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Carbon-Nitrogen Bond Formation in the Reactions of Unsaturated Molecules with $Mo(NMe_2)_4$

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Introduction

In 1971, Chisholm and Bradley published the synthesis and characterization of $Mo(NMe_2)_4$, an air and moisture sensitive compound.(2) The molecule contains four amido ligands distributed around molybdenum as pictured in Figure 1.(4). The MoN_4 and $Mo(NC_2)_4$ units have virtual T_d and D_{2d} symmetry, respectively. All the amido ligands are planar and the Mo-N distances are short, 1.93 Å, indicative of π-bonding to the metal center which achieves a formal 18 valence electron configuration. In D_{2d} symmetry the two d-electrons are paired and result in a monomeric Mo(IV) diamagnetic compound.

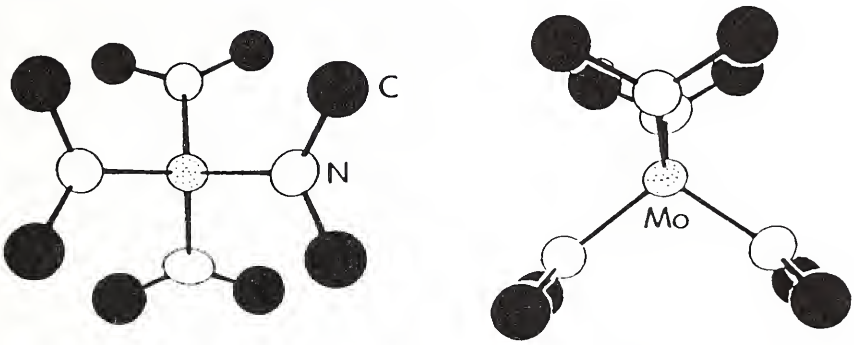

Figure 1. Two ORTEP drawings of $Mo(NMe_2)_4$ with hydrogen atoms omitted.

There are numerous molecules which have demonstrated the ability to insert into the M-N bond of a metal amide, for example: $C{\equiv}O$, $C{\equiv}NR$, CO_2, CS_2, $RC{\equiv}N$, $M_2(CO)_n$, $RN{=}O$, $RC{\equiv}CR'$, $R_2C{=}CR_2$.(7) This study was undertaken to explore the chemistry of $Mo(NMe_2)_4$ to gain fundamental insight into the reactivity of high oxidation state molybdenum species supported by strong π-bonding amido ligands towards various small unsaturated molecules. All reactions were carried out under inert atmospheres and all products are air and moisture sensitive.

Results and Discussion

Carbon Monoxide Reactions

The intense purple color of hydrocarbon solutions containing $Mo(NMe_2)_4$ changes instantaneously to brown upon exposure to carbon monoxide (>4 equiv). The ^1H and ^{13}C NMR spectra show the major diamagnetic product formed is 1,1,3,3-tetramethylurea which is consistent with a reaction pathway involving (i) $C{\equiv}O$ insertion to give a $Mo[C(O)NMe_2]$ moiety and (ii) reductive elimination by C-N bond formation: "$Mo(IV)[C(O(NMe_2](NMe_2)$" → "Mo(II)" + $(Me_2N)_2C{=}O$. A heterogeneous brown solution results when pentane is used as the solvent. Filtration of the insoluble powder and reduction of the volume of the filtrate yields a pure crystalline metal-containing compound, $Mo_3[C(O)NMe_2]_6(CO)_6(HNMe_2)_2$. A single crystal X-ray study revealed the molecular structure shown in Figure 2.

