

Reactions of Metal-to-Metal Multiple Bonds. 4.¹ μ -Acetylene-bis(cyclopentadienyl)tetracarbonyldimolybdenum Compounds. Preparations, Properties, Structural Characterizations, and Dynamical Solution Behavior

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Abstract: $\text{Cp}_2\text{Mo}_2(\text{CO})_4$, which contains a Mo-Mo triple bond, reacts with acetylenes $\text{RC}\equiv\text{CR}'$ in hydrocarbon solvents to form 1:1 adducts $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ in which the acetylenic moiety RCCR' , acting as a four-electron donor ligand, bridges two molybdenum atoms that are also joined by a Mo-Mo single bond. The reactivity order $\text{HC}\equiv\text{CH} > \text{MeC}\equiv\text{CMe} \sim \text{PhC}\equiv\text{CH} > \text{CF}_3\text{C}\equiv\text{CH} > \text{CF}_3\text{C}\equiv\text{CCF}_3 \sim \text{PhC}\equiv\text{CPh}$ has been found for 1:1 adduct formation. Three of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds, where $\text{R} = \text{H}$, Et , and Ph , have been structurally characterized by X-ray studies. There is a common $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{C}_2$ moiety having (1) a quasi-tetrahedral Mo_2C_2 core with Mo-Mo distances of 2.96–2.98 Å and (2) an asymmetric $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ unit, in which one molybdenum atom has two terminal carbonyl ligands while the other has one terminal and one semibringing carbonyl ligand. The occurrence of the semibringing carbonyl group is attributed to internal crowding. A number of these acetylene adducts have been characterized by infrared, NMR (^1H , ^{13}C , and $^{13}\text{C}\{^1\text{H}\}$), and mass spectrometry. The dynamical solution behavior of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds can be interpreted on the following assumptions. (1) A low-energy process interconverts $\text{Mo}(1)$ and $\text{Mo}(2)$, $\text{Cp}(1)$ and $\text{Cp}(2)$, and the carbonyl ligands $a = d$, $b = c$. This process allows the $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ moiety to adopt a time-averaged structure having C_2 symmetry. (2) A higher energy process effects rotation about the Mo-Mo bond. (3) The central Mo_2C_2 moiety is rigid on the NMR time scale up to 90 °C. (4) Carbonyl ligand scrambling between molybdenum atoms is not observed on the NMR time scale at temperatures up to 90 °C. (5) For certain acetylene adducts, e.g., $\text{R} = \text{R}' = \text{Et}$, an isomer different from that found in the crystalline state is also present in equilibrium in solution. In $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ the acetylene is not labile toward ligand displacement reactions (with CO and $\text{MeC}\equiv\text{CMe}$) or hydrogenation.

Introduction

The ability of acetylenes to bridge two directly bonded metal atoms is well documented in transition metal chemistry.^{3–8} Recently it was shown that acetylenes, but not olefins, would add across certain metal-to-metal triple bonds as in the reaction⁹



where $\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; and $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$.

The same type products had previously been obtained by the reaction between acetylenes and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ compounds.¹⁰ Here, as in other reactions leading to compounds containing quasi-tetrahedral M_2C_2 cores of which the C_2 portion is derived from the central carbon atoms of an acetylene, it is conceivable, and for the present cases quite likely, that unsaturated intermediates containing M-M multiple bonds are involved.

The earlier work on $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{RCCR}')$ compounds ($\text{M} = \text{Mo}$ or W) has left many important questions unresolved. For example: (1) What are the structures of these acetylene adducts?¹¹ (2) What type of dynamical solution behavior do they display?¹² (3) How do the acetylene compounds compare with the allene adducts, $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{allene})$, described in part 1¹³ of this series? (4) What restrictions, if any, are placed on the acetylenic substituents, R and R' , in reaction 1? (5) What is the nature of the bonding in the central M_2C_2 moiety? Can the M-M triple bond in $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds be described as nucleophilic or electrophilic with regard to the coordination of acetylenes? (6) Since $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds are reported to coordinate acetylenes, but not olefins, is it possible to effect a bimetallic hydrogenation of acetylenes to olefins in a catalytic cycle?¹⁴ It is to these questions that we address ourselves in this paper. Preliminary reports of parts of this work have appeared.^{15,16}

Results and Discussion

Syntheses. In this work we have used the reaction shown in eq 1 for the synthesis of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds. The ease with which the acetylene adducts form according to eq 1 depends on the acetylene used and follows the order $\text{HC}\equiv\text{CH} \sim \text{MeC}\equiv\text{CMe} \sim \text{PhC}\equiv\text{CH} > \text{CF}_3\text{C}\equiv\text{CH} > \text{CF}_3\text{C}\equiv\text{CCF}_3 \sim \text{PhC}\equiv\text{CPh}$. Thus, while $\text{HC}\equiv\text{CH}$ at 760 Torr pressure reacts virtually instantaneously at room temperature, $\text{CF}_3\text{C}\equiv\text{CCF}_3$ does not react readily even at 80 °C and 5 atm pressure in benzene. The observed reactivity order suggests that both electronic and steric factors are important, although whether this is primarily a kinetic or thermodynamic effect is uncertain. The reluctance of the highly electron-withdrawing acetylene $\text{CF}_3\text{C}\equiv\text{CCF}_3$ to react with the Mo-Mo triple bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ might suggest that the Mo-Mo moiety in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is somewhat electrophilic in its choice of acetylenes. While this may be true, it should be noted that $\text{MeOOC}\equiv\text{CCOOMe}$, which may also be considered an electrophilic acetylene,¹⁷ does readily react according to eq 1.

The acetylene $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{OH}$ reacts according to eq 1 and does not generate the carbene complex $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{L}_2$, where L represents $=\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$. Intramolecular formation of the 2-oxacyclopentylidene ligand from $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{OH}$ occurs when this acetylene coordinates to an electrophilic mononuclear metal center.¹⁸

We have found that when acetylene was added to a hydrocarbon solution containing both $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Cp}_2\text{W}_2(\text{CO})_4$ the red, crystalline product showed only homodinuclear ions in the mass spectrometer. The absence of heterodinuclear ions (Mo-W containing ions) leads us to believe that the formation of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds in reaction 1 proceeds via a direct addition of the acetylene to the dinuclear compound and does not involve mononuclear

Table I. Bond Distances in $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{C}_2\text{H}_2^a$

Mo(1)–Mo(2)	2.980 (1)	C(1,1)–C(1,2)	1.410 (6)
–C(1)	1.993 (4)	C(1,2)–C(1,3)	1.387 (7)
–C(2)	1.989 (3)	C(1,3)–C(1,4)	1.395 (8)
–C(3)	2.902 (4)	C(1,4)–C(1,5)	1.415 (7)
–C(5)	2.190 (3)	C(1,5)–C(1,1)	1.408 (7)
–C(6)	2.172 (3)		
–C(1,1)	2.308 (4)	C(2,1)–C(2,2)	1.386 (9)
–C(1,2)	2.364 (4)	C(2,2)–C(2,3)	1.41 (1)
–C(1,3)	2.363 (4)	C(2,3)–C(2,4)	1.30 (1)
–C(1,4)	2.322 (4)	C(2,4)–C(2,5)	1.36 (1)
–C(1,5)	2.310 (4)	C(2,5)–C(2,1)	1.39 (1)
		C(5)–H(5)	0.98 (6)
Mo(2)–C(3)	1.951 (4)	C(6)–H(6)	0.93 (6)
–C(4)	1.953 (4)		
–C(5)	2.122 (3)	C(1,1)–H(1,1)	0.86 (5)
–C(6)	2.203 (3)	C(1,2)–H(1,2)	0.95 (5)
–C(2,1)	2.371 (4)	C(1,3)–H(1,3)	0.69 (6)
–C(2,2)	2.306 (5)	C(1,4)–H(1,4)	0.98 (6)
–C(2,3)	2.327 (5)	C(1,5)–H(1,5)	0.94 (6)
–C(2,4)	2.351 (5)		
–C(2,5)	2.374 (5)	C(2,1)–H(2,1)	0.83 (6)
		C(2,2)–H(2,2)	0.76 (6)
C(1)–O(1)	1.135 (4)	C(2,3)–H(2,3)	0.92 (6)
C(2)–O(2)	1.135 (5)	C(2,4)–H(2,4)	0.80 (6)
C(3)–O(3)	1.157 (5)	C(2,5)–H(2,5)	0.94 (6)
C(4)–O(4)	1.137 (5)		
C(5)–C(6)	1.337 (5)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

intermediates. The detailed mechanism is unknown.

