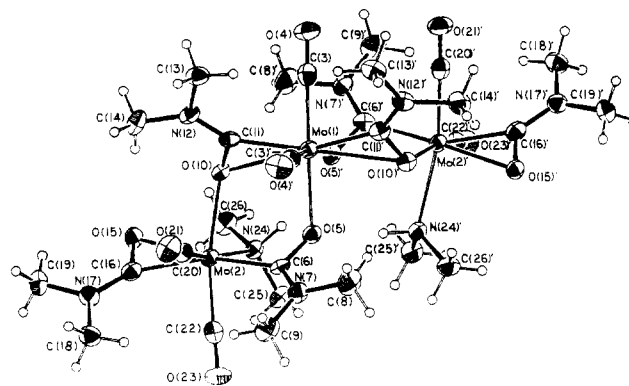


We have demonstrated that the asymmetry arising from heterobidentate ligand bonding to transition-metal clusters can be stereospecifically translated into ligand configuration. The initially observed (synthetic) de's are different than those obtained under equilibrating conditions. These results indicate the magnitudes of diastereomeric excesses that can reasonably be expected in similar cluster systems and the sensitivity of observed de's to substituents. Our observations set good precedent for the utility of the broad variety of asymmetric clusters now available<sup>1-7,21</sup> in asymmetric synthesis and catalysis.<sup>22</sup>

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**Figure 1.** An ORTEP view of the  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$  molecule giving the atomic number scheme used in the tables.

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### $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$ . An Unexpected Product Formed in the Carbonylation of $\text{Mo}(\text{NMe}_2)_4$ Displaying Three Distinct Modes of Carbamoyl-Molybdenum Bonding

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**Summary:** From the reaction between  $\text{Mo}(\text{NMe}_2)_4$  and CO (>4 equiv) in hydrocarbon solvents, the yellow crystalline compound  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$  has been obtained and characterized. In the solid state, the molecule has  $C_2$  symmetry. There are three *cis*- $\text{Mo}(\text{CO})_2$  units, two related by symmetry. Each molybdenum atom has 18 valence shell electrons and may be ascribed as oxidation state +2 in a distorted octahedral geometry considering the  $\eta^2$ -carbamoyl ligands are uninegative, occupy one coordination site, and donate four electrons. The  $\text{Mo}_3$  chain is held together by two pairs of bridging carbamoyl ligands, one of which is  $\eta^2$ -(CO)-bonded to the central molybdenum atom Mo(1) and  $\eta^1$ , oxygen-bonded to the outer molybdenum atoms Mo(2) and Mo(2)'; the other pair are  $\eta^2$ -(CO)-bonded to Mo(2)/Mo(2)' and Mo(1), respectively. NMR data indicate that the trimeric unit is retained and relatively rigid in solution.

The  $d^2$  group 4-6 metal complexes or fragments are known to be capable of binding  $\pi$ -acceptor ligands such as alkynes, olefins, carbon monoxide, diazoalkanes, and, even in some instances, dinitrogen. Well-known examples include  $\text{Cp}_2\text{Ti}(\text{CO})_2$ ,<sup>1</sup>  $[\text{Cp}^*\text{Zr}(\text{N}_2)]_2(\mu\text{-N}_2)$ ,<sup>2</sup>  $\text{Cp}^*\text{Ta}(\text{H})(\text{C}_2\text{H}_4)$ ,<sup>3</sup>  $\text{Mo}(\text{O}-t\text{-Bu})_4(\text{N}_2\text{C}_2\text{Ar}_2)$ ,<sup>4</sup> and  $[\text{WCl}_4(\text{Ph}_2\text{C}_2)]_2$ .<sup>5</sup> We are currently examining the reactivity of the coordi-

nately unsaturated,  $\pi$ -donor-stabilized,  $d^2$  complex  $\text{Mo}(\text{NMe}_2)_4$  toward  $\pi$ -acid molecules<sup>7</sup> and wish to report here our discovery of an unexpected and unusual product formed in the reaction involving carbon monoxide.

