Formation of Nitride Clusters by the Action of NO^+ on $[M_4H_3(CO)_{12}]^-$ (M = Ru, Os): the Synthesis and Structural Characterization of $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$ and $[N(PPh_3)_2][Os_4(CO)_{12}(\mu_4\text{-}N)]$

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Reaction of $[Ru_4H_3(CO)_{12}]^-$ with $NOBF_4$ in CH_2Cl_2 gives the nitride cluster $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$ as one of the products and in the analogous reaction with $[Os_4H_3(CO)_{12}]^-$ the mono-hydrido complex $[Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$ is obtained, which upon subsequent reaction with $[N(PPh_3)_2][NO_2]$ gives the anion $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$; the structures of $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$ and $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$ have been established by *X*-ray analysis.

Although the chemistry of tetra- and penta-nuclear carbide containing clusters of the elements of the iron triad is well established there has been little research into the synthesis and reactivity of the corresponding nitride species. Recently, there have been several reports on the formation of tetra-[1–3] and penta-nuclear[3] iron nitrides, but only one communication on ruthenium and osmium systems.[4] Nitrides in 'semi-open' cluster environments, such as bridging a tetranuclear 'butterfly' metal framework, are of interest because of the possibility of hydrogenation of the nitrogen,[5] and the analogy to the synthesis of ammonia on metal surfaces.

We recently reported the synthesis of nitrosyl and nitride containing clusters from the reaction of NO^+ with $[M_4H_3(CO)_{12}]^-$ (M = Ru, Os),[4] and in this communication we present an extension of this work which has produced the novel complexes $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$, $[Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$, and $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$. The reaction of the salt $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$, in CH_2Cl_2, with a stoicheiometric quantity of $NOBF_4$ gives $[Ru_4H(CO)_{12}N]$.[4] This cluster reacts with $[N(PPh_3)_2][NO_2]$ to give the anion $[Ru_4(CO)_{12}(\mu_4\text{-}N)]^-$, which has been characterised by i.r. spectroscopy, and several other as yet uncharacterised products. It has now been found that the reaction of $[Ru_4H_3(CO)_{12}]^-$ with NO^+ also yields the novel nitrido-cluster $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$, which displays i.r. carbonyl stretching frequencies at 2106(w), 2081(s), 2060(s), 2041(vs), 2031(s), 2021(m), 2004(w), and 1987(m) cm^{-1} (cyclohexane solvent), indicating that all the carbonyl groups are terminally bound to the metal atoms.† The ^1H n.m.r. spectrum at room temperature shows two singlets at δ −15.29 and −23.11 in a 2:1 ratio, indicating two different hydride environments. The mass spectrum shows a molecular ion at m/z 741 (for ^{104}Ru) and the sequential loss of 11 CO groups. A single crystal suitable for an *X*-ray analysis was obtained‡ and the molecular geometry of the complex is shown in Figure 1 which includes some important bond parameters. The crystal struc-

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† Satisfactory C, H, and N microanalyses were obtained for these compounds.

‡ *Crystal data:* $C_{11}H_3NO_{11}Ru_4$, $M = 729.4$, triclinic, $P\bar{1}$, $a = 9.554(2)$, $b = 12.743(2)$, $c = 16.012(3)$ Å, $\alpha = 91.39(2)$, $\beta = 96.23(2)$, $\gamma = 90.59(1)°$, $U = 1937.2$ Å^3, $D_c = 2.50$ g cm^{-3}, $Z = 4$, $F(000) = 1360$, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å, $\mu(Mo\text{-}K_\alpha) = 30.27$ cm^{-1}. 6274 Reflections were measured on a Syntex $P2_1$ diffractometer in the range $3.0 < 2\theta < 50.0°$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least-squares (Ru, N, C, O anisotropic, H isotropic) to $R = 0.030$, $R_w = 0.031$ for 5294 unique observed reflections $[F > 3\sigma(F)]$.

The atomic co-ordinates for this structure are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