Physical Properties. $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds are dark red, crystalline solids, sparingly soluble in alkane solvents but appreciably soluble in benzene and toluene. They are also soluble and stable for several hours in the chlorinated solvents CH_2Cl_2 and CHCl_3 . In the crystalline state they are only slowly decomposed on exposure to the atmosphere but solutions are decomposed more rapidly.

In the mass spectrometer $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ showed a molecular ion $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})^+$ as well as ions formed by the loss of carbonyl ligands, namely $\text{Cp}_2\text{Mo}_2(\text{CO})_x(\text{HCCH})^+$, where $x = 2, 1$, and 0 . The most intense ion corresponded to $\text{Cp}_2\text{Mo}_2(\text{HCCH})^+$.

In the infrared spectra several bands were observed in the region $2100\text{--}1800\text{ cm}^{-1}$ which must be due to $\nu_{\text{str}}(\text{CO})$ and $\nu_{\text{str}}(\text{C}\equiv\text{C})$. However, in the absence of appropriate isotopic labeling studies unequivocal assignments are not possible. The lowest energy band in this region is assignable to $\nu_{\text{str}}(\text{CO})$ of the semibridging carbonyl ligand (see later). IR data, analytical data, and other characterization data are recorded in the Experimental Section.

Structures. Three $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ compounds, where $\text{R} = \text{H}, \text{Et},$ and Ph , have been characterized by single-crystal X-ray studies. These compounds have the same basic structure in which there is a crosswise acetylene bridge (i.e., the central M_2C_2 moiety is quasi-tetrahedral) typical of that found in other acetylene bridged compounds such as $\text{M}_2(\text{CO})_6(t\text{-BuCCBu-}t)$, where $\text{M} = \text{Fe}^5$ and Co .^{4,5}

The atomic positional and thermal parameters for the three structures are given as Tables IX–XI in the supplementary material. For the HCCH compound, the bond distances and bond angles are listed in Tables I and II, respectively, and the full molecular structure is shown in Figure 1, which also defines the atomic numbering scheme. Figure 2 emphasizes the structure of the central quasi-tetrahedral C_2Mo_2 core.

For the EtCCEt compound the bond lengths and angles are listed in Tables III and IV, respectively, and an ORTEP drawing of the molecule is presented in Figure 3.

Table II. Bond Angles in $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{C}_2\text{H}_2^a$

Mo(2)–Mo(1)–C(1)	121.6 (1)
–C(2)	83.6 (1)
–C(3)	38.72 (8)
–C(5)	45.34 (9)
–C(6)	47.50 (9)
C(1,1)	111.1 (1)
C(1,2)	93.0 (1)
C(1,3)	108.8 (2)
C(1,4)	143.4 (2)
C(1,5)	146.6 (1)
Mo(1)–Mo(2)–C(3)	68.5 (1)
–C(4)	92.5 (1)
–C(5)	47.25 (9)
–C(6)	46.64 (9)
C(2,1)	127.2 (2)
C(2,2)	158.4 (2)
C(2,3)	161.1 (2)
C(2,4)	130.9 (2)
C(2,5)	115.8 (2)
Mo(1)–C(1)–O(1)	178.5 (3)
–C(2)–O(2)	179.3 (4)
–C(3)–O(3)	118.4 (3)
Mo(2)–C(3)–O(3)	168.5 (4)
–C(4)–O(4)	178.9 (5)
Mo(1)–C(5)–Mo(2)	87.4 (1)
Mo(1)–C(6)–Mo(2)	85.9 (1)
C(1,1)–C(1,2)–C(1,3)	107.7 (4)
C(1,2)–C(1,3)–C(1,4)	109.0 (4)
C(1,3)–C(1,4)–C(1,5)	108.1 (4)
C(1,4)–C(1,5)–C(1,1)	106.9 (4)
C(1,5)–C(1,1)–C(1,2)	108.3 (4)
C(2,1)–C(2,2)–C(2,3)	107.1 (6)
C(2,2)–C(2,3)–C(2,4)	107.7 (6)
C(2,3)–C(2,4)–C(2,5)	111.4 (6)
C(2,4)–C(2,5)–C(2,1)	107.3 (6)
C(2,5)–C(2,1)–C(2,2)	106.5 (6)
C(6)–C(5)–H(5)	139 (3)
C(5)–C(6)–H(6)	138 (3)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

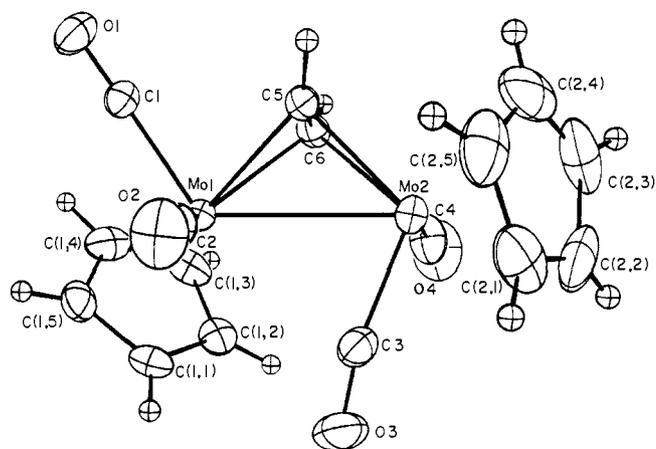


Figure 1. The molecular structure of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$. Each atom is represented by its ellipsoid (or sphere) of thermal vibration, scaled to enclose 35% of the electron density.

For the PhCCPh compound the bond lengths and angles are given in Tables V and VI and the molecular structure is shown and the atomic numbering scheme is defined in Figure 4.

Figures 1, 3, and 4 can be compared to see the essential similarity of the three structures. There are, of course, small

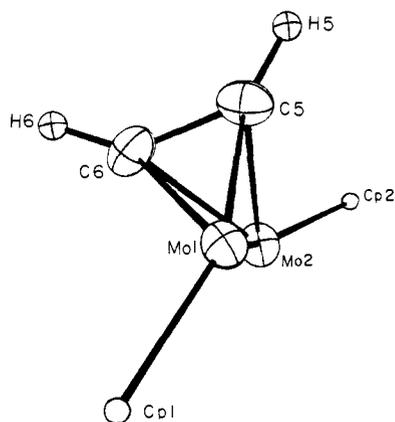


Figure 2. The central portion of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ molecule. The small circles labeled Cp1 and Cp2 represent the centroids of the $\eta^5\text{-C}_5\text{H}_5$ rings.

Table III. Bond Distances in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{Et}_2\text{C}_2)^a$

Mo(1)–Mo(2)	2.977 (1)	C(1)–O(1)	1.135 (7)
–C(1)	1.972 (7)	C(2)–O(2)	1.129 (8)
–C(2)	1.994 (8)	C(3)–O(3)	1.154 (7)
–C(4)	2.826 (6)	C(4)–O(4)	1.158 (7)
–C(5)	2.251 (6)		
–C(6)	2.188 (6)	C(5)–C(6)	1.335 (8)
		C(7)–C(5)	1.489 (8)
–C(1,1)	2.318 (6)	C(7)–C(8)	1.551 (9)
–C(1,2)	2.311 (6)	C(6)–C(9)	1.509 (8)
–C(1,3)	2.335 (6)	C(9)–C(10)	1.53 (1)
–C(1,4)	2.382 (6)		
–C(1,5)	2.362 (6)	C(1,1)–C(1,2)	1.41 (1)
Mo(2)–C(3)	1.942 (7)	C(1,2)–C(1,3)	1.45 (1)
–C(4)	1.936 (6)	C(1,3)–C(1,4)	1.42 (1)
–C(5)	2.153 (6)	C(1,4)–C(1,5)	1.40 (1)
–C(6)	2.219 (6)	C(1,5)–C(1,1)	1.43 (1)
–C(2,1)	2.341 (7)	C(2,1)–C(2,2)	1.41 (1)
–C(2,2)	2.376 (6)	C(2,2)–C(2,3)	1.40 (1)
–C(2,3)	2.375 (7)	C(2,3)–C(2,4)	1.35 (1)
–C(2,4)	2.334 (7)	C(2,4)–C(2,5)	1.41 (1)
–C(2,5)	2.308 (7)	C(2,5)–C(2,1)	1.36 (1)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

differences in detail. Thus, the Mo–Mo distances are 2.980 (1), 2.977 (1), and 2.956 (1) Å in the HCCH, EtCCEt, and PhCCPh compounds, respectively. The first two are not significantly different from each other, but the third one is about 0.020 (2) Å shorter. However, it is not evident that this small difference, though real, has any chemical significance.

