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Reactions of Metal-to-Metal Multiple Bonds. 2.[1] Reactions of Bis(cyclopentadienyl)tetracarbonyldimolybdenum with Small Unsaturated Molecules. Structural Characterization of μ-Dimethylaminocyanamide-bis(cyclopentadienyl)-tetracarbonyldimolybdenum

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Abstract: The reactivity of $Cp_2Mo_2(CO)_4$ toward CO_2, CS_2, 1,3-butadiene, N_2O, PhN=NPh, CF_3CN, CH_3CN, *i*-PrCN, $(NH_2)_2C$=NCN, H_2NCN, and Me_2NCN has been examined under conditions comparable to those which allowed preparation of various acetylene and allene adducts. Only the last two reacted, yielding dark red, crystalline products, $Cp_2Mo_2(CO)_4$-$NCNR_2$, moderately stable in air. The structural and dynamic properties of the dimethylcyanamide adduct have been studied in detail. The structure of the molecule appears to be the same in the crystal and in solution. Two $CpMo(CO)_2$ units are joined by an Mo–Mo bond (3.056 (1) Å) and a bridging Me_2NCN group that donates a nitrogen lone pair to one Mo atom and a CN π-electron pair to the other one. This structure possesses no symmetry and the NMR spectra (^{13}C, ^1H) at −40 °C accordingly show the presence of four nonequivalent CO groups, two nonequivalent CH_3 groups, and two nonequivalent Cp groups. As the temperature is raised all resonances broaden and by about 66 °C the spectrum shows time-average equivalence of the four CO groups, the two CH_3 groups, and the two Cp rings. Possible pathways for fluxionality are discussed. The substance crystallizes in space group $P2_1/n$ with unit cell dimensions $a = 8.326$ (4) Å, $b = 14.839$ (4) Å, $c = 14.875$ (4) Å, $\beta = 91.44$ (2)°, $V = 1837$ (1) Å³, and $Z = 4$. The structure was refined to $R_1 = 0.054$ and $R_2 = 0.081$ using 1998 reflections for which $I > 3\sigma(I)$.

Introduction

$Cp_2Mo_2(CO)_4$, which contains a molybdenum-to-molybdenum triple bond, has been shown[1,3] to react with allenes and acetylenes to form 1:1 adducts in which the unsaturated hydrocarbon acts as a four-electron donor spanning two directly bonded molybdenum atoms. This paper reports an extension of our studies of the reactivity of $Cp_2Mo_2(CO)_4$ toward small, unsaturated molecules, especially those containing heteroatoms, where modes of interaction other than π-electron donation might be anticipated.

Results and Discussion

We have examined the reactions of $Cp_2Mo_2(CO)_4$ with a number of small, unsaturated molecules, all of which are known to form 1:1 adducts with mononuclear transition metal complexes and are potentially capable of acting as four electron donor ligands to a bimetallic acceptor. These reactions are summarized in Table I. The experimental conditions are comparable to those required for the formation of allene[1] or acetylene[3] adducts with $Cp_2Mo_2(CO)_4$. Only the cyanamides, R_2NCN, where R = H or Me, formed stable adducts. It is not clear why the other substrates failed to react.

$Cp_2Mo_2(NCNR_2)$ Compounds (R = H and Me). The compounds $Cp_2Mo_2(CO)_4(NCNR_2)$, where R = H and Me, are dark red-brown, crystalline solids. They appear relatively stable toward the atmosphere in the solid state but are fairly rapidly decomposed by air when in solution. They are appreciably soluble in benzene and toluene but only sparingly soluble in alkane solvents. In the mass spectrum they show parent ions $Cp_2Mo_2(CO)_4(NCNR_2)^+$ followed by ions resulting from pairwise loss of CO ligands, $Cp_2Mo_2(CO)_2(NCNR_2)^+$ and $Cp_2Mo_2(NCNR_2)^+$. There is also an alternate mode of fragmentation involving loss of the $NCNR_2$ ligand to yield $Cp_2Mo_2(CO)_4^+$. The most intense ions correspond to

Figure 1. An ORTEP drawing of the molecular structure of Cp₂Mo₂(CO)₄(NCNMe₂). Atoms are represented by their ellipsoids of thermal vibration drawn to enclose 50% of the electron density.

