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Synthesis, characterization and hindered rotation of triosmium clusters $(\mu\text{-H})Os_3(CO)_{10}L[ON(CF_3)_2]$ [L = CO, CH_3CN and PhCN]

H.G. Ang, C.H. Koh and W.L. Kwik

Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511 (Singapore)

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Abstract

Bis(trifluoromethyl)nitroxyl radical reacts with $H_2Os_3(CO)_{10}L$ (L = CH_3CN, PhCN) to afford the stable derivatives $(\mu\text{-H})Os_3(CO)_{10}L[ON(CF_3)_2]$ in which single crystal X-ray structural analysis reveals that the $(CF_3)_2NO$ moiety assumes an axial terminal position. Variable-temperature ^{19}F NMR spectra suggest that rotations of the $(CF_3)_2N$ moiety about the Os–O bond are hindered due to its proximity to the neighbouring CO groups. The activation energies were estimated from the coalescence temperatures.

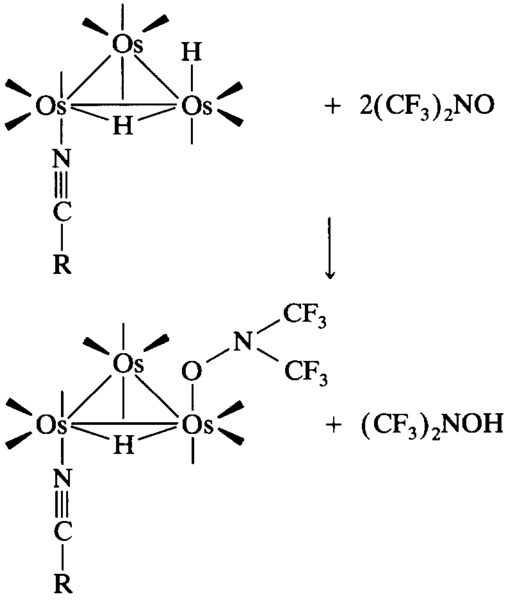
Introduction

Although bis(trifluoromethyl)nitroxyl radical reacts directly with several main group elements to form interesting derivatives [1], only a few metal complexes containing the $(CF_3)_2NO$ moiety have been reported [2–6]. Most mono- and dinuclear carbonyls undergo oxidation reactions with $(CF_3)_2NO$ to give metal nitroxides and carbon monoxide. Recently, we have shown that $(CF_3)_2NO$ radical reacts with $(\mu\text{-H})Os_3(CO)_{10}H$ to afford $(\mu\text{-H})Os_3(CO)_{10}[ON(CF_3)_2]$ (I) in which the $(CF_3)_2NO$ group resides at the axial position [7]. We report below the syntheses, X-ray structural and spectroscopic properties of two new substituted triosmium carbonyl clusters, namely $(\mu\text{-H})Os_3(CO)_{10}L[ON(CF_3)_2]$ (L = CH_3CN (II) and PhCN (III)) which represent the first examples of stable adducts of triosmium carbonyl clusters containing an organic nitrile [8].

Correspondence to: Dr. H.G. Ang, Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore.

Results and discussion

A yellow solution of (μ-H)$Os_3(CO)_{10}L$ (L = CH_3CN or PhCN) was obtained when $H_2Os_3(CO)_{10}$ was dissolved in L. Reactions of the $(CF_3)_2NO$ radical with a solution of the $H_2Os_3(CO)_{10}L$ in a 2 : 1 molar ratio readily afforded the triosmium cluster derivatives (μ-H)$Os_3(CO)_{10}L[ON(CF_3)_2]$ together with $(CF_3)_2NOH$, as shown by



where R = CH_3, C_6H_5.

Yellow crystals of II and III were obtained from the crude product by TLC followed by recrystallization from CH_2Cl_2/hexane. The structures of II and III were established on the basis of their elemental analysis (C, H, F), IR, ^1H and ^{19}F NMR data, and single crystal X-ray structural determinations.