The geometry of the alkyne unit is invariant within the experimental errors. The three C–C distances are 1.337 (5), 1.335 (8), and 1.329 (6) Å and the HCC or CCC angles are 138 (3), 134.2 (6), and 134.6 (8)°, in the order HCCH, EtCCEt, and PhCCPh. These distances are essentially the same as those in the $\text{M}_2(\text{CO})_6(t\text{-BuCCBu-}t)$ compounds,⁵ which are 1.31 (1) and 1.335 (6) Å for M = Fe and Co, respectively, but in the latter two compounds the C–C–C angles are larger, namely, in the range 144.5–145.3°. It is possible that this difference in angles may be of steric origin since the presence of a Cp group in place of a CO group greatly increases the internal crowding in this type of molecule.

This brings us to the most noteworthy structural aspect of these molecules, namely, the lack of any symmetry in the arrangement of the ligands around the C_2Mo_2 core. This lack of symmetry means that (a) the two Cp rings are not equivalent and the Cp–Mo–Mo–Cp chain is twisted, as shown most

Table IV. Bond Angles in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{Et}_2\text{C}_2)^a$

Mo(2)–Mo(1)–C(1)	124.2 (2)
–C(2)	86.9 (2)
–C(4)	39.9 (1)
–C(5)	46.1 (2)
–C(6)	47.9 (2)
–C(1,1)	136.1 (2)
–C(1,2)	150.4 (2)
–C(1,3)	115.5 (2)
–C(1,4)	92.4 (2)
–C(1,5)	101.9 (2)
Mo(1)–Mo(2)–C(3)	85.8 (2)
–C(4)	66.3 (2)
–C(5)	48.9 (2)
–C(6)	47.1 (1)
–C(2,1)	152.5 (2)
–C(2,2)	130.1 (2)
–C(2,3)	126.7 (2)
–C(2,4)	144.2 (3)
–C(2,5)	172.5 (2)
Mo(1)–C(1)–O(1)	176.0 (6)
Mo(1)–C(2)–O(2)	173.3 (6)
Mo(1)–C(4)–O(4)	116.8 (4)
Mo(2)–C(3)–O(3)	175.3 (6)
Mo(2)–C(4)–O(4)	168.1 (5)
Mo(1)–C(5)–Mo(2)	85.1 (2)
Mo(1)–C(6)–Mo(2)	85.0 (2)
C(5)–C(6)–C(9)	134.9 (6)
C(6)–C(9)–C(10)	111.4 (5)
C(6)–C(5)–C(7)	133.4 (6)
C(5)–C(7)–C(8)	114.9 (6)
C(1,1)–C(1,2)–C(1,3)	108.3 (6)
C(1,2)–C(1,3)–C(1,4)	106.4 (6)
C(1,3)–C(1,4)–C(1,5)	109.1 (6)
C(1,4)–C(1,5)–C(1,1)	109.0 (7)
C(1,5)–C(1,1)–C(1,2)	107.2 (7)
C(2,1)–C(2,2)–C(2,3)	107.6 (7)
C(2,2)–C(2,3)–C(2,4)	107.3 (8)
C(2,3)–C(2,4)–C(2,5)	109.8 (8)
C(2,4)–C(2,5)–C(2,1)	107.4 (8)
C(2,5)–C(2,1)–C(2,2)	107.9 (7)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

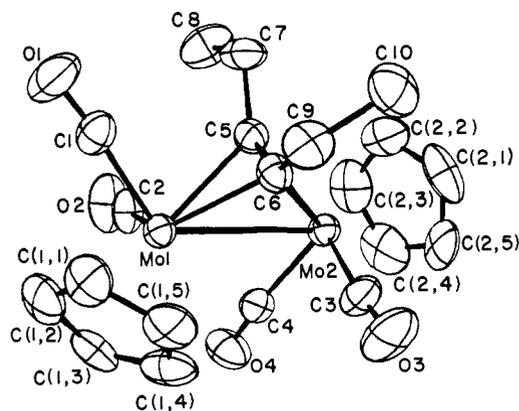


Figure 3. The molecular structure of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{EtCCEt})$. Atoms are represented by ellipsoids of thermal vibration scaled to enclose 35% of the electron density. The atom numbering scheme used in the tables is defined.

clearly in Figure 2; (b) each of the four CO groups is in a different environment, and one of them is in a semibridging posture; (c) the two halves of the RCCR moieties are not equiv-

Table V. Bond Distances in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{Ph}_2)^a$

Mo(1)–Mo(2)	2.956 (1)
–C(1)	1.994 (5)
–C(2)	1.951 (6)
–C(3)	2.871 (5)
–C(5)	2.203 (4)
–C(6)	2.192 (4)
–C(1,1)	2.350 (5)
–C(1,2)	2.302 (5)
–C(1,3)	2.294 (5)
–C(1,4)	2.327 (5)
–C(1,5)	2.385 (4)
Mo(2)–C(3)	1.949 (5)
–C(4)	1.953 (5)
–C(5)	2.148 (4)
–C(6)	2.185 (4)
–C(2,1)	2.341 (5)
–C(2,2)	2.284 (6)
–C(2,3)	2.333 (7)
–C(2,4)	2.350 (6)
–C(2,5)	2.353 (6)
C(1)–O(1)	1.135 (6)
C(2)–O(2)	1.156 (6)
C(3)–O(3)	1.151 (6)
C(4)–O(4)	1.136 (6)
C(5)–C(6)	1.329 (6)
C(5)–C(7)	1.486 (6)
C(7)–C(8)	1.401 (7)
C(8)–C(9)	1.403 (8)
C(9)–C(10)	1.380 (8)
C(10)–C(11)	1.332 (7)
C(11)–C(12)	1.407 (7)
C(12)–C(7)	1.395 (6)
C(6)–C(13)	1.488 (6)
C(13)–C(14)	1.356 (6)
C(14)–C(15)	1.416 (8)
C(15)–C(16)	1.394 (8)
C(16)–C(17)	1.323 (8)
C(17)–C(18)	1.420 (8)
C(18)–C(13)	1.368 (7)
C(1,1)–C(1,2)	1.363 (9)
C(1,2)–C(1,3)	1.423 (9)
C(1,3)–C(1,4)	1.396 (9)
C(1,4)–C(1,5)	1.375 (9)
C(1,5)–C(1,1)	1.436 (8)
C(2,1)–C(2,2)	1.37 (1)
C(2,2)–C(2,3)	1.43 (2)
C(2,3)–C(2,4)	1.35 (1)
C(2,4)–C(2,5)	1.38 (1)
C(2,5)–C(2,1)	1.43 (1)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

alent. We believe that this unsymmetrical arrangement results from internal crowding in the molecules. We have already noted that the greater bending of the RCCR moieties in these $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ molecules as compared to the $\text{M}_2(\text{CO})_6(\text{RCCR})$ types is probably also of the same origin. The solid angle required by a $\eta^5\text{-C}_5\text{H}_5$ ligand is enormously greater than that required by a CO group, which readily accounts for the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ species being more crowded than the $\text{M}_2(\text{CO})_6(\text{RCCR})$ types even though the latter have shorter M–M bonds.

In the $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{L}$ molecules where L = allene and NCNMe_2 the structures are more symmetrical;^{13,19} there is less crowding because the Mo–Mo distances are longer, viz.,

3.117 (1) and 3.056 (1) Å. The longer Mo–Mo distances are made possible by the greater “reach” of the bridging allene and cyanamide ligands. Thus, of all the known compounds in the general class under consideration internal steric factors are most severe in the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ type because of the combined effects of the size of the ligands and the small “reach” of the alkyne-type bridge.