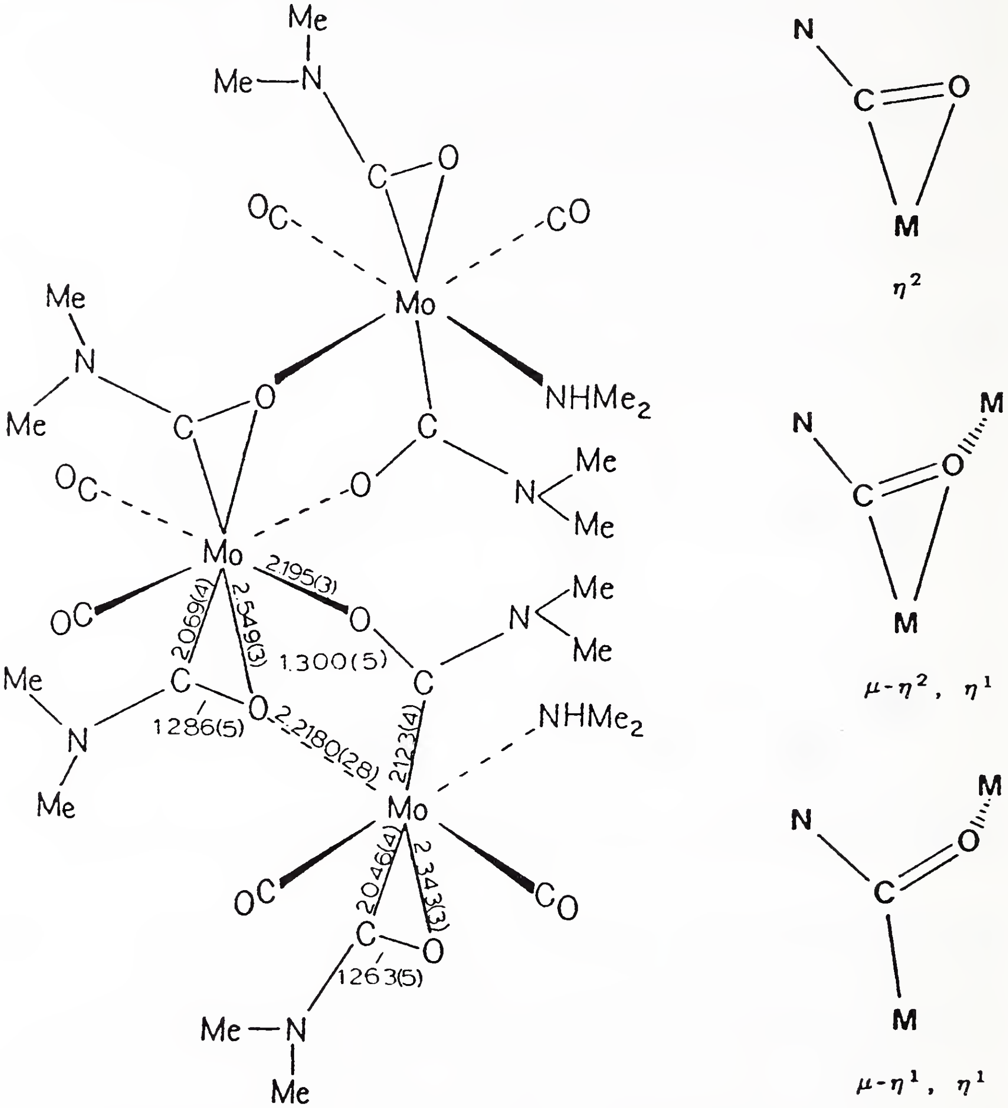

FIGURE 2. Schematic drawing of $Mo_3[C(O)NMe_2]_6(CO)_6(HNMe_2)_2$ with pertinent bond distances for the carbamoyl ligands and drawings of the three types of carbamoyl ligand bonding modes.

In the space group A2/a, the molecule has crystallographically imposed C_2 symmetry. The C_2 axis bisects the *cis*-$Mo(CO)_2$ portion of the central molybdenum atom, Mo(1), and relates the two terminal molybdenum atoms, Mo(2) and Mo(2)′, and their attendant ligands. Each molybdenum atom may be viewed as Mo(2+) if the carbamoyl ligands are counted as uninegative with the carbon-to-metal bond bearing the formal charge. Note that the terminal molybdenum atoms, Mo(2) and Mo(2)′, are bonded to three carbamoyl ligands while the central molybdenum atom, Mo(1), is bonded to four, but each molybdenum atom only makes two Mo-C bonds to carbamoyl ligands. If the η^2-(CO)-carbamoyl ligands are counted as four electron donors and all other carbon-, nitrogen-, and oxygen-to-molybdenum bonds are taken as dative two electron bonds, Mo(2) and Mo(2)′ attain 18 valence electrons while Mo(1) formally has 20 valence electrons. However, the atoms in the two carbamoyl ligands attached to Mo(1) lie in a plane, which together with the relatively long Mo(1)-O distance imply delocalized bonding. If the η^2-(CO)-carbamoyl ligands are presumed to occupy one coordination site, then the local geometry about each molybdenum atom corresponds to a distorted octahedron. The carbamoyl ligand, as seen in this one molecule, can act as an η^2-4 electron donor, a bridging, η^1-C, η^1-O, 4-electron donor, and a bridging, η^2-(CO), η^1-O, formal 6-electron donor as shown in Figure 1. The η^2-(CO) bonding mode has been seen before on a mononuclear actinide center.(5) However, the μ-η^2-(CO),η^1-O and μ-η^1-C,η^1-O are unfamilar bonding modes.

