The Stepwise Hydrogenation of a Nitrile Group on an Osmium Cluster; the X-Ray Crystal Structures of [H₂Os₃(μ₃-NCH₂CF₃)(CO)₉] and [H₄Os₃(μ₃-NCH₂CF₃)(CO)₈]

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An X-ray diffraction study of [H(μ_2-H)$_3$Os$_3$(μ_3-NCH$_2$CF$_3$)(CO)$_8$] is the first for a trinuclear cluster containing four metal-bound H atoms; this complex, together with [(μ_2-H)Os$_3$(μ_2-NHCH$_2$CF$_3$)(CO)$_{10}$] and [(μ_2-H)$_2$Os$_3$(μ_3-NCH$_2$CF$_3$)(CO)$_9$] (for which X-ray data are also presented), is obtained from the hydrogenation of CF$_3$CN on an Os$_3$ cluster, and a scheme for the mechanism of this hydrogenation is presented.

The pathways involved in the selective reduction of small molecules bound to transition metal carbonyl clusters are the subjects of recent studies.[1,2] Kaesz has outlined a partial model for the reduction of a nitrile group on a tri-iron cluster,[3] and we now report our results on the reduction of CF$_3$CN by [H$_2$Os$_3$(CO)$_{10}$] and molecular hydrogen; the results presented here take this model one stage further, and suggest that alternative pathways for the reduction are possible.

The reaction of CF$_3$CN with [H$_2$Os$_3$(CO)$_{10}$] in a sealed tube gives [(μ_2-H)Os$_3$(CO)$_{10}$\{μ_2-η^1-NC(H)CF$_3$\}] (1) and [(μ_2-H)-Os$_3$(CO)$_{10}$(μ_2-η^2-HNCCF$_3$)] (2) in 69% and 14% yields, respectively.[4] Treatment of (1) with molecular hydrogen (49 atm, 140 °C, 16 h) leads to the formation of three complexes [(μ_2-H)Os$_3$(CO)$_{10}$(μ_2-HNCH$_2$CF$_3$)] (3), [(μ_2-H)$_2$Os$_3$-(CO)$_9$(μ_3-NCH$_2$CF$_3$)] (4), and [H(μ_2-H)$_3$Os$_3$(CO)$_8$(μ_3-NCH$_2$-CF$_3$)] (5), in approximately equal yields (ca. 25%). These molecules were partially characterised by their spectroscopic properties,† and the structures have now been established by X-ray diffraction studies. The molecular structure of (3) is analogous to that of [(μ_2-H)Os$_3$(CO)$_{10}$(μ_2-NHSO$_2$C$_6$H$_4$Me)]^5 and will be published elsewhere.[6] The molecular structures of (4) and (5) are shown in Figures 1 and 2, together with some important bond parameters.‡ The structure of (4) § is closely
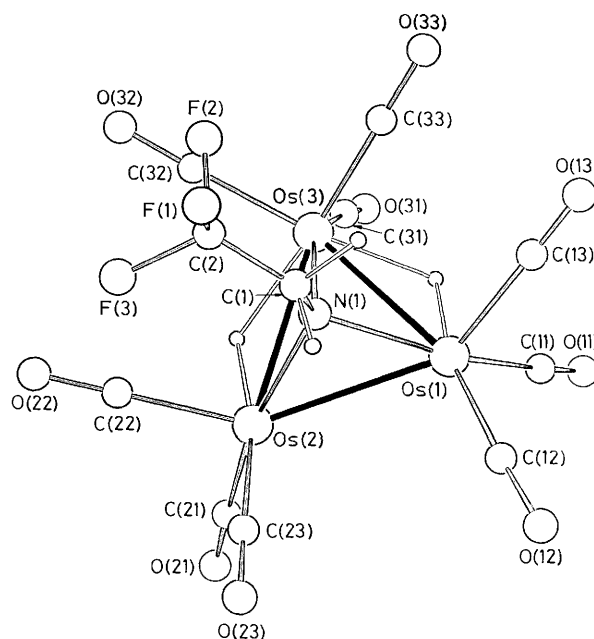

Figure 1. The structure of the complex [(μ-H)$_2$Os$_3$(μ_3-NCH$_2$CF$_3$)(CO)$_9$] (4); Os(1)–Os(2) 2.863(1), Os(1)–Os(3) 2.717(1), Os(2)–Os(3) 2.856(1), Os–N 2.056—2.119(13), and N–C(1) 1.443(23) Å. Mean Os–C = 1.915, C–O = 1.139 Å, and Os–C–O = 177°.

analogous to that of [(μ_2-H)$_2$Os$_3$(μ_3-NMe)(CO)$_9$] reported during the course of this study,[7] and that of (5) ¶ is derived from (4) by what is formally an oxidative addition involving CO loss and incorporation of a terminal and a μ_2-H atom into the cluster. The added μ_2-H atom was not located in the analysis, but is presumably located along the Os(1)–Os(3) edge of the triangle, as evidenced by the equivalence of the three

