REACTIONS INVOLVING HYDROGEN TRANSFER FROM TRIOSMIUM CLUSTERS TO AN ACTIVATED NITRILE

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Summary

The reactions of $H_2Os_3(CO)_{10}$, Ia and $H_2Os_3(CO)_9PMe_2Ph$, Ib with CF_3CN have been investigated. Both Ia and Ib react with CF_3CN to give the products $HOs_3[\mu\text{-}\eta^2\text{-}(CF_3)C=NH](CO)_9L$ and $HOs_3[\mu\text{-}\eta^1\text{-}N=C(H)CF_3](CO)_9L$, IIa, IIIa, L = CO; IIb and IIIb, L = PMe_2Ph. IIb and IIIb have been characterized crystallographically. In each, one nitrile molecule was added to the cluster and one hydride ligand was transferred to the nitrile ligand, but in IIb the hydride was transferred to the nitrogen atom to form a $CF_3C=NH$ ligand which bridges an edge of the cluster while in IIIb the hydride was transferred to the carbon atom to form a $CF_3(H)C=N$ ligand which also bridges an edge of the cluster. On the basis of spectroscopic measurements IIa and IIIa are believed to have analogous structures. An isotope scrambling experiment established that the formation of IIIa occurs by an intramolecular process. IIa was decarbonylated to yield the compound $HOs_3[\mu_3\text{-}\eta^2\text{-}(CF_3)C=NH](CO)_9$, which is believed to contain a triply-bridging iminyl ligand. IIIa reacts with PMe_2Ph to give two mono-substitution products, one of which is IIIb.

Introduction

The remarkable cluster compound $H_2Os_3(CO)_{10}$, which is formally electronically unsaturated, has been shown to form stable adducts, $H_2Os_3(CO)_{10}L$, with a variety of two-electron donors such as carbon monoxide [1], phosphines [1,2], phosphites [1], isocyanides [1,3] and even a nitrile [2]. In cases where L is an unsaturated molecule the addition may be accompanied by a rapid transfer of hydrogen from the cluster to the ligand, which could be viewed as the initial stages of hydrogenation of the ligand at a polynuclear center. Such processes have been observed for alkenes [4], alkynes [5—7], isocyanates [8], carbodiimides [9], and carbon disulfide [10]. In addition, induced hydrogen transfers have been demonstrated for isocyanide ligands [3].

Kaesz has recently shown that organonitriles are readily hydrogenated on the face of a triiron cluster [11—14], but the addition of benzonitrile to $H_2Os_3(CO)_{10}$ is reversible and no hydrogen transfer processes have yet been reported [3]. In hopes that the reduction tendency of the nitrile function would be enhanced by an electron-withdrawing substituent we have investigated the reactions of CF_3CN with $H_2Os_3(CO)_{10}$, Ia, and $H_2Os_3(CO)_9[PMe_2Ph]$, Ib.

Experimental

General

Although these compounds are not air sensitive, reactions and purifications were routinely performed under a prepurified nitrogen atmosphere. Hexane was purified by distillation from sodium-benzophenone. Other solvents were stored over 4 Å molecular sieves and saturated with nitrogen gas prior to use. Trifluoroacetonitrile was obtained from PCR (Gainesville, FL) and used without further purification. Osmium carbonyl was obtained from Strem Chemicals Inc. or prepared from OsO_4 [15]. Alumina used in chromatographic workups was Baker acid-washed aluminum oxide deactivated with 6% w/w water, unless otherwise specified. The compounds $H_2Os_3(CO)_{10}$ [16], and $H_2Os_3(CO)_9(PMe_2Ph)$ [2] were prepared by published methods.

Melting points were determined in evacuated capillary tubes using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX270 spectrometer (Table 1). Mass spectra were obtained at 20 eV on a Hewlett-Packard 5985 GC/MS using direct inlet, electron impact mode. Elemental analyses were performed by Midwest Microlab, LTD, (Indianapolis, IN).

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

$H_2Os_3(CO)_{10}$, (30.0 mg, 0.035 mmol), was dissolved in hexane solvent (30.0 ml), and the solution was stirred (23°C) under an atmosphere of CF_3CN for 12 hours. During this time the solution became pale yellow. All volatiles were removed in vacuo and the residue was chromatographed on alumina. The first yellow band was eluted with hexane and crystallized from hexane at —20°C to yield $HOs_3(\mu-\eta^1-N=C(H)CF_3)(CO)_{10}$, IIIa (11.7 mg, 35%) as yellow crystals, m.p. 172—174°C.

The second yellow band was eluted with toluene, reduced to dryness in vacuo and crystallized from hexane to give $HOs_3(\mu-\eta^2-(F_3C)C=NH)(CO)_{10}$, IIa, (10.6 mg, 32%) as yellow crystals, m.p. 184.2—186.5°C. Analysis: Found: C, 15.08; H, 0.29; N, 1.34. Calcd. for $Os_3F_3O_{10}NC_{12}H_2$, IIIa: C, 15.20; H, 0.21; N, 1.48%. Found: C, 15.92; H, 0.56; N, 1.55. Calcd. for $Os_3F_3O_{10}NC_{12}H$: IIa, C, 15.20; H, 0.21; N, 1.48%.

Reaction of $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ with CF_3CN

$H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (146 mg, 0.152 mmol) was dissolved in hexane solvent under an atmosphere of CF_3CN. The purple solution was stirred for 5 hours at r.t., during which time it changed from purple to yellow. All volatiles were removed in vacuo, and chromatography yielded two yellow bands. The

TABLE 1

SPECTRAL PROPERTIES [a]

Compound	^{1}H NMR (ppm, J in Hz)	IR (cm^{-1})
HOs$_3$[μ-η^2-(CF$_3$)C=NH](CO)$_{10}$, IIa	9.57 broad (NH), −15.15d (^3J = 1.0, OsH)	3294w ^{b}, 2115w, 2073vs, 2064s, 2036vs, 2015s, 2003m, 1981vw
HOs$_3$[μ-η^1-N=C(H)CF$_3$](CO)$_{10}$, IIIa	7.74dq (^4J = 1.0, ^3J = 4.5, CH) −14.84m (OsH)	2118w, 2080vs, 2074s, 2039vs, 2024s, 2018m, 1990w
HOs$_3$[μ-η^2-(CF$_3$)C=NH](CO)$_9$P(CH$_3$)$_2$C$_6$H$_5$, IIb	8.73 broad (NH), 7.38 m (C$_6$H$_5$), 2.26d (^2J = 9.0, CH$_3$), 2.23d (^2J = 9.0, CH$_3$'), −15.25d (^2J_p = 8.5, OsH)	3288w ^{b}, 2029m, 2053s, 2022s, 2015m(sh), 2002m(sh), 1992m(sh), 1981m(sh), 1974m(sh), 1948m
HOs$_3$[μ-η^1-N=C(H)CF$_3$](CO)$_9$P(CH$_3$)$_2$C$_6$H$_5$, IIIb	7.49m (C$_6$H$_5$), 6.23d, d, q (^4J = 1.1, ^4J = 2.4, ^3J_F = 4.9, CH 2.23d (^2J = 11.0, CH$_3$), 2.11d (^2J = 9.8, CH$_3$), −14.80d, (^2J_p = 8.6, OsH)	2012m, 2065s, 2023vs, 1988m, 1980m, 1956vw
HOs$_3$[μ_3-η^2-(CF$_3$)C=NH](CO)$_9$, IV	8.31 broad (NH), −18.08d (J = 0.7, OsH)	3287w ^{b}, 2104w, 2080s, 2054s, 2026s, 2009s, 1983w

^{a} ^{1}H NMR spectra of compounds in CDCl$_3$ at 298°K, IR spectra of ν(CO) in hexane, ±5 cm^{-1}. ^{b} ν(NH) in CDCl$_3$.

first band was eluted with hexane solvent. The second band was eluted with benzene. The first band was recrystallized from hexane to give yellow crystals of *anti*-HOs$_3$[μ-η^1-N=C(H)CF$_3$](CO)$_9$PMe$_2$Ph, IIIb, (79.3 mg 49.4% yield). M.p.