The ^1H NMR spectrum of (μ-H)$Os_3(CO)_{10}L[ON(CF_3)_2]$ displays peaks at -11.74 (s, CH_3CN) and -11.65 (s, PhCN), ppm, which are comparable to that of I (L = CO) at -14.2 (s) ppm and are indicative of the presence of bridging hydride. As shown in Fig. 1, whereas the ^{19}F NMR spectrum of I gives a doublet at room temperature (25°C), singlets were obtained for II and III. However, all three spectra similarly display a doublet each at 0°C and two sets of quartets at about -20°C. That the two CF_3 groups are magnetically non-equivalent at the low temperatures suggest that rotations of the $(CF_3)_2N$ group about the Os–O bond are hindered due to its proximity to the neighbouring axial CO groups on Os(1) and Os(2) atoms.

An estimation of the energy barrier for the hindered rotation of the $(CF_3)_2N$ group about the Os–O bond of each of the above clusters I, II and III, was made at their coalescence temperatures [9*]. The values of $\Delta G_c^\ddagger$ thus obtained were found to be 65 (CO), 62 (CH_3CN) and 63 (PhCN) kJ mol^{-1}. These values are

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* Reference number with asterisk indicates a note in the list of references.

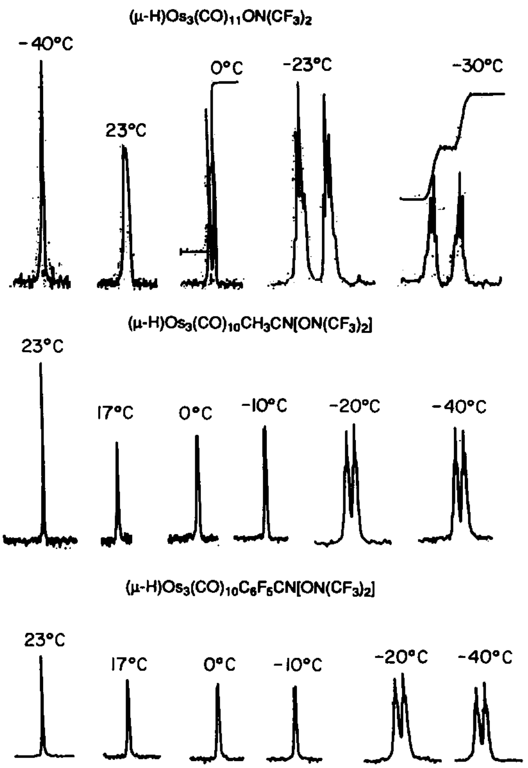


Fig. 1. Variable temperature ^{19}F NMR spectra of (top) (μ-H)$Os_3(CO)_{11}ON(CF_3)_2$, (middle) (μ-H)$Os_3(CO)_{10}CH_3CN[ON(CF_3)_2]$ and (bottom) (μ-H)$Os_3(CO)_{10}C_6F_5CN[ON(CF_3)_2]$.

somewhat higher than those reported for the fluxional exchange processes involving the two hydrides and two carbonyls in $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_{10}L$ (L = Lewis' bases) [10,11].