Table I. Attempted Reactions of Cp₂Mo₂(CO)₄

Substrate	Reaction conditions[a]	Observations
O=C=O	Sealed tube, 2 at CO₂, T = 35 °C	No reaction
S=C=S	Large excess, T = 35 °C	No reaction
H₂C=CHCH=CH₂	80–90 °C for 1 day, sealed tube	No reaction
N=N=O	80–90 °C for 1 day, sealed tube	No reaction
PhN=NPh	Large excess, T = 35 °C	No reaction
CF₃C≡N	80–90 °C for 1 day, sealed tube	No reaction
CH₃C≡N	80–90 °C for 1 day, sealed tube	No reaction
(CH₃)₂CHC≡N	Large excess, T = 35 °C	No reaction
(NH₂)₂C=NC≡N	Large excess, T = 35 °C	No reaction
(CH₃)₂NC≡N	Large excess, T = 35 °C	1:1 adduct
H₂NC≡N	Large excess, T = 35 °C	1:1 adduct

Cp₂Mo₂(NCNR₂)⁺ and Cp₂Mo₂(CO)₄⁺. This finding contrasts with the fragmentation pattern of allene adducts Cp₂Mo₂(CO)₄(allene) which do *not* show loss of allene.

In the infrared spectrum several bands are observed in the region 2200–1600 cm⁻¹. (See Experimental Section for details.) These absorption bands must be associated with stretching vibrations of the carbonyl and cyanamide ligands. These observations parallel the findings of Bock,[4,5] who prepared the first transition metal carbonyl dialkylcyanamide complexes having empirical formula (R₂NCN)Ni(CO). Originally these compounds were believed[4,5] to adopt the dimeric structure shown in I. However, a subsequent crystallographic

I

study showed[6] that the piperidine cyanamide Ni-(C₅H₁₀NCN)CO has a trimeric structure with a triangulo Ni₃ core, terminally bonded carbonyl ligands, and bridging cyanamide ligands. Each cyanamide could be considered to form an N σ bond to one nickel atom and a C≡N μ bond to the other nickel atom as shown in II.

II

In view of the interesting bonding possibilities that exist for the Mo₂(NCNMe₂) moiety and the interesting dynamical solution behavior indicated by NMR studies (discussed later) we proceeded directly toward a full structural characterization of Cp₂Mo₂(CO)₄(NCNMe₂).

Structure of Cp₂Mo₂(CO)₄(NCNMe₂). The molecular structure as determined by x-ray crystallography is shown in Figure 1. The crystal is composed of these molecules packed with normal nonbonded contacts. The atomic positional coordinates and thermal vibration parameters are listed in Table II, and bond distances and bond angles are listed in Tables III and IV. The molecules occupy general positions in the unit cell and therefore have no crystallographically imposed symmetry. Nor are there any approximate symmetry elements, as Figure 1 shows, because of the orientation of the Me₂NCN

ligand. The Cp₂Mo₂(CO)₄ portion of the molecule does, however, come close to having a C_2 axis perpendicular to the center of the Mo–Mo bond such that rotation exchanges the C(1)O(1)/C(3)O(3) and C(2)O(2)/C(4)O(4) pairs of CO groups, the pair of Cp groups, and the Mo atoms. This local C_2 symmetry is violated mainly by the fact that the Mo(1)-Mo(2)-C(3) angle, 65.6°, is appreciably smaller than the Mo(2)-Mo(1)-C(1) angle, 85.1°.

Each molybdenum atom is bonded to one essentially planar η^5-C₅H₅ ring (metal to Cp carbon distances range from 2.29 (1) to 2.40 (1) Å) and to two essentially linear carbonyl groups with M–C–O angles ranging from 170.0 (8) to 178.0 (8)°. It is interesting to note that the carbonyl group that deviates most from linearity, Mo(2)-C(3)-O(3) = 170.0 (8)°, also has the smallest M–M–C angle, Mo(1)-Mo(2)-C(3) = 65.6 (3)°; however, with an Mo(1)-C(3) distance of 2.861 (9) Å, there is presumably little or no electronic interaction and the position of this carbonyl is presumably due primarily to intramolecular steric factors.

