The Reaction of NO^+ with some Anions of Osmium and Ruthenium: Synthesis and *X*-Ray Characterization of $[H_3Os_4(CO)_{12}(\mu_2\text{-}NO)]$ and $[HRu_4N(CO)_{11}P(OMe)_3]$

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Reaction of $[H_3Os_4(CO)_{12}]^-$ with $NOBF_4$ in CH_2Cl_2 gives the nitrosyl cluster $[H_3Os_4(CO)_{12}(\mu\text{-}NO)]$ in which the NO ligand has been shown by *X*-ray analysis to adopt a unique bonding mode bridging the wing-tips of a butterfly arrangement of metal atoms; the analogous reaction of $[H_3Ru_4(CO)_{12}]^-$ with $NOBF_4$ gives instead the nitrido-cluster $[HRu_4N(CO)_{12}]$ in low yield, whose formulation has been confirmed by an *X*-ray analysis of the derivative $[HRu_4N(CO)_{11}P(OMe)_3]$.

The ability of the nitrosyl ligand to function as a one or a three electron donor allows it to adopt either a bent or linear geometry, respectively, in mononuclear metal complexes.[1] In metal clusters many more bonding modes are possible, but to date few nitrosyl containing clusters have been synthesized. We recently reported the reaction of the trinuclear anions $[HM_3(CO)_{11}]^-$ (M = Os, Ru) with NO^+ to yield the neutral derivatives $[HM_3(CO)_{10}(\mu\text{-}NO)]$,[2] and the synthesis of the dinitrosyl clusters $[Os_3(CO)_{10}(\mu\text{-}NO)_2]$ and $[Os_3(CO)_9(NO)_2]$ from $[Os_3(CO)_{12}]$.[3] The synthesis of the tetranuclear iron containing species $[FeRu_3(CO)_{12}(NO)]^-$ and $[Fe_4N(CO)_{11}(NO)]$ was recently reported by Gladfelter;[4] the NO ligand adopts a terminal, linear bonding mode in these molecules. We now report the reaction of the anions $[H_3M_4(CO)_{12}]^-$ (M = Os, Ru) with $NOBF_4$ in CH_2Cl_2 which yields either a nitrosyl containing cluster (M = Os), or a nitrido-cluster (M = Ru).

The salt $[PPN][H_3Os_4(CO)_{12}]$ [PPN = $(Ph_3P)_2N$] was dissolved in CH_2Cl_2 or tetrahydrofuran (THF), the solution degassed, and a stoicheiometric amount of freshly sublimed $NOBF_4$ added as a solid. Reduction of the solution volume, and cooling to −20 °C overnight gave the crystals of $[H_3Os_4(CO)_{12}(\mu\text{-}NO)]$ (**1**) in *ca.* 30% yield. This behaviour is in contrast to the reaction of $[H_3Os_4(CO)_{12}]^-$ with $NOBF_4$ in MeCN in which the nitrosonium ion acts simply as an oxidizing agent and yields the cation $[H_3Os_4(CO)_{12}(MeCN)_2]^+$.[5] Complex (**1**) exhibits carbonyl i.r. stretching frequencies at 2110w, 2084s, 2065s, 2016s, and 2006sh cm^{-1} in CH_2Cl_2. The presence of a bridging NO ligand was indicated by a broad absorption at 1603 cm^{-1}; this is resolved into two components in the solid state (Nujol mull). No parent ion was detected in the mass spectrum of (**1**), however peaks due to fragments consistent with the above formulation were observed. The ^1H n.m.r. spectrum of (**1**) (−30 °C, CD_2Cl_2) revealed two sharp singlets of intensity ratio 2 : 1 at δ −14.89 and −17.95 respectively due to the hydride ligands. *X*-Ray analysis[†,‡] has shown the complex to possess the structure shown in Figure 1, and reveals that the nitrosyl ligand adopts a unique bonding mode bridging the wing-tips of a butterfly arrangement of metal atoms. The NO ligand acts as a three-electron donor and the cluster is a 62 electron system making it formally isoelectronic with most other butterfly complexes of the iron triad.[6] The nitrogen atom is within bonding distance of only the wing-tip osmium atoms so that the overall structure is very similar to that of the halogen derivative $[H_3Os_4(CO)_{12}I]$.[7] The anions $[H_3M_4(CO)_{12}]^-$ (M = Os, Ru) exist in solution as a mixture of two isomers which differ only in the position of the hydride ligands.[8,9] Complex (**1**) apparently does not exhibit such isomerism as the ^1H n.m.r. data are consistent with the C_2 symmetry observed in the solid state with the H-ligands bridging the three longer Os–Os bonds.