TABLE 2

CRYSTALLOGRAPHIC DATA FOR X-RAY DIFFRACTION STUDIES

A) Compound	IIb	IIIb
Formula	Os$_3$PF$_3$O$_9$NC$_{19}$H$_{13}$	Os$_3$PF$_3$O$_9$NC$_{19}$H$_{13}$
Temperature ($\pm 5^\circ$C)	22	22
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.944(4)	9.105(2)
b (Å)	16.612(2)	16.069(4)
c (Å)	15.610(2)	18.263(5)
β (deg)	109.68(2)	89.89(3)
V (Å^3)	2672(2)	2672(2)
M. wt.	1057.9	1057.9
$\rho_{calcd.}$ (g/cc)	2.63	2.63
B) Measurement of intensity data		
Radiation	Mo-$K\alpha$ (0.71073 Å)	
Monochromator	Graphite	
Detector aperture (mm)		
Horizontal ($A + B \tan\theta$):		
A	3.0	3.0
B	1.0	1.0
Vertical:	4.0	4.0
Crystal faces:	010, 0$\overline{1}$0, 011, 0$\overline{1}\overline{1}$	100, $\overline{1}$00, 011, 0$\overline{1}\overline{1}$
	01$\overline{1}$, 0$\overline{1}\overline{1}$, $\overline{2}$12, 2$\overline{1}$2	$\overline{1}$2$\overline{2}$, 12$\overline{2}$, 1$\overline{1}$0
Crystal size: (mm)	0.10 × 0.19 × 0.27	0.33 × 0.31 × 0.38
Crystal orientation:	normal to 20$\overline{1}$; 7.0°	normal to 01$\overline{1}$; 14.4
Direction; deg from ϕ-axis		
Reflection measured	+h, +k, +l	+h, +k, ±l
Max. 2θ ($^\circ$)	48	50
Scan type	moving crystal-stationary counter	
ω-Scan width:		
$A + 0.347 \tan\theta$ $A =$ ($^\circ$)	0.80	0.80
Background:	1/4 additional scan at each end of scan	
ω-Scan rate (variable)		
Max$^\circ$/min	10.0	10.0
Min$^\circ$/min	2.6	2.6
No. reflections	4527	4983
measured		
Data used ($F^2 \geqslant 3.0\sigma(F)^2$)	2214	2857
C) Treatment of data		
Decay correction		
Max.	1.03	—
Min.	0.99	—
Absorption correction (cm^{-1})	152.6	152.6
Grid	14 × 6 × 10	8 × 8 × 14
Transmission coef.		
Max.	0.26	0.093
Min.	0.09	0.027
P-factor	0.02	0.02
Final residuals R	0.034	0.051
R_w	0.033	0.055
E.s.d. of unit weight	1.51	2.64
Largest shift error value on final cycle	0.10	0.05
Largest peak in final diff. Fourier (e/Å^3)	0.48	1.19

TABLE 3

POSITIONAL AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR HOs₃[μ-η²-(CF₃)C=NH](CO)₉PMe₂Ph, IIb

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Os(1)	0.21638(6)	0.62271(5)	0.358644(4)	—	C(8)	-0.185(1)	0.4925(11)	0.2201(9)	5.9(4)
Os(2)	0.15200(5)	0.49327(4)	0.22069(3)	—	C(9)	-0.080(1)	0.6284(11)	0.1855(9)	6.0(4)
Os(3)	-0.04358(6)	0.55747(5)	0.28612(4)	—	C(10)	0.189(1)	0.6630(9)	0.2312(8)	4.0(3)
P	0.33383(4)	0.4555(3)	0.1881(3)	—	C(11)	0.419(1)	0.5378(9)	0.1516(8)	4.4(3)
F(1)	0.208(1)	0.7553(7)	0.1125(7)	—	C(12)	0.509(1)	0.5887(11)	0.2163(9)	6.0(4)
F(2)	0.132(1)	0.7990(7)	0.2130(8)	—	C(13)	0.561(2)	0.6545(12)	0.1872(10)	6.9(5)
F(3)	0.331(1)	0.7755(7)	0.2465(9)	—	C(14)	0.528(2)	0.6706(12)	0.0975(10)	6.7(4)
O(1)	0.497(1)	0.6807(10)	0.4267(8)	10.8(4)	C(15)	0.443(2)	0.6244(12)	0.0337(10)	6.9(4)
O(2)	0.252(1)	0.5425(9)	0.5414(8)	9.4(4)	C(16)	0.388(1)	0.5568(11)	0.0601(9)	5.7(4)
O(3)	0.086(2)	0.7725(11)	0.3992(10)	13.3(5)	C(17)	0.465(2)	0.4124(13)	0.2847(11)	8.6(5)
O(4)	-0.049(1)	0.4356(8)	0.0474(6)	6.9(3)	C(18)	0.314(2)	0.3765(14)	0.1029(12)	8.8(6)
O(5)	0.166(1)	0.3302(9)	0.3113(7)	8.8(3)	C(19)	0.216(2)	0.7475(13)	0.1959(11)	7.6(5)
O(6)	-0.178(1)	0.6655(9)	0.3871(7)	9.2(4)	H(171)	0.5000	0.4375	0.3320	6.0
O(7)	0.040(1)	0.4266(8)	0.4346(7)	8.1(3)	H(172)	0.5386	0.3933	0.2702	6.0
O(8)	-0.273(1)	0.4519(8)	0.1775(7)	8.0(3)	H(173)	0.4337	0.3651	0.3101	6.0
O(9)	-0.110(1)	0.6713(8)	0.1202(7)	7.1(3)	H(181)	0.2500	0.3945	0.0410	6.0
N	0.166(1)	0.6094(8)	0.1661(7)	4.9(3)	H(182)	0.2758	0.3275	0.1177	6.0
C(1)	0.389(2)	0.6693(13)	0.4023(12)	8.7(6)	H(183)	0.3916	0.3603	0.0919	6.0
C(2)	0.239(2)	0.5781(12)	0.4717(11)	7.5(5)	H(12)	0.5363	0.5770	0.2836	6.0
C(3)	0.140(2)	0.7169(15)	0.3901(14)	11.0(7)	H(13)	0.6205	0.6919	0.2286	6.0
C(4)	0.034(1)	0.4569(11)	0.1155(9)	5.9(4)	H(14)	0.5959	0.7158	0.0760	6.0
C(5)	0.153(2)	0.3968(12)	0.2781(10)	6.8(5)	H(15)	0.4164	0.6406	-0.0308	6.0
C(6)	-0.124(2)	0.6245(12)	0.3512(10)	7.1(5)	H(16)	0.3291	0.5230	0.0128	6.0
C(7)	0.010(2)	0.4775(11)	0.3810(10)	6.4(4)	H(1)	0.8594	0.1250	0.3945	6.0

Anisotropic thermal parameters [a]

