Conversion of a Nitrile Ligand into an Amido Group on a Cluster Surface; X-Ray Characterisation of [HOs₄(CO)₁₂{ μ_3 -N(CO)Me}MPPh₃] (M = Au or Cu)

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The reaction of $[H_3Os_4(CO)_{12}(NCMe)_2]^+$ with $[N(PPh_3)_2]NO_2$ yields $[HOs_4(CO)_{12}\{\mu_3-N(CO)Me\}]^-$ by a novel conversion of an acetonitrile ligand into an amido group on the cluster surface; the anion reacts with $[MPPh_3]^+$ (M = Au or Cu) to produce the neutral derivatives $[HOs_4(CO)_{12}\{\mu_3-N(CO)Me\}(MPPh_3)]$ which have been characterised by X-ray diffraction.

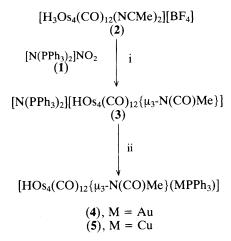
The interaction of $[N(PPh_3)_2]NO_2$ (1) with metal clusters has been developed as a method for enhancing cluster reactivity. The following reactions of (1) have been observed: (i) nucleophilic nitrosylation of $M_3(CO)_{12}$ (M = Ru or Os), $H_3Os_4(CO)_{12}(\mu-I)$, $Ru_5C(CO)_{15}$, $Ru_6C(CO)_{17}$, and $Os_{10}C-(CO)_{24}I_2$; (ii) double deoxygenation of (1) to form nitrido and isocyanate derivatives of Co, Rh, and Ir carbonyl clusters;² (iii) deprotonation of hydrido carbonyl metal clusters;³ (iv) incorporation of the nitrite ion within the cluster unit in $Os_3(CO)_{11}(\mu-CH_2)$;⁴ (v) catalysis of substitution reactions in triruthenium compounds by (1).⁵

The reaction of the bis-acetonitrile cation [H₃Os₄-(CO)₁₂(NCMe)₂]⁺ (2) with (1) has been reported to afford the anionic species [HOs₄(CO)₁₂(NCMe)₂]⁻, on the basis of spectroscopic data.⁶ Our recent investigation of this process has revealed a novel type of interaction in which oxygen is transferred from the nitrite ion to a co-ordinated acetonitrile ligand. The reaction is summarised in Scheme 1. Although incorporation of an amido group into a triosmium cluster can be achieved by displacement of the acetonitrile ligands in

 $Os_3(CO)_{10}(NCMe)_2$ in the presence of the appropriate amide under refluxing conditions,⁷ the reaction herein reported represents an unprecedented example of the conversion of an acetonitrile ligand into an amido group on a cluster surface. The anionic species $[HOs_4(CO)_{12}\{\mu_3\text{-N}(CO)Me\}]^-$ (3) was obtained in 50% yield as its $[N(PPh_3)_2]^+$ salt from the reaction of (2) with (1) in acetonitrile at room temperature.† Reaction of the cations $[MPPh_3]^+$ (M=Au or Cu), formed from Ph_3PMCl in the presence of $Tl[PF_6]$, with (3) in CH_2Cl_2 solution at room temperature yields the neutral species $[HOs_4(CO)_{12}\{\mu_3\text{-N}(CO)Me\}(MPPh_3)]^+$ [M=Au (4), or Cu (5)].

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[†] Spectroscopic data: i.r., $v(CO)(CH_2Cl_2)$, (3) 2045s, 2010s, 1992s, 1968sh, 1932sh, and 1658 cm⁻¹ (amide); (4) 2096m, 2066s, 2029vs, 1989s, 1968sh, 1949sh, and 1600 cm⁻¹ (amide); (5) 2088m, 2060s, 2027vs, 1990s, and 1600 cm⁻¹ (amide); ¹H n.m.r. (CDCl₃), δ (3) 2.67 (Me, s) and -16.02 (OsH, s); (4) 2.58 (Me, s) and -18.57 (OsH, s); (5) 2.58 (Me, s) and -18.20 (OsH, s); satisfactory elemental analysis was obtained for (3).



Scheme 1. Reagents and conditions: i, MeCN, 1 h; ii, Ph₃PMCl, TlPF₆, CH₂Cl₂, 30 min.

In order to determine the ligand distributions and the metal framework geometry an X-ray study of both (4) and (5) was undertaken.‡ Suitable crystals of (3) could not be obtained. The structural determination revealed that (4) and (5) are strictly isostructural.

The metal atom polyhedron is constituted of an Os_4 'butterfly' capped on one external triangular face by the PPh_3M ligand (M = Au or Cu). The N(CO)Me ligand is found to adopt an unprecedented bonding mode with the N atom bridging two edges of the Os_4 'butterfly' wings (see Figure 1) so that the whole ligand system is displaced on one side of the 'butterfly' core. In (4) and (5) the N atom is required to supply four electrons to the cluster orbitals in order to reach the number of 62 electrons necessary for electron-precise 'butterfly' species. The M atom is believed to bridge the M boson evident displacement of the M bond lengthening effect which usually accompanies formation of M2-M4 bridges on metal clusters. The presence of the capping heteroatoms somewhat