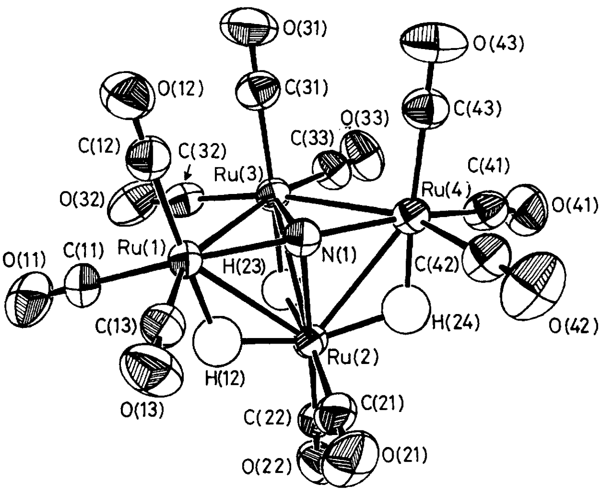


Figure 1. The molecular structure of $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$. Bond lengths (values for the second molecule given in square brackets): Ru(1)–Ru(2), 2.783(1) [2.794(1)]; Ru(1)–Ru(3), 2.794(1) [2.789(1)]; Ru(2)–Ru(3), 2.811(1) [2.810(1)]; Ru(2)–Ru(4), 2.794(1) [2.797(1)]; Ru(3)–Ru(4), 2.798(1) [2.790(1)]; Ru(1)–N(1), 1.972(4) [1.962(4)]; Ru(2)–N(1), 2.020(4) [2.013(4)]; Ru(3)–N(1), 2.092(4) [2.102(4)]; Ru(4)–N(1), 1.953(4) [1.954(4)]; Ru(1)–H(12), 1.71(6) [1.82(6)]; Ru(2)–H(23), 1.79(5) [1.89(5)]; Ru(2)–H(24), 1.74(6) [1.61(5)]; Ru(3)–H(23), 1.83(5) [1.79(5)]; Ru(4)–H(24), 1.65(6) [1.86(5)] Å; bond angles Ru(1)–N(1)–Ru(4), 174.0(2) [173.4(2)]; Ru(1)–H(12)–Ru(2), 113(3) [108(3)]; Ru(2)–H(23)–Ru(3), 102(3) [100(2)]; Ru(2)–H(24)–Ru(4), 111(3) [107(3)]°. The dihedral angle between Ru(1)Ru(2)Ru(3) and Ru(2)Ru(3)Ru(4) planes is 108.6 [108.2]°.

ture contains two independent but structurally equivalent molecules per asymmetric unit. The complex is formally a 62 electron system and the four Ru atoms adopt the expected 'butterfly' geometry. The nitride, N(1), caps the 'butterfly' and is bonded to all four metal atoms. One hydride, H(23), bridges the Ru(2)–Ru(3) 'hinge' bond while the other two bridge 'wing-tip'–'hinge' metal–metal bonds [Ru(1)–Ru(2) and Ru(3)–Ru(4)] on the same side of the molecule. The metal atom, Ru(2), which is associated with all three bridging hydrides is also co-ordinated to two terminal carbonyl groups while each of the other three Ru atoms are co-ordinated to three. The bond parameters within the Ru_4N core are similar to those in $[Ru_4(\mu\text{-}H)(CO)_{11}(\mu_4\text{-}N)P(OMe)_3]$,[4] and the presence of two additional hydride bridged Ru–Ru bonds has little effect on the core geometry. The differences between Ru(wing-tip)–Ru(hinge) and Ru(hinge)–Ru(hinge) bond lengths are not as marked as for the corresponding Fe–Fe distances in $[Fe_4H(CO)_{12}N]$[3] where the average values are 2.62(1) and 2.54(2) Å respectively. The Fe(wing-tip)–N–Fe(wing-tip) angle of 178.4(6)° in the latter complex is significantly closer to linearity than the corresponding angle in $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$.

In the analogous reaction of $[Os_4H_3(CO)_{12}]^-$ with NO^+ the major product has been found to be $[Os_4H_3(CO)_{12}(NO)]$;[4] however the nitrido cluster $[Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$ has now been isolated in 10% yield from the same reaction. This cluster exhibits i.r. carbonyl stretching frequencies at 2069(vs), 2055(m), 2011(w), and 1989(m) cm^{-1} (hexane solvent), and the mass spectrum shows a molecular ion at m/z 1119, and the sequential loss of 12 CO groups followed by the loss of 14 mass units corresponding to an N atom. These data are similar to those reported for the ruthenium analogue, $[Ru_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$, suggesting that the two complexes have similar structures. It is significant that $[Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$ also appears to be produced on keeping dichloromethane or tetrahydrofuran solutions of $[Os_4H_3(CO)_{12}(NO)]$ for several days at room temperature.

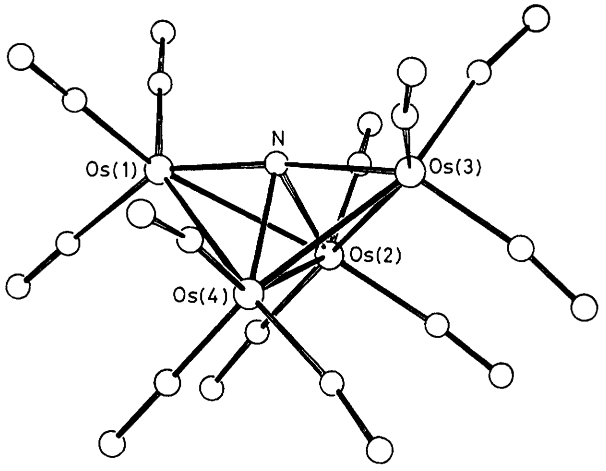
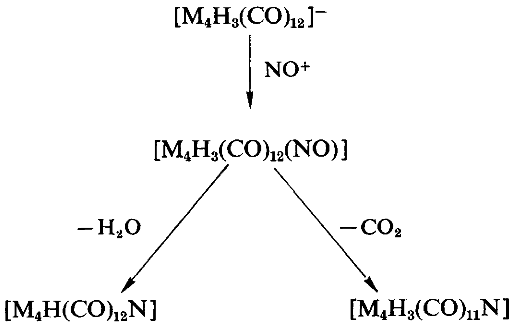


