The Reduction of (μ_2-NO) in [$Ru_3(CO)_{10}(\mu_2$-$NO)_2$] by Carbon Monoxide; Evidence for the Formation of a Triruthenium Nitrido Intermediate, and the Structural Characterisation of [$Ru_4N(CO)_{12}(\mu_2$-NO)] and [$Ru_4N(CO)_{12}(\mu_2$-NCO)]

Julian P. Attard, Brian F. G. Johnson,* Jack Lewis, Julian M. Mace, and Paul R. Raithby

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

The cluster [$Ru_3(CO)_{10}(\mu_2$-$NO)_2$] reacts with CO to form the species [$Ru_3(CO)_{12}$], [$Ru_3(CO)_{10}(\mu_2$-NO)(μ_2-NCO)], [$Ru_4N(CO)_{12}(\mu_2$-NO)], and [$Ru_4N(CO)_{12}(\mu_2$-NCO)], evidence suggesting the formation of a reactive nitrido- or nitrene–nitrosyl intermediate; *X*-ray analysis shows that both of the tetranuclear nitrido species adopt a 64-electron 'butterfly' structure in which the 'hinge' metal–metal vector is long and supports a (μ_2-NO) or a (μ_2-NCO) bridging group.

The reactions of nitric oxide bonded to a metal cluster provide a useful analogy for the corresponding reactions on a heterogeneous surface.[1] One such reaction is the reduction of NO, which has been investigated for a trinuclear ruthenium cluster with molecular hydrogen,[2] and for tetranuclear ruthenium and osmium clusters internally.[3,4] Here we report the reduction of (μ_2-NO) with carbon monoxide, and offer evidence to suggest the formation of a reactive triruthenium nitrido- or nitrene–nitrosyl intermediate, evidence which may help to clarify the method of nitrosyl reduction in these clusters.

The dinitrosyl cluster [$Ru_3(CO)_{10}(\mu_2$-$NO)_2$] (**1**) reacts with CO under mild conditions (1 atm, 110 °C, 9 h) to give four neutral products, (**2**), (**3**), (**4**), and (**5**), in varying amounts [equation (1)].

$$\begin{aligned}\underset{(\mathbf{1})}{[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]} \xrightarrow{CO} & \underset{(\mathbf{2}),\,5\%}{[Ru_3(CO)_{12}]} \\ & + \underset{(\mathbf{3}),\,30\%}{[Ru_4N(CO)_{12}(\mu_2\text{-}NO)]} \\ & + \underset{(\mathbf{4}),\,5\%}{[Ru_4N(CO)_{12}(\mu_2\text{-}NCO)]} \\ & + \underset{(\mathbf{5}),\,5\%}{[Ru_3(CO)_{10}(\mu_2\text{-}NO)(\mu_2\text{-}NCO)]} \qquad (1)\end{aligned}$$

Compound (**2**) was readily identified as [$Ru_3(CO)_{12}$] on the basis of its i.r. spectrum in the ν_{CO} region. Compound (**3**) was identified as [$Ru_4N(CO)_{12}(\mu_2$-NO)] primarily by mass spectroscopy, a parent ion appearing at m/z = 796 (^{104}Ru), together with peaks corresponding to the loss of twelve CO groups and an NO group. In addition its i.r. spectrum in the ν_{CO} region is similar to that observed for the related compound [$HM_4N(CO)_{12}$] (M = Ru or Os),[3,4] (Table 1). Crystals of (**3**) suitable for *X*-ray analysis†‡ were obtained, and the molecular geometry of the complex is shown in Figure 1, which includes some important bond parameters. The crystal structure contains two independent but structurally equivalent molecules per asymmetric unit. The four Ru atoms

---

† *Crystal data:* (**3**) $C_{12}N_2O_{13}Ru_4$, M = 784.4, triclinic, space group $P\bar{1}$ (no. 2), a = 9.775(1), b = 13.954(1), c = 16.536(2) Å, α = 98.02(1), β = 97.19(1), γ = 107.70(1)°, U = 2094.4 Å^3, D_c = 2.48 g cm^{-3}, Z = 4, $F(000)$ = 1464, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 28.13 cm^{-1}. 7829 Reflections measured on a Stoe–Siemens four-circle diffractometer in the range $5.0 < 2\theta < 50.0°$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full-matrix least-squares (Ru, N, and O anisotropic) to R = 0.037, R_w = 0.041 for 5936 unique observed reflections [$F > 4\sigma(F)$].