Atom	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Os(1)	4.59(3)	5.06(4)	5.19(3)	-0.18(3)	1.00(2)	-1.84(3)
Os(2)	3.61(2)	3.01(3)	4.14(2)	-0.08(3)	1.41(2)	-0.27(3)
Os(3)	3.95(3)	5.41(4)	4.34(2)	0.53(3)	1.51(2)	-0.36(3)
P	4.6(2)	4.2(2)	6.6(2)	0.1(2)	2.6(1)	-0.7(2)
F(1)	23(1)	4.9(6)	12.2(6)	-0.6(7)	8.6(5)	2.6(5)
F(2)	10.4(7)	4.4(6)	18.0(8)	1.8(6)	5.0(6)	1.5(6)
F(3)	8.9(7)	6.7(7)	20(1)	-2.7(6)	3.6(7)	-0.1(7)

[a] The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

TABLE 4

INTERATOMIC DISTANCES WITH E.s.d.'s FOR $HOs_3[\mu\text{-}\eta^2\text{-}(CF_3)C=NH](CO)_9PMe_2Ph$, IIb

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)—Os(2)	2.956(1)	P—C(11)	1.82(1)
Os(1)—Os(3)	2.895(1)	C(11)—C(12)	1.43(2)
Os(2)—Os(3)	2.870(1)	C(12)—C(13)	1.38(2)
Os(1)—C(1)	1.88(2)	C(13)—C(14)	1.35(2)
Os(1)—C(2)	1.85(2)	C(14)—C(15)	1.35(2)
Os(1)—C(3)	1.92(2)	C(15)—C(16)	1.40(2)
Os(1)—C(10)	2.02(1)	C(16)—C(11)	1.39(2)
Os(2)—C(4)	1.82(1)	C(1)—O(1)	1.17(2)
Os(2)—C(5)	1.83(2)	C(2)—O(2)	1.20(2)
Os(2)—N	2.14(1)	C(3)—O(3)	1.13(2)
Os(2)—P	2.347(4)	C(4)—O(4)	1.20(1)
Os(3)—C(6)	1.91(2)	C(5)—O(5)	1.21(2)
Os(3)—C(7)	1.93(2)	C(6)—O(6)	1.16(2)
Os(3)—C(8)	1.86(2)	C(7)—O(7)	1.16(2)
Os(3)—C(9)	1.90(2)	C(8)—O(8)	1.18(2)
N—C(10)	1.31(1)	C(9)—O(9)	1.20(2)
C(10)—C(19)	1.57(2)		
C(19)—F(1)	1.28(2)		
C(19)—F(2)	1.33(2)		
C(19)—F(3)	1.35(2)		
P—C(17)	1.82(2)		
P—C(18)	1.82(2)		

121—124°C. The second band was recrystallized from hexanes to give $HOs_3\text{-}[\mu\text{-}\eta^2\text{-}(CF_3)C=NH](CO)_9PMe_2Ph$, IIb, (6.9 mg, 4.3%). M.p. 123—126°C.

Isotope labeling reaction

25.9 mg (0.0304 mmol) of $H_2Os_3(CO)_{10}$ and 25.8 mg (0.0302 mmol) of $D_2Os_3(CO)_{10}$ (isotopically >99% as determined by a calibrated ^1H NMR measurement) was treated with CF_3CN as described above. After reaction, the solvent was removed. An ^1H NMR spectrum of the residue showed full H—H coupling between the hydride ligand and the C—H proton in IIIa and implied the absence of any intermolecular H—D scrambling in the reaction. A ^2H NMR spectrum confirmed the presence of the product $IIIa\text{-}d_2$ also in this reaction. The ^1H NMR spectrum also showed full H—H coupling between the hydride ligand and N—H proton in IIa, but we were unable to confirm the presence of the N—D resonance in the ^2H NMR spectrum.

Thermolysis of IIa

Exposure of 4.57 mg (0.0482 mmol) of IIa to refluxing octane for 16 hours resulted in CO loss and the formation of what we believe to be a cluster containing a triply-bridging $(H)N=CCF_3$ ligand. The reaction mixture was concentrated and chromatographed on a short column of alumina. Elution of a yellow band with hexane/methylene chloride (3/1, v/v) yielded a yellow solid (4.14 mg, 93%) M.p. 134—136°C. Analysis: Found: C, 14.58; H, 0.23; N, 1.85. Calcd. for $Os_3F_3O_9NC_{11}H_2$: C, 14.37; H, 0.22; N, 1.52%.

TABLE 5

INTERATOMIC ANGLES WITH e.s.d.'s FOR HOs$_3$[μ-η^2-(CF$_3$)C=NH](CO)$_9$PMe$_2$Ph, IIb

Atoms	Angle (deg.)	Atoms	Angle (deg)
Os(2)—Os(1)—Os(3)	58.73(2)	Os(1)—Os(2)—C(5)	108.6(5)
Os(1)—Os(2)—Os(3)	59.58(2)	Os(3)—Os(2)—N	88.3(3)
Os(1)—Os(3)—Os(2)	61.69(2)	Os(3)—Os(2)—P	169.4(1)
Os(2)—Os(1)—C(10)	66.7(4)	Os(3)—Os(2)—C(4)	93.5(4)
Os(2)—Os(1)—C(1)	117.6(5)	Os(3)—Os(2)—C(5)	92.0(5)
Os(2)—Os(1)—C(2)	109.0(5)	N—Os(2)—P	88.2(3)
Os(2)—Os(1)—C(3)	139.7(6)	N—Os(2)—C(4)	94.2(5)
Os(3)—Os(1)—C(10)	86.6(3)	N—Os(2)—C(5)	174.1(6)
Os(3)—Os(1)—C(1)	176.2(6)	P—Os(2)—C(4)	96.7(4)
Os(3)—Os(1)—C(2)	91.2(5)	P—Os(2)—C(5)	90.5(5)
Os(3)—Os(1)—C(3)	87.0(6)	C(4)—Os(2)—C(5)	91.6(7)
C(10)—Os(1)—C(1)	92.6(6)	Os(1)—Os(3)—C(6)	98.2(5)
C(10)—Os(1)—C(2)	175.7(6)	Os(1)—Os(3)—C(8)	87.2(5)
C(10)—Os(1)—C(3)	92.9(7)	Os(1)—Os(3)—C(7)	161.2(4)
C(1)—Os(1)—C(2)	89.4(7)	Os(1)—Os(3)—C(9)	89.7(4)
C(1)—Os(1)—C(3)	96.7(9)	Os(2)—Os(3)—C(6)	159.8(5)
C(2)—Os(1)—C(3)	90.7(8)	Os(2)—Os(3)—C(7)	86.9(4)
Os(1)—Os(2)—N	66.3(3)	Os(2)—Os(3)—C(8)	99.6(4)
Os(1)—Os(2)—P	109.9(1)	Os(2)—Os(3)—C(9)	84.8(4)
Os(1)—Os(2)—C(4)	93.5(4)	C(6)—Os(3)—C(7)	94.0(6)
C(6)—Os(3)—C(8)	100.6(6)	C(17)—P—C(18)	101.9(8)
C(6)—Os(3)—C(9)	94.2(7)	C(17)—P—C(11)	104.0(7)
C(7)—Os(3)—C(8)	90.5(6)	C(18)—P—C(11)	106.3(7)
C(7)—Os(3)—C(9)	171.6(6)	P—C(11)—C(12)	121.0(10)
C(8)—Os(3)—C(9)	89.9(6)	P—C(11)—C(16)	121.2(10)
N—C(10)—C(19)	110.2(11)	C(16)—C(11)—C(12)	117.7(13)
Os(1)—C(10)—N	117.6(10)	C(11)—C(12)—C(13)	120.0(13)
Os(1)—C(10)—C(19)	131.1(10)	C(12)—C(13)—C(14)	120.1(15)
Os(2)—N—C(10)	109.0(8)	C(13)—C(14)—C(15)	122.1(16)
C(10)—C(19)—F(1)	119.3(16)	C(14)—C(15)—C(16)	119.7(15)
C(10)—C(19)—F(2)	106.1(14)	C(15)—C(16)—C(11)	120.4(13)
C(10)—C(19)—F(3)	110.8(15)	Os(1)—C(1)—O(1)	177.5(17)
F(1)—C(19)—F(2)	108.6(17)	Os(1)—C(2)—O(2)	174.2(15)
F(1)—C(19)—F(3)	107.2(17)	Os(1)—C(3)—O(3)	172.7(21)
F(2)—C(19)—F(3)	103.8(16)	Os(2)—C(4)—O(4)	175.2(13)
Os(2)—P—C(17)	113.7(5)	Os(2)—C(5)—O(5)	171.6(14)
Os(2)—P—C(18)	115.1(6)	Os(3)—C(6)—O(6)	177.0(15)
Os(2)—P—C(11)	114.5(4)	Os(3)—C(7)—O(7)	176.5(15)
		Os(3)—C(8)—O(8)	178.9(12)
		Os(3)—C(9)—O(9)	175.9(13)