For comparison, the bond distances for the three types of carbamoyl are given in Figure 2. The Mo-C distances of the η^2-ligated carbamoyl ligands are notably shorter than the Mo-C distance of the μ-η^1,η^1-ligand. The C-O distances follow the same relative order as the Mo-C distances. It is interesting to note that the two η^2-carbamoyl ligands are orientated such that their respective $(C_2NCO)Mo$ units are essentially planar. These planes roughly bisect each of the cis-$Mo(CO)_2$ angles.

Isocyanide Reations [$C\equiv NR$ (R = Me, Et, Pr^i, Bzl)]

The intense purple color of hydrocarbon solutions containing $Mo(NMe_2)_4$ changes instantaneously to brown upon exposure to isocyanides, C≡ (where R = Me, Et, Pr^i, Bzl). Observations by ^1H and ^{13}C NMR spectroscopy show the major diamagnetic products formed are 1,1,3,3-tetramethyl-2-alkylguanidines (alkyl- = Me, Et, Pr^i, Bzl), analogous to tetramethylurea, the product formed in the reaction between $Mo(NMe_2)_4$ and $C\equiv O$. The product is consistent with a reaction pathway involving (i) $C\equiv NR$ insertion to give a $Mo[Me_2NCNR]$ moiety and (ii) reductive elimination together with C-N bond formation: "$Mo(IV)[Me_2NCNR](NMe_2)$" $\rightarrow$ Mo (II) + $(Me_2N)_2C=NR$. Unreacted $Mo(NMe_2)_4$ in the reaction mixture decomposes to form $HNMe_2$ and other unidentified compounds.

To identify the formation of 1,1,3,3-tetramethyl-2-alkylguanidine (alkyl = Me, Et, Pr^i, and Bzl), 1,1,2,3,3-pentamethylguanidine was synthesized independently, and was added to an NMR tube containing the reaction mixture of $Mo(NMe_2)_4$ and $C\equiv NMe$. The resonances in the reaction mixture assigned to 1,1,2,3,3-pentamethylguanidine increased in intensity relative to the solvent protio impurity. The methyl groups of 1,1,3,3-tetramethyl-2-alkylguanidine species have a characteristic pair of singlets (*ca.* δ 2.48 ppm) in the ^1H NMR spectrum which are derived from the diastereotopic methyl groups.

tert-Butyl Isocyanide Reactions

In hydrocarbon solutions $Mo(NMe_2)_4$ reacts rapidly with $C\equiv NBu^t$ (*ca.* 4 equiv) at ambient temperatures producing $Mo_2(\mu\text{-}NMe_2)_2(CNBu^t)_8$ as a red-brown crystalline solid in an isolated 50% yield. When the reaction is carried out in a deuterated solvent, the filtrate shows resonances in the ^1H and ^{13}C NMR spectra assignable to 1,1,3,3-tetramethyl-2-*tert*-butylguanidine. The proposed balanced chemical equation is:

$$2Mo(NMe_2)_4 + 11C\equiv NBu^t \dashrightarrow Mo_2(\mu\text{-}NMe_2)_2(CNBu^t)_8 + 3Me_2NC(=NBu^t)NMe_2$$

Upon first examination, the infrared spectrum (mineral oil mull or KBr pellet) does not appear clean; bands assignable to C-N multiple bonds appear at 2045(m brd), 1920(m sh brd), and 1795(vs brd) cm^{-1}. The ^1H NMR integral intensities showed the presence of one amido ligand to four icocyanide ligands. The isocyanide ligands are in two environments and exchange positions (T_c = 34.8°, $\triangle G\ddagger$ = 14.9 ± 0.3 kcal/mol) consistent with axial-equatorial ligand exchange.(8) The NMR data are consistent with an edge-shared bioctahedral d^5-d^5 dimer with briding amido ligands and four terminal isocyanide ligands on each molybdenum atom. The molecular configuration was uncertain due to the broad bands in the infrared spectrum. Therefore, a crystal structure determination was undertaken.

The molecular structure of $Mo_2(\mu\text{-}NMe_2)_2(CNBu^t)_8$ is shown in Figure 3. The structure contains a crystallographically imposed C_2 axis through the bridging nitrogen atoms.