The Mo–Mo distance here, 3.056 (1) Å, is intermediate between those in the Cp₂Mo₂(CO)₄(RC≡CR) compounds,[3b,c] 2.977 (1), 2.984 (1) Å, and that in Cp₂Mo(CO)₄(allene), 3.117 (1) Å. It seems likely that these distances are determined by the bonding geometry of the bridging ligands in an obvious way. The "crosswise" acetylene has the smallest "reach" and the allene the longest, with that of Me₂CNC intermediate.

Bonding in the Bridging System. The Me₂NCN molecule itself is not fully characterized structurally. In the experimental study,[7] linearity of the NCN group was assumed. This was also the case with H₂NCN,[8] although for F₂NCN a slight bend (174°) was directly observed.[9] This bend is such as to preserve a plan of symmetry containing the NCN group and bisecting the FNF angle. Minimal basis set Hartree–Fock calculations[10] suggest that there might be similar but smaller (ca. 3°) bends in H₂NCN and Me₂NCN. For all three molecules experiment and theory agree that the amine nitrogen atom has a markedly pyramidal configuration. The observed H₃C–N, N–C, and C–N distances are 1.462, 1.351, and 1.160 Å. On the basis of these structural parameters, the electronic structure can be formulated as a resonance hybrid of III and IV, viz.,

$$R_2N\!-\!C\!\equiv\!N: \longleftrightarrow R_2\overset{+}{N}\!=\!C\!=\!\overset{..}{\underset{..}{N}}$$

III   IV

in which III predominates.

The Me₂NCN ligand in Cp₂Mo₂(CO)₄(Me₂NCN) has a markedly different configuration. It is now essentially planar (mean deviation of atoms from the plane: 0.02 Å), but markedly bent at the NCN carbon atom (135°). The Me₂N–C distance is perhaps slightly (ca. 0.015 Å) shorter while the C–N distance is distinctly longer (0.08 Å). It is also important to note that the ligand plane and the Mo(1)-Mo(2)-N(1) plane

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	0.5648 (1)	0.377 64 (6)	0.263 24 (6)	0.0133 (1)	0.004 18 (4)	0.003 85 (4)	−0.0011 (1)	0.0007 (1)	−0.000 82 (7)
Mo2	0.4293 (1)	0.239 11 (5)	0.129 59 (6)	0.0110 (1)	0.002 98 (3)	0.0034 (4)	0.0011 (1)	−0.0010 (1)	−0.000 15 (7)
O1	0.812 (1)	0.2281 (6)	0.3189 (7)	7.3 (2)					
O2	0.898 (1)	0.4498 (7)	0.2106 (7)	8.0 (2)					
O3	0.358 (1)	0.1827 (6)	0.3255 (7)	7.4 (2)					
O4	0.060 (1)	0.2284 (7)	0.1350 (7)	7.5 (2)					
N1	0.4999 (9)	0.3784 (5)	0.1289 (5)	0.014 (1)	0.0031 (4)	0.0041 (4)	−0.002 (1)	0.001 (1)	0.0010 (6)
N2	0.2744 (10)	0.4270 (5)	0.0412 (6)	0.015 (1)	0.0035 (4)	0.0059 (5)	0.004 (1)	−0.002 (1)	0.0005 (7)
C5	0.371 (1)	0.3703 (6)	0.0862 (6)	0.012 (1)	0.0038 (5)	0.0036 (4)	0.002 (1)	0.002 (1)	−0.0005 (7)
C1	0.714 (1)	0.2838 (8)	0.2983 (8)	5.4 (3)					
C2	0.768 (1)	0.4213 (8)	0.2293 (8)	5.0 (2)					
C3	0.389 (1)	0.2121 (8)	0.2533 (8)	5.0 (2)					
C4	0.203 (1)	0.2332 (8)	0.1318 (8)	4.9 (2)					
C6	0.302 (1)	0.5235 (8)	0.0450 (8)	5.3 (2)					
C7	0.134 (2)	0.3931 (9)	−0.0113 (9)	6.1 (3)					
C8	0.316 (1)	0.3965 (8)	0.3387 (9)	5.7 (3)					
C9	0.343 (1)	0.4751 (8)	0.2914 (8)	5.5 (3)					
C10	0.488 (2)	0.5146 (9)	0.3213 (9)	6.5 (3)					
C11	0.553 (2)	0.4618 (10)	0.3923 (9)	6.6 (3)					
C12	0.453 (2)	0.3883 (9)	0.4041 (10)	6.5 (3)					
C13	0.679 (2)	0.2001 (10)	0.0696 (10)	7.0 (3)					
C14	0.575 (2)	0.2112 (9)	−0.0042 (9)	6.2 (3)					
C15	0.460 (2)	0.1472 (9)	0.0034 (9)	5.9 (3)					
C16	0.488 (2)	0.0933 (10)	0.0824 (10)	7.1 (3)					
C17	0.632 (2)	0.1317 (11)	0.1216 (11)	7.7 (4)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