Reaction of IIIa with PMe$_2$Ph

9.7 mg (0.07 mmol) of PMe$_2$Ph was added to a solution of IIIa (65 mg; 0.0686 mmol) in heptane solvent. The solution was heated to reflux for 2 hours. All volatiles were removed in vacuo, and the residue was taken up in CDCl$_3$ and examined by ^{1}H NMR spectroscopy which showed it to be an approximately equimolar mixture of two compounds. One of these was IIIb. The other was subsequently shown to be another substitutional isomer [17]. The solution was chromatographed over alumina to give one yellow band. Crystallization from hexane gave 58.2 mg, 80.2% combined yield of IIIb and its isomer. IIIb and its isomer could be isolated in pure form by separating crystals.

TABLE 6

POSITIONAL AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR $anti$-HOs[μ-η^2-N=C(H)CF$_3$)CO)$_9$PMe$_2$Ph, IIIb

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Os(1)	0.12952(9)	0.18924(5)	0.09643(4)	—	C(8)	0.499(3)	0.198(2)	−0.078(1)	7.1(6)
Os(2)	0.38856(8)	0.28810(5)	0.09097(4)	—	C(9)	0.224(2)	0.257(2)	−0.072(1)	6.0(6)
Os(3)	0.32872(9)	0.17173(6)	−0.02394(4)	—	C(10)	0.098(2)	0.380(1)	0.058(1)	5.0(5)
P	0.40926(6)	0.3759(5)	0.1936(3)	—	C(11)	0.262(2)	0.448(1)	0.206(1)	4.2(4)
F(1)	−0.109(1)	0.461(1)	0.0534(10)	—	C(12)	0.127(2)	0.425(2)	0.242(1)	5.9(5)
F(2)	−0.138(1)	0.348(1)	0.1073(9)	—	C(13)	0.011(3)	0.478(2)	0.251(1)	6.3(6)
F(3)	−0.118(1)	0.344(1)	−0.0054(9)	—	C(14)	0.024(3)	0.552(2)	0.224(2)	8.1(7)
O(1)	0.165(2)	0.003(1)	0.1256(9)	7.9(4)	C(15)	0.138(3)	0.579(2)	0.185(2)	9.8(9)
O(2)	−0.049(2)	0.212(1)	0.2366(9)	7.3(4)	C(16)	0.271(3)	0.528(2)	0.177(1)	6.5(6)
O(3)	−0.122(2)	0.150(1)	−0.0055(10)	8.6(5)	C(17)	0.424(3)	0.321(2)	0.279(1)	7.0(6)
O(4)	0.537(2)	0.409(1)	−0.0108(10)	8.2(5)	C(18)	0.572(3)	0.444(2)	0.191(2)	8.2(7)
O(5)	0.668(2)	0.202(1)	0.1363(9)	6.7(4)	C(19)	−0.063(2)	0.383(1)	0.051(1)	5.9(6)
O(6)	0.183(2)	0.033(1)	−0.117(10)	8.1(5)	H(171)	0.3418	0.2910	0.2988	6.0
O(7)	0.493(2)	0.046(1)	0.0755(9)	7.6(4)	H(172)	0.4684	0.3571	0.3121	6.0
O(8)	0.601(2)	0.214(1)	−0.1106(10)	8.0(5)	H(173)	0.5027	0.2772	0.2676	6.0
O(9)	0.161(2)	0.312(1)	−0.0996(9)	7.8(4)	H(181)	0.5996	0.4785	0.1660	6.0
N	0.164(2)	0.314(1)	0.071(1)	5.2(4)	H(182)	0.6486	0.4041	0.2002	6.0
C(1)	0.150(2)	0.075(1)	0.114(1)	5.5(5)	H(183)	0.5581	0.4717	0.2408	6.0
C(2)	0.024(2)	0.205(1)	0.183(1)	5.2(5)	H(12)	0.1166	0.3700	0.2616	6.0
C(3)	−0.026(2)	0.167(1)	0.032(1)	5.9(5)	H(13)	−0.0736	0.4585	0.2758	6.0
C(4)	0.480(2)	0.357(2)	0.027(1)	6.0(6)	H(14)	−0.0647	0.5845	0.2269	6.0
C(5)	0.561(2)	0.237(1)	0.115(1)	4.9(5)	H(15)	0.1190	0.6345	0.1709	6.0
C(6)	0.240(2)	0.089(1)	−0.079(1)	6.0(6)	H(16)	0.3673	0.5514	0.1493	6.0
C(7)	0.435(2)	0.099(1)	0.037(1)	5.3(5)	H(10)	0.1408	0.4347	0.0649	6.0

Anisotropic thermal parameters [a]

Atom	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Os(1)	3.82(3)	4.53(4)	2.94(3)	−0.07(3)	−0.45(3)	0.01(3)
Os(2)	3.25(3)	4.42(4)	2.75(3)	0.43(3)	0.05(2)	−0.29(3)
Os(3)	4.69(3)	5.57(4)	2.66(3)	1.50(3)	−0.52(4)	−0.74(3)
P	4.7(2)	4.9(3)	3.4(2)	0.2(2)	−0.3(2)	−0.8(2)
F(1)	6.7(8)	9(1)	18(1)	2.3(7)	0.8(9)	4(1)
F(2)	5.2(6)	9.1(9)	11(1)	0.9(6)	0.6(7)	2.4(8)
F(3)	6.6(7)	22(2)	11(1)	5.4(9)	−5.1(6)	−6(1)

[a] The form of the anisotropic thermal parameter is exp[$-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^{*}b^{*} + B_{13}hla^{*}c^{*} + B_{23}klb^{*}c^{*})$].