Because of the crowding one CO group is forced into the region close to the Mo–Mo bond and opposite the bridging alkyne. This positioning of one CO has as a necessary consequence the unsymmetrical arrangement of the rest of the ligands.

It should be noted that this is not the first time that a purely steric explanation has been proposed to account for the occurrence of a semibridging carbonyl ligand. Vahrenkamp²⁰ made such a proposal for $\text{Mn}_2(\text{CO})_6(\text{C}_5\text{H}_5)\text{As}(\text{CH}_3)_2$. However, in the latter there must be some ambiguity since the dimanganese compound is necessarily polar, to some extent, and the semibridging CO might be caused, at least in part, by the necessity of equalizing charge distribution.

NMR Spectra. ¹H, ¹³C, and ¹³C[H] spectra have been obtained for a number of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds in the temperature range –100 to 90 °C. NMR data are recorded in the Experimental Section. ¹³C NMR spectra were obtained partly from samples with ¹³C at the natural abundance level and partly from samples 30% enriched in ¹³C, $\text{Cp}_2\text{Mo}_2(*\text{CO})_4(\text{RCCR}')$. The most interesting aspect of the spectra is their temperature dependence, which will be discussed presently. In general the chemical shift values and the qualitative features of the spectra in the slow exchange limits are fully and straightforwardly consistent with the structures.

For the coordinated alkynes the ¹³C shifts and, for the HCCH' compound, the ¹J_{13C-1H} coupling constant merit comment. The shifts of the acetylenic ¹³C resonances (see Experimental Section for details) are upfield from those of the free acetylenes, e.g., 61.9 ppm for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ compared with 71.6 ppm in HCCH itself,²¹ where shifts are downfield from Me₄Si. There is a change in the C–H coupling constant from 249 Hz for free HCCH to 216 Hz for the bound HCCH. Since ¹J_{13C-1H} values generally provide a reliable indication of hybridization of carbon in the C–H bond,²¹ this observation suggests that there is a small but significant rehybridization in the direction $\text{Csp} \rightarrow \text{Csp}^2$ (¹J_{13C-1H} = 156 Hz in the $\text{CH}_2=\text{CH}_2$) upon complexation. We conclude that the acetylene to metal bonding in the Mo_2C_2 moiety must utilize predominantly carbon 2p orbitals. This, of course, is quite consistent with the nonlinearity of the bound alkyne moieties.

Dynamic Stereochemistry in Solution. The experimental spectra in the ¹³CO region over temperature ranges from the slow exchange limit (or the lowest attainable temperature, whichever is higher) to the fast exchange limit for the four $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds (with R = R' = H; R = R' = Ph; R = H, R' = Ph; and R = R' = Et) are shown in Figures 5–8. It will be seen that the one feature common to all three with a symmetrical alkyne is that at the highest temperatures all four CO groups are time-average equivalent. For the HCCPh compound the CO groups are still of two types, even at 80 °C, without any evidence of interconversion.

We shall now show that all of these spectra are consistent with the following postulates:

(1) There is in each case a low-energy process that interconverts Mo(1) with Mo(2), Cp(1) with Cp(2), and the a,d and b,c pairs of carbonyl ligands. This process is shown schematically in Figure 9. Once this process becomes rapid on the NMR time scale the molecules have effective NMR symmetry equivalent to that of $\text{Cp}_2\text{Mo}_2(\text{allene})$,¹³ namely, C₂ symmetry.

Table VI. Bond Angles in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{Ph}_2)^a$

Mo(2)-Mo(1)-C(1)	87.7 (1)	C(6)-C(5)-C(7)	135.4 (4)
-C(2)	122.0 (2)	C(5)-C(7)-C(8)	122.0 (4)
-C(3)	39.0 (1)	C(7)-C(8)-C(9)	119.9 (5)
-C(5)	46.4 (1)	C(8)-C(9)-C(10)	119.7 (5)
-C(6)	47.4 (1)	C(9)-C(10)-C(11)	121.0 (6)
-C(1,1)	104.6 (2)	C(10)-C(11)-C(12)	121.2 (5)
-C(1,2)	137.6 (2)	C(11)-C(12)-C(7)	119.4 (4)
-C(1,3)	149.6 (2)	C(12)-C(7)-C(8)	118.8 (4)
-C(1,4)	115.2 (2)	C(12)-C(7)-C(5)	119.2 (4)
-C(1,5)	93.3 (2)	C(5)-C(6)-C(13)	133.8 (4)
Mo(1)-Mo(2)-C(3)	68.1 (1)	C(13)-C(14)-C(15)	121.1 (5)
-C(4)	87.7 (2)	C(14)-C(15)-C(16)	117.6 (5)
-C(5)	48.0 (1)	C(15)-C(16)-C(17)	122.3 (6)
-C(6)	47.6 (1)	C(16)-C(17)-C(18)	118.9 (6)
-C(2,1)	134.2 (3)	C(17)-C(18)-C(13)	120.9 (5)
-C(2,2)	161.8 (3)	C(18)-C(13)-C(14)	119.2 (5)
-C(2,3)	161.9 (3)	C(18)-C(13)-C(6)	120.5 (4)
-C(2,4)	134.7 (2)	C(1,1)-C(1,2)-C(1,3)	107.6 (5)
-C(2,5)	122.6 (2)	C(1,2)-C(1,3)-C(1,4)	107.7 (6)
Mo(1)-C(1)-O(1)	178.8 (4)	C(1,3)-C(1,4)-C(1,5)	109.0 (5)
-C(2)-O(2)	175.5(5)	C(1,4)-C(1,5)-C(1,1)	107.0 (6)
-C(3)-O(3)	118.5 (4)	C(1,5)-C(1,1)-C(1,2)	108.8 (6)
Mo(2)-C(3)-O(3)	168.6 (4)	C(2,1)-C(2,2)-C(2,3)	108.2 (7)
-C(4)-O(4)	176.9 (5)	C(2,2)-C(2,3)-C(2,4)	107.2 (8)
Mo(1)-C(5)-Mo(2)	85.6 (1)	C(2,3)-C(2,4)-C(2,5)	110.2 (8)
Mo(1)-C(6)-Mo(2)	85.0 (1)	C(2,4)-C(2,5)-C(2,1)	107.0 (7)
		C(2,5)-C(2,1)-C(2,2)	107.2 (8)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

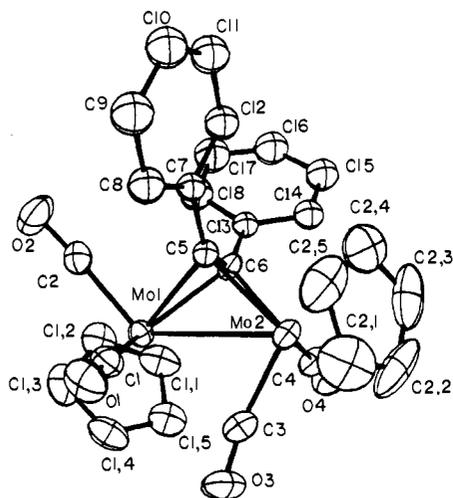


Figure 4. The molecular structure of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PhCCPh})$. Atoms are represented by their ellipsoids of thermal vibration, scaled to enclose 35% of their electron density.

(2) A process of higher energy in which there is at least partial rotation about the Mo-Mo bond. There is effective C_{2v} symmetry in the $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ moiety when both this and the lower energy process are proceeding rapidly, and the enantiomers, shown in Figure 10, are interconverted.

(3) The central Mo_2C_2 polyhedron is rigid on the NMR time scale up to at least 90°C .

(4) Carbonyl scrambling between molybdenum atoms is not rapid on the NMR time scale up to at least 90°C .

(5) For $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{EtCCEt})$ an isomer different from that found in the crystalline state is also present in solution.

