5)	143.3(9)
Os(2)-Os(1)-C(13)	145.1(5)	143.4(8)
Os(3)-Os(1)-C(13)	95.2(5)	96.9(8)
Os(1)-Os(2)-C(21)	120.6(5)	123.2(8)
Os(3)-Os(2)-C(21)	122.6(5)	125.9(8)
Os(1)-Os(2)-C(22)	143.3(6)	93(2) *
Os(3)-Os(2)-C(22)	94.9(6)	139(2) *
Os(1)-Os(2)-C(23)	101.0(5)	152(1) *
Os(3)-Os(2)-C(23)	147.2(5)	103(1) *
Os(1)-Os(3)-C(31)	107.9(5)	119.6(9)
Os(2)-Os(3)-C(31)	115.4(6)	121.7(9)
Os(1)-Os(3)-C(32)	94.0(5)	95.8(7)
Os(2)-Os(3)-C(32)	147.5(6)	143.9(7)
Os(1)-Os(3)-C(33)	154.8(6)	148.0(7)
Os(2)-Os(3)-C(33)	101.0(6)	96.5(8)
N-Os(1)-C(11)	154(1)	165(1)
N-Os(1)-C(12)	105(1)	97(1)
N-Os(1)-C(13)	98(1)	98(1)
N-Os(2)-C(21)	165(1)	168(1)
N-Os(2)-C(22)	98(1)	93(2) *
N-Os(2)-C(23)	100(1)	105(1) *
N-Os(3)-C(31)	153(1)	162(1)
N-Os(3)-C(32)	101(1)	98(1)
N-Os(3)-C(33)	107(1)	102(1)
C(11)-Os(1)-C(12)	99(1)	93(1)
C(11)-Os(1)-C(13)	90(1)	92(1)
C(12)-Os(1)-C(13)	93(1)	92(1)
C(21)-Os(2)-C(22)	93(1)	93(2) *
C(21)-Os(2)-C(23)	89(1)	84(1) *
C(22)-Os(2)-C(23)	92(1)	87(1) *
C(31)-Os(3)-C(32)	92(1)	92(1)
C(31)-Os(3)-C(33)	96(1)	90(1)
C(32)-Os(3)-C(33)	93(1)	92(1)
(*b*) Os-C-O (carbonyl)		
Range	173—179(1)	170—178(2)
Mean	176.9	174.8
(*c*) Ligand geometry		
Os(1)-N-Os(2)	87.0(5)	88.1(6)
Os(1)-N-Os(3)	81.2(4)	87.8(6)
Os(2)-N-Os(3)	85.2(5)	87.9(5)
C(1)-N-Os(1)	126(1)	115(1)
C(1)-N-Os(2)	130(1)	135(1)
C(1)-N-Os(3)	130(1)	127(1)
N-C(1)-C(2)	125(2)	115(2)
C(1)-C(2)-F		
Range	110—116(2)	109—127(3)
Mean	113.7	119.5
F-C(2)-F		
Range	102—107(2)	92—103(3)
Mean	103.7	96.2

* Disorder in compound (5).

Table 7. Selected bond lengths (Å) for some $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ compounds containing an Os_2X three-membered ring

X	X-bridged Os-Os	Other Os-Os	Os-X	Other	Ref.
$CHCH{=}NEt_2$	2.785	2.866	2.15		*a*
		2.870	2.16		
$NHCH_2CF_3$ [b]	2.792	2.848	2.150	1.460 ($N-CH_2$)	This work
		2.851	2.166		
$CHCH_2PMe_2Ph$	2.800	2.869			*c*
		2.873			
$C{=}CPh(PMe_2Ph)$	2.802	2.870	2.096	1.356	13
		2.873	2.103	(C=C)	
$C{=}NHBu^t$	2.812	2.859	2.043	1.298	*d*
		2.867	2.066	(C=N)	
$N{=}CHCF_3$	2.813	2.828	2.065	1.271	*e*
		2.845	2.078	(N=C)	
$NHSO_2(C_6H_4Me\text{-}p)$	2.814	2.847	2.145		*f*
		2.858	2.162		

[a] M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1979, **18**, 848. [b] Compound (3). [c] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 1141. [d] R. D. Adams and N. M. Golembeski, *Inorg. Chem.*, 1979, **18**, 2255. [e] Z. Dawoodi, M. J. Mays, and A. G. Orpen, *J. Organomet. Chem.*, 1981, **219**, 251. [f] M. R. Churchill, F. J. Hollander, J. R. Shapely, and J. B. Keister, *Inorg. Chem.*, 1980, **19**, 1272.

membered $Os_2(\mu\text{-}X)$ unit. The Os-X distances for both C and N are similar, but differ according to whether the bridging atom is sp^3 or sp^2 hybridised, with mean Os-X distances of 2.155 and 2.075 Å respectively (Table 7).

