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Synthesis, and ^{19}F NMR and X-ray structural studies of triosmium clusters (μ-H)Os$_3$(CO)$_{10}$L[ON(CF$_3$)$_2$] (L = PPh$_3$, AsPh$_3$ and SbPh$_3$)

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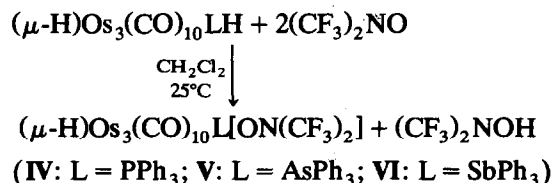(Received September 25, 1992; in revised form October 31, 1992)

Abstract

Bis(trifluoromethyl)nitroxyl radical reacts with H$_2$Os$_3$(CO)$_{10}$L (L = PPh$_3$, AsPh$_3$, SbPh$_3$) to afford the derivatives (μ-H)Os$_3$(CO)$_{10}$L[ON(CF$_3$)$_2$] in which the (CF$_3$)$_2$NO moiety is revealed by single crystal X-ray determinations to assume an axial position. Variable-temperature ^{19}F NMR spectral studies indicate that the two CF$_3$ groups of the (CF$_3$)$_2$N moiety become magnetically different at lower temperature due to restricted rotation about the N–O bond. The activation energies estimated from the coalescence temperatures are 54.4 and 52.3 kJ/mole for (μ-H)Os$_3$(CO)$_{10}$PPh$_3$[ON(CF$_3$)$_2$] and for (μ-H)Os$_3$(CO)$_{10}$AsPh$_2$-[ON(CF$_3$)$_2$] respectively.

1. Introduction

Recently, we have shown that (CF$_3$)$_2$NO radical reacts with (μ-H)Os$_3$(CO)$_{10}$HL (L = CO (**I**), CH$_3$CN (**II**) and PhCN (**III**)) to afford (μ-H)Os$_3$-(CO)$_{10}$[ON-(CF$_3$)$_2$]L where the (CF$_3$)$_2$NO group resides in the axial position [1,2]. We report below the syntheses, X-ray structural and spectroscopic properties of three new substituted triosmium carbonyl clusters, namely (μ-H)Os$_3$(CO)$_{10}$L[ON(CF$_3$)$_2$] (L = PPh$_2$ (**IV**), AsPh$_3$ (**V**), SbPh$_3$ (**VI**)).

Reactions of (CF$_3$)$_2$NO radical with H$_2$Os$_3$(CO)$_{10}$L (L = PPh$_3$, AsPh$_3$, SbPh$_3$] in a 2 : 1 molar ratio readily afford the triosmium cluster derivatives (μ-H)Os$_3$-(CO)$_{10}$L[ON(CF$_3$)$_2$] together with (CF$_3$)$_2$NOH, as shown by the equation:

$$(\mu\text{-H})Os_3(CO)_{10}LH + 2(CF_3)_2NO$$

$$\downarrow {\scriptstyle \begin{array}{c} CH_2Cl_2 \\ 25°C \end{array}}$$

$$(\mu\text{-H})Os_3(CO)_{10}L[ON(CF_3)_2] + (CF_3)_2NOH$$

(**IV**: L = PPh$_3$; **V**: L = AsPh$_3$; **VI**: L = SbPh$_3$)

Yellow crystals of **IV**, *V* and *V*I were obtained in over 60% yield from the crude products by TLC followed by recrystallisation using CH$_2$Cl$_2$/hexane. **IV**, **V** and **VI**

have been characterised by elemental analysis (C, H, F), IR and ^{1}H and ^{19}F NMR spectroscopic data and single crystal X-ray structural analysis.