‡ The atomic co-ordinates for this work are available 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.

Table 1. I.r. data in the carbonyl region unless noted otherwise.

Compound	ν/cm^{-1}	Ref.
$[Ru_4N(CO)_{12}(\mu_2\text{-}NO)]$ (**3**)[a]	2070s, 2064s, 2052m, 2032s, 2023mw, 2011vw, 2003w, 1997m, 1978vw, 1964vw; ν(NO): 1523w[b]	
$[HRu_4N(CO)_{12}]$	2065vs, 2050m, 2024s, 2013w(sh), 1994m, 1961vw[c]	3
$[HOs_4N(CO)_{12}]$	2069vs, 2055m, 2020s, 2011w, 1989m[b]	4
$[Ru_4N(CO)_{12}(\mu_2\text{-}NCO)]$ (**4**)[a]	2099vw, 2070s(sh), 2066vs, 2053w, 2023s, 2015w(sh), 1994w; ν(NCO): 2203vs[b]	
$[Ru_3(CO)_{10}(\mu_2\text{-}NO)(\mu_2\text{-}NCO)]$ (**5**)[a]	2108w, 2082vs, 2068s, 2039s, 2022ms, 2000m(sh); ν(NCO): 2206vs. ν(NO): 1507w(br)[d]	
$[HRu_3(CO)_{10}(\mu_2\text{-}NO)]$	2109w, 2070vs, 2064s, 2033vs, 2027m, 2019s, 1998w; ν(NO): 1550w[c]	8
$[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$	2110w, 2077s, 2068s, 2061(sh), 2038s, 2030s, 2026(sh), 2015w, 2000m; ν(NO): 1524w, 1508m[c]	9

[a] Satisfactory C, H, and N microanalyses were obtained. [b] Hexane. [c] Cyclohexane. [d] CH_2Cl_2.

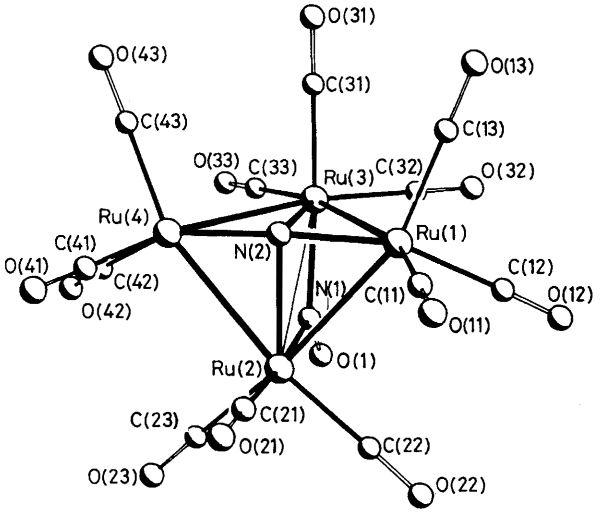


Figure 1. The molecular structure of $[Ru_4N(CO)_{12}(\mu_2\text{-}NO)]$ (**3**). Bond lengths (values for the second molecule given in square brackets): Ru(1)–Ru(2), 2.823(1) [2.831(1)]; Ru(1)–Ru(3), 2.827(1) [2.826(1)]; Ru(2)–Ru(3), 3.249(1) [3.244(1)]; Ru(2)–Ru(4), 2.821(1) [2.825(1)]; Ru(3)–Ru(4), 2.826(1) [2.814(1)]; Ru(1)–N(2), 1.906(5) [1.909(5)]; Ru(2)–N(2), 2.163(5) [2.169(5)]; Ru(3)–N(2), 2.171(6) [2.152(5)]; Ru(4)–N(2), 1.896(5) [1.894(5)]; Ru(2)–N(1), 2.025(6) [2.032(6)]; Ru(3)–N(1), 2.011(6) [2.034(6)]; N(1)–O(1), 1.227(7) [1.204(6)] Å. Bond angles: Ru(1)–N(2)–Ru(4), 173.0(3) [173.5(2)]; Ru(2)–N(1)–Ru(3), 107.2(2) [105.8(2)]; Ru(2)–N(1)–O(1), 125.5(5) [126.6(5)]; Ru(3)–N(1)–O(1), 127.3(5) [127.5(5)°]. The dihedral angle between the Ru(1)Ru(2)Ru(3) and Ru(2)Ru(3)Ru(4) planes is 69.6 [69.6]°.