TABLE 7

INTERATOMIC DISTANCES WITH e.s.d.s FOR *anti*-HOs$_3$[μ-η^1-N=C(H)CF$_3$](CO)$_9$(P(CH$_3$)$_2$(C$_6$H$_5$), IIIb

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)—Os(2)	2.845(1)	C(19)—F(3)	1.312(18)
Os(1)—Os(3)	2.861(2)'	P—C(11)	1.785(13)
Os(2)—Os(3)	2.864(1)	P—C(17)	1.798(16)
Os(1)—C(1)	1.876(16)	P—C(18)	1.841(18)
Os(1)—C(2)	1.864(14)	C(11)—C(12)	1.441(17)
Os(1)—C(3)	1.882(15)	C(12)—C(13)	1.363(19)
Os(1)—N	2.075(12)	C(13)—C(14)	1.300(21)
Os(2)—P	2.353(3)	C(14)—C(15)	1.326(24)
Os(2)—C(4)	1.819(16)	C(15)—C(16)	1.476(23)
Os(2)—C(5)	1.826(13)	C(16)—C(11)	1.383(18)
Os(2)—N	2.119(11)	C(1)—O(1)	1.186(16)
Os(3)—C(6)	1.854(16)	C(2)—O(2)	1.193(15)
Os(3)—C(7)	1.888(14)	C(3)—O(3)	1.139(15)
Os(3)—C(8)	1.883(17)	C(4)—O(4)	1.190(16)
Os(3)—C(9)	1.886(16)	C(5)—O(5)	1.187(14)
N—C(10)	1.247(15)	C(6)—O(6)	1.199(16)
C(10)—C(19)	1.465(19)	C(7)—O(7)	1.215(15)
C(19)—F(1)	1.331(17)	C(8)—O(8)	1.138(17)
C(19)—F(2)	1.352(17)	C(9)—O(9)	1.163(16)

Crystallographic analyses

Crystals of IIb and IIIb suitable for diffraction measurements were obtained from hexane solutions by cooling to −20°C. Crystals were mounted in thin-walled glass capillaries. All diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite mono-chromatized Mo-$K\alpha$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index and least-squares routines. The space groups were determined from the systematic absences observed during data collection. Crystal data and data collections parameters are listed in Table 2. All data processing was performed on a Digital PDP 11/45 computer by using the Enraf Nonius SDP program library. Absorption corrections of a Guassian integration type were done for both structures. Neutral atom scattering factors were calculated by the standard procedures [18a]. Anomalous dispersion corrections were applied for all nonhydrogen atoms [18b]. All structures were solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were calculated on the basis of idealized geometry. Contributions from such atoms were included in structure factor calculations but their positions were not refined. Full-matrix least-squares refinements minimized the function $\Sigma_{hkl}w$-$(|F_{obs}| - |F_{calc}|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = (F^2_{obs})/2F_{obs}$ and $\sigma(F^2_{obs}) = [\sigma(I_{raw})^2 + (PF^2_{obs})^2]^{1/2}/Lp$. All atoms heavier than oxygen were refined with anisotropic temperature factors. All other atoms were refined with isotropic temperature factors only. Final fractional atomic coordinates, thermal parameters, interatomic distances and angles with errors obtained from the inverse

TABLE 8

INTERATOMIC ANGLES WITH e.s.d.s FOR $anti$-HOs$_3$[μ-η^1-N=C(H)CF$_3$](CO)$_9$(P(CH$_3$)$_2$C$_6$H$_5$), IIIb

Atoms	Angle (deg)	Atoms	Angle (deg)
Os(1)—Os(2)—Os(3)	60.15(2)	Os(2)—Os(3)—C(6)	161.9(5)
Os(2)—Os(1)—Os(3)	60.25(2)	Os(2)—Os(3)—C(7)	82.8(4)
Os(1)—Os(3)—Os(2)	59.60(2)	Os(2)—Os(3)—C(8)	94.6(5)
Os(2)—Os(1)—N	47.9(3)	Os(2)—Os(3)—C(9)	87.7(5)
Os(2)—Os(1)—C(1)	118.0(4)	C(6)—Os(3)—C(7)	95.9(6)
Os(2)—Os(1)—C(2)	112.2(4)	C(6)—Os(3)—C(8)	103.5(7)
Os(2)—Os(1)—C(3)	135.2(5)	C(6)—Os(3)—C(9)	92.7(6)
Os(3)—Os(1)—N	80.2(3)	C(7)—Os(3)—C(8)	91.6(7)
Os(3)—Os(1)—C(1)	88.4(4)	C(7)—Os(3)—C(9)	170.5(6)
Os(3)—Os(1)—C(2)	171.4(4)	C(8)—Os(3)—C(9)	90.4(7)
Os(3)—Os(1)—C(3)	88.7(4)	N—C(10)—C(19)	121.7(14)
N—Os(1)—C(1)	165.3(5)	C(10)—C(19)—F(1)	110.2(14)
N—Os(1)—C(2)	97.6(5)	C(10)—C(19)—F(2)	115.3(14)
N—Os(1)—C(3)	99.0(6)	C(10)—C(19)—F(3)	115.5(14)
C(1)—Os(1)—C(2)	92.2(6)	Os(2)—P—C(17)	113.8(6)
C(1)—Os(1)—C(3)	90.0(6)	Os(2)—P—C(18)	113.8(6)
C(2)—Os(1)—C(3)	99.9(6)	Os(2)—P—C(11)	115.2(4)
Os(1)—Os(2)—N	46.6(3)	C(17)—P—C(18)	104.5(6)
Os(1)—Os(2)—P	112.0(1)	C(11)—P—C(17)	105.6(7)
Os(1)—Os(2)—C(4)	138.0(5)	C(11)—P—C(18)	102.8(7)
Os(1)—Os(2)—C(5)	116.7(4)	P—C(11)—C(12)	122.2(11)
Os(3)—Os(2)—N	79.5(3)	P—C(11)—C(16)	120.6(11)
Os(3)—Os(2)—P	172.1(1)	C(11)—C(12)—C(13)	124.3(14)
Os(1)—N—C(10)	142.5(10)	C(12)—C(13)—C(14)	116.5(16)
Os(2)—N—C(10)	131.8(10)	C(13)—C(14)—C(15)	125.5(20)
Os(3)—Os(2)—C(4)	90.8(5)	C(14)—C(15)—C(16)	120.5(20)
Os(3)—Os(2)—C(5)	92.6(4)	C(15)—C(16)—C(11)	115.7(15)
N—Os(2)—P	95.6(3)	C(16)—C(11)—C(12)	117.2(12)
N—Os(2)—C(4)	102.4(5)	Os(1)—C(1)—O(1)	179.2(10)
N—Os(2)—C(5)	163.3(5)	Os(1)—C(2)—O(2)	176.0(13)
P—Os(2)—C(4)	96.4(5)	Os(1)—C(3)—O(3)	176.4(15)
P—Os(2)—C(5)	90.5(4)	Os(2)—C(4)—O(4)	173.4(14)
C(4)—Os(2)—C(5)	92.3(6)	Os(2)—C(5)—O(5)	174.8(12)
Os(1)—Os(3)—C(6)	102.3(5)	Os(3)—C(6)—O(6)	176.1(14)
Os(1)—Os(3)—C(7)	86.3(4)	Os(3)—C(7)—O(7)	173.7(13)
Os(1)—Os(3)—C(8)	154.2(5)	Os(3)—C(8)—O(8)	179.6(10)
Os(1)—Os(3)—C(9)	87.9(5)	Os(3)—C(9)—O(9)	177.9(13)

matrix calculated on the final cycle of least-squares refinement are listed in Tables 3—8. Structure factor amplitudes are available for both structures *.