In contrast, when $[H_3Ru_4(CO)_{12}]^-$ reacts with $NOBF_4$ in CH_2Cl_2 the nitrido-cluster $[HRu_4N(CO)_{12}]$ (**2**) is formed in low yield. Reaction of the anions $[HRu_3(CO)_{11}]^-$, $[HRu_4(CO)_{13}]^-$, or $[Ru_4(CO)_{13}Cl]^-$ with NO^+ also gives this product in low yield. The mass spectrum of (**2**) shows the

$[HRu_4N(CO)_{12}]$
(**2**)

parent ion as well as regular loss of CO; the ^1H n.m.r. spectrum displays a signal at δ −24.33 characteristic of a bridging hydride ligand, and the i.r. spectrum in cyclohexane displays C–O stretching frequencies at 2065vs, 2050m, 2024s, 2013w(sh), 1994m, and 1961vw cm^{-1}. Suitable crystals of this complex were not obtained for *X*-ray analysis, but good single crystals of the phosphite derivative $[HRu_4N(CO)_{11}P(OMe)_3]$ (**3**) were obtained. This complex was synthesized along with the di- and the tri-substituted

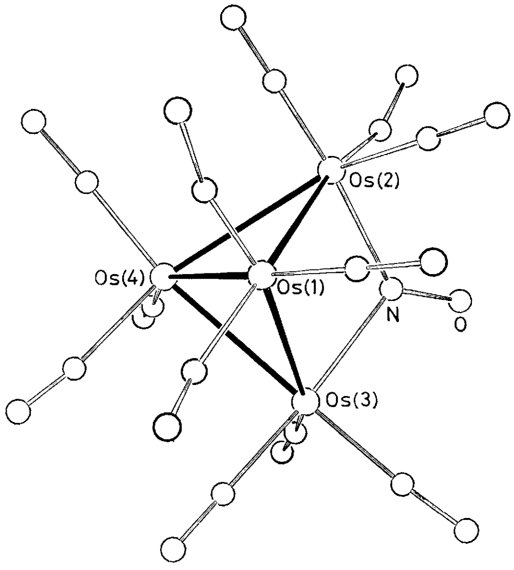

Figure 1. The molecular structure of $[H_3Os_4(CO)_{12}(\mu\text{-}NO)]$ (**1**). Averaged bond lengths for the two independent molecules: Os(1)–Os(2) 2.856(5), Os(1)–Os(3) 3.019(5), Os(1)–Os(4) 2.960(5), Os(2)–Os(4) 3.010(5), and Os(3)–Os(4) 2.849(5) Å. Average Os–ligand bond lengths are Os–C 1.86(2) and Os–N 2.10(2) Å. The hydride ligands bridge the Os(1)–Os(3), Os(1)–Os(4), and Os(2)–Os(4) bonds.