make a dihedral angle of 42°.

The above facts lead us to propose the following interpretation of the bonding. The CN group donates an electron pair from the nitrogen atom to Mo(1) and a pair of CN π-bonding electrons to Mo(2). The drift of so much electron density away from the CN group causes a significant lengthening of the C–N bond and enhances the participation of the lone pair of the amine nitrogen in π bonding to the carbon atom, thus slightly shortening the Me$_2$N–C bond and making the configuration about that atom planar. In other words, the importance of resonance form IV relative to III is enhanced because the accumulation of charge on the terminal nitrogen atom at the expense of the amine nitrogen atom is now useful in making the ligand a better donor.

This interpretation of the bonding within the Me$_2$NCN ligand also provides a ready explanation for the 42° dihedral angle mentioned above. The lone pairs on the terminal nitrogen atom in IV lie above and below the plane of the CN π bond that is being used to bind the CN group to Mo(2). Therefore, in order to have one of these lone pairs oriented toward Mo(1), the Me$_2$NCN plane must be tilted appreciably away from the Mo(1)-Mo(2)-N(1) plane, as observed.

The bonding in the bridging cyanamide system in [Ni(C$_5$H$_{10}$NCN)CO]$_3$ appears to be considerably different in details according to the very terse report of the structure.[6] In this case, the electronic structure seems to be represented almost exclusively by III (>N–C = 1.45 Å, C≡N = 1.13 Å) and the bonding to the nickel atoms involves donation of an sp lone pair on N and a π-electron pair of the C≡N bond. The amine nitrogen atom appears to be (but is not stated to be) quite pyramidal and the NCN angle is 151°.

NMR Studies. At 35 °C in toluene-d_8 both compounds show a single resonance for the cyclopentadienyl protons. The dimethylamino compound shows a single resonance for the NMe$_2$ protons. On lowering the temperature, the cyclopentadienyl resonance broadens and then splits into two sharp signals of equal intensity ($T_c \approx -25$ °C). Similar behavior is observed for the NMe$_2$ resonance, which becomes a two-line spectrum (1:1) below −30 °C.

^{13}C NMR spectra were obtained for the compound

Table III. Bond Distances (Å) in Cp$_2$Mo$_2$(CO)$_4$(Me$_2$NCN)[a]

Atoms	Distance	Atoms	Distance
Mo(1)–Mo(2)	3.056 (1)	Mo(2)–C(17)	2.33 (1)
–N(1)	2.056 (6)	C(1)–O(1)	1.20 (1)
–C(5)	3.054 (7)	C(2)–O(2)	1.20 (1)
–C(1)	1.929 (10)	C(3)–O(3)	1.20 (1)
–C(2)	1.894 (9)	C(4)–O(4)	1.20 (1)
–C(3)	2.861 (9)	C(5)–N(1)	1.236 (9)
–C(8)	2.40 (1)	–N(2)	1.335 (9)
–C(9)	2.39 (1)	N(2)–C(6)	1.45 (1)
–C(10)	2.30 (1)	–C(7)	1.48 (1)
–C(11)	2.29 (1)	C(8)–C(9)	1.39 (1)
–C(12)	2.32 (1)	–C(12)	1.49 (1)
Mo(2)–N(1)	2.149 (5)	C(10)–C(9)	1.41 (1)
–C(5)	2.103 (5)	–C(11)	1.41 (1)
–C(3)	1.921 (9)	C(11)–C(12)	1.39 (1)
–C(4)	1.889 (9)	C(13)–C(14)	1.39 (1)
–C(13)	2.36 (1)	–C(17)	1.34 (2)
–C(14)	2.39 (1)	C(15)–C(14)	1.35 1)
–C(15)	2.34 (1)	–C(16)	1.43 (2)
–C(16)	2.33 (1)	C(16)–C(17)	1.44 (2)

[a] Atoms are labeled as in Figure 2. Numbers in parentheses are the estimated standard deviations of the least significant digits.