^{1}H NMR spectra of **IV**, **V** and **VI** display peaks at −13.8(d), −14.2(s) and −14.2(s) ppm, respectively, all of which are indicative of the presence of bridging hydride. The variable temperature ^{19}F NMR spectra are summarised in Fig. 1. Whereas singlets are obtained at room temperature (25°C) in the spectra of **IV** and **V**, the spectra at low temperatures display two quartets for **IV** and a doublet for **V** (Fig. 1). Similar temperature dependence of ^{19}F NMR has been observed for **I**, **II** and **III** and this has been rationalised on the basis of restricted rotation of the (CF$_3$)$_2$N moiety about the N–O bond [1,2]. The ^{19}F NMR spectra for **VI**, however, remain as a singlet throughout the temperature range employed. The variations of ^{1}H and ^{13}C NMR in H$_2$Os$_3$(CO)$_{10}$ and H$_2$Os$_3$(CO)$_{10}$L (L = Lewis bases) [3,4] have been rationalised in terms of fluxional exchange processes involving the two hydrides and two carbonyls. The activation energies for **IV** and **V** as estimated from the coalescence temperature [5] are 54.4 and 52.3 kJ mol^{-1} respectively which are similar to those of **I**, **II** and **III** (65.1, 62.1 and 63.3 kJ mol^{-1} respectively).

The molecular structures of **IV**, **V** and **VI** have been determined by single-crystal X-ray diffraction and are shown in Figs. 2–4. Selected bond distances and angles
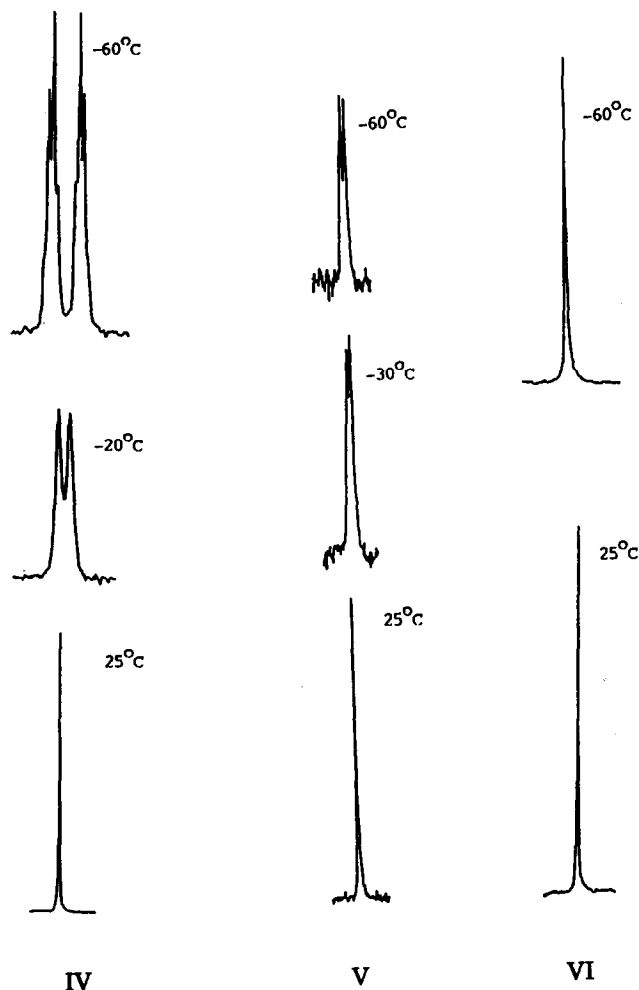
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Fig. 1. Variable-temperature ¹⁹F NMR spectra of IV: (μ-H)Os₃-(CO)₁₀(PPh₃)[ON(CF₃)₂], V: (μ-H)Os₃(CO)₁₀(AsPh₃)[ON(CF₃)₂], VI: (μ-H)Os₃(CO)₁₀(SbPh₃)[ON(CF₃)₂].