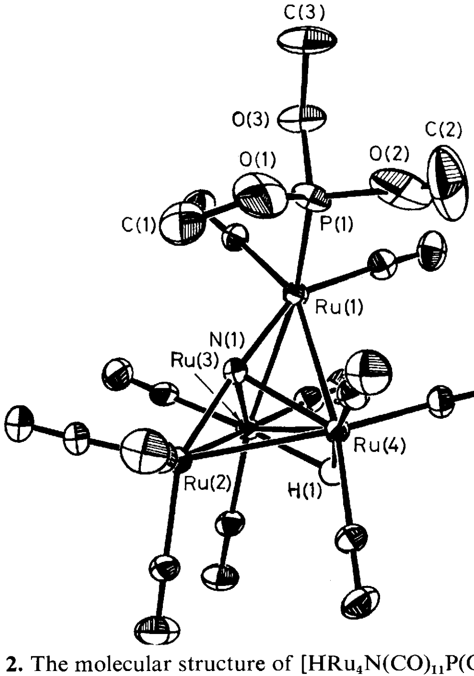

Figure 2. The molecular structure of $[HRu_4N(CO)_{11}P(OMe)_3]$ (**3**). Bond lengths: Ru(1)–Ru(3) 2.832(1), Ru(1)–Ru(4) 2.801(1), Ru(2)–Ru(3) 2.773(1), Ru(2)–Ru(4) 2.770(1), Ru(3)–Ru(4) 2.804(1), Ru(1)–P(1) 2.244(2), Ru(1)–N(1) 1.913(5), Ru(2)–N(1) 1.941(5), Ru(3)–N(1) 2.105(5), Ru(4)–N(1) 2.114(4), Ru(3)–H(1) 1.76(7), and Ru(4)–H(1) 1.88(7) Å. Bond angles: Ru(1)–N(1)–Ru(2) 173.2(3) and Ru(3)–H(1)–Ru(4) 101(3)°.

[†] *Crystal data*: $C_{12}H_3NO_{13}Os_4$, M = 1129.95, triclinic, space group $C\bar{1}$, a = 27.934(4), b = 16.738(3), c = 8.933(2) Å, α = 89.92(2), β = 90.08(2), γ = 94.75(2)°, Z = 8, U = 4162.3 Å^3, D_c = 3.61 g cm^{-3}, θ-range 3—25°, $I/\sigma(I) \geqslant 3.0$, present R-value 0.096 for 3437 absorption corrected reflections [μ(Mo-K_α) = 234.17 cm^{-1}]. Although the gross features are well established, refinement of the structure has proved very difficult owing to the presence of two independent molecules related by pseudo-translational symmetry. For the unit cell used (with the b and c axes reversed) this approximates to the non-standard monoclinic space group $P2_1/n$. There is a slight (*ca.* 5%) disorder of the metal atoms of both molecules corresponding to different orientations of the cluster.

[‡] The atomic co-ordinates for compound (**1**) are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany, and for compound (**3**) 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.

derivatives from the reaction of $[HRu_4N(CO)_{12}]$ with $P(OMe)_3$ in refluxing cyclohexane. The parent ion corresponding to $[HRu_4N(CO)_{11}P(OMe)_3]$ was seen in the mass spectrum. The *X*-ray analysis‡§ of this complex was performed and the results are shown in Figure 2. The complex contains a butterfly arrangement of metal atoms and the nitride ligand functions as a five electron donor bonded to all four ruthenium atoms. The structure is analogous, therefore, to the formally isoelectronic species $[Fe_4N(CO)_{12}]^-$ [4] and $[HFe_4N(CO)_{12}]$.[10]

The isolation of $[H_3Os_4(CO)_{12}(NO)]$ suggests the intermediacy of this, or a similar complex, in the conversion of NO into a nitride ligand in $[HRu_4N(CO)_{12}]$. If the cluster bound NO can alter its bonding mode and behave as a traditional, bent, one electron donor, interaction between the oxygen atom of the NO and adjacent carbonyl or hydride ligands is possible; elimination of CO_2 or H_2O could then account for nitride formation as previously proposed.[11] Similar processes have been used to explain carbide formation in metal clusters.[12] In such a proposal, steric considerations are important and might explain the preferential formation of the nitrosyl cluster in the case of osmium, and the nitrido-species as observed for ruthenium and iron. In this connection it is interesting to note that protonation of $[FeRu_3(CO)_{12}NO]^-$ yields the nitride derivative $[HFeRu_3N(CO)_{12}]$ rather than the corresponding neutral nitrosyl containing species.[11]

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§ *Crystal data*: $C_{14}H_{10}NO_{14}PRu_4$, $[Ru_4(H)N(CO)_{11}P(OMe)_3]$, $M = 851.48$, monoclinic, space group $P2_1/c$, $a = 13.396(3)$, $b = 13.762(3)$, $c = 13.407(4)$ Å, $\beta = 98.89(2)°$, $U = 2441.96$ Å^3, $F(000) = 1612$, $D_c = 2.31$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) = 24.78 cm^{-1}. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least squares to $R = 0.041$ for 3730 reflections with $I/\sigma(I) \gg 2.0$.