DALTON COMMUNICATION

Synthesis and characterization of triosmium clusters containing a nitrite ligand; crystal and molecular structures of $[N(PPh_3)_2][Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$

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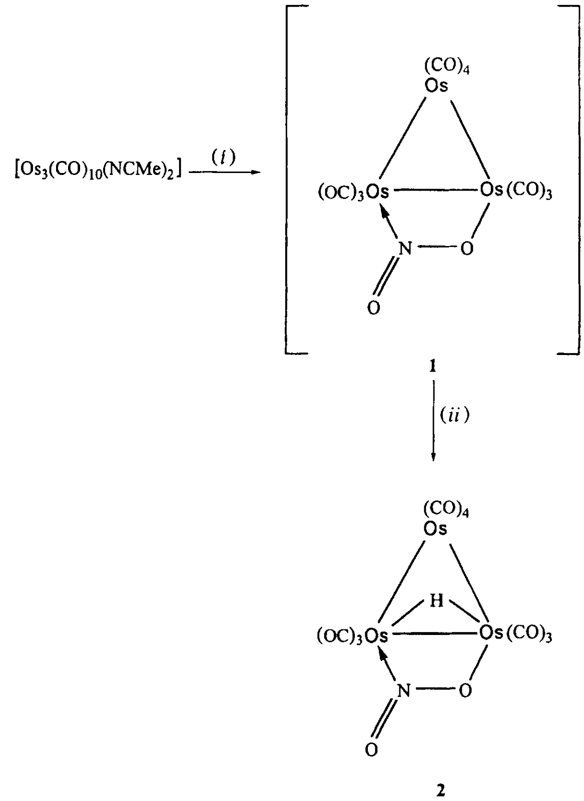
The cluster $[Os_3(CO)_{10}(NCMe)_2]$ reacted with $[N(PPh_3)_2]NO_2$ in CH_2Cl_2 to give a novel red-orange complex $[N(PPh_3)_2][Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ in moderate yield, which underwent protonation with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 to give the neutral complex $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ in high yield; X-ray crystal-structure analyses have shown that both clusters contain a μ-η^2-bridging nitrite ligand.

It has been shown that the nitrite ligand can co-ordinate to metal centres in various co-ordination modes.[1,2] This ligand is also capable of undergoing oxygen transfer to an adjacent carbonyl group.[3] It is believed that transition-metal nitrite clusters may be a useful model for investigating the mechanism of NO_2 reduction and oxygen-transfer reactions to an unsaturated carbon atom. The chemistry of transition-metal nitrite complexes is well studied for Co, Ni, Cu, Pd, Pt and Re.[1–10] However, nitrite complexes of osmium are relatively rare. Therefore, we would like to investigate the chemistry of osmium-nitrite clusters. Herein, we report the synthesis and full characterization of $[N(PPh_3)_2][Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ **1** and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ **2**.

The cluster $[Os_3(CO)_{10}(NCMe)_2]$, dissolved in CH_2Cl_2, was treated with one equivalent of $[N(PPh_3)_2]NO_2$ at 40 °C. The yellow solution was stirred under an argon atmosphere and heated to reflux for 45 min to give a red-orange solution. This was concentrated under reduced pressure and the orange product $[N(PPh_3)_2][Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ **1** isolated and purified by thin-layer chromatography (TLC) on alumina plates using CH_2Cl_2–*n*-hexane (70:30, v/v) as eluent. It was recrystallized by slow evaporation of a cyclohexane–CH_2Cl_2 solution at room temperature to give red-orange, rod-shaped crystals in 65% yield (Found: C, 38.75; H, 2.05; N, 1.90; P, 4.10. Calc. for $C_{46}H_{30}N_2O_{12}Os_3P_2$: C, 38.45; H, 2.10; N, 1.95; P, 4.30%). The complex anion of **1** undergoes protonation with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at room temperature in an argon atmosphere. The orange solution changed to yellow immediately and it was stirred for 30 min for complete reaction. The solution was concentrated under reduced pressure and separated by TLC on silica plates using CH_2Cl_2–*n*-hexane (60:40, v/v) as eluent. The crude yellow product was recrystallized by slow evaporation of an *n*-hexane–$CHCl_3$ solution at room temperature to give yellow microcrystals of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ **2** in 90% yield (Found: C, 13.55; H, <0.3; N, 1.70. Calc. for $C_{10}HNO_{12}Os_3$: C, 13.40; H, 0.10; N, 1.55%) (Scheme 1). Single-crystal X-ray analyses were carried out to determine the molecular structures of **1** and **2**.†