Let us now examine the spectra of the individual compounds in the light of these ideas. The spectra for the HCCH and MeCCMe compounds are very similar and we shall discuss

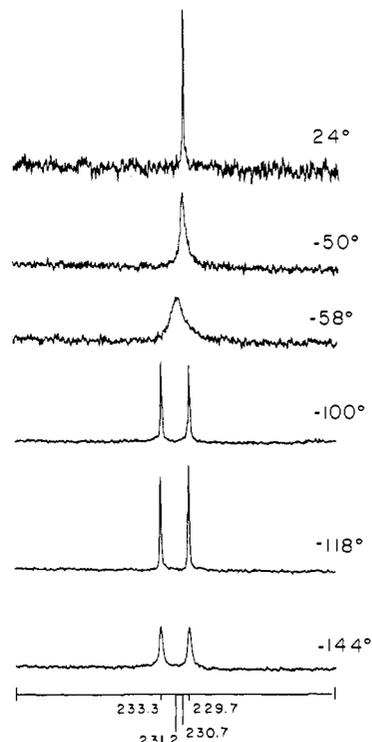


Figure 5. ^{13}CO NMR spectra for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ at various temperatures. Carbon-13 is at the natural abundance level. Chemical shifts are in parts per million downfield from Me_4Si .

explicitly only the former. It is clear from Figure 5 that even at the lowest temperature attained for the HCCH compound the low-energy process is still relatively rapid, although the two lines observed show considerable broadening, suggesting that coalescence might occur $20\text{--}30^\circ\text{C}$ below -144°C .

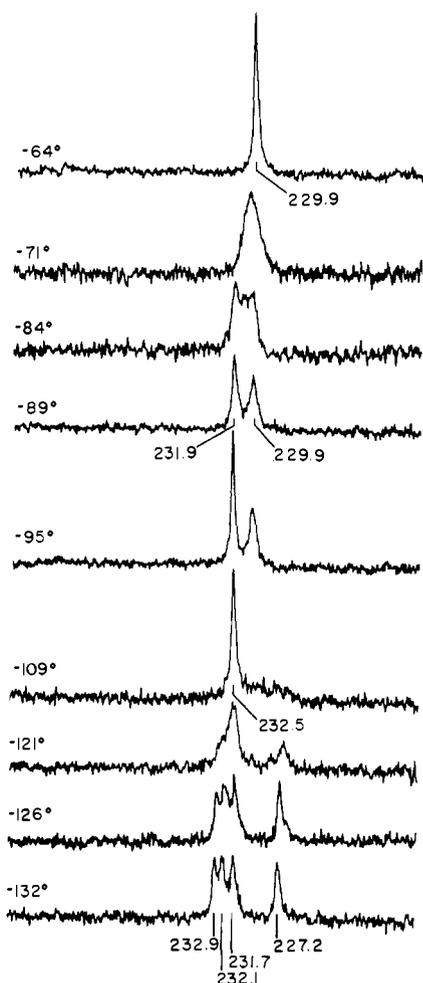


Figure 6. ^{13}CO NMR spectra (natural abundance level) for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PhCCPh})$. Chemical shifts are in parts per million downfield from Me_4Si .

Throughout the temperature range -90 to -144 °C the Cp ^{13}C resonance is a sharp singlet. Figure 11 shows the ^{13}C spectrum of the HCCH compound in the CO region at -90 °C for a sample with 30% enrichment of ^{13}C in the CO groups. The satellites due to ^{13}C - ^{13}C coupling are clearly visible showing that the nonequivalent pairs of CO groups are in the same molecule. On the assumption that only geminal coupling could account for such splittings, this constitutes further support for our postulate (1). By computer fitting of the spectra in Figure 5 the activation parameters for the higher energy process were found and are listed in Table VII.

The spectra for the PhCCPh and $\text{MeO}_2\text{CCCCO}_2\text{Me}$ compounds are rather similar and we shall refer explicitly to those for the PhCCPh compound shown in Figure 6. Here we reach, or closely approach, the slow exchange limit for the low-energy process and the ^{13}CO spectrum shows four lines of equal intensity as required by the structure shown in Figure 4. Between -132 °C and about -90 °C the low-energy process (Figure 9) causes the four lines to coalesce to two but before the appropriate spectrum with two lines of equal width can be fully developed the next process supervenes causing these two lines to coalesce to one. We have been able to match the entire range of spectral changes shown in Figure 6 by computer-simulated spectra, employing the exchange schemes implied by Figures 9 and 10, from which the activation parameters were derived. These, too, are listed in Table VII.

It is the spectra for the PhCCH compound, Figure 7, which provide direct support for postulates (3) and (4). At -100 °C

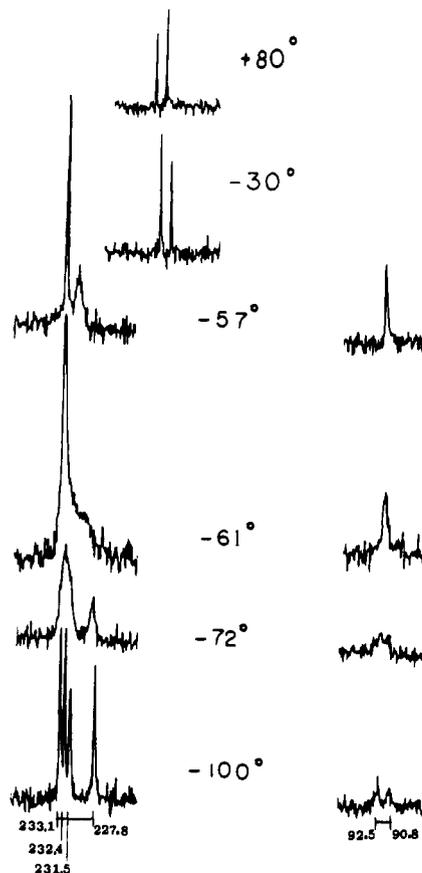


Figure 7. ^{13}C NMR spectra of $\text{Cp}_2\text{Mo}_2\text{Mo}_2(\text{PhCCH})$ in the CO region (left) and Cp region (right). Chemical shifts are in parts per million downfield from Me_4Si . The solvent is toluene- d_8 and the CO carbons are enriched to 30% ^{13}C . In the range -50 to 90 °C the two lines in the CO region show a $J_{^{13}\text{C}-^{13}\text{C}}$ coupling of ca. 5.5 Hz when displayed on a broader scale.

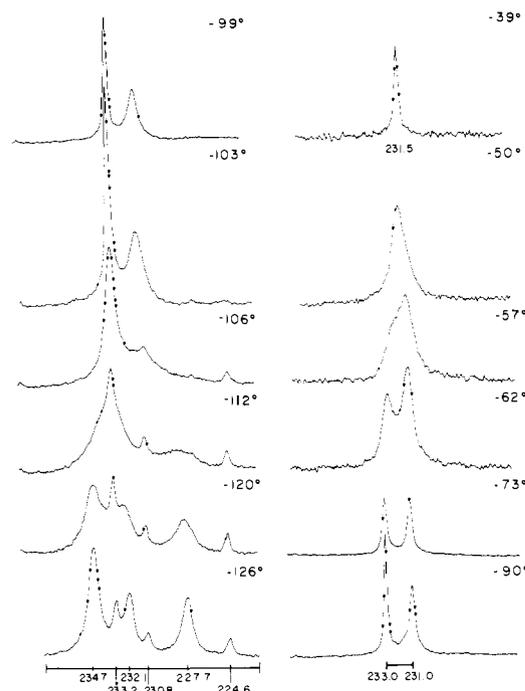


Figure 8. The ^{13}CO NMR spectrum of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{EtCCEt})$ at various temperatures. The chemical shifts are in parts per million downfield from Me_4Si .

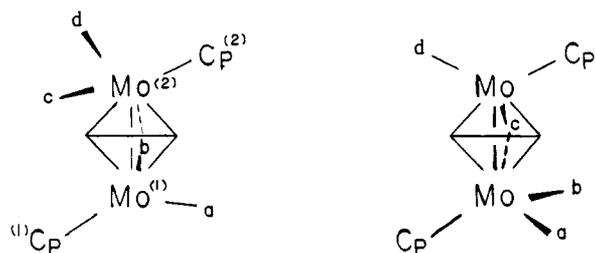


Figure 9. A schematic representation of the postulated low-energy rearrangement. The two structures shown are identical but chiral. The process interconverts Mo(1) with Mo(2), Cp(1) with Cp(2), and the $a \rightleftharpoons d$ and $b \rightleftharpoons c$ pairs of CO groups.

