The Reduction of (μ_2-NO) in [$HRu_3(CO)_{10}(\mu_2$-NO)] to (μ_3-NH) and (μ_2-NH_2) by Molecular Hydrogen

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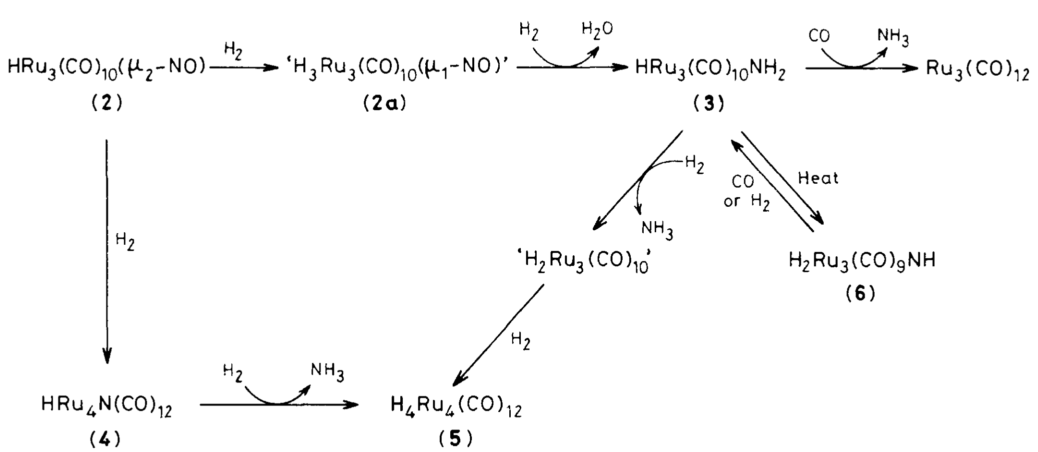
[$HRu_3(CO)_{11}]^-$ reacts with $NOBF_4$ in moist MeCN to generate $HRu_3(CO)_{10}NO$, $HRu_3(CO)_{10}NH_2$, and $HRu_4N(CO)_{12}$; the same products, together with $H_2Ru_3(CO)_9NH$ and $H_4Ru_4(CO)_{12}$, are observed in the direct hydrogenation of $HRu_3(CO)_{10}NO$.

The reduction of nitric oxide by hydrogen on a heterogeneous surface is not a well understood reaction. Here we report the reduction of co-ordinated μ_2-NO to μ_3-NH and μ_2-NH_2 in a *triangulo*-ruthenium cluster, an observation which may shed some light on the method by which the reduction of NO occurs.

Previously we have described the preparation of $HRu_3(CO)_{10}NO$ from the reaction of $NOBF_4$ with [$HRu_3(CO)_{11}]^-$.[1] Here we report that the reaction between [$HRu_3(CO)_{11}]^-$ and $NOBF_4$ in moist acetonitrile, in addition to the expected compound, also gave, in an unprecedented fashion, the compound $HRu_3(CO)_{10}NH_2$.



Scheme 1

Table 1. I.r. absorptions ($\nu_{max.}/cm^{-1}$) in the carbonyl region (cyclohexane solvent).

(**2**) $HRu_3(CO)_{10}NO$	2109w, 2070vs, 2064s, 2033vs, 2027m, 2019s, 1998w; ν(NO): 1550w
(**3**) $HRu_3(CO)_{10}NH_2$	2100w, 2064vs, 2051s, 2034vw, 2024s, 2010vs, 2002s, 1991w, 1982w
(**4**) $HRu_4N(CO)_{12}$	2065vs, 2050m, 2024s, 2013w, sh, 1994m, 1961vw
(**5**) $H_2Ru_3(CO)_9NH$	2114m, 2078s, 2055vs, 2044s, 2010vs, 1999s, 1987w

Reaction of $[HRu_3(CO)_{11}]^-$ (**1**) with $NOBF_4$ in moist MeCN results in the formation, in addition to $Ru_3(CO)_{12}$, of a mixture of compounds (**2**), (**3**), and (**4**) [equation (1)].

$$\underset{(\mathbf{1})}{[HRu_3(CO)_{11}]^-} \xrightarrow[NOBF_4]{} \underset{(\mathbf{2})}{HRu_3(CO)_{10}NO} + \underset{(\mathbf{3})}{HRu_3(CO)_{10}NH_2} + \underset{(\mathbf{4})}{HRu_4N(CO)_{12}} \quad (1)$$