Results

Two products formulated as, HOs$_3$[μ-η^2-(CF$_3$)C=NH](CO)$_{10}$, IIa and HOs$_3$-[μ-η^1-N=C(H)CF$_3$](CO)$_{10}$, IIIa on the basis of IR and ^{1}H NMR spectroscopies,

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* The tables of final observed and calculated structure factor amplitudes have been deposited as NAPS Document No. 03849 (23 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $5.75 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

elemental analyses and X-ray crystallographic analyses of their PMe$_2$Ph deriva-
tives, have been isolated from the reaction of Ia with CF$_3$CN at room tempera-
ture. The corresponding PMe$_2$Ph derivatives, HOs$_3$[μ-η^2-(CF$_3$)C=NH](CO)$_9$(PMe$_2$-
Ph), IIb and HOs$_3$(μ-η^1-N=C(H)CF$_3$)(CO)$_9$(PMe$_2$Ph), IIIb were isolated from the
reaction of Ib with CF$_3$CN (see Scheme 1).

IR analyses if IIa and IIb show prominent absorptions at 3295 and 3290
cm^{-1} which can be assigned to N—H stretching vibrations. Such absorptions

SCHEME 1
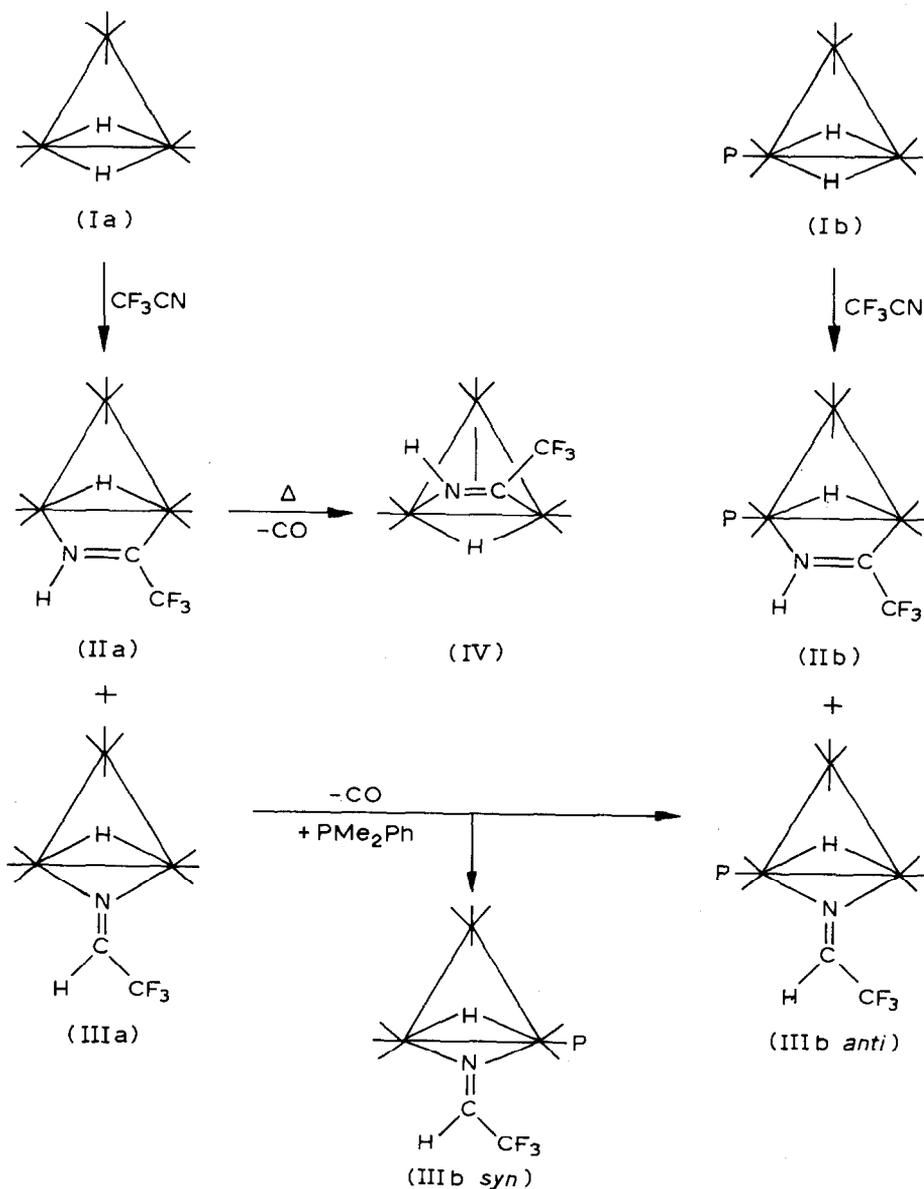
were not observed in IIIa or IIIb. The ^{1}H NMR spectra of IIa and IIb show broad low-field resonances at δ = 9.57 and 8.73 ppm, respectively. The broadening can be attributed to quadrupole relaxation caused by the proximate nitrogen atom. High-field resonances at δ = −15.15 ppm, doublet (J(H—H) = 1.0 Hz), and −15.25, doublet (J(P—H) = 8.5 Hz), can be assigned to the bridging hydride ligands in IIa and IIb, respectively. The ^{1}H NMR spectrum of IIIa shows a doublet of quartets, δ = 7.74 ppm (J(H—F) = 4.5 Hz, J(H—H) = 1.0 Hz) due to a single proton coupled to the three fluorine atoms of the CF$_3$ group and the hydride ligand. A high-field multiplet δ = −14.84 ppm is attributed to a bridging hydride ligand. The ^{1}H NMR spectrum of IIIb shows a low-field multiplet δ = 6.23 ppm which is coupled to the fluorine atoms, J(H—F) = 4.9 Hz, the phosphorus atom J(P—H) = 2.4 Hz, and the hydride ligand J(H—H) = 1.1 Hz. The hydride ligand appears as a doublet, δ = −14.80 ppm, J(P—H) = 8.5 Hz. Two methyl resonances from the phosphine ligand indicate that the methyl groups are diastereotopic.

The molecular structure of IIb is shown in Fig. 1. The molecule contains a triangular cluster of three metal atoms with a N-hydrido, C-trifluoromethyliminyl ligand bridging one edge. The unbridged Os—Os distances at 2.895(1) Å and 2.870(1) Å are significantly shorter than the bridged Os—Os distance, which is 2.956(1) Å. However, all three distances are similar to the Os—Os single bond distance of 2.877(3) Å found in Os$_3$(CO)$_{12}$ [19].