Cp$_2$Mo$_2$(*CO)$_4$(NCNMe$_2$), where *CO represents CO 30% enriched in ^{13}C. At 66 °C there was a single cyclopentadienyl carbon resonance (δ 94.45 ppm) and a single, somewhat broad, carbonyl resonance (δ 242,68 ppm). On lowering the temperature, the carbonyl carbon resonance broadened and at probe temperature (35 °C) was barely visible above the base line, but the cyclopentadienyl carbon signal remained sharp. At −20 °C the cyclopentadienyl carbon resonance had broadened and four carbonyl carbon resonances were apparent. At −40 °C a low-temperature limiting spectrum was observed consisting of four CO resonances of equal intensity (δ 248.29, 247.08, 241.87, and 237.24 ppm) and two Cp-carbon resonances of equal intensity (δ 95,08 and 94.00 ppm). These spectral changes are shown in Figure 2. Not shown in Figure 2 are the NMe$_2$ carbon signals, which appeared as a single resonance
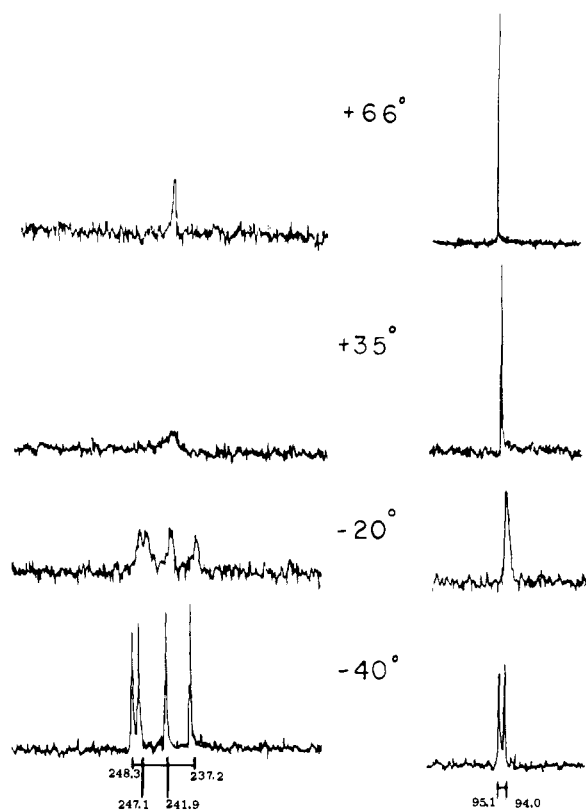
Figure 2. ^{13}C NMR spectra recorded at various temperatures in toluene-d_8 for Cp$_2$Mo$_2$(*CO)$_4$(NCNMe$_2$) showing the carbonyl (left) and cyclopentadienyl carbon (right) signals. The ^{13}CO enrichment was ca. 30%.

at 35 °C (δ 41.45 ppm) and two resonances of equal intensity at −40 °C (δ 41.86 and 40.88 ppm).

These observations are entirely consistent with the presence in solution of the structure found in the solid. They furthermore show that this molecule is stereochemically nonrigid to a high degree. In order for the two cyclopentadienyl ligands to be equivalenced, the bridging Me$_2$NCN ligand must be the key participant in a fluxional process of the type shown in eq 1. This