The molecular structures of II and III were determined by single-crystal X-ray diffraction, and that for III is shown in Fig. 2. Both II and III were found to be isomorphous with (μ-H)(H)$Os_3(CO)_{10}P(C_6H_5)_3$ [12] and (μ-H)(H)$Os_3(CO)_{10}$(CN-t-C_4H_9) [13]. As has been found for I, the $(CF_3)_2NO$ group bonds to the Os(3) atom at the axial terminal position in II and III. The Os(3)–O(1) bond distance falls into a narrow range of 2.104–2.115 Å. The nearly linear PhCN [N(2)–C(2)–C(111) = 177(16)°] and CH_3CN [N(2)–C(3)–C(4) = 171.3(40)°] ligands are located at the axial coordination sites perpendicular to the Os_3 triangle and on the opposite side of the triangle from the terminal $(CF_3)_2NO$ moiety. Tables 1 and 2 list some selected bond distances and angles, respectively, of I, II and III. In general the Os–Os distances are similar to those of the parent compound (μ-H)(H)$Os_3(CO)_{10}$ [14] but somewhat shorter than those in the adduct containing the isocyanide. Notably, the averages of the Os(1)–Os(3) and Os(2)–Os(3) bond lengths are nearly the same for I, II and III. The $(CF_3)_2NO$ group in III inclines at a somewhat larger angle (86.8°) to the Os_3 triangle than the corresponding angles in I (84.0°) and II (84.5°). However, it is interesting to note that on the Os(1) and Os(2), the axial CO groups on the same side of the Os_3 triangle as the $(CF_3)_2NO$

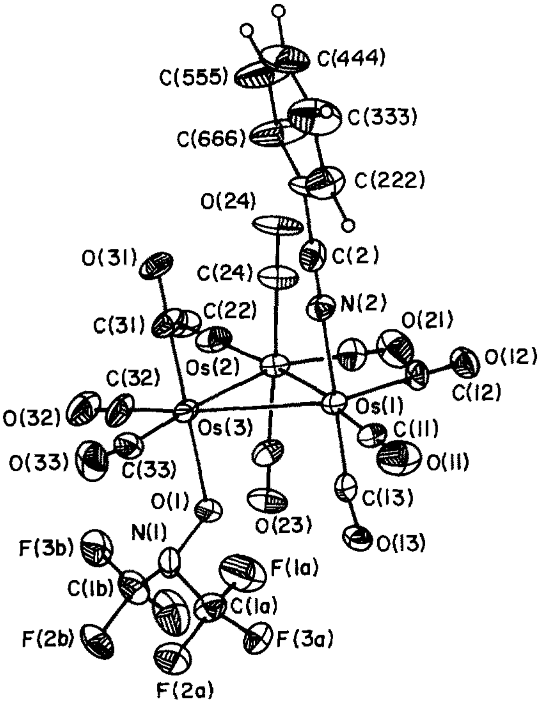
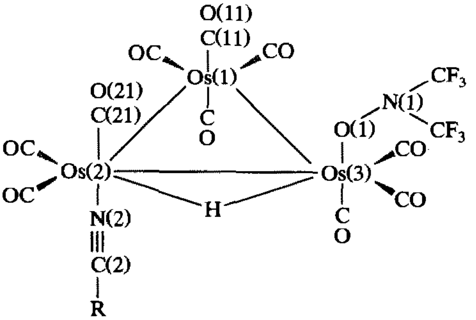


Fig. 2. The crystal and molecular structure of $Os_3(CO)_{10}[PhCN][ON(CF_3)_2]$, showing the numbering scheme.

Table 1

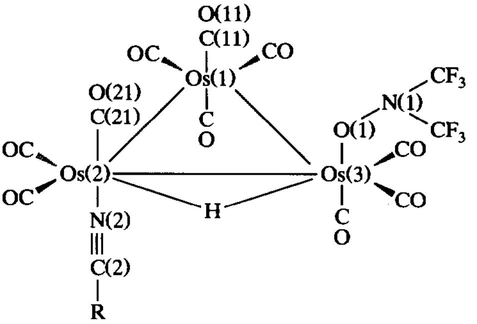
Selected bond lengths (Å) for $(\mu\text{-}H)Os_3(CO)_{10}L[ON(CF_3)_2]$ (L = CO, CH_3CN, PhCN)



	CO	CH_3CN	PhCN
Os(1)–Os(2)	2.901(1)	2.874(2)	2.876(1)
Os(1)–Os(3)	2.845(1)	2.860(2)	2.862(2)
Os(2)–Os(3)	2.999(1)	2.977(2)	2.982(2)
Os(3)–O(1)	2.107(8)	2.104(21)	2.115(9)
N(1)–O(1)	1.419(13)	1.442(34)	1.415(17)
Os(2)–N(2)	–	2.139(32)	2.073(13)
N(2)–C(2)	–	1.158(47)	1.158(20)