The N-hydrido, C-trifluoromethyliminyl ligand bridges the Os(1)—Os(2) bond in axial coordination sites. The nitrogen atom is coordinated solely to Os(2) and the carbon atom solely to Os(1). The C(10)—N bond is formally double
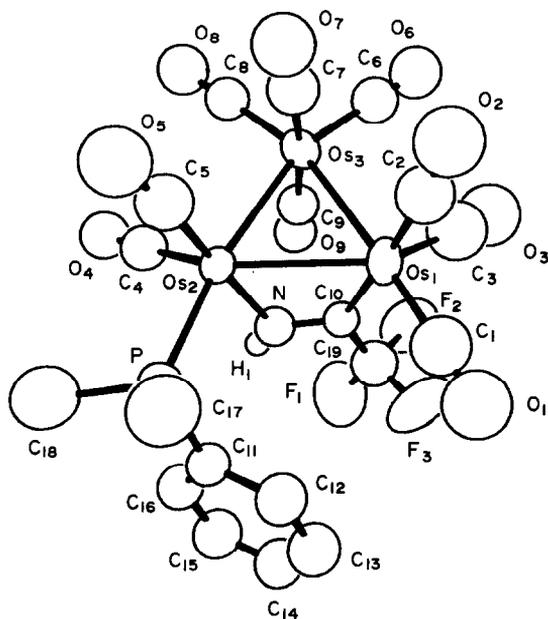
Fig. 1. An ORTEP diagram of HOs$_3$-[μ-η^2-(CF$_3$)C=NH](CO)$_9$P(CH$_3$)$_2$C$_6$H$_5$, IIb, showing 50% probability ellipsoids.

and this is supported by the short internuclear distance of 1.31(1) Å. This molecule is structurally similar to the compounds $HOs_3(\mu\text{-}\eta^2\text{-}PhC{=}NMe)(CO)_{10}$ [20] and $HOs_3(\mu\text{-}\eta^2\text{-}HC{=}NPh)(CO)_9[P(OMe)_3]$ [3], both of which also contain an iminyl ligand bridging the edge of a triangular cluster of osmium atoms. The C=N distances in these molecules are 1.278(10) and 1.32(1) Å, respectively.

The hydrogen atom on the nitrogen atom and the hydride ligand were not observed crystallographically. The position of the former was calculated on the basis of idealized geometry. The hydride ligand is believed bridging the Os(1)—Os(2) bond in the cavity circumscribed by the carbonyls C(1)—O(1), C(2)—O(2), C(5)—O(5) and the phosphine ligand.

Overall the molecule contains nine carbonyl ligands arranged such that Os(3) has four, Os(1) has three, and Os(2) has two, and the dimethylphenylphosphine ligand. This is the same distribution of ligands that exists in Ib [22], and H_2Os_3-$(CO)_9(CN\text{-}t\text{-}Butyl)$ [23]. This implies that the CF_3CN ligand has entered into bonding with the cluster without disturbing the original ligand structure of the cluster except for the hydride ligands. In the crystal IIb consists of discrete molecules. The two shortest intermolecular contacts are between carbonyl oxygen atoms at 2.90(2) and 2.98(2) Å.

An ORTEP drawing of IIIb is shown in Fig. 2. The molecule contains a triangular cluster of three osmium atoms. In contrast to IIb, the bridged osmium—osmium bond in IIIb is slightly shorter (2.845(1) Å) than the unbridged osmium—osmium bonds (2.861(1) and 2.864(1) Å). This is not surprising since Churchill
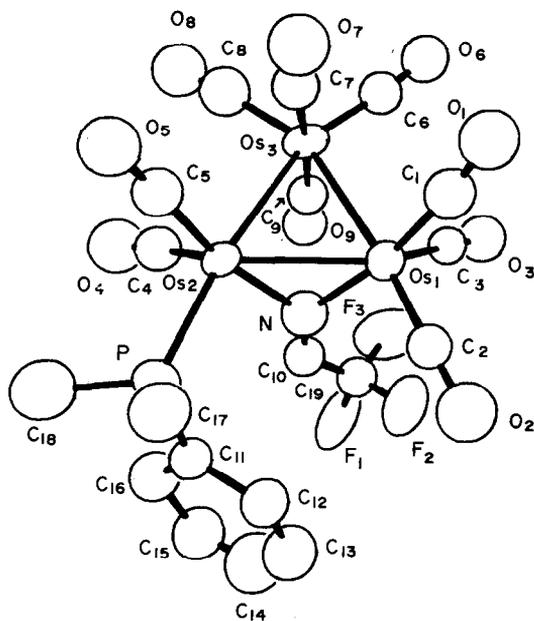
Fig. 2. An ORTEP diagram of $HOs_3\text{-}[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9P(CH_3)_2C_6H_5$, IIIb, showing 50% probability ellipsoids.

has shown for a number of triosmium clusters where two metal atoms are bridged by a ligand with only one atom in the bridge that the bridged metal—metal bond is often shorter than the unbridged metal—metal bonds [24]. The single bridging atom in IIIb is the nitrogen atom of a C-trifluoromethyl-C-hydridoalkylidenimino ligand, $CF_3(H)C=N$. The C(10)—N bond is formally double and this is supported by the short internuclear distance of 1.247(15) Å. This distance is similar to those of related ligands found in the molecules Mn_2-$[\mu-\eta^1-N=C(CF_3)_2]_2(CO)_7$, 1.259(9) and 1.258(9) Å [25] and $Fe_2[\mu-\eta^1-N=C$-$(p$-tol$)_2](CO)_6$, 1.24(2) and 1.29(2) Å [26]. In $Re_2[\mu-\eta^1-N=C(H)Me](CO)_6dpm$ a longer C=N distance of 1.39(6) Å was observed, but the error on this value is rather large [27]. Interestingly, this last compound was prepared by the addition of MeCN to the unsaturated dinuclear dihydrido compound $H_2Re_2(CO)_6$-dpm.

The hydrogen atom on C(10) was not observed crystallographically, but its location there is supported by a low-field ^1H NMR resonance which is coupled to the fluorine atoms on the nitrile group and the nonlinearity of the nitrile group at the cyano carbon. This nonlinearity produces a conformation which positions the CF_3 group *anti* to the osmium atom which contains the phosphine ligand. The single hydride ligand was not observed crystallographically either, but it is believed to bridge the Os(1)—Os(2) bond in the cavity circumscribed by the carbonyls C(1)—O(1), C(2)—O(2), C(5)—O(5) and the phosphine ligand. Nine carbonyls are distributed such that Os(3) has four, Os(1) has three, and Os(2) has two plus the phosphine ligand. In the crystal IIIb consists of discrete molecules. The shortest intermolecular contact was between a carbonyl oxygen atom and a fluorine atom at 2.98(1) Å.

The gross arrangement of the carbonyl and phosphine ligands in both IIb and IIIb is the same as that in found in Ib. This implies that the nitrile molecule has entered the coordination sphere of the cluster and one hydride ligand has been transferred to it in processes which do not disturb the remaining ligand structure of the cluster. We expect that the formations of IIb and IIIb occur in two-step sequences (i.e. additions followed by hydrogen transfers). Adducts A and B, which contain one terminal and one bridging hydride ligand, are structures which could be formed by the addition of CF_3CN to Ib [13] (see Scheme 2). A π-bonded nitrile ligand is postulated since it has been shown previously that CF_3CN coordinates to noble metals in this fashion [28]. In IIb the nitrogen atom is coordinated to the osmium bearing the phosphine ligand. Thus, A would seem to be the most probable adduct that would lead to IIb. The attack of CO on the isocyanide derivatives $H_2Os_3(CO)_9$ CNR also proceeds by addition to the substituted osmium atom [3].

The observation of coupling between the hydrogen atom on the reduced nitrile ligand and the hydride ligand in IIIa permits the use of an isotope scrambling experiment to test the molecularity of the reaction. A 1 : 1 mixture of Ia and $D_2Os_3(CO)_{10}$ was allowed to react with CF_3CN. An ^1H NMR spectrum of the reaction mixture which contained both IIa and IIIa showed full H—H coupling diagnostic of the molecule $HOs_3[\mu-N=C(H)CF_3](CO)_{10}$. Formation of the analogous dideuterio compound was confirmed by ^2H NMR spectroscopy. We thus conclude that the hydrogen transfer process for the formation IIIa is largely (certainly >95%) if not exclusively, intramolecular.