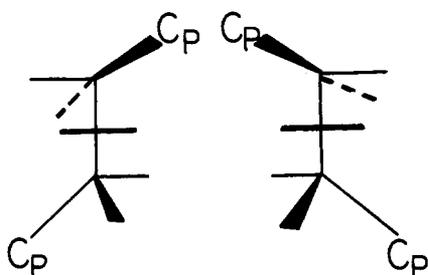


Figure 10. A schematic representation of the two enantiomers of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ type molecule.

the ^{13}C O spectrum consists of four lines (1:1:1:1) and there are two (1:1) Cp lines. This is obviously consistent with a frozen structure akin to those (Figures 1–4) of the structurally characterized molecules, but it is also consistent with the rapid occurrence of the low-energy process (1) since this process does *not* equivalence Mo(1) with Mo(2), Cp(1) with Cp(2), nor any pair of CO groups when the alkyne is unsymmetrical, i.e., of the RCCR' type. Thus, we obtain no information as to whether process (1) is already occurring rapidly at -100°C in this compound or not. In view of the behavior of the HCCH, MeCCMe, and PhCCPh compounds it seems reasonable to believe that process (1) is already occurring fairly rapidly at -100°C .

In any event, on raising the temperature above -100°C for the PhCCH compound we see the four-line CO spectrum coalesce to a two-line spectrum and the two Cp resonances coalesce to one. This can be explained by simultaneous and rapid occurrence of both the low- and the high-energy process. The fact that the two-line CO spectrum persists, with sharp lines, at 80°C rules out the occurrence of any rearrangement of the central Mo_2C_2 unit that would switch the phenyl group from one side to the other and thus abolish the diastereotopic character of the CO groups. It also means that internuclear CO scrambling, unless it is of an unlikely type in which only the two members of each equivalent pair interchange with each other, does not occur.

The apparent rigidity of the central M_2C_2 moiety and lack of CO scrambling in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR}')$ compounds find a direct parallel in the allene adducts,¹³ $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{allene})$. For example, the CO spectrum for the compound

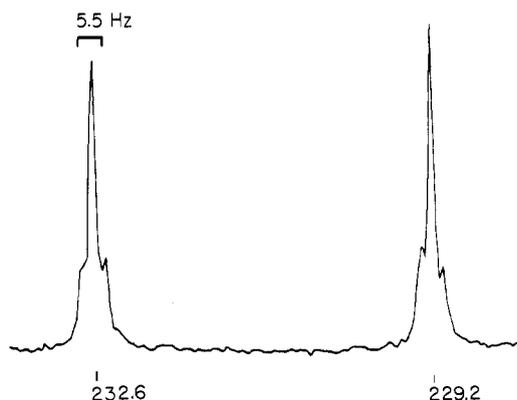


Figure 11. The ^{13}C NMR spectrum of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ in the CO region obtained at -90°C in toluene- d_8 , showing $J_{^{13}\text{C}-^{13}\text{C}} \sim 5\text{ Hz}$, δ in parts per million relative to Me_4Si . The CO groups are enriched to 30% ^{13}C .

$\text{Cp}_2\text{Mo}_2(*\text{CO})_4(\text{MeCH}=\text{C}=\text{CH}_2)$, which is shown in Figure 12, consists of four carbonyl resonances; the Mo_2C_3 moiety must be rigid and CO scrambling slow on the NMR time scale even at 90°C .²²

The variable temperature ^{13}C NMR spectra for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{EtCCEt})$, Figure 8, show several carbonyl resonances at low temperatures. On raising the temperature to -50°C these collapse to give a single CO resonance.

As rotation about the Mo–Mo bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ compound slows, three time-averaged *dl* pairs of isomers may be thermally accessible and must exist in equilibrium with each other. See Figure 13. Thus, there is a possibility of observing ten CO resonances and four Cp resonances even if process (1) is rapid. As (1) becomes slow on the NMR time scale, that is to say, a structure having one semibridging carbonyl ligand becomes frozen out, more isomers are possible. It is fruitless to speculate further upon the spectra for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{EtCCEt})$, other than to note that the combined effect of both the low- and high-energy processes leads to the rapid interconversion of all isomers above -57°C .

Reactions of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$. Coordination of an acetylene to a transition metal center generally leads to activation of the carbon–carbon triple bond. Reactions of acetylenes with mononuclear transition metal complexes have yielded an abundance of interesting products. Compounds of the type $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ provide a good starting point for the study of reactions of acetylenes coordinated to dinuclear metal centers. With this in mind, we carried out the following reactions.

Displacement Reactions. A benzene solution of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ was reacted with CO (1 atm) and $\text{MeC}\equiv\text{CMe}$ in separate experiments. No reaction occurred in either case and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ was recovered.

Attempted Hydrogenation. Since acetylenes, but not olefins, will coordinate to the $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ moiety, there exists the potential for the catalytic hydrogenation of acetylenes to olefins.¹⁴ Consequently, we reacted $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ with molecular hydrogen. In benzene at room temperature and 1 atm H_2 , no reaction was observed. At $70\text{--}80^\circ\text{C}$ and 50 atm

Table VII. Activation Parameters^a

Compound	E_a , kcal/mol	$\log A$	ΔH^\ddagger , kcal/mol	ΔG^\ddagger_{298} , kcal/mol	ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹
$\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{PhCCPh}$					
low-energy process	8.1 (2)	13.3 (3)	1.6 (4)	7.8 (2)	7.3 (2)
high-energy process	10.3 (2)	13.5 (3)	2.1 (4)	9.9 (2)	9.3 (2)
$\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{HCCH}$	10.7 (2)	13.4 (3)	1.6 (4)	10.2 (2)	9.8 (2)

^a Esd's given in parentheses occur in the least significant digit.

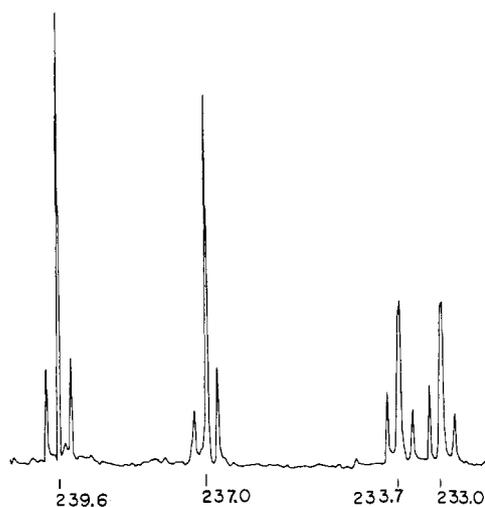


Figure 12. ^{13}C NMR spectra of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{MeCH}=\text{C}=\text{CH}_2)$ in the CO region obtained at 40 °C in toluene- d_6 , showing four carbonyl carbon resonances and $J_{^{13}\text{C}-^{13}\text{C}} \approx 10$ Hz. The spectrum remains unchanged at 90 °C. The CO groups are enriched to 30% in ^{13}C .

H_2 in benzene a small amount of ethylene was formed but extensive decomposition of the organometallic species occurred under these conditions. Formation of ethylene was not increased in a separate experiment when $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ was reacted with a 1:1 mixture of H_2 and $\text{HC}\equiv\text{CH}$ at 70 °C and 50 atm for a period of 18 h. We conclude that the acetylene in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ is quite tightly bound and not readily displaceable. These findings are not altogether surprising since in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ molybdenum attains an 18-electron valence shell configuration and, moreover, the central Mo_2C_2 moiety is saturated. We anticipate greater reactivity when the M_2C_2 moiety is unsaturated as is the case, for example, in $\text{Fe}_2(\text{CO})_6(t\text{-BuCCBu-}t)$, which contains an acetylene bridging an iron-iron double bond,^{5,23} and $\text{W}_2(\text{CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$, which contains bridging carbyne ligands and a planar central W_2C_2 core.^{24,25}

Experimental Section

General Procedures. All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere in vacuo using standard Schlenk techniques.²⁶ Solvents (benzene, toluene, and pentane) were dried and purged of molecular oxygen by distillation from sodium-potassium amalgam (25% Na to 75% K by weight), benzophenone, and phenyl ether. The molybdenum and tungsten compounds are slightly air-sensitive in solution. Samples were stored and handled in a Vacuum Atmospheres Co. Dri Lab System.