The structures of (4) and (5) are similar, with each molecule having an approximate isosceles triangle of metal atoms and with all the carbonyl ligands terminal in each case. The structure of (4) is closely related to that of the methylnitrene complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NMe)(CO)_9]$ [15] with the NCH_2CF_3 ligand triply bridging. In (4) the H-bridged Os(1)-Os(2) and Os(1)-Os(3) edges are longer by around 0.14 Å than the remaining Os-Os bond, and reasonable positions were located for the hydride and the methylene hydrogen atoms. The bridging hydrogen atoms were not located in the analysis of (5) but are presumably positioned along each of the Os-Os edges of the triangle as evidenced by the equivalence of the three Os-Os bond lengths of 2.861, 2.862, and 2.870 Å. Selected bond parameters of some μ_3-X trinuclear clusters are presented in Table 8 and show a mean H-bridged M-M distance of 2.873 Å and a mean unbridged M-M distance of 2.753 Å. The terminal H atom in (5) is disordered between the sites occupied by C(22) and C(23) in (4), leading to a half occupancy of these sites by carbonyl groups on (5) [Figure 3(*a*) and (*b*)], the disorder being accompanied by a slight disorder in the CF_3 group. The Os-N distances for (4) and (5) are in the range 2.050—2.119 Å similar to both the mean Os-μ_3-N and Ru-μ_3-C distances in $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NMe)(CO)_9]$ [15] and $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CCl)(CO)_9]$ [16] of 2.075 and 2.061 Å respectively. The C-N distances in both (4) and (5) are as expected for a single C-N bond.[17]

Although other trinuclear clusters containing four metal-bound H atoms have been synthesised,[18-20] (5) is the first for which an *X*-ray analysis reveals the presence of a terminal hydride ligand. The structure of (5) is, however, related to that of $[Ir_3H_7\{Ph_2P(CH_2)_3PPh_2\}_3]^{2+}$ which contains one terminal hydride ligand on each metal atom.[21]

A Partial Model for the Hydrogenation of a Nitrile on a Cluster.—The isolation of complexes (1)—(5) suggests a partial model for the hydrogenation of a nitrile on a triosmium complex (Scheme) which differs in several respects from that proposed by Andrews and Kaesz[4] for hydrogenation of a nitrile on a tri-iron complex. Thus in the Kaesz scheme, insertion of MeCN into $[Fe_3H(CO)_{11}]^-$ to give $[Fe_3(\mu_3\text{-}\eta^2\text{-}MeC{=}NH)(CO)_9]^-$ is followed by a separate protonation step and subsequent isomerisation of the protonated complex, prior to hydrogenation with molecular hydrogen to give $[Fe_3(\mu\text{-}H)(\mu_3\text{-}NEt)(CO)_9]$. Hydrogenation of CF_3CN by $[Os_3H_2(CO)_{10}]$ is more straightforward in that the separate protonation step is not required, and the most fully hydrogenated product (5) is obtained from (1) in the presence of molecular hydrogen in a one-step reaction. A further difference between our model and that of Kaesz is that hydrogenation of CF_3CN by H_2 and $[Os_3H_2(CO)_{10}]$ is proposed to proceed *via* the μ-alkylideneimino-complex (1), whereas hydrogenation of CH_3CN by H_2 and $[Fe_3H(CO)_{11}]^-$ proceeds *via* a μ_3-alkylideneimino-complex. We cannot entirely exclude the possibility that (4) is also formed from (1), in part, *via* the hydrogenation of an analogous intermediate μ_3-alkylideneimino-complex which is not present in significant concentrations at the conclusion of the hydrogenation reaction. This seems unlikely however, since, although (1) does lose CO on thermolysis at >150 °C to give $[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}NCHCF_3)(CO)_9]$ in low yield (together with extensive decomposition to Os metal),[5] it can be recovered unchanged from refluxing octane solution (125 °C) after several hours.