The ^1H NMR spectrum of complex **1** in CD_2Cl_2 reveals the absence of metal hydride and the IR spectrum that only terminal carbonyl ligands are present. The solid-state IR (KBr disc) spectrum contains weak bands at 1116 and 1440 cm^{-1} attributed to $\nu(NO_2)$.‡ A perspective view of complex **1** is shown in Fig. 1. The Os(1) atom has four terminal ligands while the other two osmium atoms, Os(2) and Os(3) are bonded to three terminal carbonyl ligands and a nitrite ligand bridges them in a μ-η^2 mode. The metal framework is an irregular



Scheme 1 (*i*) $[N(PPh_3)_2]NO_2$, 40 °C; (*ii*) $HBF_4{\cdot}Et_2O$, room temperature

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† Crystal data: **1**, $C_{46}H_{30}NO_{12}Os_3P_2$, M = 1435.30, triclinic, space group $P\bar{1}$ (no. 2), a = 11.055(1), b = 12.301(1), c = 18.914(2) Å, α = 71.18(2), β = 73.18(2), γ = 85.28(2)°, U = 2336.4(8) Å^3, Z = 2, D_c = 2.040 g cm^{-3}, $F(000)$ = 1348, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 82.64 cm^{-1}, dimensions 0.22 × 0.24 × 0.38 mm, 4230 observed diffractometer data [$I > 3\sigma(I)$], ψ-scan absorption correction, structure solved by direct methods (SIR 88)[11] and Fourier-difference techniques, refined by full-matrix least-squares analysis (Os, P, O and C on the cluster anion anisotropic) to R = 0.062, R' = 0.072, $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o)^2]$; **2**, $C_{10}HNO_{12}Os_3$, M = 897.72, monoclinic, space group $P2_1/c$ (no. 14), a = 9.385(3), b = 9.672(3), c = 19.029(5), β = 90.08(2)°, U = 1727.4(7) Å^3, Z = 4, D_c = 3.452 g cm^{-3}, $F(000)$ = 1568, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 220.60 cm^{-1}, dimensions 0.23 × 0.28 × 0.40 mm. Crystal system is monoclinic as the Laue symmetry $2/m$ is although the β angle is *ca.* 90°; 1396 observed diffractometer data [$I > 3\sigma(I)$], ψ-scan absorption correction, structure solved and refined as for **1** to R = 0.032, R' = 0.027, $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o)^2]$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/62.

‡ Spectroscopic data for **1**: IR [ν(CO), CH_2Cl_2] 2119w, 2082s, 2071m, 2023vs, 2011vs, 1988s and 1951s cm^{-1}; IR [$\nu(NO_2)$, KBr] 1440w and 1116w cm^{-1}; negative-ion FAB mass spectrum m/z 898 (calc. 898); ^1H NMR (CD_2Cl_2) δ 7.24–7.41 (m, 30 H, phenyl H).