Table 2

Selected bond angles (deg) for (μ-H)$Os_3(CO)_{10}L[ON(CF_3)_2]$ (L = CO, CH_3CN, PhCN)



	CO	CH_3CN	PhCN
Os(1)–Os(2)–Os(3)	57.6(1)	58.5(1)	58.5(1)
Os(1)–Os(3)–Os(2)	59.5(1)	58.9(1)	58.9(1)
Os(2)–Os(1)–Os(3)	62.9(1)	62.6(1)	62.6(1)
Os(3)–O(1)–N(1)	115.0(6)	116.5(16)	114.6(8)
Os(1)–Os(3)–O(1)	86.1(2)	85.0(6)	89.1(3)
Os(2)–Os(3)–O(1)	83.6(2)	84.1(6)	84.5(3)
Os(3)–Os(1)–C(11)	88.4(4)	87.3(12)	84.1(5)
Os(3)–Os(2)–C(21)	88.5(3)	92.6(11)	89.5(6)
Os(1)–C(11)–O(11)	175.5(10)	177.8(30)	173.6(16)
Os(2)–C(21)–O(21)	172.3(10)	176.6(29)	173.2(16)
Os(2)–N(2)–C(2)	–	167.2(30)	174.7(13)
N(2)–C(2)–R	–	171.3(40)	177.0(16)

group assume average inclination angles to the Os_3 triangle of 88.5°, 90.0° and 86.8° for I, II and III, respectively. Thus it would appear that it is the interplay of the various structural parameters that determines the relative ease of rotation of the $(CF_3)_2N$ group about the Os–O bond as ascertained from the variable temperature ^{19}F NMR spectra.

Experimental

The starting materials $H_2Os_3(CO)_{10}$ [15] and $(CF_3)_2NO$ [1] were prepared by published methods and the latter was handled in a conventional vacuum line fitted with greaseless PTFE O-ring taps. The solvents for the reactions were distilled under nitrogen from appropriate drying agents. Thin layer chromatography was performed in air on plates coated with silica (Merck Kieselgel 60GF). IR spectra were recorded on a Perkin-Elmer 983G spectrometer and NMR data were collected in $CDCl_3$ on a Jeol FX 90Q FT NMR spectrometer. ^1H NMR was measured with respect to TMS and ^{19}F NMR with respect to CF_3COOH.

Crystal data for II

$[C_{14}H_4N_2O_{11}F_6Os_3]$, monoclinic, $P2_1/c$, $a = 13.392(7)$, $b = 8.889(4)$, $c = 19.673(9)$ Å, $\beta = 95.960(0)°$, $U = 2329.0(2)$ Å^3, $Z = 4$. $D_c = 3.022$ g cm^{-3}, $\mu = 164.52$ cm^{-1}; $T = 25°C$, Siemens R3m/v, Mo-K_α. Of 4383 data ($3.5 \leq 2\theta \leq 50.0°$), 3939 were independent ($R_{int} = 4.01\%$) and 2344 were observed $|5\sigma(F_o)|$. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized. $R(F) = 6.73\%$, $R_w(F) = 8.77\%$, GOF = 0.96. $\Delta/\sigma = 0.202$, $\Delta/\sigma_{max} = 0.003$. SHELXTL software was used for all computations. An empirical (psi-scan) correction was performed. The ratio of the transmission coefficients was 4.33. Tables of atomic coordinates, thermal parameters, bond parameters and structure factors are available as supplementary material.