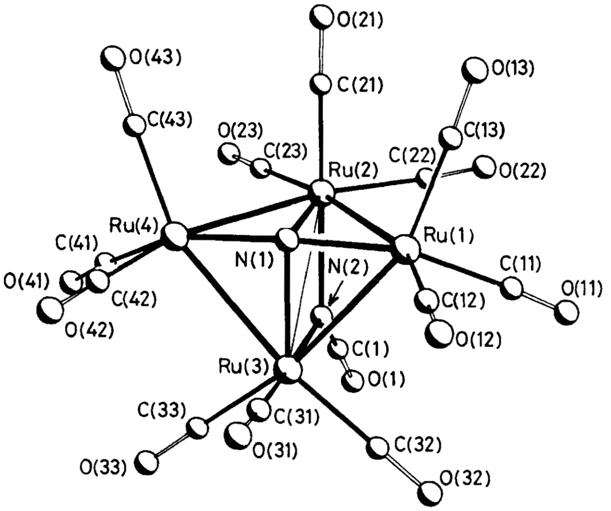


Figure 2. The molecular structure of $[Ru_4N(CO)_{12}(\mu_2\text{-}NCO)]$ (**4**). Bond lengths: Ru(1)–Ru(2), 2.817(1); Ru(1)–Ru(3), 2.814(1); Ru(2)–Ru(3), 3.239(1); Ru(2)–Ru(4), 2.826(1); Ru(3)–Ru(4), 2.807(1); Ru(1)–N(1), 1.903(3); Ru(2)–N(1), 2.132(3); Ru(3)–N(1), 2.132(3); Ru(4)–N(1), 1.901(3); Ru(2)–N(2), 2.154(4); Ru(3)–N(2), 2.179(4); N(2)–C(1), 1.185(6); C(1)–O(1), 1.161(6) Å. Bond angles: Ru(1)–N(1)–Ru(4), 174.9(2); Ru(2)–N(2)–Ru(3), 96.8(1); Ru(2)–N(2)–C(1), 134.9(3); Ru(3)–N(2)–C(1), 128.0(3); N(2)–C(1)–O(1), 177.9(5)°. The dihedral angle between the Ru(1)Ru(2)Ru(3) and Ru(2)Ru(3)Ru(4) planes is 68.9°.

adopt a 'butterfly' geometry, and the nitride, N(2), caps the 'butterfly' and is bonded to all four metal atoms. The nitrosyl ligand bridges the Ru(2)–Ru(3) 'hinge' vector, which is elongated [3.249(1) Å; molecule 2, 3.244(1) Å], and there appears to be no direct metal–metal interaction, in agreement with the molecule being an electron-rich 64-electron system (*cf.* $[HRu_4N(CO)_{11}\{P(OMe)_3\}]$ with a 1-electron donor hydride ligand and a 'hinge' bond length of 2.804 Å[3]). This is in keeping with the behaviour observed for the cluster $[Ru_4(CO)_8(Pr^iN{=}CHCH{=}NPr^i)_2]$,[5] a 64-electron system with an elongated hinge vector (2.994 Å). However, a number of anomalous 64-electron systems are known,[6] for example $[Os_4(CO)_{12}(\mu_3\text{-}S)_2]$, which has two elongated 'hinge'–'wingtip' metal–metal vectors to give a molecule with C_2 symmetry.