(1)
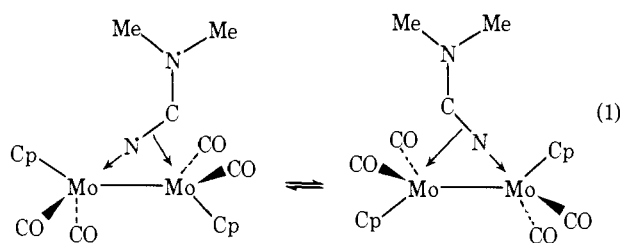
process, which interconverts enantiomers, may be achieved through a transition state or intermediate having a μ-C≡N ligand bridging the Mo$_2$ center in a manner similar to that found in acetylene adducts Cp$_2$Mo$_2$(CO)$_4$(RC≡CR).[3b,c] Enantiomerization, however, need not equivalence all the carbonyl ligands; indeed, if this were the only fluxional process one might anticipate a two-line (1:1) spectrum for the carbonyl carbon signals. Either the reaction pathway leading to enantiomerization or some other process of comparable free energy of activation causes an equivalency of all carbonyl ligands.

Experimental Section

General Procedures. All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo using standard Schlenk techniques.[11] Solvents (benzene, toluene, and pentane) were dried and freed from molecular oxygen by distillation from sodium–potassium amalgam (25% Na to 75% K by

Table IV. Bond Angles (deg) in Cp$_2$Mo$_2$(CO)$_4$(Me$_2$NCN)[a]

Atoms	Angle	Atoms	Angle
Mo(2)–Mo(1)–C(1)	85.1 (3)	C(5)–Mo(2)–N(1)	33.8 (2)
–C(2)	112.0 (3)	Mo(1)–C(1)–O(1)	176.9 (8)
–N(1)	44.6 (2)	Mo(1)–C(2)–O(2)	178.0 (8)
–C(8)	94.2 (2)	Mo(2)–C(3)–O(3)	170.0 (8)
–C(9)	104.3 (2)	Mo(2)–C(4)–O(4)	178.5 (8)
–C(10)	137.4 (3)	Mo(1)–N(1)–	93.2 (2)
		Mo(2)	
–C(11)	152.6 (3)	–C(5)	134.6 (5)
–C(12)	118.9 (3)	Mo(2)–N(1)–C(5)	71.1 (4)
Mo(1)–Mo(2)–C(3)	65.6 (3)	Mo(2)–C(5)–N(1)	75.2 (4)
–C(4)	111.8 (3)	–N(2)	150.3 (6)
–C(5)	69.8 (2)	N(1)–C(5)–N(2)	134.6 (7)
–N(1)	42.2 (2)	C(5)–N(2)–C(6)	120.7 (7)
–C(13)	95.6 (3)	–C(7)	120.8 (7)
–C(14)	118.1 (3)	C(6)–N(2)–C(7)	118.6 (7)
–C(15)	150.2 (3)	C(8)–C(9)–C(10)	110.0 (9)
–C(16)	138.1 (3)	C(9)–C(10)–C(11)	108.3 (9)
–C(17)	103.7 (3)	C(10)–C(11)–	108.3 (9)
		C(12)	
C(1)–Mo(1)–C(2)	75.3 (4)	C(11)–C(12)–C(8)	107.9 (9)
–N(1)	114.7 (3)	C(12)–C(8)–C(9)	105.5 (9)
C(2)–Mo(1)–N(1)	87.4 (3)	C(13)–C(14)–	106.1 (10)
		C(15)	
C(3)–Mo(2)–C(4)	77.0 (4)	C(14)–C(15)–	111.2 (9)
		C(16)	
–C(5)	116.3 (3)	C(15)–C(16)–	103.0 (10)
		C(17)	
–N(1)	105.0 (3)	C(16)–C(17)–	108.5 (11)
		C(13)	
C(4)–Mo(2)–C(5)	80.1 (3)	C(17)–C(13)–	111.2 (11)
		C(14)	
–N(1)	108.5 (3)		

[a] Atoms are labeled as in Figure 2. Numbers in parentheses are the estimated standard deviations of the least significant digits.

weight), benzophenone, and phenyl ether. Samples were stored and handled in a Vacuum Atmospheres Co. Dri-Lab System.

Materials. [CpMo(CO)$_3$]$_2$ was synthesized by the established route.[12] Subsequent thermolysis caused loss of two COs to give [CpMo(CO)$_2$]$_2$ as reported earlier.[3a]

(CH$_3$)$_2$NCN was purchased from Columbia Organics; H$_2$C= CHCH=CH$_2$ and CO$_2$ were obtained from Matheson. CF$_3$C≡N was purchased from PCR, Inc. All the other organics were from Aldrich. ^{13}CO (90% ^{13}C) was obtained from Prochem Ltd.