Fig. 2. The crystal and molecular structure of Os₃(CO)₁₀(PPh₃)-[(CF₃)₂NO] showing the numbering scheme.

are given in Table 1. Whereas the structures of IV and VI are isomorphous with H₂Os₃(CO)₁₁ and Os₃(CO)₁₂, V crystallises out as $P\bar{1}$ with two inequivalent molecules in the unit cell. As has been found for I, II and III, the (CF₃)₂NO moiety bonds to an Os atom at an axial position in IV, V and VI. The effect of the bridging hydride and the bulky MPh₃ group has been to increase the separation of the two osmium atoms containing the (CF₃)₂NO group and the MPh₃ moiety respectively, resulting in this being the longest Os–Os distance in each of the three clusters. These bond distances are also longer than the corresponding Os–Os distances in I, II and III; and for cluster IV, it is comparable to that of 3.019 Å in (μ-H)HOs₃(CO)₁₀-PPh₃ [6]. On the other hand, the shortest Os–Os distance is the Os–Os edge bearing the unsubstituted Os and that bonded to the (CF₃)₂NO group. Hence the presence of the (CF₃)₂NO group at the Os has caused the Os–Os distance to be significantly shorter than the

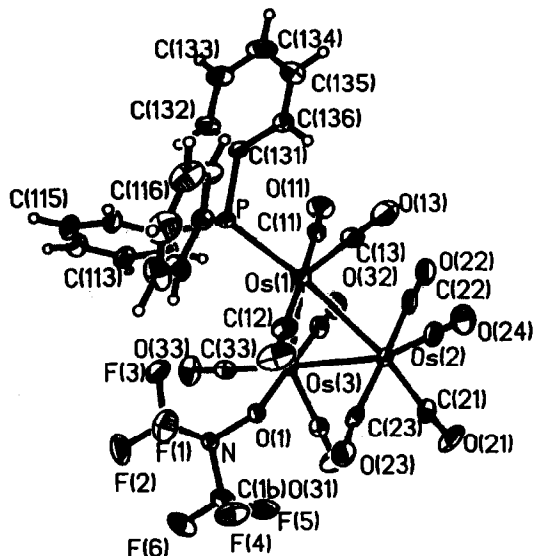average Os–Os distance of 2.877 Å in Os₃(CO)₁₂ [7]. The third edge, which ranges from 2.866–2.905 Å for these three clusters, decreases in the order M = P > As > Sb.

The Os–O(1) bond distance falls within a narrow range of 2.068–2.114 Å, and is comparable to that of 2.107(8) Å in I [1]. This bond is long, presumably due to the electron withdrawing nature of the CF₃ groups. The N(1)–O(1) distance in each case is also very similar to that of I. On the other hand, the Os–M distance decreases in the order M = Sb > As > P. And for cluster IV, the Os–P distance is comparable to that in (μ-H)HOs₃(CO)₁₀PPh₃ and in Os₃(CO)₁₁PPh₃ [8], which also happens to be 2.370 Å in each case.

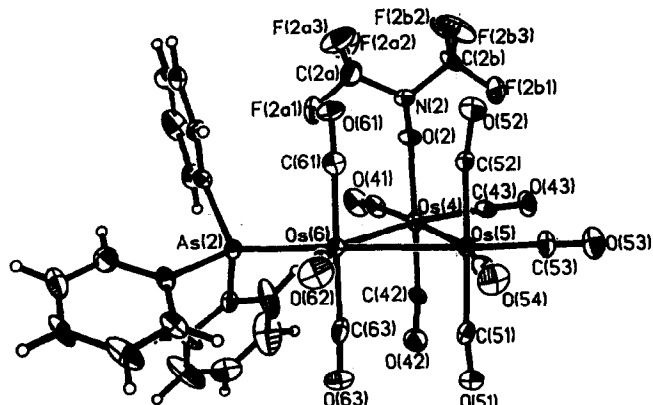The carbonyl groups are essentially linear, and the axial Os–C distances are longer than the equatorial