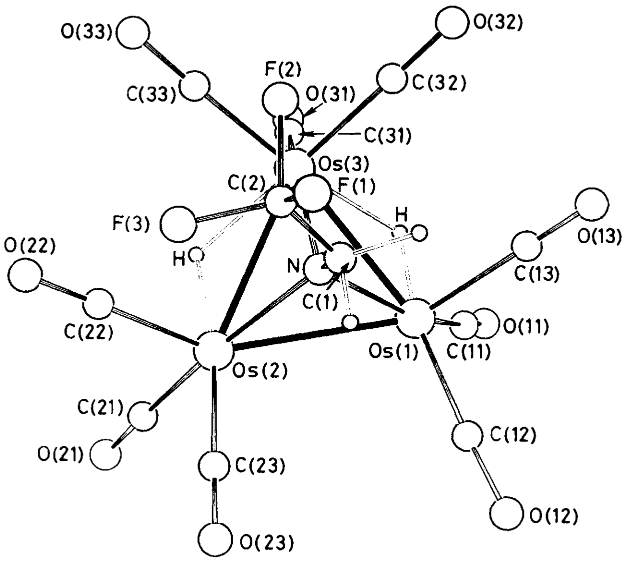


Figure 2. Molecular structure of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9]$ (4) including the numbering scheme

Table 8. Selected bond lengths (Å) for some M_3 clusters containing an μ_3-X ligand

Compound	H-bridged M−M	Other M−M	M−X	Ref.
$[Ru_3H_3(\mu_3\text{-}CCl)(CO)_9]$	2.8523		2.067	16
	2.8527		2.056	
$[Os_3H_2(\mu_3\text{-}NMe)(CO)_9]$	2.8612	2.7498	2.070	15
			2.081	
$[Os_3H_2(\mu_3\text{-}S)(CO)_9]$	2.908	2.764	2.393	*a*
	2.922		2.395	
			2.382	
$[Os_3H(\mu_3\text{-}S)(CO)_9]^-$	2.899	2.766	2.396	*b*
		2.769	2.401	
			2.369	
(4)	2.863	2.717	2.056	This work
	2.856		2.119	
			2.101	
(5)	2.862		2.067	This work
	2.870		2.050	
	2.861		2.072	

[a] B. F. G. Johnson, J. Lewis, D. Pippard, P. R. Raithby, G. M. Sheldrick, and K. D. Rouse, *J. Chem. Soc., Dalton Trans.*, 1979, 616. [b] B. F. G. Johnson, J. Lewis, D. Pippard, and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1978, **34**, 3767.