The intense purple color of hydrocarbon solutions containing the extremely air- and moisture-sensitive compound  $\text{Mo}(\text{NMe}_2)_4$  changes virtually instantaneously to brown upon exposure to carbon monoxide (>4 equiv). By  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy the main diamagnetic product formed is 1,1,3,3-tetramethylurea that suggests a reaction pathway involving (i) CO insertion to give a  $\text{Mo}[\text{C}(\text{O})\text{NMe}_2]$  moiety and (ii) reductive elimination by C-N bond formation " $\text{Mo}(\text{IV})[\text{C}(\text{O})\text{NMe}_2(\text{NMe}_2)] \rightarrow \text{Mo}(\text{II}) + (\text{Me}_2\text{N})_2\text{CO}$ ". When pentane is used as the solvent, an inhomogeneous brown solution results. Filtering this powder and reducing the volume of the filtrate yield the only isolable pure metal-containing compound  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{HNMe}_2)_2$ ,<sup>8</sup> 5-20% yield.

The infrared spectrum was suggestive of (i)  $\nu(\text{NH})$  at  $3225\text{ cm}^{-1}$  for the coordinated  $\text{Me}_2\text{NH}$  ligand, (ii) *cis*- $\text{Mo}(\text{CO})_2$  units,  $\nu(\text{CO}) = 1948$  and  $1925\text{ cm}^{-1}$  in the integral ratio 0.68,<sup>9</sup> and (iii) carbamoyl ligands<sup>10</sup> having  $\nu(\text{NCO})$  bands at 1585, 1530, and  $1500\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum allowed the identification of a bound  $\text{HNMe}_2$  ligand having diastereotopic methyl groups and three different carbamoyl ligands, each with two *NMe* carbons, implying restricted rotation about the  $\text{Me}_2\text{N}-\text{CO}$  bond. Even when the temperature is increased to  $60^\circ\text{C}$ , all resonances in the  $^1\text{H}$  NMR spectrum are well-defined with no noticeable line broadening as might have been anticipated for a fluxional molecule. The  $^{13}\text{C}\{^1\text{H}\}$  spectrum of the  $^{13}\text{CO}$ -labeled compound was complicated by  $^{13}\text{C}-^{13}\text{C}$  coupling between carbamoyl-carbamoyl, carbonyl-carbonyl, and carbamoyl-carbonyl carbon atoms. Identification of the carbamoyl carbon atoms,  $\text{Me}_2\text{N}-\text{CO}$ , was made possible by the fact that  $^3J_{^{13}\text{C}-^1\text{H}}$  coupling causes broadening in the proton-coupled  $^{13}\text{C}$  NMR spectra. Three of the six signals

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(7) A reaction involving 2,6-dimethylphenyl isocyanide,  $\text{CNAr}$  (4 equiv), has been found to give a tetrakis( $\eta^2$ -amidino) complex  $\text{Mo}(\eta^2\text{-C}(\text{NMe}_2)\text{N}(\text{Ar})_2)_4$ : Chisholm, M. H.; Hammond, C. E.; Huffman, J. C.; Ho, D., submitted for publication in *J. Am. Chem. Soc.*

(8) Anal. Calcd (Found): C, 34.37 (34.57); H, 5.15 (5.04); N, 11.45 (11.47).  $^1\text{H}$  NMR data (toluene- $d_6$  at  $22^\circ\text{C}$ ):  $\delta$  3.61 (septet, 2 H,  $\text{HNMe}_2$ ), 3.16 (s, 6 H,  $\text{NMe}_2$ ), 3.13 (s, 6 H,  $\text{NMe}_2$ ), 3.06 (s, 6 H,  $\text{NMe}_2$ ), 3.05 (s, 6 H,  $\text{NMe}_2$ ), 2.98 (s, 6 H,  $\text{NMe}_2$ ), 2.97 (s, 6 H,  $\text{NMe}_2$ ), 2.61 (d, 6 H,  $\text{HNMe}_2$ ), 2.44 (d, 6 H,  $\text{HNMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR spectral data using  $^{13}\text{CO}$  ( $\text{CDCl}_3$  at  $22^\circ\text{C}$ ):  $\delta$  240.76 (m, 2 C, carbonyl), 239.05 (m, 2 C, carbamoyl), 235.63 (t, 2 C, carbonyl), 233.93 (m, 2 C, carbonyl), 230.24 (t, 2 C, carbamoyl), 210.47 (m, 2 C, carbamoyl).