Physical Measurements. Elemental analyses were performed by Chemalytics, Inc. Infrared spectra were obtained from Nujol mulls between CsI or NaCl plates using a Perkin-Elmer 283 spectrometer.

^{1}H NMR spectra were recorded on a Varian A-60 spectrometer equipped with a variable temperature probe. Temperatures were calibrated with methanol (low temperature) or ethylene glycol (high temperatures). ^{1}H chemical shifts are reported using C$_6$D$_6$ (δ 7.24) as a reference. Variable temperature NMR spectra were measured in toluene-d_8.

^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer using toluene-d_8 as a reference and recorded in the Fourier mode.

Mass spectra were obtained using an AEI MS9 mass spectrometer by the method method of direct insertion (200–300 °C).

Preparation of [CpMo(CO)$_2$]$_2$H$_2$NC≡N. [CpMo(CO)$_2$]$_2$ (0.4167 g, 0.96 mmol) was dissolved in toluene (20 mL). Cyanamide (0.040 g, 0.96 mmol) was dissolved in warm toluene (10 mL) and added to the magnetically stirred solution. After 4 h the solvent was removed by vacuum. Recrystallization from toluene/pentane gave Cp$_2$Mo$_2$CO)$_4$(NCNH$_2$), 0.3976 g, 87% yield.

Anal. Calcd for C$_{15}$H$_{12}$N$_2$O$_4$Mo$_2$: C, 39.83; H, 2.55. Found: C, 41.1; H, 2.48. IR data 2212 (m), 2157 (m), 1950 (s), 1926 (w), 1900 (m), 1845 (sh), 1635 (br), 1565 cm^{-1} (br). ^{1}H NMR (benzene-d_6) δ 4.78 (Cp).

Preparation of [CpMo(CO)$_2$]$_2$(CH$_3$)$_2$NCN. [CpMo(CO)$_2$]$_2$ (0.4248 g, 0.979 mmol) was dissolved in toluene (20 mL). (CH$_3$)$_2$NCN (1 mL, ca. 10 mmol) was added to the magnetically stirred solution. An im-

mediate color change from red-brown to violet occurred. After stirring for 5 h the volume of the solvent was reduced by vacuum and hexane was added. Black needles (0.4080 g, 81% yield) crystallized from solution.

Anal. Calcd for $C_{17}H_{16}N_2O_4Mo_2$: C, 40.49; H, 3.20. Found: C, 40.6; H, 3.01. IR data 2220 (w), 1963 (w), 1932 (m), 1900 (s), 1829 (s), 1813 (m), 1705 cm^{-1} (br). ^{1}H NMR (benzene-d_6, 30 °C) δ 5.09 (Cp), 3.00 (Me); uncor Me$_2$NCN 2.13 (Me). ^{13}C NMR (toluene-d_8, probe temperature) 242.68 (CO) broad, 94.95 (Cp), 41.45 ppm (Me). ^{13}C NMR (toluene-d_8, −40 °C) δ 248.29, 247.08, 241.87, and 237.24 (CO), 95.08 and 94.00 (Cp), 41.86 and 40.88 ppm (Me). Mass spectral data m/e 504 [Cp$_2$Mo$_2$(CO)$_4$Me$_2$NCN]$^+$, medium; 448 [Cp$_2$Mo$_2$(CO)$_2$Me$_2$NCN]$^+$, strong; 434 [Cp$_2$Mo$_2$(CO)$_4$]$^+$, strong; 406 [Cp$_2$Mo$_2$(CO)$_3$Me$_2$NCN]$^+$, v small.

Isotopically Labeled Compounds. Labeled compounds [CpMo(*CO)$_3$]$_2$ and [CpMo(*CO)$_2$]$_2$ were prepared by reacting [CpMo(CO)$_2$]$_2$ with ^{13}CO to give [CpMo(*CO)$_3$]$_2$ which was then refluxed in m-xylene under a N$_2$ purge to produce [CpMo(*CO)$_2$]$_2$. The labeled [CpMo(*CO)$_2$]$_2$ was then allowed to react with dimethylcyanamide to produce the ^{13}CO labeled compounds.

