

A New Low Co-ordination Mode for Nitrogen in a Nitrido Metal Cluster: X-Ray Crystal Structure of $[\text{Mo}_3(\text{N})(\text{O})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_3]$

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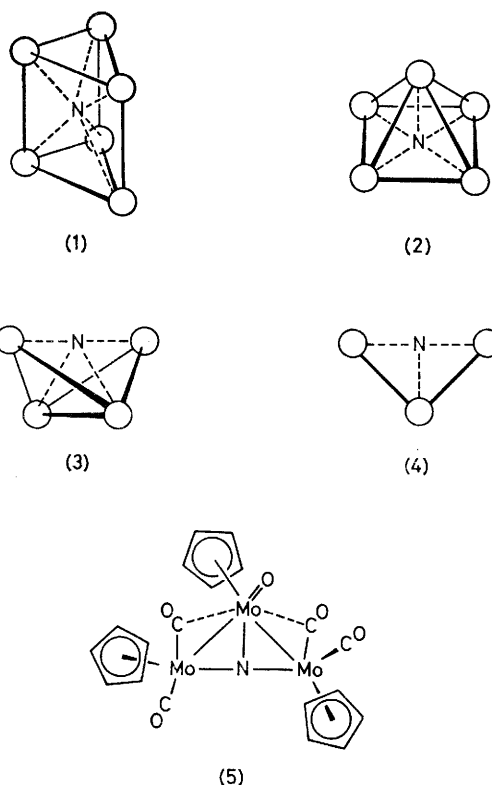
Heating $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with ethyl diazoacetate yields $[\text{Mo}_3(\text{N})(\text{O})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_3]$, shown by X-ray diffraction to contain a nitrogen atom with T-shaped co-ordination, bound to three molybdenum atoms.

Metal clusters containing nitrogen co-ordinated only to metal atoms (nitrides) are of interest as possible models for nitrogen on a metal surface. To date, clusters have been identified with six-co-ordinate interstitial nitrogen (1),¹ and five- and four-co-ordinate exposed nitrogen (2)² and (3).^{2,3} We now describe a new member of this class of compounds, containing potentially more reactive three-co-ordinate nitrogen with the unprecedented geometry (4).

Heating the formally triple metal-metal bonded $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with ethyl diazoacetate in boiling toluene provides dark green, air-stable, crystalline $[\text{Mo}_3(\text{N})(\text{O})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_3]$ (5) in 5% yield. The i.r. spectrum gave indications of terminal (1911s) and semi-bridging (1854m) CO ligands and of an Mo=O bond (902s cm^{-1}), while the ^1H n.m.r. spectrum [τ 4.00 (s, 5 H) and 4.38 (s, 10 H)] showed there to be three cyclopentadienyl groups, two of which appeared equivalent. Mass spectrometry and elemental analyses required the presence of a nitrogen atom and this was established by X-ray diffraction.

Crystal data: $\text{C}_{19}\text{H}_{15}\text{Mo}_3\text{NO}_5$, $M = 625.2$, monoclinic, space group $P2_1/c$, $a = 19.510(7)$, $b = 12.621(4)$, $c = 17.791(5)$ Å, $\beta = 115.31(3)^\circ$, $U = 3960(2)$ Å³. $Z = 8$; $F(000) = 2416$, $D_c = 2.097$ g cm^{-3} , Mo- K_α X-radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 18.57$ cm^{-1} . The structure was solved by heavy atom (direct and Fourier) methods and refined by the blocked-cascade least-squares technique using the SHELXTL program package. For 6312 unique observed [$I > 2\sigma(I)$] data, measured at 200 K on a Nicolet $P3m$ diffractometer in the range $4 \leq 2\theta \leq 53^\circ$, the current residual R is 0.024 †

The structure of one of the two crystallographically independent molecules is shown in Figure 1; the other molecule



differs only in the orientation of the cyclopentadienyl ligand attached to Mo(3). The central feature of the molecule is a nitrogen atom with T-shaped co-ordination [$\text{Mo}(2)\text{-N}(1)\text{-Mo}(3)$ 172° ; $\text{Mo}(1)\text{-N}(1)\text{-Mo}(3) = \text{Mo}(1)\text{-N}(1)\text{-Mo}(2) = 94^\circ$] to three molybdenum atoms with which it is essentially co-planar [$\text{N}(1)$ lies 0.012 Å out of the Mo_3 plane on the same side as O(1)]. The Mo-N distances are all somewhat shorter

† Atomic co-ordinates are available on request 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.