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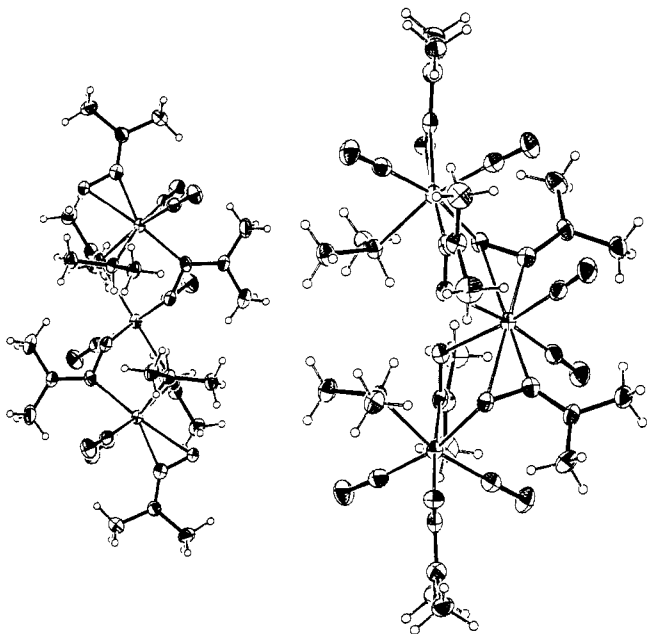
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**Figure 2.** Two ORTEP views of the  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$  molecule showing the coplanarity of the trans carbamoyl ligands.

in the region 210–240 ppm (relative to  $\text{Me}_4\text{Si}$ ) thus broadened could be assigned to the  $\text{Me}_2\text{NCO}$  ligands.<sup>8</sup>

The spectroscopic data, together with the elemental analytical data, require, at minimum, a trinuclear structure,  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$ , though the detailed connectivity of the various groups could not reliably be ascertained. Accordingly, a single-crystal X-ray study was undertaken,<sup>11</sup> and this revealed the molecular structure shown in Figure 1.

In the space group  $A2/a$ , the molecule has crystallographically imposed  $C_2$  symmetry. The  $C_2$  axis bisects the *cis*- $\text{Mo}(\text{CO})_2$  moiety of the central molybdenum atom  $\text{Mo}(1)$  and relates the two terminal molybdenum atoms  $\text{Mo}(2)$  and  $\text{Mo}(2)'$  and their attendant ligands. Each molybdenum atom may be viewed as  $\text{Mo}(2+)$  if the carbamoyl ligands are counted as uninegative with the carbon-to-metal bond bearing the formal charged character. Note the terminal molybdenum atoms  $\text{Mo}(2)$  and  $\text{Mo}(2)'$  are bonded to three carbamoyl ligands while the central molybdenum atom  $\text{Mo}(1)$  is bonded to four, but each molybdenum atom only makes two  $\text{Mo}-\text{C}$  bonds to carbamoyl ligands. If the  $\eta^2(\text{CO})$ -carbamoyl ligands are counted as 4-electron donors and all other carbon-, nitrogen-, and oxygen-to-molybdenum bonds are taken as dative 2-electron bonds,  $\text{Mo}(2)$  and  $\text{Mo}(2)'$  attain a share of 18 valence electrons while  $\text{Mo}(1)$  has formally 20 valence electrons. However, the atoms  $\text{C}(11)$ ,  $\text{O}(10)$ ,  $\text{C}(11)'$ ,  $\text{O}(10)'$ , and  $\text{Mo}(1)$  all lie in a plane, which together with the relatively long  $\text{Mo}(1)-\text{O}(10)$ ,  $\text{O}(10)'$  distances implies a delocalized bonding situation with a lone pair on the oxygen atoms. If  $\eta^2(\text{CO})$ -carbamoyl ligands are taken to occupy one coordination site, then the local geometry about each molybdenum atom corresponds to a distorted octahedron. This rather satisfying situation for molybdenum is achieved because of the remarkable flexibility and accommodating nature of the carbamoyl ligand which, as seen in this one molecule, can act as a  $\eta^2$ , 4-electron donor,<sup>12</sup>

(11) Crystal data for  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$  at  $-154^\circ\text{C}$ : space group  $A2/a$ ,  $a = 24.261(4)$  Å,  $b = 18.198(2)$  Å,  $c = 9.246(1)$  Å,  $\beta = 96.09(0)^\circ$ ,  $Z = 4$ ,  $d_{\text{calc}} = 1.601$  g  $\text{cm}^{-3}$ . A total of 2643 unique data points were collected of which 2380 had  $I > \sigma(I)$  and were used in the refinement,  $R(F) = 0.0289$  and  $R_w(F) = 0.0341$ .