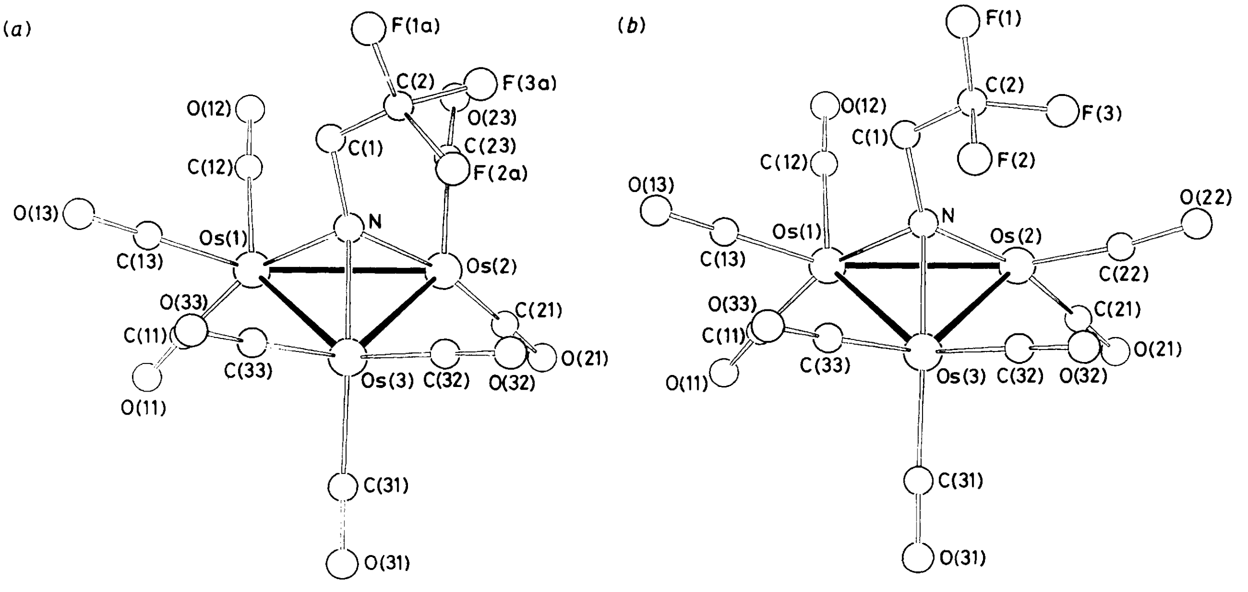
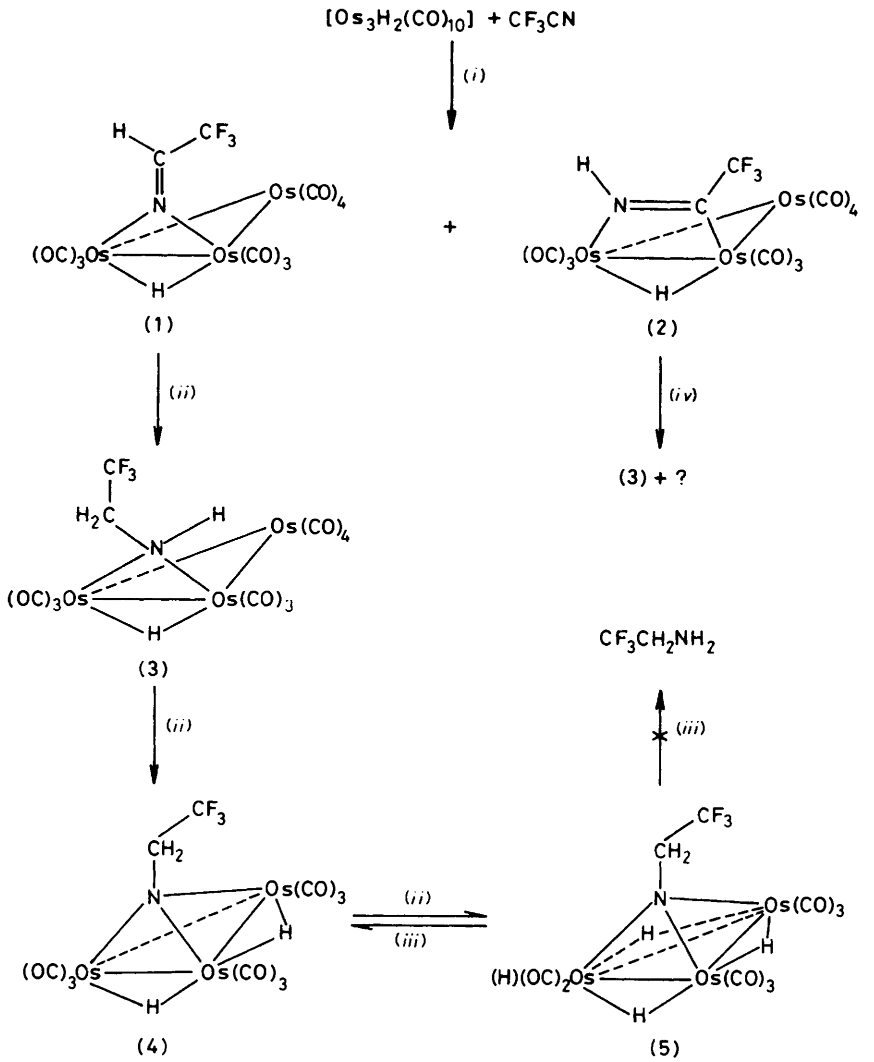


Figure 3. Molecular structure of $[Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ (5) including the numbering scheme. (*a*) The molecule with the terminal hydride atom in the position of carbonyl C(22) and (*b*) the hydride in the position part occupied by carbonyl C(23)



Scheme. (*i*) 80 °C, 15 h; (*ii*) hexane, H_2 (49 atm, 140 °C, 16 h); (*iii*) CD_2Cl_2, CO (50 atm, 140 °C, 18 h); (*iv*) hexane, H_2 (23 atm, 120 °C, 16 h)

A final point of difference in the reaction of MeCN with $[Fe_3H(CO)_{11}]^-$ as compared to the reaction of CF_3CN with $[Os_3H_2(CO)_{10}]$ is that, in the latter reaction, the final product of hydrogenation (5) contains an extra molecule of H_2, in the form of two additional metal-bound hydride ligands. This difference is presumably associated with the well known greater facility with which, in a given oxidation state, third row as compared to first row transition metals undergo oxidative addition reactions.