† Selected spectroscopic data: Compound (3), v$_{CO}$ (C$_6$H$_{14}$) 2106w, 2069vs, 2054s, 2033m, 2023s, 2008sh, 2005s, 1997sh, 1993s, and 1981m cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$) δ 7.65 (1H, s, NH), 4.18 (2H, m, CH), and −14.84 (1H, s, OsH). Compound (4), v$_{CO}$ (C$_6$H$_{14}$) 2119m, 2082s, 2056vs, 2035vs, 2010sh, 2005vs, 1992s, 1976m, and 1953w cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$) δ 4.48 [2H, q, ^{3}J(HF) 8 Hz, CH_2] and −18.57 (1H, s, OsH). Compound (5), v$_{CO}$ (C$_6$H$_{14}$) 2122w, 2104s, 2045m, 2043m, 2034vs, 2026sh, 2022m, 1964w, and 1957m cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$) δ 4.77 [2H, q, ^{3}J(HF) 7 Hz, CH_2], −12.29 [1H, d, ^{3}J(HH) 10 Hz, OsH], −16.11 [1H, d, ^{3}J(HH) 10 Hz, OsH], −17.85 (1H, s, OsH), and −19.01 (1H, s, OsH).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Crystal data for (4): C$_{11}$H$_4$F$_3$NO$_9$Os$_3$, M = 921.76, monoclinic, a = 9.383(2), b = 12.388(2), c = 16.171(3) Å, β = 97.79(2)°, U = 1862.32 Å^3, D_c = 3.279 g cm^{-3}, Z = 4, F(000) = 1612, μ(Mo-K_α) = 196.87 cm^{-1}, Mo-K_α radiation, space group $P2_1/c$. 3091 reflections [$I > 3\sigma(I)$] were collected on a Philips PW1100 4-circle diffractometer (3 ≤ θ ≤ 25°) and were corrected for absorption. The structure was solved by the Patterson method and refined by full matrix least-squares to an R value of 0.051 [R_w = 0.053 with $w = 1/\sigma^2(F_0)$] and 245 parameters.