Compound (**2**) was shown to be the expected nitrosyl derivative. The i.r. and ^1H n.m.r. spectrum of this molecule are consistent with a *triangulo*-structure in which the NO and H ligands occupy bridging positions, and this has been confirmed by an *X*-ray crystal structure determination of the tri-substituted trimethyl phosphite derivative.[1] More surprising and unexpected was the formation of the μ_2-NH_2 compound. Cluster (**3**) has been obtained in moderate yields, and the trinuclear formulation, $HRu_3(CO)_{10}NH_2$, has been confirmed by mass spectroscopy. This result clearly indicated that a facile reduction of the μ_2-NO ligand in (**2**) was occurring during the reaction.

The cluster $[HRu_3(CO)_{11}]^-$ is known to be strongly basic and to be a good source of the H^- ligand.[2] Treatment of (**2**) with either $[HRu_3(CO)_{11}]^-$, or $[HRu_3(CO)_{11}]^-$ in the presence of CO, did not bring about the formation of (**3**), indicating that the $-NH_2$ group did not arise from the nucleophilic addition of H^- to co-ordinated μ_2-NO. We suspected that the formation of (**3**) in the reaction of $[HRu_3(CO)_{11}]^-$ with $NOBF_4$ arose from the fortuitous presence of HBF_4 (due to moist MeCN). Furthermore, co-ordinated NO has been shown to undergo electrophilic addition by H^+ to generate $-NHOH$ and $-NH_2OH$.[3] However, in this case, we were able to show that direct addition of H^+ to $HRu_3(CO)_{10}NO$ did not bring about the required reduction.

Keister has shown that at low temperatures $[HRu_3(CO)_{11}]^-$ adds H^+, and above −30 °C forms $H_2Ru_3(CO)_{11}$.[4] On warming to room temperature this complex decomposes to produce $Ru_3(CO)_{12}$ and presumably H_2. We therefore considered the possibility that H_2 was the reductant in equation (1), and that this was formed according to equations (2) and (3). The reaction of $HRu_3(CO)_{10}NO$ with H_2 (1 atmos; 100 °C) gave four neutral products (**3**), (**4**), (**5**) and (**6**) [equation (4)].

$$[HRu_3(CO)_{11}]^- + H^+ \longrightarrow H_2Ru_3(CO)_{11} \quad (2)$$

$$H_2Ru_3(CO)_{11} \longrightarrow Ru_3(CO)_{12} + H_2 \quad (3)$$

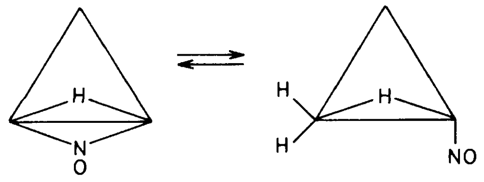
$$\underset{(\mathbf{2})}{HRu_3(CO)_{10}NO} + H_2 \longrightarrow \underset{(\mathbf{3})}{HRu_3(CO)_{10}NH_2} + \underset{(\mathbf{4})}{HRu_4N(CO)_{12}} + \underset{(\mathbf{5})}{H_4Ru_4(CO)_{12}} + \underset{(\mathbf{6})}{H_2Ru_3(CO)_9NH} \quad (4)$$

Compound (**5**) was shown to be $H_4Ru_4(CO)_{12}$ on the basis of its spectroscopic data. Compound (**3**) was identified as $HRu_3(CO)_{10}NH_2$ by a combination of spectroscopic methods. Thus, the mass spectrum shows the molecular ion at *m/z* 609 (^{104}Ru), followed by the sequential loss of 10 CO groups; the ^1H n.m.r. spectrum shows a resonance arising from the hydrido-ligand at δ −13.96, and, finally, the i.r. spectrum (Table 1) is similar to those observed for the osmium analogue $HOs_3(CO)_{10}NH_2$,[5] and other, related, $HM_3(CO)_{10}X$ systems.