Fig. 3. The crystal and molecular structure of Os₃(CO)₁₀(AsPh₃)-[(CF₃)₂NO] showing the numbering scheme.
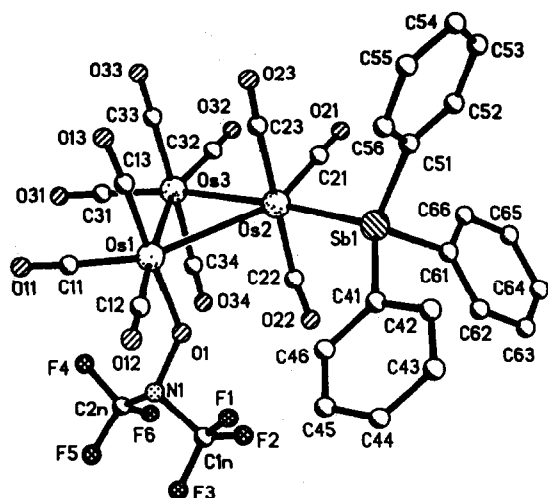
Fig. 4. The crystal and molecular structure of Os₃(CO)₁₀(SbPh₃)-
[(CF₃)₂NO] showing the numbering scheme.

Os–C distance, except for those on the Os, which is linked to the (CF₃)₂NO group. In fact the axial CO group that is *trans* to the nitroxy group has the shortest Os–C distance of all the CO groups.

2. Experimental details

The starting materials H₂Os₃(CO)₁₀ [9] and (CF₃)₂-NO [10] 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 CDCl₃ on a Jeol FX 90Q FT NMR spectrometer. ^{1}H NMR was measured with respect to TMS and ^{19}F NMR with respect to CF₃COOH.

2.1. Crystal data for IV

[C₃₀H₁₅NO₁₁F₆POs₃], monoclinic, $P2_1/c$, $a = 8.576(2)$, $b = 22.644(5)$, $c = 18.467(4)$ Å, $\beta = 91.85$ (3)°, $U = 3584.3$ (14) Å³, $Z = 4$. $D_c = 2.374$ g cm⁻³, $\mu = 107.54$ cm⁻¹; $T = 25$°C, Siemens R3m/v, Mo Kα. Of 6742 data ($3.0 \leq 2\theta \leq 50.0$°), 6136 were independent ($R_{int} = 2.78\%$) and 4479 were observed $|6\sigma(F_o)|$. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealised. $R(F) = 3.52\%$, $R(_wF) = 4.81\%$, GOF = 0.88. $\Delta/\sigma = 0.387$, $\Delta/\sigma_{max} = 0.096$. SHELXTL software used for all computations [11]. 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.
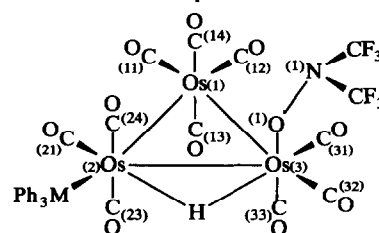
2.2. Crystal data for V

[C₃₀H₁₅NO₁₁F₆AsOs₃], triclinic, $P\bar{1}$, $a = 10.882$ (2), $b = 15.022$ (3), $c = 22.839$ (5) Å, $\alpha = 106.07$ (3)°, $\beta = 92.64$ (3)°, $\gamma = 91.62$ (3)°, $U = 3580.6$ (12) Å³. $Z = 4$, $D_c = 2.458$ g cm⁻³, $\mu = 116.37$ cm⁻¹; $T = 25$°C, Siemens R3m/v, Mo Kα. Of 12870 data ($3.5 \leq 2\theta \leq 45$°), 1220 were independent ($R_{int} = 1.96\%$) and 6853 were observed $|6\sigma(F_o)|$. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealised $R(F) = 4.05\%$, $R(_wF) = 4.58\%$, GOF = 1.07. $\Delta/\sigma = 0.036$, $\Delta/\sigma_{max} = 0.003$. SHELXTL software used for all computations [11]. An expirical (psi-scan) correction was performed. The

TABLE 1. Selected bond lengths (Å) and bond angles with e.s.d.s for (μ-H)Os₃(CO)₁₀L[ON(CF₃)₂] (L = CO, PPh₃, AsPh₃, SbPh₃)