SCHEME 2   99

(II b)

(III b)
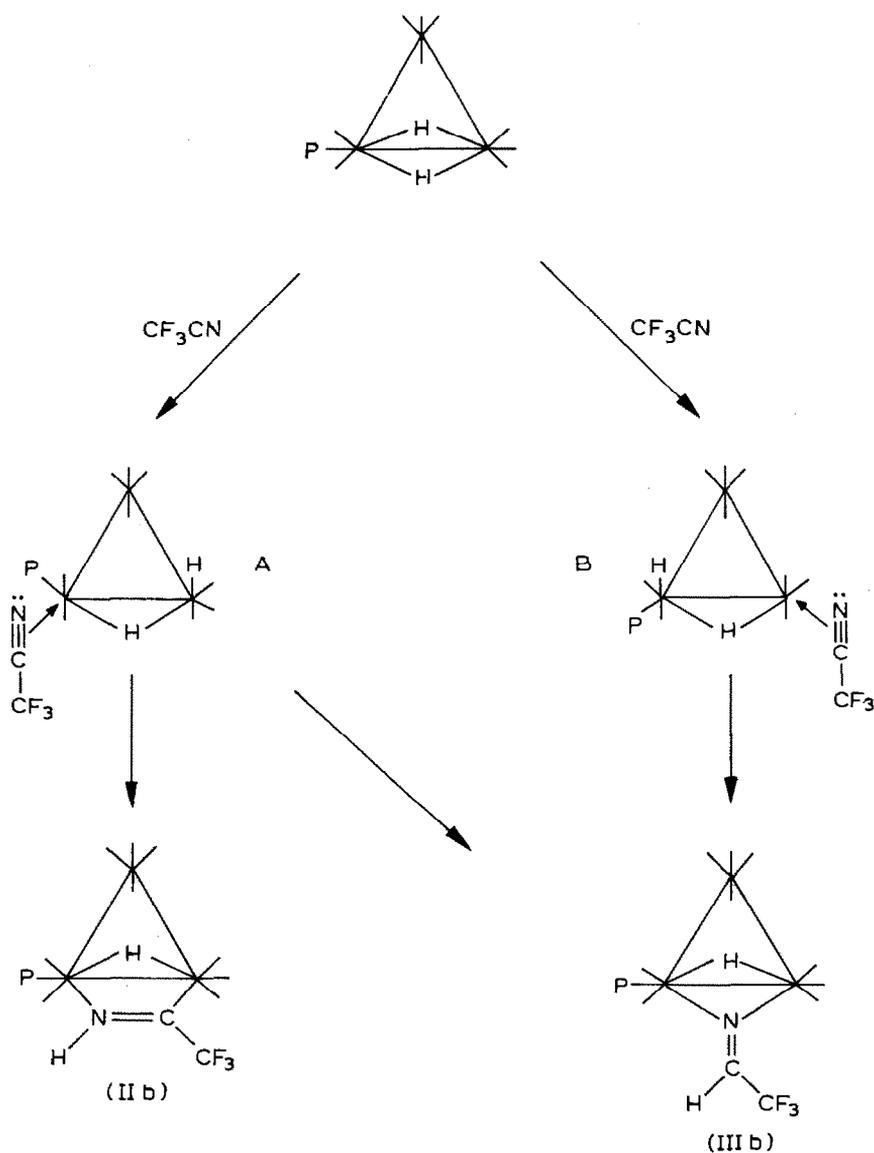
In A or B only the bridging hydride ligand is proximate to the nitrile ligand. The intramolecularity of the formation of IIIa suggests that it may be the bridging hydride ligand which is transferred to the nitrile ligand, although we cannot rule out the possibility of intramolecular ligand scrambling processes which could result in isomers of A and B that might allow the transfer of a terminal hydride ligand. We also observed that IIa and IIIa cannot be interconverted. This implies that they are formed by different processes.

When heated, IIa is decarbonylated and transformed into $HOs_3(\mu_3\text{-}\eta^2\text{-}CF_3CNH)$ $(CO)_9$, IV, which is believed to contain a triply-bridging CF_3CNH ligand. This is supported by the observation of an N—H stretching vibration at 3290 cm^{-1}, a

broad low-field ^{1}H NMR signal at $\delta = 8.31$ ppm and a bridging metal hydride resonance at $\delta = -18.08$ ppm. This molecule is similar to the iron complex $HFe_3(\mu_3-\eta^2-CH_3C=NH)(CO)_9$, V, prepared and structurally studied by Kaesz [12]. The transformation IIa to IV is analogous to that which was observed between the molecules $HOs_3(\mu-\eta^2-HC=NPh)(CO)_{10}$ and $HOs_3(\mu_3-\eta^2-HCNPh)$-$(CO)_9$ [3]. Kaesz was also able to prepare the molecule $HFe_3[\mu_3-\eta^1-N=C(H)-CH_3](CO)_9$, VI, which contains a triply-bridging $N=C(H)CH_3$ ligand [12]. We have tried to convert IIIa into an analog of VI by thermolytic decarbonylation, but have not been successful.

The alkylidenimino ligands in IIIa and IIIb are electronically equivalent to the alkenyl ligands found in the molecules $HOs_3(\mu-\eta^2-CH=C(H)R)(CO)_{10}$, VII, in which the alkenyl ligand is σ-bonded to one osmium atom and π-bonded to the other, C. While a similar bonding arrangement, D, could be envisaged for

(C) (D) (E)
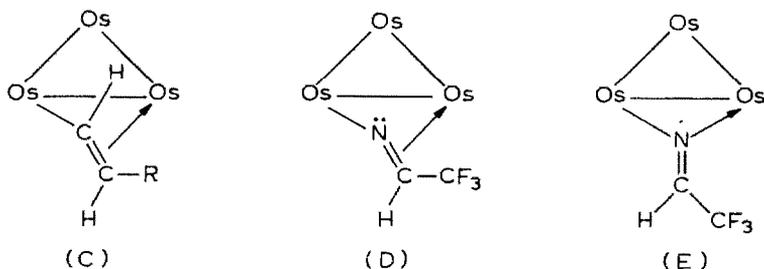
the alkylidenimino ligand, the arrangement E which utilizes the lone pair of electrons on the nitrogen atom is apparently the preferred form. It has been shown that phosphines will react with the complexes VII by addition to the alkenyl ligand [39,30]. The adduct $HOs_3(\mu-CHCH_2PMe_2Ph)(CO)_{10}$ has been characterized crystallographically [29]. We tested IIIa for a similar reaction with PMe_2Ph, but found that only substitution to give *anti*-IIIb and a *syn* isomer [17] (not observed in reaction of Ib with CF_3CN) had occurred.

Since Ia does not readily transfer hydrogen to other nitriles [2,27] our present results support our original notion that CF_3CN is an activated nitrile which is more susceptible to hydrogen reductions than ordinary nitriles. It is interesting that IIa could be converted into IV, which is an analog of V. The IIa to IV transformation thus permits an entry into the regime of the triply-bridging ligands. Presumably, a sequence of further reduction reactions analogous to those observed by Kaesz for the iron compounds will follow, but we have not pursued this. We have not been able to convert IIIa into an analog of VI. This raises the possibility that if further reduction could be produced it might be confined to the edge of the cluster. It would be interesting to see in what ways such a reduction might differ from those which have been observed on the face of a trinuclear cluster [11—13].

As this work neared completion we became aware of similar results that had been obtained in the laboratories of Professor M.J. Mays, University Chemical Laboratories, Cambridge [31].

Acknowledgments

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