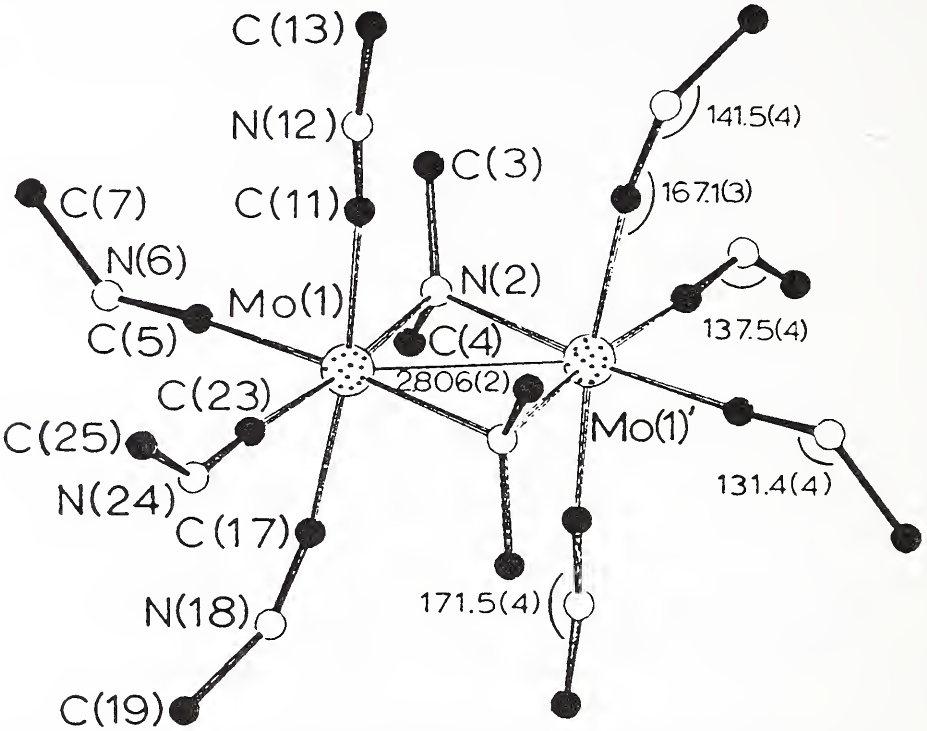

FIGURE 3. Ball-and-stick drawing of $Mo_2(\mu\text{-}NMe_2)_2(CNBu^t)_8$. The *tert*-butyl metyl carbon atoms and all hydrogen atoms are not shown. Pertinent bond distances (Å) and angles (°) are: Mo(1)-N(2) 2.212(3), Mo(1)-N(2)' 2.230(3), Mo(1)-C(5) 1.996(4), Mo(1)-C(23) 2.017(4), Mo(1)-C(17) 2.065(4), Mo(1)-C(11) 2.131(4), C(5)-N(6) 1.213(5), C(23)-N(24) 1.192(5), C(17)-N(18) 1.188(5), C(11)-N(12) 1.166(5), Mo(1)-N(2)-Mo(1)' 78.35(11), N(2)-Mo-N(2)' 101.65(11).

Molybdenum has been reduced from Mo(IV) to Mo(I), presumably by reductive C-N bond formation of $Me_2NC(=NBu^t)NMe_2$. The two molybdenum atoms are in pseudo octahedral environments sharing an edge with a Mo-Mo distance of 2.806 Å corresponding to a Mo-Mo single bond.(3) For comparison we note that related compounds $Mo_2(\mu\text{-}X)_2(CO)_8$, where X = SBu^t (6) and I,(1) have Mo-Mo distances of 2.984 Å and 3.164 Å, respectively. There are four types of isocvanide ligands in the solid state structure accounting for the broad bands in the infrared spectrum.

It is interesting to note that the analogous $Mo_2(\mu\text{-}SBu^t)_2(CNBu^t)_8$ species can be synthesized from $Mo(SBu^t)_4$ and $CNBu^t$, although no crystal structure determination has been undertaken.(6)

Xylyl Isocyanide Reactions

Hydrocarbon solutions of $Mo(NMe_2)_4$ react rapidly with C≡Nxylyl (4 equiv.) at ambient temperatures to give $Mo(\eta^2\text{-}C(NMe_2)Nxylyl)_4$, isolable as pure red-brown crystals in *ca.* 60% yield on cooling the reaction solution to -15 °C.