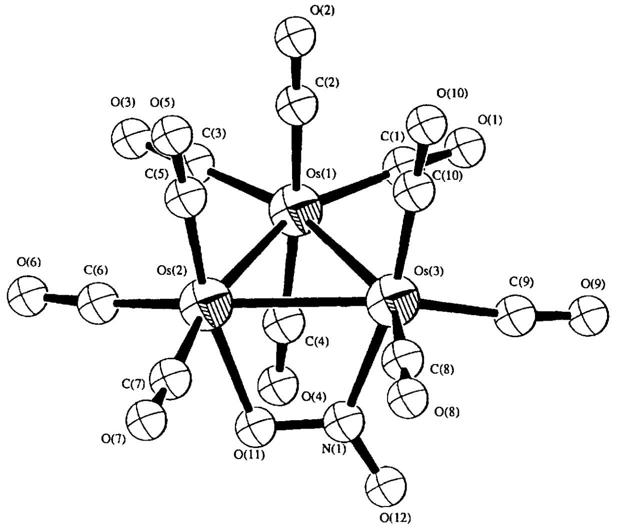

Fig. 1 Molecular structure of $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]^-$ **1** showing the atom-numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) (the sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4): Os(1)–Os(2) 2.849(1), Os(2)–Os(3) 2.714(1), Os(1)–Os(3) 2.882(1), Os(2)–O(11) 2.16(2), Os(3)–N(1) 2.12(2), N(1)–O(12) 1.21(2) and N(1)–O(11) 1.28(2); Os(2)–Os(1)–Os(3) 56.55(3), Os(1)–Os(2)–Os(3) 62.34(3), Os(1)–Os(3)–Os(2) 61.11(3), Os(1)–Os(3)–N(1) 85.1(5), Os(1)–Os(2)–O(11) 86.7(5), Os(2)–Os(3)–N(1) 69.1(5), Os(3)–Os(2)–O(11) 71.6(5), Os(3)–N(1)–O(11) 113(1), Os(2)–O(11)–N(1) 105(1), O(11)–N(1)–O(12) 116(2) and Os(3)–N(1)–O(12) 129(1); C(5)–Os(2)–Os(3)–C(8) 85(1), C(5)–Os(2)–Os(3)–C(10) −5(1), C(7)–Os(2)–Os(3)–C(8) −7(1) and C(7)–Os(2)–Os(3)–C(10) −97(1)

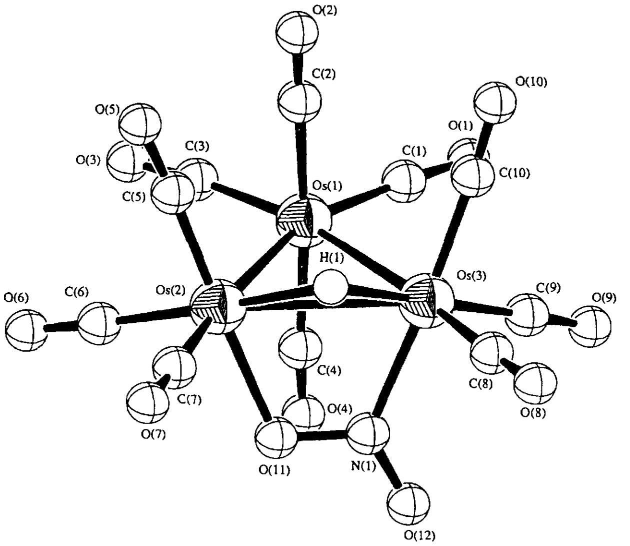

Fig. 2 Molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NO_2)]$ **2** showing the atom-numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) (positive sign as in Fig. 1): Os(1)–Os(2) 2.842(1), Os(1)–Os(3) 2.851(2), Os(2)–Os(3) 2.906(1), Os(2)–O(11) 2.13(1), Os(3)–N(1) 2.11(2), N(1)–O(11) 1.28(2) and N(1)–O(12) 1.21(2); Os(2)–Os(1)–Os(3) 61.38(3), Os(1)–Os(2)–Os(3) 59.46(3), Os(1)–Os(3)–Os(2) 59.16(3), Os(1)–Os(3)–N(1) 88.7(5), Os(2)–Os(3)–N(1) 67.0(5), Os(3)–N(1)–O(11) 114(1), Os(3)–N(1)–O(12) 129(1), Os(1)–Os(2)–O(11) 88.7(4), Os(3)–Os(2)–O(11) 68.0(4), Os(2)–O(11)–N(1) 110(1) and O(11)–N(1)–O(12) 115(1); C(5)–Os(2)–Os(3)–C(8) 96(1), C(5)–Os(2)–Os(3)–C(10) −6(1), C(7)–Os(2)–Os(3)–C(8) −3(1) and C(7)–Os(2)–Os(3)–C(10) −106(1)