L	CO	PPh₃	ᵃ AsPh₃	SbPh₃
Os(1)–Os(2)	2.901(1)	2.905(1)	2.893(1)	2.866(4)
			2.899(1)	
Os(1)–Os(3)	2.845(1)	2.844(1)	2.851(1)	2.845(4)
			2.844(1)	
Os(1)–Os(3)	2.999(1)	3.011(1)	3.020(1)	3.005(5)
			3.043(1)	
Os(3)–O(1)	2.107(8)	2.113(7)	2.130(10)	2.114(13)
			2.068(10)	
N(1)–O(1)	1.419(3)	1.420(10)	1.412(18)	1.418(25)
			1.412(16)	
Os(2)–M	–	2.370(3)	2.473(2)	2.609(4)
			2.481(2)	
Os(1)–Os(2)–Os(3)	57.6(1)	57.4(1)	56.6(1)	57.9(1)
			57.1(1)	
Os(1)–Os(3)–Os(2)	59.5(1)	59.4(1)	59.0(1)	58.6(1)
			58.9(1)	
Os(2)–Os(1)–Os(3)	62.9(1)	63.2(1)	63.4(1)	63.5(1)
			64.0(1)	
Os(3)–Os(1)–N(1)	115.0(6)	113.7(5)	114.4(7)	115.8(11)
			117.6(7)	
Os(1)–Os(3)–O(1)	86.1(2)	88.2(2)	86.2(3)	84.5(4)
			87.6(3)	
Os(2)–Os(3)–O(1)	83.6(2)	85.2(2)	86.7(3)	84.6(4)
			85.2(3)	
Os(3)–Os(2)–M	116.1(4)	120.0(1)	111.6(1)	119.3(1)
			109.4(1)	

ᵃ the unit cell of (μ-H)Os₃(CO)₁₀AsPh₃[ON(CF₃)₂] has been found to contain two independent molecules

Structure of (μ-H)Os₃(CO)₁₀MPh₃[ON(CF₃)₂]

ratio of the transmission coefficients was 2.14. Tables of atomic coordinates, thermal parameters, bond parameters and structure factors are available as supplementary material.

2.3. Crystal data for VI

[C$_{30}$H$_{15}$NO$_{11}$F$_6$SbOs$_3$], monoclinic, $P2_1/c$, $a = 17.09(3)$, $b = 9.726(8)$, $c = 22.010(12)$ Å, $\beta = 98.94$ (9)°, $U = 3613(6)$ Å^3, $Z = 4$. $D_c = 2.522$ g cm^{-3}, $\mu = 113.62$ cm^{-1}; $T = 25°C$, Siemens R3m/v, Mo Kα. Of 6958 data ($3.0 \leq 2\theta \leq 50.0°$), 6323 were independent ($R_{int} = 5.74\%$) and 3204 were observed $|4\sigma(F_o)|$. The structure was solved by direct methods. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealised. $R(F) = 5.51\%$, $R(_wF) = 4.70\%$, GOF = 1.32. $\Delta/\sigma = 1.209$, $\Delta/\sigma_{max} = 0.160$. SHELXTL software was used for all computations [11]. An empiricial (psi-scan) correction was performed. The ratio of the transmission coefficients was 1.56. Tables of atomic coordinates, thermal parameters, bond parameters and structure factors are available as supplementary material.