‡ Crystal data: (4) [and, in square brackets, (5)] C₃₂H₁₉AuNO₁₃Os₄P $[C_{32}H_{19}CuNO_{13}Os_4P], M = 1614.2[1480.7], monoclinic [monoclinic],$ space group C_2/c [C_2/c], a = 25.681(7) [25.318(6)], b = 16.069(1)[15.964(4)], c = 18.265(2) [18.347(7)] Å, $\beta = 90.90(1)^{\circ}$ [91.80(2)°], U = 7536.5 [7411.9] Å³, Z = 8 [8], $D_c = 2.84$ [2.65] g cm⁻³, $F(000) = 1.80(2)^{\circ}$ 5760 [5360], $\mu(\text{Mo-}K_{\alpha}) = 168 [138] \text{ cm}^{-1}$; $\theta \text{ range } 2.5 - 25^{\circ} [2.5 - 25^{\circ}]$ final R value 0.052 [0.035], R_w 0.057 [0.036] for 4332 [2391] out of 7088 [6989] absorption-corrected independent reflections $[F_o > 5\sigma(F_o)]$ (transmission range 29—100% [44—100%]). Intensity data for both structures were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω -2 θ scan method. Space group choices were based on systematic absences and confirmed by successful refinement. Metal and phosphorus atoms were allowed to vibrate anisotropically, all light atoms isotropically. Phenyl groups of the PPh₃ ligands were treated as rigid bodies (\(C-C-C 120°, C-C 1.40 Å); H-atoms were added in calculated positions and not refined, though their contributions to the structure factors were taken into account. The structures were solved by combined use of Patterson and direct methods; for all calculations the SHELX10 package was used. Residual peaks of ca. 1 and 3 e Å⁻³ were observed in the vicinity of the heavy atoms for (5) and (4), respectively, for (4) this being attributed to a non-completely satisfactory absorption correction. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

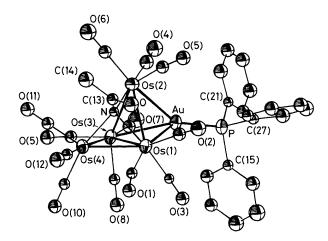


Figure 1. ORTEP drawing of $HOs_4(CO)_{12}\{N(CO)Me\}AuPPh_3$ (4) showing 50% thermal ellipsoids. The C atoms of the CO groups have the same numbers as the corresponding O atoms. Complex (5) is isostructural. Structural parameters for (4) (M = Au) [and (5) (M = Cu) in square brackets]: Os(1)-Os(2) 2.955(1) [2.864(1)], Os(1)-Os(3) 2.939(1) [2.885(1)], Os(2)-Os(3) 2.908(1) [2.891(1)], Os(1)-Os(4) 2.759(1) [2.768(1)], Os(3)-Os(4) 2.785(1) [2.775(1)], Os(1)-M 2.762(1) [2.646(3)], Os(2)-M 2.814(1) [2.709(3)], Os(3)-M 2.940(1) [2.745(3)], Os(3)-M 2.940(1) [2.745(3)], Os(3)-M 2.95(2) [1.87(2)], mean Os(3)-M 2.95(2) [1.87(2)], mean Os(3)-M 2.96(2) [1.87(2)], Os(3)-M 2.96(3) [1.17(2)], Os(3)-M 2.97(3) [1.17(2)], Os(3)-M 2.97(4) [1.17(2)], Os(3)-M 2.97(1) [1.17(2)], Os(3)-M 2.97(1)

obscures the effect of the H bridge. In fact all three Os-Os bonds involved in the heteroatomic tetrahedron appear to be longer than those of the uncapped face [mean 2.880(1), 2.772(1); and 2.934(1), 2.772(1) Å for M = Cu and Au, respectively]. Moreover, the steric requirements of the H atom may account for the asymmetric location of the N(CO)Me group with respect to the 'butterfly' open edge.

The feature of major interest is the stereochemistry and geometry of the amido group. The average Os–N distances [2.10(2), 2.12(1) Å for M = Cu, and Au, respectively] agree well with the values reported for other systems containing Os–N bonds such as $H_3Os_4(CO)_{12}(\mu$ -NO) [2.10(2) Å]⁸ and $[H_3Os_4(CO)_{12}(NCMe_2)]^+$ [2.12(1) Å]⁶ while they appear to be slightly shorter than in $[Os_3(CO)_{10}(\mu$ -CH₂)(μ -NCO)⁻[2.19(1) Å].⁴

The ligand is strictly planar and the hybridisation of the C atom is sp². Bond distances within the system show values expected for N-C and C-C single bonds and for C=O double bonds. Relevant structural parameters are given in the caption to Figure 1. It is noteworthy that the presence of the bridging ligand causes an appreciable decrease of the angle between the 'butterfly' wings [mean Os(2)-Os(N)-Os(4) (N 1,3) 79.3 and 79.5° for (4) and (5), respectively] with respect to the unsupported metal core of the parent [H₃Os₄(CO)₁₂-(NCMe)₂]+ (mean 93.0°).6

The spectroscopic properties of (3) are consistent with the presence of a co-ordinated amido group.† Since the addition of PPh₃M fragments does not usually lead to alterations of metal framework or ligand distribution⁹ it is possible that the amido ligand in (3) is bonded in a similar fashion to that observed in (4) and (5); the available data, however, do not allow an unambiguous assignment in this respect.

Although the mechanism of the interaction between (1) and (2) has not been established, this reactivity shows the dual behaviour of the nitrite ion as both as deprotonating and a nucleophilic reagent.

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