Crystal data for III

$[C_{19}H_6N_2O_{11}F_6Os_3]$, monoclinic, $P2_1/c$, $a = 10.661(3)$, $b = 15.107(6)$, $c = 17.128(5)$ Å, $\beta = 102.470(0)°$, $U = 2693.5(15)$ Å^3, $Z = 4$. $D_c = 2.766$ g cm^{-3}, $\mu = 142.35$ cm^{-1}; $T = 25$°C, Siemens R3m/v, Mo-K_α. Of 3926 data ($3.5 \leq 2\theta \leq 45.0°$), 3531 were independent ($R_{int} = 5.24\%$) and 2637 were observed $|4\sigma(F_o)|$. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized. $R(F) = 3.80\%$, $R_w(F) = 4.73\%$, GOF = 0.95, $\Delta/\sigma = 0.078$, $\Delta/\sigma_{max} = 0.006$. SHELXTL software was used for all computations. An empirical (psi-scan) correction was performed. The ratio of the transmission coefficients was 1.38. Tables of atomic coordinates, thermal parameters, bond parameters and structure factors are available as supplementary material.

Synthesis of (μ-H)$Os_3(CO)_{10}[CH_3CN][(CF_3)_2NO]$

$H_2Os_3(CO)_{10}$ (35 mg, 41 μmol) was dissolved in CH_3CN in a reaction vessel and the solution was degassed. Excess CH_3CN was removed and 10 ml of CH_2Cl_2, followed by $(CF_3)_2NO$ (15 mg, 90 μmol) was condensed into the yellow solid of (μ-H)$HOs_3(CO)_{10}CH_3CN$ at liquid nitrogen temperature. The mixture was warmed up to room temperature and after stirring for 30 min, the solvent and volatile components were removed under vacuum. The solid residue was dissolved in CH_2Cl_2 and chromatographed on TLC plates using a CH_2Cl_2/hexane (4:6) mixture as eluent. The yellow solid extracted from the major band ($R_f = 0.41$) was recrystallized from CH_2Cl_2/hexane to afford yellow crystals of (μ-H)$Os_3(CO)_{10}$-$[CH_3CN][ON(CF_3)_2]$. Yield: 20 mg, 46%. Anal. Found: C, 15.85; H, 0.25; N, 2.17; F, 10.95. $C_{14}H_4N_2O_{11}F_6Os_3$ calc.: C, 15.84; H, 0.38; N, 2.64; F, 10.75%. IR (cyclohexane): ν(C–O) 2115w, 2078vs, 2068m, 2036vs, 2020s, 2007m, 1996m, 1980w, 1955w; ν(C–F) 1185w; ν(N–O) 1038w; ν(C–N) 957w cm^{-1}. ^{1}H NMR: δ 2.50 (s, CH_3), −11.74 (s, Os–H) ppm.

Synthesis of (μ-H)$Os_3(CO)_{10}[PhCN][(CF_3)_2NO]$

A similar procedure as above was applied for the reaction of (μ-H)$HOS_3(CO)_{10}$PhCN (prepared from 64 mg, 75 μmol of $H_2OS_3(CO)_{10}$) with $(CF_3)_2NO$ (24 mg, 142 μmol). Yellow crystals of (μ-H)$Os_3(CO)_{10}$[PhCN] $[ON(CF_3)_2]$ were obtained from the major band ($R_f = 0.45$) upon TLC of the crude product and further recrystallization from CH_2Cl_2/hexane. Yield: 24 mg, 29%. Anal. Found: C, 20.80; H, 0.71, F: 10.60. $C_{19}H_6N_2O_{11}F_6Os_3$ calc.: C, 20.31; H, 0.53; F, 10.15%. IR (cyclohexane): ν(C–O) 2114w, 2078vs, 2069m, 2036vs, 2020s, 2007m, 2000m, 1980w, 1960w; ν(C–F) 1180w; ν(N–O) 1017w; ν(C–N) 955w cm^{-1}. ^{1}H NMR: δ 7.59 (m, 5H, C_6H_5), −11.65 (s, Os–H) ppm.

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