Compound (**6**) was identified as $H_2Ru_3(CO)_9NH$ by its mass spectrum [M^+, *m/z* 581 (^{104}Ru)], and its i.r. spectrum (Table 1). This is similar to that of $H_2Os_3(CO)_9(\mu_3\text{-}NPh)$ which shows bands at 2115w, 2083s, 2056s, 2034m, 2010s, 1988m, and 1977w cm^{-1} (hexane solution).[6] Compound (**4**) has been fully characterised as $HRu_4N(CO)_{12}$, previously observed in reaction (1), and as a product of the reaction of $[H_3Ru_4(CO)_{12}]^-$ with $NOBF_4$.[7]

In a separate experiment (carried out in a high-pressure i.r. cell), the reaction was monitored by following the change in i.r. spectrum with time. At a hydrogen pressure of approximately 50 atmospheres, a smooth transformation of (**2**) into the observed products [with the exception of (**4**)] was observed.

In further experiments we have found the following. (i) $H_2Ru_3(CO)_9NH$ reacts with H_2 under pressure to produce $HRu_3(CO)_{10}NH_2$ and $H_4Ru_4(CO)_{12}$. (ii) The same cluster reacts with CO under pressure to form $HRu_3(CO)_{10}NH_2$. (iii)



(2) **(2a)**

On reaction with CO under pressure, $HRu_3(CO)_{10}NH_2$ forms $Ru_3(CO)_{12}$. (iv) $HRu_3(CO)_{10}NH_2$ produces $H_4Ru_4(CO)_{12}$ on reaction with H_2 under pressure. (v) On heating, $HRu_3(CO)_{10}NH_2$ forms some $H_2Ru_3(CO)_9NH$. (vi) $HRu_4N(CO)_{12}$ produces $H_4Ru_4(CO)_{12}$ on reaction with H_2 under pressure. These reactions lead us to propose the mechanism shown in Scheme 1.

Reactions in this scheme include oxidative-addition of H_2 to $HRu_3(CO)_{10}(\mu_2\text{-NO})$ (**2**) to form $H_3Ru_3(CO)_{10}(\mu_1\text{-NO})$ (**2a**), and the subsequent reduction would presumably follow the sequence shown in equation (5).

$$\begin{tikzcd} H_3Ru_3(CO)_{10}(\mu_1\text{-NO}) \arrow[r] & HRu_3(CO)_{10}(NHOH) \arrow[d, "H_2"] \\ HRu_3(CO)_{10}NH_2 & H_3Ru_3(CO)_{10}(NHOH) \arrow[l, "-H_2O"'] \end{tikzcd} \qquad (5)$$

Reaction of $HRu_3(CO)_{10}NH_2$ with more H_2 is then considered to lead first to NH_3 and $H_2Ru_3(CO)_{10}$, which by analogy with $H_2Os_3(CO)_{10}$ is expected to be converted rapidly into $H_4Ru_4(CO)_{12}$[8] [equation (6)]. A measure of support for this pathway is given by the fact that the loss of a nitrosyl oxygen in the elements of water has previously been observed for a cluster system $[H_3Os_4(CO)_{12}NO \rightarrow HOs_4N(CO)_{12}]$.[9]

$$HRu_3(CO)_{10}NH_2 \xrightarrow{H_2} H_2Ru_3(CO)_{10} \xrightarrow{H_2} H_4Ru_4(CO)_{12} \qquad (6)$$

Alternatively, the reaction may proceed *via* the formation of a nitride intermediate [equation (7)]. To us, this appears a less likely pathway, because of the relative amounts of (**3**) and (**6**) produced (40 : 3%) given the necessity of (**6**) to scavenge CO from the system. However, the loss of a nitrosyl oxygen as

$$\begin{tikzcd} HRu_3(CO)_{10}(\mu_2\text{-NO}) \arrow[r, "H_2", "-CO_2"'] & \text{'}H_3Ru_3(CO)_9N\text{'} \arrow[d] \\ HRu_3(CO)_{10}NH_2 & H_2Ru_3(CO)_9NH \arrow[l, "{[CO]}"'] \end{tikzcd} \qquad (7)$$

CO_2 has been observed for a cluster system $[HOs_4(CO)_{13}NO \rightarrow HOs_4N(CO)_{12}]$,[9] and H-transfer onto the N-atom of a cluster nitride is implied by the formation of $H_4Ru_4(CO)_{12}$ from $HRu_4N(CO)_{12}$ above. Thus we cannot, at this stage, differentiate between these two possibilities.

In connection with the above, it is interesting that, unlike the ruthenium case, $HOs_4N(CO)_{12}$, on treatment with H_2 under pressure, brings about H-addition and CO-loss to give a moderate yield of the new compound $H_3Os_4N(CO)_{11}$. This cluster, of which the ruthenium analogue is known,[9] has been identified by its spectroscopic data.

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