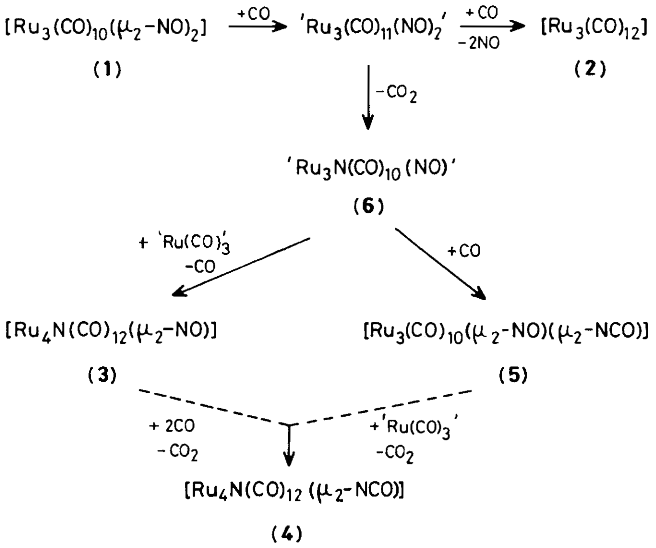
Only one other example of a mixed nitrosyl–nitrido cluster has been reported, *viz* $[Fe_4N(CO)_{11}(NO)]$.[7] Two possible structures have been suggested for this iron compound: either a tetrahedron of metal atoms with a terminal NO on one vertex and a 3-electron donor μ_3-nitrogen bridging the opposite face, or more likely, a 5-electron donor μ_4-nitrogen bridging a 'butterfly' of metal atoms with a terminal NO group. The latter structure would tie in with that observed for $[Ru_4N(CO)_{12}(NO)]$, there being one 2-electron donor CO group difference between them.

Compound (**4**) was identified as $[Ru_4N(CO)_{12}(\mu_2\text{-}NCO)]$ by mass spectroscopy, a parent ion appearing at m/z = 808 (^{104}Ru), and from its i.r. spectrum, which in the carbonyl region is similar to that of $[Ru_4N(CO)_{12}(\mu_2\text{-}NO)]$ above (Table 1). This suggests that the bridging nitrosyl group in (**3**) has been replaced by a bridging isocyanate ligand. This has been confirmed by *X*-ray analysis‡§ of a single crystal of (**4**), and the molecular geometry of the complex is shown in Figure 2 together with some important bond parameters. As expected, the nitride caps a 'butterfly' of four Ru atoms, with the isocyanate ligand bridging an elongated Ru(2)—Ru(3) 'hinge' vector [3.239(1) Å].

Compound (**5**) was identified as $[Ru_3(CO)_{10}(\mu_2\text{-}NO)(\mu_2\text{-}NCO)]$ by mass spectroscopy, a parent ion appearing at m/z = 664 (^{104}Ru). The i.r. spectrum (Table 1) indicates that all the carbonyl groups are terminally bound, and is similar to those of other $[M_3(CO)_{10}XY]$ species such as $[HRu_3(CO)_{10}(NO)]$[8] and $[Ru_3(CO)_{10}(NO)_2]$[9] (Table 1). This suggests that the cluster adopts a triangular geometry with the nitrosyl and isocyanate ligands bridging the same edge. As the molecule is a 50-electron system, it may be expected that this Ru–Ru vector will be formally non-bonded, as in $[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$.[10] It is interesting to note that this is the first example of a $[M_3(CO)_{10}XY]$ system where X and Y are both 3-electron donors and different.

When the reaction time is increased, improved yields of compound (**4**) are obtained, but less of (**3**). This suggests that (**4**) is formed from (**3**). However, (**3**) has been shown to be stable with respect to CO under these reaction conditions, implying a more complicated reaction pathway. Under more vigorous conditions (50 atm, 110 °C, 9 h), $[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$ reacts to give $[Ru_3(CO)_{12}]$ only, no nitrogen-containing products being observed.