$$Mo(NMe_2)_4 + 4CNxylyl \text{ -----> } Mo(\eta^2\text{-}C(NMe_2)Nxylyl)_4$$

Crystallization from toluene yields a 1:1 solvate. The infrared spectrum of the crystalline product showed no bands assignable to $\nu(C\equiv N)$ in the region 2200-1900 cm^{-1}, indicative of C-N or C-C double bond stretches. The ^1H NMR spectrum revealed eight signals of equal integral intensity assignable to methyl groups (NMe_2 and $ArMe_2$), while the ^{13}C NMR spectrum revealed two resonances of equal intensity at δ 213 and 194 ppm assignable to NCN carbons, four amido methyl carbons (*D* 44.8, 43.6, 38.3, and 37.9 ppm), and four aryl-methyl carbons (δ 20.5, 19.9, 19.1, and 18.1 ppm), all of roughly equal intensity.

The molecular structure of $Mo(\eta^2\text{-}C(NMe_2)Nxylyl)_4$ is shown in Figure 4. The central $Mo(\eta^2\text{-}C(NC_2)NC)_4$ skeleton looking down the virtual C_2 axis, which bisects the C(18)-Mo-C(44) angle, is shown in Figure 5. There are two types of amidino ligands. One type haws shorter Mo-C and Mo-N distances relative to the other, but each is bonded to the metal atom in a η^2 manner. The amidino ligands having the shorter Mo-C and Mo-N distances have longer η^2-(C-N) distances than those with long Mo-C and Mo-N distances. The amido nitrogen to isocyanide carbon (Me_2N-CNxylyl) distances are all essentially the same, which together with the planarity of the C_2NCN moieties are indicative of extensive π-delocalization with the ligand.

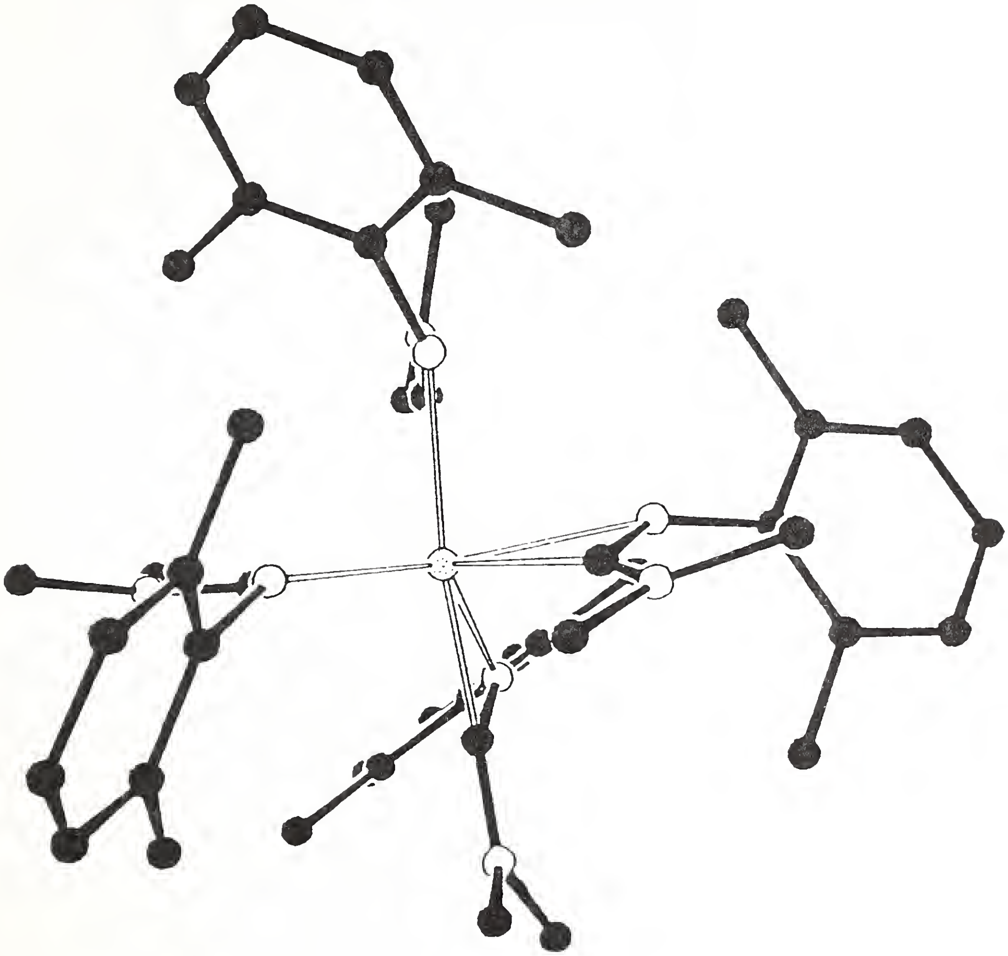

FIGURE 4. Ball-and-stick dragram of $Mo(\eta^2\text{-}C(NMe_2)Nxylyl)_4$ molecule showing the alignment of the four η^2-CN ligands. Viewed down the *z* axis, NCN units are aligned in a pairwise manner along *xz* and *yz* planes.