**Table I. Pertinent Bond Distances (Å) for the Carbamoyl Ligands in  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{HNMe}_2)_2$**

	$\eta^2$ <sup>a</sup>	$\mu-\eta^1, \eta^2$ <sup>b</sup>	$\mu-\eta^1, \eta^1$ <sup>c</sup>
Mo-C	2.046 (4)	2.069 (4)	2.123 (4)
Mo(1)-O		2.549 (3)	2.195 (3)
Mo(2)-O	2.343 (3)	2.218 (3)	
C-O	1.263 (5)	1.286 (5)	1.300 (5)
C-N	1.317 (6)	1.335 (5)	1.339 (5)

<sup>a</sup>  $\text{O}(15)$ ,  $\text{C}(16)$ ,  $\text{N}(17)$ . <sup>b</sup>  $\text{O}(10)$ ,  $\text{C}(11)$ ,  $\text{N}(12)$ . <sup>c</sup>  $\text{O}(5)$ ,  $\text{C}(6)$ ,  $\text{N}(7)$ .

a bridging,  $\eta^1\text{-C}$ ,  $\eta^1\text{-O}$ , 4-electron donor, and a bridging,  $\eta^2(\text{CO})$ ,  $\eta^1\text{-O}$ , formal 6-electron donor. The  $\eta^2(\text{CO})$  and  $\mu-\eta^1, \eta^1$  bonding modes have been seen before in mononuclear actinide<sup>13</sup> and di- and polynuclear transition-metal carbonyl chemistry,<sup>14</sup> respectively. We are not, however, familiar with any prior example of the  $\mu$ -6-electron donor mode. The latter is stereochemically and electronically similar to the bridging  $\eta^2, \eta^1(\text{CN})$  moiety in  $\text{W}_2(\text{OCH}_2\text{-t-Bu})_6(\text{NCNMe}_2)_3$ .<sup>15</sup>

A comparison of bond distances for the three types of carbamoyl ligands is given in Table I. (1) The  $\text{Mo}-\text{C}$  distances of the  $\eta^2$ -ligated carbamoyl ligands are notably shorter than those of the  $\text{Mo}-\text{C}$  distance of the  $\mu-\eta^1, \eta^2$ -ligand. The short  $\text{Mo}-\text{C}$  distances, 2.04–2.06 Å, are in the range commonly found for 4-electron,  $\pi$ -donor alkynes bonded to Mo and W atoms.<sup>16</sup> (2) The  $\text{C}-\text{O}$  distances follow the order of  $\text{Mo}-\text{C}$  distances. It is also interesting to note that the two  $\eta^2$ -carbamoyl ligands are orientated such that their respective  $(\text{C}_2\text{NCO})\text{Mo}$  units are essentially planar. These planes roughly bisect each of the *cis*- $\text{Mo}(\text{CO})_2$  angles. See Figure 2. This situation is reminiscent of the coplanarity of the trans  $\pi$ -donor alkoxide<sup>17</sup> ligands in  $\text{L}_2\text{Mo}(\text{OR})_2(\text{CO})_2$  that also contain  $d^4$  *cis*- $\text{Mo}(\text{CO})_2$  functionalities. An analogous electronic explanation<sup>18</sup> can be forwarded on the basis of an orbital splitting diagram of the  $e_{2g}^4$  configuration and the  $\pi$ -donor properties of the carbamoyl ligands.

Finally, we note that the formation of  $\text{Mo}_3[\text{C}(\text{O})\text{NMe}_2]_6(\text{CO})_6(\text{HNMe}_2)_2$  represents a rare example of CO insertion into a metal–amide bond,<sup>13,19</sup> though this may be only a formal view of the reaction since the overall stoichiometric and reaction patterning remains to be established.<sup>20</sup>

**Supplementary Material Available:** Tables of fractional coordinates, anisotropic thermal parameters, and complete listings of bond distances and angles (4 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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