# Heteronuclear Metal Cluster Nitrides *via* NO Cleavage

**Neil D. Feasey and Selby A. R. Knox***

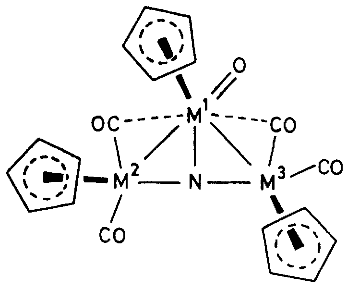
*Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.*

Heating $[M(CO)_2(NO)(\eta\text{-}C_5H_5)]$ and $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) together at 200 °C yields metal cluster nitrides $[M_3(N)(O)(CO)_4(\eta\text{-}C_5H_5)_3]$ ($M_3$ = $Mo_3$, $Mo_2W$, $MoW_2$, and $W_3$); isotopic labelling reveals that the co-ordinated oxygen does not evolve from NO, whose oxygen appears in $CO_2$.

We recently reported the structural identification of the cluster compound $[Mo_3(N)(O)(CO)_4(\eta\text{-}C_5H_5)_3]$ (**1**), containing nitrogen with an unprecedented T-shaped geometry.[1] Its unusual synthesis, from $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and ethyl diazoacetate, led us to investigate more rational routes to this class of cluster with an exposed low-co-ordinate nitrogen of potentially high reactivity. The presence of both N and O co-ordinated in (**1**) suggested experiments with the nitrosyls $[M(CO)_2(NO)(\eta\text{-}C_5H_5)]$ (M = Cr, Mo, W) as precursors, with a view to effecting NO bond cleavage. For the molybdenum and tungsten compounds this has been achieved in reaction with $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) which give (**1**), its tritungsten analogue (**2**), and the rare heteronuclear species (**3**) and (**4**).

Heating (200 °C, *ca.* 1 h, no solvent, evacuated glass tube) $[Mo(CO)_2(NO)(\eta\text{-}C_5H_5)]$ with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, and $[W(CO)_2(NO)(\eta\text{-}C_5H_5)]$ with $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$, gave (**1**) and new dark-blue crystalline air-sensitive $[W_3(N)(O)(CO)_4(\eta\text{-}C_5H_5)_3]$ (**2**), respectively, in low yield. Under these conditions $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) decarbonylates to triple metal–metal bonded $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$, which we take to be an active reagent. Heating $[M(CO)_2(NO)(\eta\text{-}C_5H_5)]$ alone does not afford (**1**) or (**2**). I.r. [1 938w, 1 893s, and 1 833m,br. $cm^{-1}$ ($CH_2Cl_2$ solution)], $^1H$ n.m.r. [$\delta$ 5.64 (s, 10 H) and 6.12 (s, 5 H) ($CDCl_3$ solution)], and mass [$(P - nCO)^+$; $n$ = 0,2,3,4] spectra identify (**2**) as structurally very similar to (**1**), with both terminal and semi-bridging CO ligands and the same fluxional process which averages the environments of the $\eta\text{-}C_5H_5$ ligands on $M^2$ and $M^3$.

The first heteronuclear metal cluster nitride $[PtRh_{10}(N)$-




(1) $M^1 = M^2 = M^3 = Mo$
(2) $M^1 = M^2 = M^3 = W$
(3) $M^1 = W, M^2 = M^3 = Mo$
(4) $M^1 = Mo, M^2 = M^3 = W$

$(CO)_{21}]^{3-}$ was reported very recently, and contains five-co-ordinate nitrogen.[2] The new heteronuclear clusters $[Mo_2W(N)(O)(CO)_4(\eta\text{-}C_5H_5)_3]$ (**3**) and $[MoW_2(N)(O)(CO)_4(\eta\text{-}C_5H_5)_3]$ (**4**), with three co-ordinate nitrogen, may be obtained either by heating (conditions as above) $[Mo(CO)_2(NO)(\eta\text{-}C_5H_5)]$ with $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ or $[W(CO)_2(NO)(\eta\text{-}C_5H_5)]$ with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$. These dark-blue crystalline compounds are air-sensitive, especially in solution, but less so than (**2**). The i.r. spectra [(**3**): 1 955w, 1 909s, and 1 859m,br.; (**4**): 1 950w, 1 897s, and 1 849m,br. $cm^{-1}$ ($CH_2Cl_2$ solution)] reveal that they have the same basic structure as (**1**) and (**2**). The $MoW_2$ complex (**4**) shows three cyclopentadienyl signals in the $^1H$ n.m.r. spectrum [$\delta$ 5.48 (s, 5 H), 5.73 (s, 5 H), and 6.13 (s, 5 H) ($CDCl_3$ solution)] and a strong Mo=O stretch in the i.r. [914s $cm^{-1}$ (Nujol mull)], establishing the arrangement of metal atoms depicted and the absence of fluxionality. For the $Mo_2W$ complex the $^1H$ n.m.r. spectrum [$\delta$ 5.57 (s, 10 H) and 6.15 (s, 5 H)] identifies two $\eta\text{-}C_5H_5$ groups as being equivalent, probably on a time-average basis, and points to the arrangement (**3**).

It is attractive to visualise the nitrido-cluster being formed by addition of two $[M(CO)_2(\eta\text{-}C_5H_5)]$ radicals to a sixteen-electron $[M(N)(O)(\eta\text{-}C_5H_5)]$ species generated by thermolysis of $[M(CO)_2(NO)(\eta\text{-}C_5H_5)]$. However, the cluster formation is clearly much more complicated. Heating together $[Mo(CO)_2(NO)(\eta\text{-}C_5H_5)]$, labelled with 13.8% $N^{18}O$, and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ provides (**1**) containing no $^{18}O$ detectable by i.r. or mass spectroscopy. It is therefore apparent that the M=O unit found in the nitrido-clusters does not derive from NO, but from one of several other possible sources ($O_2$, $H_2O$, glassware). Nitrido–metal carbonyl clusters have been obtained previously[3–5] from nitrosyl complexes and it was suggested[5] that nitrosyl oxygen could appear in $CO_2$. We can now confirm this possibility. The heating together of $[Mo(CO)_2(N^{18}O)(\eta\text{-}C_5H_5)]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ does produce $CO^{18}O$, identified by mass spectroscopy.

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