$Mo(\eta^2\text{-}C(NMe_2)Nxylyl)_4$ provides the first example of 1 a formal insertion of an isocyanide ligand into a M-N bond of a transition-metal amide, 2 a homoleptic

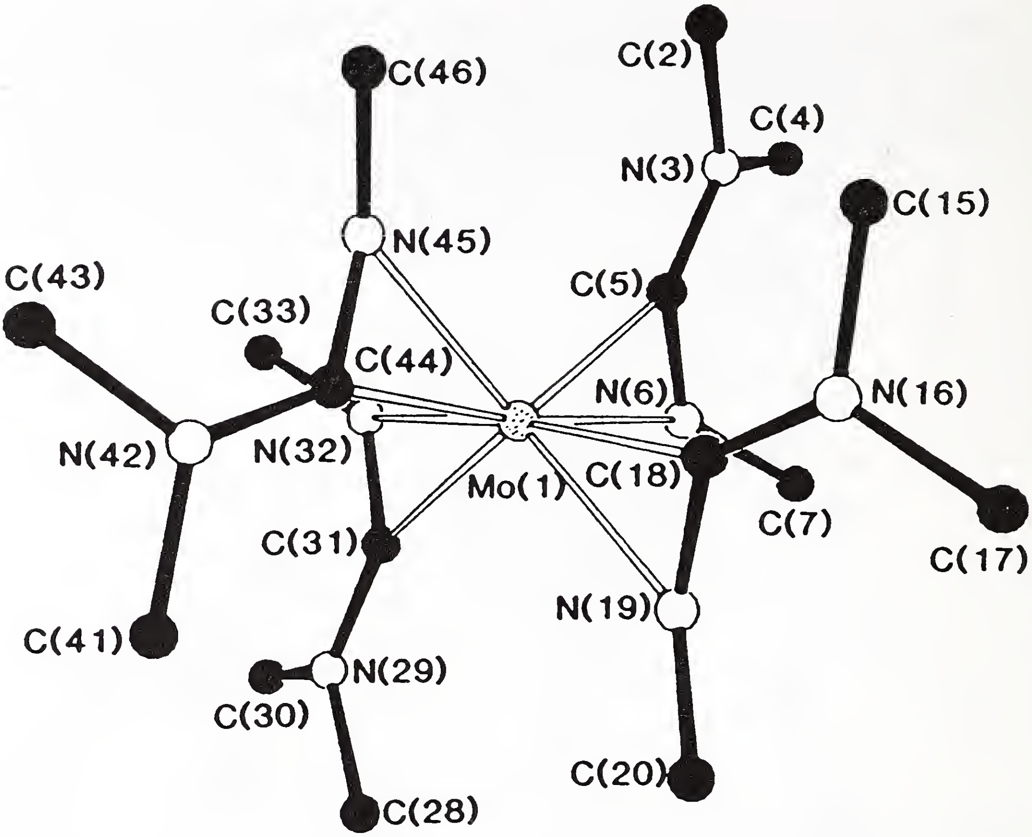

FIGURE 5. View of the central $Mo(\eta^2\text{-}C(NC_2)NC)$ moiety showing the atom number scheme. Pertinent distances (Å): for short Mo-C and Mo-N, Mo-C(18) 2.032(3), Mo-N(19) 2.205(2), Mo-C(44) 2.024(3), Mo-N(45) 2.181(2), η^2-(C-N) 1.336(7) (av); for long Mo-C and Mo-N, Mo-C(5) 2.111(3), Mo-N(6) 2.278(2), Mo-C(31) 2.116(3), Mo-N(32) 2.294(2), η^2-(C-N) 1.297(3) (av) and Me_2N-CNxylyl 1.335(6) (av).

metalloamidine complex, and 3 structural characterization of the $\eta^2\text{-}C(NC_2)NR'$ ligand. It also provides an example of a C_2 isomer of a distorted dodecahedral $Mo(\eta^2\text{-}CN)_4$ unit which is one of six possible *mmmm* isomers.(9)

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