Materials. $[\text{CpMo}(\text{CO})_3]_2$ was synthesized by the established route.²⁷ $[\text{CpW}(\text{CO})_3]_2$ was synthesized by a procedure whereby $\text{CpW}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$ is pyrolyzed to $[\text{CpW}(\text{CO})_3]_2$.²⁸ $[\text{CpMo}(\text{CO})_2]_2$ and $[\text{CpW}(\text{CO})_2]_2$ were prepared in a standard manner by thermolysis.⁹

$\text{HC}\equiv\text{CH}$ was purchased from Matheson. 3-Phenyl-2-propyn-1-ol was purchased from Chemical Samples Co. ^{13}C O (90% ^{13}C) was purchased from Prochem Ltd. All other organic reagents used during this work were purchased from Aldrich Chemical Co.

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. ^1H NMR spectra were obtained using a Varian A-60 spectrometer equipped with a variable temperature probe. Temperatures were calibrated with methanol (low temperature) or ethylene glycol (high temperatures). ^1H chemical shifts are reported using C_6D_6 (7.248 ppm) as a reference. ^{13}C NMR spectra were obtained from a Varian XL-100 spectrometer using C_6D_6 as a reference and recorded in the Fourier mode. Variable temperature ^{13}C NMR were measured in toluene- d_8 with 10% added Freon-11.

$[\text{CpMo}(\text{CO})_2]_2\text{HC}\equiv\text{CH}$. $[\text{CpMo}(\text{CO})_2]_2$ (1.1158 g, 2.44 mmol) was dissolved in toluene (25 mL). $\text{HC}\equiv\text{CH}$ was bubbled through the

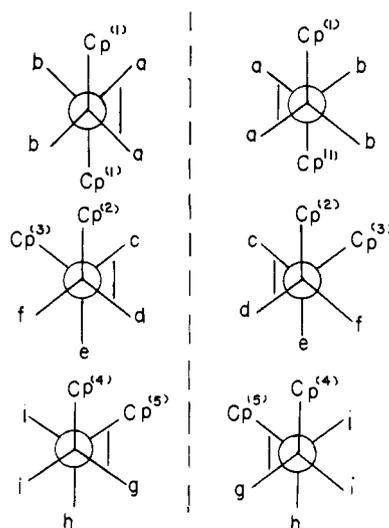


Figure 13. Schematic representations of the three *dl* isomers (rotamers) which may arise when the $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{C}_2$ moiety of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$ adopts a time-averaged structure with C_{2v} symmetry.

solution for 1 min. After 4 h of magnetically stirring this solution, the toluene was taken off and the residue was recrystallized from toluene/pentane: yield 62%; IR 1985 s, 1965 w, 1925 s, 1905 s, 1835 s cm^{-1} ; ^1H NMR (benzene- d_6) δ 4.97 (Cp), 4.67 ($\text{HC}\equiv\text{CH}$); ^{13}C NMR (benzene- d_6) at ambient temperature 230.18 (CO), 90.81 (Cp where $J_{\text{C-H}} = 178$ Hz), 61.88 ($\text{H}-\text{C}\equiv$ where $J_{\text{C-H}} = 216$ Hz), uncoordinated $\text{HC}\equiv\text{CH}$ 71.62 ppm ($J_{\text{C-H}} = 249$ Hz); at -90 °C 232.57 (t) and 229.19 ppm (t) with $J_{\text{C-C}} = 5.5$ Hz.

$[\text{CpMo}(\text{CO})_2]_2\text{HC}\equiv\text{CCF}_3$. This was prepared in essentially the same way: IR 2010 m, 1960 s, 1930 m, 1905 s, 1895 s, 1840 sh cm^{-1} ; ^1H NMR (benzene- d_6) δ 5.43 ($\text{HC}\equiv\text{CCF}_3$), 4.96 (Cp) at ca. 35 °C; ^{13}C NMR benzene- d_6) 230.04 and 226.67 (C), 90.95 ppm (Cp where $J_{\text{C-H}} = 180$ Hz) at ca. 35 °C; ^{19}F NMR (toluene- d_8) -47.2 ppm (CCl_3F standard) at ca. 35 °C; at -90 °C (toluene- d_8 and CCl_3F) single peak (-47.2 ppm).

Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{O}_4\text{F}_3\text{Mo}_2$: C, 38.66; H, 2.10. Found: C, 38.8; H, 2.34.

$[\text{CpMo}(\text{CO})_2]_2\text{MeC}\equiv\text{CMe}$. This was prepared by the same general procedure as were the preceding compounds: IR 1979 m, 1961 w, 1915 sh, 1908 s, 1841 s cm^{-1} ; ^1H NMR (benzene- d_6) δ 4.90 (Cp), 2.43 (Me) at ca. 35 °C; ^{13}C NMR ambient temperature δ 91.5, $J_{\text{C-H}} = 180$ Hz (Cp), 230.8 (CO), 82.6, $J_{\text{C-H}} = 7.5$ Hz ($\equiv\text{C}-$), 22.4, $J_{\text{C-H}} = 130$ Hz ($-\text{C}\text{H}_3$). For free but-2-yne ($\equiv\text{C}-$) 73.9 ppm.

Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Mo}_2$: C, 44.28; H, 3.31. Found: C, 44.5; H, 3.51.

$[\text{CpMo}(\text{CO})_2]_2\text{CH}_3\text{OC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{OCH}_3$. $[\text{CpMo}(\text{CO})_2]_2$ (0.2000 g, 4.6 mmol) was dissolved in toluene (20 mL). Dimethyl acetylenedicarboxylate (1.0 mL, 8 mmol) was added to the magnetically stirred solution. After 4 h the solvent was removed by vacuum and the residue was pumped overnight to remove any excess dimethyl acetylenedicarboxylate. Recrystallization from toluene/pentane yielded red crystals (42%): IR 2009 w, 2001 w, 1975 s, 1962 m, 1945 s, 1925 s, 1860 m, 1670 s cm^{-1} ; ^1H NMR (benzene- d_6) δ 5.04 (Cp), 3.62 (MeO-) at ca. 35 °C; ^{13}C NMR (toluene- d_8) ambient temperature 230.12 (CO), 90.84 (Cp), 61.96 ppm ($-\text{C}\equiv\text{C}-$). At -101 °C: 231.31, 228.22, 226.31, and 222.43 ppm (CO), all broad.

Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_8\text{Mo}_2$: C, 41.68; H, 2.80. Found: C, 41.9; H, 3.01.

$[\text{CpMo}(\text{CO})_2]_2\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OH}$. This was prepared in a similar way: IR 1976 s, 1900 sh, 1890 s, 1837 sh cm^{-1} ; ^1H NMR δ 5.97 ($\text{HC}\equiv\text{C}-$), 4.95 (Cp); ^{13}C NMR (benzene- d_6) 91.29 (Cp where $J_{\text{C-H}} = 180$ Hz), 87.21 ppm ($\text{HC}\equiv\text{C}-$ where $J_{\text{C-H}} = 210$ Hz). Uncoordinated $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OH}$ $J_{\text{C-H}} = 249$ Hz.

Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_5\text{Mo}_2$: C, 42.87; H, 3.20. Found: C, 42.9; H, 3.28.

$[\text{CpMo}(\text{CO})_2]_2\text{PhC}\equiv\text{CH}$. See ref 9 for preparation, IR, and ^1H NMR. ^{13}C NMR (toluene- d_8) at 35 °C, 231.34 and 229.85 (CO) ($J_{\text{C-C}} \approx 6$ Hz), 91.76 ppm (Cp); at -100 °C 232.99, 232.30, 231.42, and 227.79 (CO), 92.83 ppm (Cp).