triangle. The Os(1)–Os(2) and Os(1)–Os(3) distances [2.849(1) and 2.882(1) Å, respectively] are significantly longer than the bridged Os(2)–Os(3) bond [2.714(1) Å]. The Os(2)–Os(3) bond length is also shorter than the corresponding Os–Os bond [2.751(1) Å] in the related anion $[Os_3(CO)_{10}NO]^-$.[12] The μ-η²-bridging nitrite ligand is bound onto the Os(2)–Os(3) edge *via* the Os(2)–O(11) and Os(3)–N(1) bonds with bond lengths 2.16(2) and 2.12(2) Å, respectively. The geometry of the $\mu\text{-}\eta^2\text{-}NO_2$ ligand in **1** is O(11)–N(1)–O(12) [116(2)], Os(3)–N(1)–O(12) [129(1)] and Os(3)–N(1)–O(11) [113(1)°] which compare with O(1)–N(1)–O(2) [116(1)], Pt(2)–N(1)–O(1) [112(1)] and Pt(2)–N(1)–O(2) [121(7)°] for a platinum complex with a μ-η²-bridging nitrite ligand.[10] The dihedral angle between the plane defined by the bridging nitrite ligand and the Os(1)–Os(2)–Os(3) plane is 96.7°. All the terminal carbonyl ligands are essentially linear, with the Os–C–O bond angles between 172 and 178°. Complex **1** has 48 cluster valence electrons as the bridging NO_2^- acts as a four-electron donor. It is electron precise according to the effective atomic number rule.

The ¹H NMR spectrum of a solution of complex **2** in CD_2Cl_2 reveals the presence of a metal hydride at δ −12.05.§ The IR spectrum shows that the ν(CO) and $\nu(NO_2)$ stretching bands are shifted to higher wavenumbers and this is consistent with the weaker π-back bonding from the triangular metal framework to the carbonyl and nitrite ligands upon protonation. The solid-state IR (KBr disc) spectrum also shows two bands at 1134w and 1496m cm⁻¹ attributed to $\nu(NO_2)$. A perspective view of complex **2** is shown in Fig. 2. The three osmium atoms define an irregular triangle, Os(1)–Os(2) and Os(1)–Os(3) are 2.842(1) and 2.851(2) Å, respectively, with Os(2)–Os(3) the longest at 2.906(1) Å. The μ-η²-bridging nitrite ligand also bridges the Os(2)–Os(3) edge *via* the bonds Os(3)–N(1) [2.11(2)] and Os(2)–O(11) [2.13(1) Å]. The dihedral angle between the plane defined by the bridging nitrite ligand and the Os(1)–Os(2)–Os(3) plane is 102.3°. The terminal carbonyl ligands are almost linear with bond angles of 174 and 178°. We are currently investigating the chemical and electrochemical properties of these nitrite-containing clusters.

Acknowledgements

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§ Spectroscopic data for **2**: IR [ν(CO), CH_2Cl_2] 2119w, 2082vs, 2071s, 2035vs, 2024s and 1991m cm⁻¹; IR [$\nu(NO_2)$, KBr] 1496m and 1134w cm⁻¹; negative-ion FAB mass spectrum *m/z* 898 (calc. 898); ¹H NMR (CD_2Cl_2) δ −12.05 (s, Os-H).