Figure 2. The structure of the $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$ anion. Important bond lengths are: Os(1)–Os(2) 2.811(2); Os(1)–Os(4) 2.816(2); Os(2)–Os(3) 2.811(2); Os(2)–Os(4) 2.728(2); Os(3)–Os(4) 2.793(2); Os(1)–N 1.93(2); Os(2)–N 2.13(2); Os(3)–N 1.98(2); Os(4)–N 2.10(2) Å. The dihedral angle between the planes Os(1)Os(2)Os(4) and Os(2)Os(3)Os(4) is 105.4°. The 'wing-tip' Os(1) · · · Os(3) distance is 3.903 Å.



Scheme 1

When $[Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$ is treated with $[N(PPh_3)_2][NO_2]$ the expected nitrosyl-nitrido complex is not formed, but deprotonation occurs to give the monoanion $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$ which may be crystallised as the $[N(PPh_3)_2]^+$ salt. This anion shows i.r. carbonyl stretching frequencies at 2068(w), 2040(s), 2006(s), 1994(vs), and 1971(w) cm^{-1} (CH_2Cl_2 solvent). A single crystal suitable for an X-ray analysis§ was obtained and the results are shown in Figure 2 together with some important bond parameters. The Os complex is isostructural with the anion $[Fe_4(CO)_{12}(\mu_4\text{-}N)]^-$,[1] with three carbonyl groups per Os atom, and thus the overall geometry approximates to C_{2v} symmetry. Also, as in the Fe analogue, the Os(hinge)–N distance is significantly longer than the Os(wing-tip)–N distance, average values being 2.12 and 1.95 Å respectively for the Os complex, and 1.90 and 1.77 Å in the Fe complex.

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§ *Crystal data:* $[C_{36}H_{30}NP_2][C_{12}NO_{12}Os_4]$, M = 1649.5, monoclinic, $P2_1/c$, a = 17.290(3), b = 16.292(3), c = 17.716(3) Å, β = 96.21(2)°, U = 4961.2 Å^3, D_c = 2.21 g cm^{-3}, Z = 4, $F(000)$ = 3048, $\mu(\text{Mo-}K_\alpha)$ = 99.17 cm^{-1}. Data were collected with a Philips PW1100 diffractometer in the range $6.0 < 2\theta < 50.0°$, present R factor 0.0568 for 3895 reflections $[I > 3\sigma(I)]$ corrected for absorption.

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

These results suggest that there are two possible pathways for nitride formation in these systems (Scheme 1). $[M_4H_3(CO)_{12}(NO)]$ is isolated for M = Os, $[M_4H_3(CO)_{11}N]$ for M = Ru, and $[M_4H(CO)_{12}N]$ for both M = Ru and Os. The ruthenium nitrosyl adduct appears to be unstable at room temperature,¶ and forms a nitride by the loss of the elements of H_2O or CO_2, the latter route being favoured. For M = Os the nitrosyl complex can be isolated at room temperature, and forms the nitride *via* 'H_2O' loss. This is favoured over 'CO_2' loss which is not observed in this case.** Although it has been suggested previously that nitrides can be formed by the loss of either H_2O or CO_2,[6] this is the first evidence for both pathways existing as alternatives in the same system.

We thank Dr. E. Constable for running the ^1H n.m.r. spectra. We are grateful to the S.E.R.C., British Petroleum (J. M. M.), I.C.I. (W. J. H. N.), Penn Chemicals Ltd. (M. C.), and the Consejo Nacional de Investigaciones Cientificas y Technologious (C.O.N.I.C.I.T.) (J. P.) for financial support.

Received, 16th March 1983; Com. 345

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¶ At −30 °C, the nitride complex is not formed, but as yet uncharacterized products are produced.

** *Note added in proof*: We have recently found, however, that the anion $[Os_4H(CO)_{13}]^-$ reacts with NO^+ to give $[Os_4H(CO)_{13}(NO)]$; this nitrosyl complex loses 'CO_2' on heating to form the nitride cluster $[Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)]$ (R. M. Sorrell and M. J. Taylor, unpublished results).