Reactions of Cp$_2$Mo$_2$(CO)$_4$. A. With CS$_2$. To a toluene solution of Cp$_2$Mo$_2$(CO)$_4$ (0.05 g, 0.1 mmol Cp$_2$Mo$_2$(CO)$_4$ in 0.5 mL of toluene) contained in an NMR tube was added CS$_2$ (0.2 mL). The mixture was monitored by NMR spectroscopy. No reaction was detected after 1 day. The contents of the tube were dried under vacuum and an IR spectrum was recorded in a Nujol mull. Only starting material was present.

B. With N$_2$O. Cp$_2$Mo$_2$(CO)$_4$ (0.5 g, 0.1 mmol) was dissolved in C$_6$D$_6$ (0.3 mL) and placed in an NMR tube. N$_2$O (0.2 mmol) was condensed into the NMR tube which was then sealed. The sealed tube was heated to 90 °C for 1 day and monitored as above by NMR and IR spectroscopy. No evidence of a reaction product was seen.

C. With Ph$_2$N$_2$. Cp$_2$Mo$_2$(CO)$_4$ (0.1 g, 0.2 mmol) was dissolved in toluene (5 mL). PhN=NPh (0.2 g, 1.0 mmol) was added with magnetic stirring. After 1 day NMR and IR spectroscopy indicated that only starting materials were present.

D. With Other Compounds. The other reactions listed in Table I were carried out in a similar manner.

Crystal Selection and X-Ray Data Collection. Crystals of Cp$_2$Mo$_2$(CO)$_4$(Me$_2$NCN) were immersed in mineral oil. A crystal measuring ca. 0.25 × 0.25 × 0.40 mm was cleaved from a larger crystal and mounted by wedging it in a thin-walled glass capillary under mineral oil. The ω scans of several intense reflections showed peak widths at half-height of ca. 0.2°.

Cell constants and axial photographs showed that the crystal belonged to the monoclinic system with a = 8.326 (4) Å, b = 14.839 (4) Å, c = 14.875 (4) Å, β = 91.44 (2)°, and V = 1837 (1) Å^3. The volume agrees with that anticipated for Z = 4. The above lattice constants as well as the orientation matrix used for data collection were determined from the diffractometer settings of 15 reflections having 5.5° < 2θ(Mo Kα) < 22.5°.

Data were collected at 22 ± 2 °C using a Syntex P$\bar{1}$ autodiffractometer, with graphite-monochromatized Mo Kα (λ = 0.710 730 Å) radiation and the θ–2θ scan technique. Scans were recorded using variable scan rates of from 4 to 24° per minute, depending upon the intensity of the reflection, and scan ranges from Mo Kα_1 − 1.0° to Mo Kα_2 + 1.0°. The ratio of background to scan time was 0.5. A total of 2576 unique reflections having 0° < 2θ(Mo Kα) < 46° were measured of which 1998 had $I > 3\sigma(I)$ and were used in subsequent structure solution and refinement. The intensities of three standard reflections measured after each 87 reflections during data collection

showed no significant change. The intensities were reduced to a set of relative $|F_o|^2$ values for use in structure solution and refinement.[13] No corrections were made for absorption (μ = 13.64 cm^{-1}).

During data collection the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, were noted, uniquely determining the space group to be $P2_1/n$ (a nonstandard setting of $P2_1/c$, no. 14).

Structure Solution and Refinement. The positions of the two crystallographically independent molybdenum atoms were determined from the solution of the three-dimensional Patterson function. Three cycles of least-squares refinement of the Mo atom positional parameters yielded discrepancy indices of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.228$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.317$$

The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. A value of 0.07 for p was used in the calculation[13] of the weights, w. A difference Fourier map revealed the positions of the remaining nonhydrogen atoms.

The structure was refined to convergence using anisotropic thermal parameters for the Mo atoms and the N–C–N atoms of the dimethylcyanamide ligand. Final discrepancy indices were R_1 = 0.054 and R_2 = 0.081. The esd of an observation of unit weight was 1.843. During the final least-squares refinement cycle, no parameter shifted by more than 0.09σ. A final difference Fourier map revealed no peaks of chemical significance.

Supplementary Material Available. A table of observed and final calculated structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

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