2.4. Synthesis of (μ-H)Os$_3$(CO)$_{10}$(PPh$_3$)[ON(CF$_3$)$_2$] (IV)

A mixture of H$_2$Os(CO)$_{10}$ (32.6 mg, 38.2 μmol) and PPh$_3$ (10 mg, 38.2 μmol) was dissolved in 10 ml CH$_2$Cl in a reaction vessel which was first evacuated. A yellow solution of (μ-H)Os$_3$(CO)$_{10}$PPh$_3$H was obtained instantaneously. The solution was stirred for five minutes after which (CF$_3$)$_2$NO (20.5 mg, 122 μmol) was condensed in at liquid nitrogen temperature. The resultant mixture was warmed up to room temperature and stirred vigorously for 30 mins, before the solvent and volatile components were removed under vacuum. The solid residue was dissolved in CH$_2$Cl$_2$ and chromatographed on TLC plates using CH$_2$Cl$_2$/hexane (4:6) mixture as eluent. The yellow solid extracted from the major band ($R_f = 0.60$) was recrystallised from CH$_2$Cl$_2$/hexane to afford yellow crystals of (μ-H)Os$_3$(CO)$_{10}$(PPh$_3$)ON(CF$_3$) yield: 29 mg; 60%. Anal. Found: C, 27.98; H, 1.24; N, 1.36; F, 9.20. C$_{30}$H$_{16}$O$_{12}$F$_6$POs$_3$ calc.: C, 28.09; H, 1.25; N, 1.09; F, 8.90%. IR (cyclohexane) ν(C–O) 2117m, 2079s, 2066s, 2035vs, 2022vs, 2012s, 2004m, 1992w, 1980w, 1971w, ν(N–O) 1185w; ν(C–N) 955w cm^{-1}. ^{1}H NMR: δ 7.53 (m, C$_6$H$_6$), −13.79 (d, Os–H) ppm.

2.5. Synthesis of (μ-H)Os$_3$(CO)$_{10}$(AsPh$_3$)[ON(CF$_3$)$_2$] (V)

A similar procedure as above was applied for the reaction of (μ-H)HOs$_3$(CO)$_{10}$(AsPh$_3$) (prepared from 32.0 mg, 39.9 μmol of H$_2$Os$_3$(CO)$_{10}$) with (CF$_3$)$_2$NO

(13.7 mg, 81.5 μmol). Yellow crystals of (μ-H)Os$_3$(CO)$_{10}$(AsPh$_3$)[ON(CF$_3$)$_2$] were obtained from the major band ($R_f = 0.62$) upon TLC of the crude product and further recrystallisation from CH$_2$Cl$_2$/hexane yield: 36.2 mg, 68.4%. Anal. Found: C; 27.29; H, 1.22; N, 1.08; F, 8.5V. C$_{30}$H$_{16}$O$_{12}$F$_6$AsOs$_3$ calc.: C, 27.16; H, 1.21; N, 1.06; F, 8.60%. IR (cyclohexane) ν(C–O) 2117m, 2079s, 2066s, 2035vs, 2021vs, 2012s, 2004m, 1991w, 1980w, 1970w; ν(N–O) 1078w; ν(C–N) 955w cm^{-1}. ^{1}H NMR: δ 7.51 (m, C$_6$H$_5$), −13.88 (s, Os–H) ppm.

2.6. Synthesis of (μ-H)Os$_3$(CO)$_{10}$(SbPh$_3$)[ON(CF$_3$)$_2$] (VI)

A similar procedure as for IV was applied for the reaction of (μ-H)HOs$_3$(CO)$_{10}$(SbPh$_3$) (prepared from 36.4 mg, 42.7 μmol of H$_2$Os$_3$(CO)$_{10}$) with (CF$_3$)$_2$NO (19.7 mg, 117 μmol). Yellow crystals of (μ-H)Os$_3$-(CO)$_{10}$(SbPh$_3$)[ON(CF$_3$)$_2$] were obtained from the major band ($R_f = 0.64$) upon TLC of the crude product and further recrystallisation from CH$_2$Cl$_2$/hexane yield: 40.0 mg, 68.3%. Anal. Found: C; 26.38; H, 1.12; N, 1.06; F, 8.78. C$_{30}$H$_{16}$O$_{12}$F$_6$SbOs$_3$ calc.: C, 26.23; H, 1.17; N, 1.02; F, 8.30%. IR (cyclohexane) ν(C–O) 2115m, 2079s, 2067s, 2035vs, 2022vs, 2012s, 2003m, 1991w, 1981w, 1952w; ν(N–O) 1068w; ν(C–N) 956w cm^{-1}. ^{1}H NMR: δ 7.54 (m, C$_6$H$_5$), −14.24 (s, Os–H) ppm.

Acknowledgments

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