These reactions lead us to suggest that reductive carbonylation of one nitrosyl ligand in $[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$ (**1**) gives a reactive triruthenium nitride or nitrene intermediate '$Ru_3N(CO)_{10}(NO)$' (**6**), of the type previously considered for the formation of NCO from NO systems.[11] This subsequently reacts with either CO (directly or by migration from the metal framework) to yield $[Ru_3(CO)_{10}(\mu_2\text{-}NO)(\mu_2\text{-}NCO)]$ (**5**), or with a mononuclear ruthenium fragment (from decomposition of cluster species under reaction conditions) to yield $[Ru_4N(CO)_{12}(\mu_2\text{-}NO)]$. (**3**). The product $[Ru_4N(CO)_{12}(\mu_2\text{-}NCO)]$ (**4**) must be produced by reduction of both nitrosyls on (**1**). This is a unique observation. There is no evidence for similar behaviour in dinitrosyl mononuclear complexes. It is not clear whether the isocyanate group or the tetraruthenium nitride framework is produced first, *i.e.*, whether the reaction proceeds *via* (**5**) or (**3**). However, the absence of any product identifiable as $[Ru_3(CO)_{10}(\mu_2\text{-}NCO)_2]$, and the variation in yield of (**3**) and (**4**) with time, imply that the former is less likely. The absence of any nitrogen-containing products when the reaction is repeated under 50 atm of CO suggests that nitrosyl reduction may be effected intramolecularly by cluster-bound CO rather than by free CO, the latter forming $[Ru_3(CO)_{12}]$ when present in large excess. These reaction pathways are summarised in Scheme 1.



Scheme 1

Compound (**3**) has been previously reported as a minor product in the preparation of $[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$ (**1**) from $[Ru_3(CO)_{12}]$ and NO, but was not completely characterised.[10] It may be produced by the attack on (**1**) of the CO liberated in the reaction, or by NO attack on $[Ru_3(CO)_{12}]$ producing an intermediate which can react to produce (**3**), or displace CO to yield (**1**).

The intermediacy of a triruthenium nitride species has been suggested for the hydrogenation of $[HRu_3(CO)_{10}(NO)]$,[2,12] but it is not clear whether the initial step is oxidative addition of hydrogen[2] or loss of CO concurrent with H-migration to the nitrosyl oxygen.[12] This work supports the existence of such an intermediate, and indicates that it is formed *via* addition of a ligand to the cluster, which is consistent with the known ability of nitrosyl ligands to activate a cluster to nucleophilic attack.[13]

We thank the S.E.R.C. (J. P. A.) and Corpus Christi College, Cambridge (J. M. M.), for financial support.

Received, 5th August 1985; Com. 1161

References

1 R. Eisenberg and D. E. Hendriksen, *Adv. Catal.*, 1979, **28**, 79.
2 B. F. G. Johnson, J. Lewis, and J. M. Mace, *J. Chem. Soc., Chem. Commun.*, 1984, 186.
3 D. Braga, B. F. G. Johnson, J. Lewis, J. M. Mace, M. McPartlin, J. Puga, W. J. H. Nelson, P. R. Raithby, and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1982, 1081.
4 M. A. Collins, B. F. G. Johnson, J. Lewis, J. M. Mace, J. Morris, M. McPartlin, W. J. H. Nelson, J. Puga, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1983, 689.
5 L. H. Staal, L. H. Polm, K. Vrieze, F. Ploeger, and C. H. Stam, *Inorg. Chem.*, 1981, **20**, 3590.
6 R. D. Adams and L-W. Yang, *J. Am. Chem. Soc.*, 1982, **104**, 4115, and references cited therein.
7 D. E. Fjare and W. L. Gladfelter, *Inorg. Chem.*, 1981, **20**, 3533.
8 B. F. G. Johnson, P. R. Raithby, and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1980, 99.
9 J. R. Norton, D. Valentine, Jr., and J. P. Collman, *J. Am. Chem. Soc.*, 1969, **91**, 7537.
10 J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 1972, **11**, 382.
11 M. L. Blohm and W. L. Gladfelter, *Organometallics*, 1985, **4**, 45.
12 W. L. Gladfelter, personal communication.
13 B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.*, 1978, **160**, 263.

---

§ *Crystal data*: (**4**) $C_{13}N_2O_{13}Ru_4$, M = 796.43, monoclinic, space group $P2_1/a$ (non-standard setting of $P2_1/c$; no. 14), a = 13.072(1), b = 10.701(1), c = 15.364(1) Å, β = 90.97(1)°, U = 2148.9 Å^3, D_c = 2.46 g cm^{-3}, Z = 4, $F(000)$ = 1488, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ = 27.43 cm^{-1}. 8301 Reflections measured on a Stoe–Siemens four-circle diffractometer in the range $5.0 < 2\theta < 50.0°$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full-matrix least-squares (Ru, N, C, and O anisotropic) to R = 0.029, R_w = 0.034 for 3573 unique observed reflections [$F > 4\sigma(F)$].