$[\text{CpMo}(\text{CO})_2]_2\text{PhC}\equiv\text{CCH}_2\text{OH}$ was prepared like the

Table VIII. Summary of Crystallographic Data

compd	Cp ₂ Mo ₂ (CO) ₄ Et ₂ C ₂	Cp ₂ Mo ₂ (CO) ₄ C ₂ (C ₆ H ₅) ₂	Cp ₂ Mo ₂ (CO) ₄ C ₂ H ₂
formula weight	516.26	612.35	460.15
a, Å	9.262 (2)	34.693 (1)	10.395 (2)
b, Å	13.773 (4)	9.000 (3)	17.171 (7)
c, Å	15.581 (3)	16.228 (3)	8.653 (2)
β, deg	105.41 (2)	110.57 (4)	94.38 (3)
V, Å ³	1916.3 (8)	4743 (1)	1540 (1)
Z	4	8	4
density (calcd), g/cm ³	1.794	1.715	1.984
crystal size, mm	0.17 × 0.15 × 0.13	0.50 × 0.39 × 0.20	0.41 × 0.52 × 0.70
absorption coefficient, cm ⁻¹	13.106	10.730	16.123
space group	P2 ₁ /n	C2/c	P2 ₁ /n
range of 2θ	0° < 2θ ≤ 45.0°	0° < 2θ ≤ 45.0°	0° < 2θ ≤ 65.0°
number of reflections collected	2327	3364	5644
number of reflections > 3σ	2029	2628	3876
number of variables	235	247	235
R ₁	0.036	0.046	0.038
R ₂	0.057	0.074	0.049
esd of observation of unit weight	1.382	1.858	1.101

MeO₂CC≡CCO₂Me compound: IR 1989 m, 1922 s, 1846 m, 1830 br cm⁻¹; ¹H NMR (toluene-*d*₈) ambient δ 5.14 (Cp), 4.47 (-CH₂-). -60 °C: broadening of -CH₂- region. -110 °C: collapse of -CH₂- region; Cp has split into 2 broad peaks (~10 Hz apart).

Anal. Calcd for C₂₃H₁₈O₅Mo₂: C, 48.78; H, 3.21. Found: C, 48.8; H, 3.31.

Isotopically Labeled Compounds. Labeled compounds [CpMo(*CO)₃]₂ and [CpMo(*CO)₂]₂ were prepared by reacting [CpMo(CO)₂]₂ with ¹³CO to give [CpMo(*CO)₃]₂ which was then refluxed in *m*-xylene under a N₂ purge to produce [CpMo(*CO)₂]₂. The labeled [CpMo(*CO)₂]₂ was then reacted with acetylenes to produce the ¹³CO labeled compounds, Cp₂Mo₂(*CO)₄(RCCR').

Reactions of [CpMo(CO)₂]₂HC≡CH. With CO. An NMR tube containing [CpMo(CO)₂]₂HC≡CH (0.1 g, 0.2 mmol) and C₆D₆ (0.3 mL) had CO bubbled through the solution for 1 min. The NMR and IR spectra indicated that no reaction had occurred.

The reactions with H₂ and H₂ + HC≡CH (1 atm) were performed in a similar manner.

With MeC≡CMe. An NMR tube was prepared as above. MeC≡CMe (0.2 mmol, ~2 atm) was condensed into the NMR tube, which was then sealed by torch. After 1 day at room temperature, no reaction had occurred. However, heating the tube to 105 °C for 12 h caused a reaction to occur yielding many products which were not characterized.

With H₂. H₂ + HC≡CH (50 atm, 70–80 °C). These reactions were carried out in NMR tube experiments in benzene-*d*₆ and followed by ¹H NMR spectroscopy.³¹ Formation of ethylene was easily detectable in this manner.

X-ray Crystallography. The crystallographic studies were conducted in the same manner for all three compounds. Crystallographic data are collected in Table VIII. The crystal class, cell dimensions, and space groups were established in a routine manner by examination on a Syntex P1 automated diffractometer, operating at 23 ± 2 °C, and the same instrument was then used to collect intensity data. Molybdenum Kα radiation, monochromatized by a graphite crystal in the incident beam, was used throughout. The centering and autoindexing procedures have been described previously.²⁹ In each case ω scans of several intense reflections had widths at half-height of ≤ 0.25°, and θ-2θ scans were used to measure intensities. Variable scan rates of 4.0–24.0°/min and a scan range of 1.0° above and below the Kα₁ and Kα₂ peaks, respectively, were used. Background measurements were made at both limits of each scan, with equal time intervals for background and peak counting. Intensities of three standard reflections were measured periodically. They showed no significant variations during data collection for any of the compounds. The data were corrected for Lorentz and polarization effects,³⁰ but because of the low linear absorption coefficients no absorption corrections were applied.

Solution and Refinement³⁰ of the Structures. Three-dimensional Patterson maps were used to determine the positions of the molybdenum atoms for each compound. The molybdenum positions were refined using least squares and subsequent difference Fourier maps

revealed the approximate positions of all remaining nonhydrogen atoms. The discrepancy factors listed in Table VIII are defined as follows:

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$$

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

The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, *w*, equal to $4F_o/\sigma(F_o^2)$. All structure factor calculations and least-squares refinements were executed using only those reflections for which $F_o^2 > 3\sigma(F_o^2)$. Atomic scattering factors were those of Cromer and Waber.³¹ Anomalous dispersion effects were included in the scattering factors of molybdenum.³² The structures were refined to convergence by the full-matrix least-squares procedure with anisotropic temperature factors for all nonhydrogen atoms except the phenyl carbon atoms in the diphenylacetylene compound. For the ethyne compound, hydrogen positions were calculated and included in the final refinement using fixed isotropic temperature factors.

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Supplementary Material Available: A listing of structure factors, and the atomic positional and thermal parameters for the three structures (43 pages). Ordering information is given on any current masthead page.

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Infrared Spectra of the Argon-Matrix Isolated Alkali Halide Salt/Ammonia Complexes. Spectrum of the NH_3M^+ Cation

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Abstract: The reaction products of alkali halide and cyanide salt molecules with NH_3 in argon matrices have been investigated and characterized by infrared spectroscopy. Four product bands were detected and assigned to two N-H stretching modes, an NH_3 symmetric deformation mode, and an NH_3 rocking mode in the complex. Analysis of the cation and anion dependences of these bands, and comparison to transition metal ammine complexes, has led to a proposed structure of the form $\text{NH}_3\text{M}^+\cdot\text{X}^-$, with the interaction involving the attraction of the alkali metal cation to the nitrogen lone pair, while a hydrogen bonding interaction is *not* indicated.

Introduction

Recently, a study was reported in which the argon matrix-isolated complexes of alkali metal halide salt molecules with H_2O were studied,¹ to investigate the interactions between alkali metal cations and Lewis bases. It is of interest to extend these studies to other Lewis bases, and in particular NH_3 , to more completely characterize this interaction. Also, Devlin and co-workers have carried out several studies in this area,²⁻⁴ first through the investigation of alkali nitrate and chlorate ion pairs in glassy NH_3 , and secondly through the investigation of the interaction of the ion pairs with NH_3 in argon matrices, at 3-20% NH_3 in Ar. They conclude that in each case the interaction is through the lone pair on the NH_3 molecule to the alkali metal cation, and that the interaction is consistently stronger for NH_3 than H_2O . Finally, transition metal ammine complexes are available as models for these complexes.⁵⁻⁷

Consequently, a number of reactions were carried out in argon matrices, to thoroughly characterize the 1:1 reaction product.

Experimental Section

The apparatus used for the present studies is identical with that used previously,¹ NH_3 (Matheson), ND_3 (Merck), and $^{15}\text{NH}_3$ (Merck,

95.2% ^{15}N) were all condensed into a stainless steel finger at 77 K, and volatile impurities pumped off. Argon, without further purification, was used as matrix gas in all experiments.

The alkali halide and cyanide salts employed were NaCl (Mallinckrodt, analytical reagent), KCl (Allied, reagent), KBr (Fisher), KCN (Fisher), RbCl (Fairmount), CsCl (Fisher), CsF (Alfa), CsBr (Orion), and CsI (Harshaw). These salts were loaded in a stainless steel Knudsen cell and heated to generate a pressure of about 1μ for deposition into Ar/ NH_3 matrices. Operating temperatures follow: NaCl, 600 °C; KCl, 550 °C; KBr, 525 °C; KCN, 550 °C; RbCl, 525 °C; CsCl, 500 °C; CsBr, 500 °C; CsF, 500 °C. Matrix samples were deposited onto a CsI cold window for 20-30 h at between 14 and 16 K, before final spectra were recorded.

Results

Before the reaction products of the salt molecules with NH_3 were investigated, the argon matrix spectra of NH_3 and its isotopic counterparts were recorded. The spectra were complex, owing to both dimerization and inversion structure, so that multiple bands were observed in the region of the NH_3 fundamentals, especially for ν_2 . The spectra obtained here, and shown in Figure 1, agree well with literature spectra of NH_3 in argon.^{8,9} Similar spectra were recorded for samples of Ar/ $^{15}\text{NH}_3 = 250$ and Ar/ $\text{ND}_3 = 250$, with band positions again in agreement with reported literature values. The spectra also