¶ Crystal data for (5): C$_{10}$H$_6$F$_3$NO$_8$Os$_3$, M = 895.76, monoclinic, a = 17.387(3), b = 8.137(2), c = 26.142(3) Å, β = 99.15(2)°, U = 3651.47 Å^3, D_c = 3.258 g cm^{-3}, Z = 8, F(000) = 3136, μ(Mo-K_α) = 200.75 cm^{-1}, Mo-K_α radiation, space group $C2/c$. 1944 reflections [$I > 3\sigma(I)$] were collected on a Philips PW1100 4-circle diffractometer (3 ≤ θ ≤ 25°) and were corrected for absorption. The structure was solved by the Patterson method and refined by full matrix least-squares to an R value of 0.046 [R_w = 0.046 with $w = 1/\sigma^2(F_0)$] and 151 parameters.
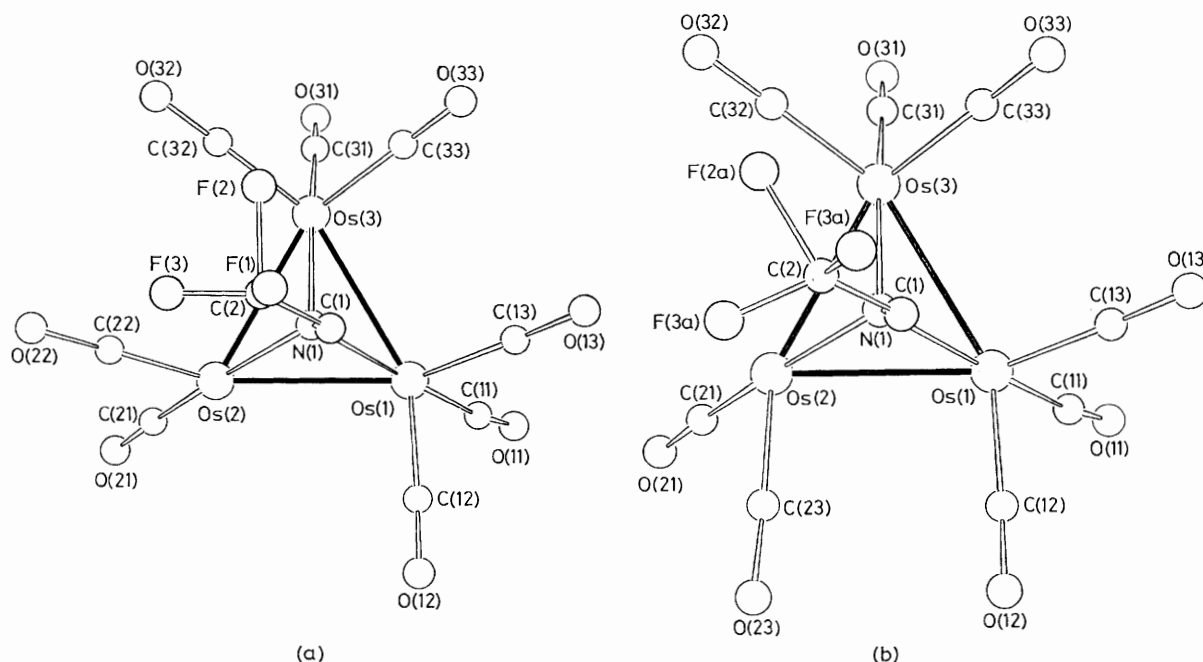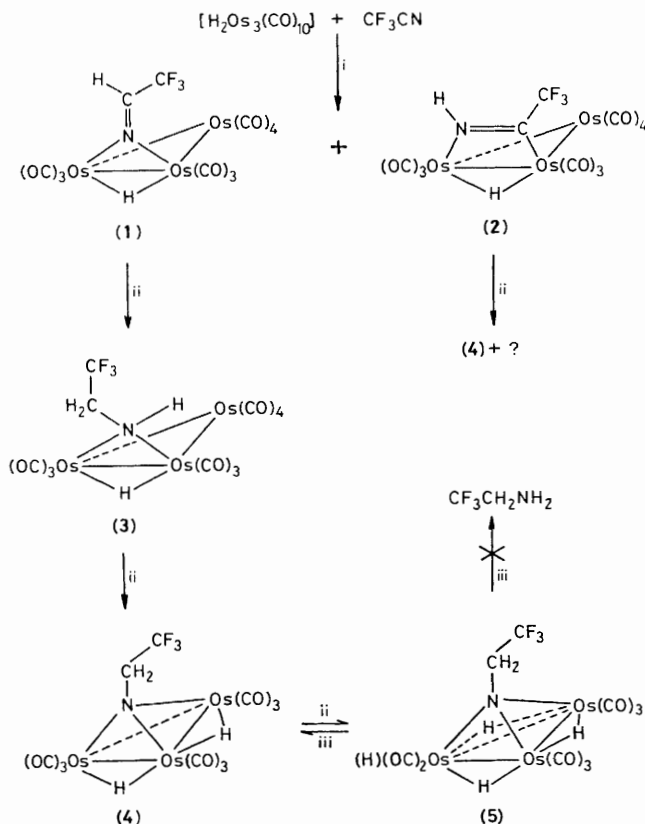
Figure 2. The structure of the complex $[(\mu\text{-}H)_3HOs_3(\mu_3\text{-}NCH_2CF_3)(CO)_8]$ **(5)**, showing the disorder between the terminal Os–H and carbonyl ligands on Os(2); Os(1)–Os(2) 2.862(1), Os(1)–Os(3) 2.870(1), Os(2)–Os(3) 2.861(1), Os–N 1.900—2.072(20), and N–C(1) 1.48(2) Å. Mean Os–C = 1.892, C–O = 1.172 Å, and Os–C–O = 176°.

Scheme 1. *Reagents and conditions:* 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).

Os–Os bond lengths in **(5)** and their non-equivalence in **(4)**. The terminal H atom 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 2(a) and (b)]. The N–C bond lengths in **(4)** and **(5)** are as expected for a single N–C bond.

Although other trinuclear clusters containing four metal-bound H atoms have been synthesised[8–10] **(5)** is the first for which an *X*-ray analysis reveals the presence of a terminal H 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 H ligand on each metal atom.[11]

The isolation of **(1)**, **(3)**, **(4)**, and **(5)** suggests a model for the hydrogenation of a nitrile ligand on a trinuclear cluster as shown in Scheme 1. The model differs from that outlined by Kaesz[3] in that the hydrogenation of a μ_2-alkylideneimino rather than a μ_3-alkylideneimino ligand is proposed. We cannot exclude the possibility, however, that **(4)** is also formed from **(1)**, in part, *via* the hydrogenation of an intermediate μ_3-ligand complex, which is not present in significant concentrations at the conclusion of the hydrogenation reaction.

Attempts to complete the cycle by treating **(5)** with CO (50 atm, 140 °C, 18 h) were unsuccessful. Instead **(4)** is regenerated in quantitative yields illustrating the stability of this nitrene-capped cluster. The formation of **(5)** does demonstrate, however, that the oxidative addition of molecular hydrogen to clusters, to give highly hydrogenated species containing terminally-bound H atoms, is a feasible pathway in the selective reduction of small molecules.

The reduction of **(2)** by molecular hydrogen gives **(4)** (80%) and two other complexes in yields too low to permit adequate characterisation.

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