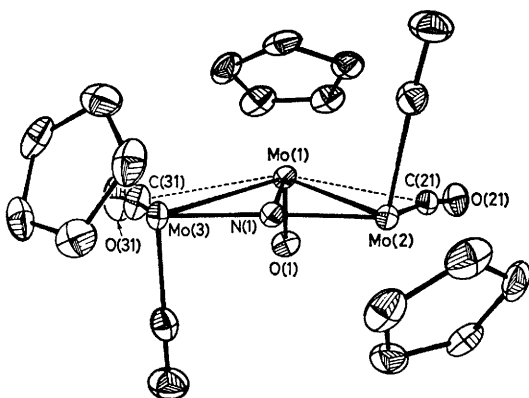


Figure 1. Molecular structure of $[\text{Mo}_3(\text{N})(\text{O})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_3]$ (**5**); molecule **1** is illustrated, with cyclopentadienyl hydrogen atoms omitted for clarity. Important averaged bond distances: Mo(1)–Mo(2) 2.851(2), Mo(1)–Mo(3) 2.848(2), Mo(1)–N(1) 1.972(4), Mo(2)–N(1) 1.914(4), Mo(3)–N(1) 1.928(4), Mo(1)–O(1) 1.708(4), Mo(1)–C(21) 2.658(5), Mo(1)–C(31) 2.802(5) Å; angles: Mo(2)–N(1)–Mo(3) 171.8(2), Mo(1)–N(1)–Mo(2) 94.4(2), Mo(1)–N(1)–Mo(3) 93.8(2), Mo(2)–C(21)–O(21) 170.6(4), Mo(3)–C(31)–O(31) 173.1(3)°.

than typically observed for Mo–N(sp) single bonds (*ca.* 2.13 Å), as expected if there are both σ and π components in the bonding. The Mo(1)–Mo(2) and Mo(1)–Mo(3) distances are at the lower end of the range observed for Mo–Mo single bonds (2.7–3.2 Å) and each is semi-bridged by a carbonyl ligand, C(21)O(21) and C(31)O(31) respectively. Molybdenum atoms Mo(2) and Mo(3) also bear a terminal CO ligand, but Mo(1) carries an oxygen atom at a typical Mo=O distance.

It is interesting to note that the nitrido-cluster (**5**) contains two molybdenum atoms [Mo(2) and Mo(3)] in environments characteristic of low-oxidation state chemistry and another [Mo(1)] in a high formal oxidation state. In fact, (**5**) may be considered to be derived *formally* from combination of a sixteen-electron $(\eta\text{-C}_5\text{H}_5)(\text{O})\text{Mo}\equiv\text{N}$ fragment with $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$. The addition of four π electrons of the Mo \equiv N bond and two electrons of the nitrogen lone pair across the Mo \equiv Mo triple bond then results in a net Mo(2)–Mo(3) bond order of zero, just as addition of four-electron donor alkynes to $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ reduces the Mo–Mo bond order to

unity.⁵ Whether nitrido-metal clusters can actually be generated by a combination of this kind is under investigation.

The cyclopentadienyl ligands on Mo(2) and Mo(3) are clearly inequivalent in the solid state, but the ¹H n.m.r. spectrum between –100 and +30 °C shows them to be equivalent in solution. It is likely that this arises from a rapid exchange of the terminal and semibridging carbonyl bonding modes associated with each of these molybdenum atoms, with corresponding rotation of the cyclopentadienyl groups from one side of the Mo₃N plane to the other, leading to their time-average equivalence. Such dynamic behaviour closely parallels the low-energy process exhibited by the alkyne adducts $[\text{Mo}_2(\text{CO})_4(\mu\text{-C}_2\text{R}_2)(\eta\text{-C}_5\text{H}_5)_2]$,⁵ which generates C₂ molecular symmetry. For both complexes the process may be viewed as rotation of the Mo(CO)₂($\eta\text{-C}_5\text{H}_5$) moieties relative to C \equiv C or Mo \equiv N units.

The unexpected formation of (**5**) from the reaction of $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with ethyl diazoacetate is presently mechanistically obscure, but may follow bridging of the Mo₂ unit by CH(CO₂Et)N₂ through nitrogen, as with Ph₂CN₂,⁴ with simultaneous co-ordination of ketonic oxygen to molybdenum. Other syntheses of nitrido-metal clusters have employed NO⁺ as a reagent or co-ordinated NO as a nitrogen source.^{1–3} However, the reaction of $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with NO gas provides only $[\text{Mo}(\text{CO})_2(\text{NO})(\eta\text{-C}_5\text{H}_5)]$.

The exposed nature of the nitrogen atom in (**5**), and its low co-ordination number, promise higher reactivity than those nitrogen atoms in (**1**), (**2**), and (**3**). Current investigations of the protonation and hydrogenation of (**5**) are directed towards determining whether this is indeed the case.

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