Attempts to complete a model catalytic cycle by treating (5) with CO (50 atm, 140 °C, 18 h) led to the regeneration of (4) in quantitative yields, illustrating the stability of this nitrene-capped complex. The reductive elimination of μ_3-capping ligands in trinuclear clusters is, in fact, rarely observed, but it is not without precedent (*e.g.* the reaction of $[Ru_3H_3\{\mu_3\text{-}\eta^2\text{-}C(O)Me\}(CO)_9]$ with H_2 and CO under forcing conditions to give $[Ru_3(CO)_{12}]$ and Me_2O).[22] This present study demonstrates that the oxidative addition of hydrogen to μ_3-ligand capped clusters to give highly hydrogenated species such as (5) containing terminally bound H atoms is a feasible pathway in such reductive elimination reactions.

Complex (2) is the minor product of the reaction of CF_3CN with $[Os_3H_2(CO)_{10}]$ and the limited amount of material available restricted the scope of our hydrogenation studies on it. The fact that (3) is formed as the major product of hydrogenation * is probably due to the slightly less severe operating conditions which were employed.† Alternatively it is possible that (2) is not hydrogenated directly and that isomerisation to give (1) or thermolysis to give a μ_3-HN=CCF$_3$ ligand-capped cluster [5] is necessary before hydrogenation can take place leading to a slower reaction. Complex (2) showed no tendency to isomerise to (1), however, during thermolysis experiments.[5]

Experimental

Unless otherwise stated, all experiments were carried out in an atmosphere of dry nitrogen. Dry, oxygen-free solvents were used when appropriate. Dichloromethane and hexane were distilled from calcium hydride and stored over 4 Å molecular sieves. Octane was washed with concentrated H_2SO_4, shaken

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* In the preliminary communication [7] an error in the preparation of the manuscript led to (4) being stated as the major product.

† Complex (2) decomposes to Os metal under the conditions employed in the hydrogenation of (1).

Table 9. Fractional atomic co-ordinates for $[Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}]$ (3)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.223 75(4)	0.124 56(5)	0.369 91(6)	C(24)	0.177 3(12)	0.036 5(15)	0.128 5(18)
Os(2)	0.123 64(4)	0.134 03(5)	0.142 23(6)	O(24)	0.209 3(9)	−0.024 7(11)	0.122 1(13)
Os(3)	0.265 57(4)	0.223 41(5)	0.241 52(6)	C(31)	0.213 6(12)	0.324 7(15)	0.178 3(14)
C(11)	0.189 7(11)	0.006 7(14)	0.364 2(16)	O(31)	0.177 6(8)	0.388 1(9)	0.139 2(12)
O(11)	0.170 7(10)	−0.056 2(10)	0.364 3(14)	C(32)	0.357 5(11)	0.285 8(14)	0.324 2(16)
C(12)	0.293 7(13)	0.121 0(11)	0.520 4(19)	O(32)	0.408 4(10)	0.332 6(12)	0.365 9(14)
O(12)	0.338 0(9)	0.117 9(11)	0.612 0(11)	C(33)	0.284 4(12)	0.200 3(13)	0.125 2(15)
C(13)	0.146 0(12)	0.167 7(13)	0.396 5(17)	O(33)	0.298 1(11)	0.174 7(13)	0.058 7(13)
O(13)	0.098 0(10)	0.192 4(11)	0.413 8(15)	N	0.310 4(8)	0.103 0(10)	0.322 0(11)
C(21)	0.041 6(14)	0.064 4(14)	0.129 4(18)	C(1)	0.389 6(11)	0.096 0(13)	0.407 5(16)
O(21)	−0.011 5(10)	0.021 5(12)	0.116 1(15)	C(2)	0.443 7(13)	0.082 9(18)	0.362 8(21)
C(22)	0.089 8(13)	0.164 2(18)	−0.004 7(18)	F(1)	0.517 2(7)	0.074 0(11)	0.441 1(14)
O(22)	0.071 4(9)	0.186 9(13)	−0.091 8(13)	F(2)	0.446 0(8)	0.150 0(11)	0.301 8(13)
C(23)	0.079 3(11)	0.235 1(13)	0.168 6(16)	F(3)	0.426 8(10)	0.017 2(12)	0.300 3(18)
O(23)	0.051 4(9)	0.296 2(10)	0.183 3(13)				

Table 10. Fractional atomic co-ordinates for $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2CF_3)(CO)_9]$ (4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.344 77(6)	0.256 50(6)	0.221 11(4)	O(31)	0.296 2(15)	−0.101 4(11)	0.144 9(10)
Os(2)	0.041 40(6)	0.244 70(5)	0.168 23(4)	C(32)	0.424 8(17)	0.134 8(16)	0.043 6(11)
Os(3)	0.248 41(6)	0.130 53(5)	0.087 63(4)	O(32)	0.532 7(15)	0.137 3(13)	0.015 7(11)
C(11)	0.436 0(22)	0.155 2(23)	0.304 8(13)	C(33)	0.139 8(18)	0.100 6(17)	−0.017 8(12)
O(11)	0.482 9(23)	0.091 3(20)	0.346 5(13)	O(33)	0.077 5(14)	0.080 1(14)	−0.083 3(8)
C(12)	0.351 4(18)	0.383 0(16)	0.288 4(11)	N(1)	0.218 1(12)	0.296 6(10)	0.111 5(7)
O(12)	0.362 5(17)	0.457 9(15)	0.332 9(9)	C(1)	0.234 6(24)	0.390 7(15)	0.061 1(10)
C(13)	0.528 1(17)	0.285 2(16)	0.186 6(10)	C(2)	0.174 2(34)	0.403 8(28)	−0.017 8(17)
O(13)	0.633 2(14)	0.304 0(14)	0.165 4(9)	F(1)	0.205 3(20)	0.493 2(12)	−0.055 3(8)
C(21)	−0.085 2(18)	0.172 6(14)	0.237 3(12)	F(2)	0.223 6(28)	0.323 1(15)	−0.068 9(8)
O(21)	−0.156 5(15)	0.133 3(12)	0.278 7(11)	F(3)	0.028 6(27)	0.390 8(23)	−0.032 3(12)
C(22)	−0.101 6(17)	0.248 3(15)	0.072 1(13)	H(13)	0.3730	0.1606	0.1809
O(22)	−0.190 4(15)	0.248 4(14)	0.015 0(10)	H(23)	0.0672	0.1442	0.1197
C(23)	−0.019 7(17)	0.378 8(16)	0.206 7(10)	H(1a)	0.2187	0.4347	0.1022
O(23)	−0.056 5(15)	0.460 0(10)	0.231 1(9)	H(1b)	0.3483	0.4208	0.0577
C(31)	0.278 3(17)	−0.017 3(13)	0.120 5(12)				

Table 11. Fractional atomic co-ordinates for $[Os_3H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ (5)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.194 44(5)	0.142 90(10)	−0.142 79(3)	O(12)	0.355 5(11)	−0.017 0(25)	−0.118 7(7)
Os(2)	0.123 26(5)	−0.167 91(11)	−0.171 29(4)	C(13)	0.214 3(14)	0.294 1(31)	−0.089 1(10)
Os(3)	0.032 89(5)	0.091 01(11)	−0.136 58(3)	O(13)	0.228 5(12)	0.390 1(28)	−0.054 3(9)
N	0.135 0(8)	−0.027 8(20)	−0.105 3(5)	C(21)	0.111 8(14)	−0.250 7(31)	−0.237 2(9)
C(1)	0.166 1(13)	−0.056 3(34)	−0.049 9(9)	O(21)	0.105 0(11)	−0.301 0(23)	−0.279 4(7)
C(2)	0.125 9(22)	−0.166 7(49)	−0.025 7(11)	C(22) *	0.219 9(39)	−0.289 1(85)	−0.148 7(26)
F(1) *	0.149 3(20)	−0.230 0(43)	0.020 3(15)	O(22) *	0.283 6(32)	−0.370 9(67)	−0.142 1(21)
F(1a) *	0.146 7(29)	−0.176 7(65)	0.030 8(20)	C(23) *	0.070 4(15)	−0.351 4(34)	−0.157 0(10)
F(2) *	0.058 0(14)	−0.087 8(32)	−0.011 4(9)	O(23) *	0.036 6(14)	−0.464 0(32)	−0.147 2(10)
F(2a) *	0.040 8(24)	−0.186 3(57)	−0.034 4(17)	C(31)	−0.045 5(15)	0.205 7(34)	−0.183 3(10)
F(3) *	0.082 2(19)	−0.305 8(39)	−0.048 5(11)	O(31)	−0.087 7(12)	0.269 6(27)	−0.216 4(8)
F(3a) *	0.138 1(28)	−0.329 3(55)	−0.036 9(17)	C(32)	0.028 7(13)	0.242 6(32)	−0.082 5(10)
C(11)	0.226 2(13)	0.297 8(29)	−0.192 5(9)	O(32)	0.027 4(11)	0.338 0(24)	−0.049 2(8)
O(11)	0.237 6(9)	0.390 6(21)	−0.221 5(6)	C(33)	−0.044 5(13)	−0.046 2(30)	−0.114 9(9)
C(12)	0.295 4(16)	0.048 9(35)	−0.125 6(10)	O(33)	−0.093 7(12)	−0.127 4(24)	−0.102 9(7)

* Partial occupancy.

with Na_2CO_3, and stored over sodium wire. Infrared spectra were recorded on Perkin-Elmer 257 or 577 spectrometers 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 tris(perfluoroheptyl)-s-triazine introduced indirectly as calibrant. ^1H N.m.r. spectra were recorded 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. High pressure work was carried out in a Roth 100-cm^3 stainless steel laboratory autoclave using a glass liner. This was vented at least three times with the reactant gas prior to filling.

All chromatography was carried out on commercial Merck t.l.c. plates coated with a 0.25-mm layer of silica. The plates were loaded by careful application of the mixture in dichloromethane and products were also extracted with this solvent.

Hydrogenation of (1).—A solution of (1) (0.150 g, 0.16 mmol) was treated with hydrogen gas (49 atm, 140 °C) in an autoclave for 16 h. It was then taken to dryness, redissolved in the minimum quantity of CH_2Cl_2 and placed on t.l.c. plates. Several elutions with CH_2Cl_2–hexane (1 : 9) gave (decreasing R_f values, approximate percentage yields in parentheses) (3) (30%), (4) (25%), and (5) (20%). Crystals of (3) and (4) suitable for *X*-ray studies were prepared by cooling warm, saturated hexane solutions at room temperature. Crystals of (5) were obtained by slow evaporation of a dilute pentane solution at −5 °C.

Hydrogenation of (2).—A solution of (2) (0.05 g, 0.05 mmol) in hexane (20 cm^3) was treated with hydrogen gas (23 atm, 120 °C) in an autoclave for 16 h. The reaction mixture was then taken to dryness, redissolved in the minimum quantity of CH_2Cl_2, and placed on t.l.c. plates. One elution with CH_2Cl_2–hexane (1 : 9) gave a bright yellow band (together with several faint yellow bands at lower R_f values) which was crystallised by cooling a warm saturated hexane solution to room temperature to give (3) (*ca.* 80%).

Carbonylation of (5).—A solution of (5) (0.02 g, 0.02 mmol) in CD_2Cl_2 (5 cm^3) was treated with CO (50 atm, 140 °C) in an autoclave for 18 h. At the end of this period a ^1H n.m.r. spectrum of the reaction solution showed that complete conversion of (5) to (4) had occurred. Following the n.m.r. measurement a t.l.c. experiment, eluting with CH_2Cl_2–hexane showed the presence of only one band, with an identical R_f value to (4).

Molecular Structure Determinations.—Details of crystal parameters, data collection parameters, and refinement data for compounds (3), (4), and (5) are summarised in Table 2. The method of data collection used the technique previously described.[13]

All the data sets were corrected for Lorentz-polarisation factors and for each structure a semi-empirical absorption correction based on a pseudo-ellipsoid model was applied. Neutral atom scattering factors were employed throughout.[23] The structures were solved using programs written by Professor G. M. Sheldrick.[24]

The three structures were solved by Patterson synthesis and refined by full-matrix least squares. In the structures of (3) and (4) all the non-hydrogen atoms were assigned anisotropic thermal parameters during refinement. In (5) the Os, N, C(1), and C(2) atoms were assigned anisotropic thermal parameters. The structure of (5) showed the terminal hydride ligand attached to Os(2) to be disordered over two sites [see Figure 3(*a*) and (*b*)] together with a slight disorder in the position of the CF_3 group.

The final atomic co-ordinates for (3), (4), and (5) are presented in Tables 9, 10, and 11, respectively.

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