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Reactions of Metal-to-Metal Multiple Bonds. 1. μ-Allene-bis(cyclopentadienyl)tetracarbonyldimolybdenum and -ditungsten Compounds. Preparation, Properties, and Structural Characterization

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Abstract: The reaction of $Cp_2M_2(CO)_4$ compounds (M = Mo and W), which contain M–M triple bonds, with allenes leads to the 1:1 adducts $Cp_2M_2(CO)_4(C_3H_4)$, where M = Mo and W, and $Cp_2Mo_2(CO)_4(allene')$ where allene' = $MeCH=C=CH_2$ and $MeCH=C=CHMe$. These new compounds have been characterized by infrared spectroscopy, mass spectroscopy, NMR spectroscopy (^1H, ^{13}C, and $^{13}C[H]$), and in the case of $Cp_2Mo_2(CO)_4(C_3H_4)$ by single-crystal x-ray crystallography. The compound crystallizes in the nonstandard space group Pn with $a = 10.932$ (2) Å, $b = 7.776$ (2) Å, $c = 10.015$ (1) Å, $\beta = 107.82$ (2)°, and $V = 810.5$ (5) Å^3. Full-matrix least-squares refinement gave final discrepancy factors $R_1 = 0.030$ and $R_2 = 0.046$. For $Cp_2Mo_2(CO)_4(C_3H_4)$ the Mo–Mo distance is 3.117 (1) Å and the molecule has virtual C_s symmetry with the rotational axis passing through the central allenic carbon atom and the center of the Mo–Mo bond. The allene is V-shaped (C–C–C = 146°) and may be considered to form one olefin–metal bond to each molybdenum atom. NMR data indicate that in solution the compounds $Cp_2M_2(CO)_4(allene)$ adopt a structure akin to that found in the solid state for $Cp_2Mo_2(CO)_4(C_3H_4)$; enantiomerization and CO site exchange are slow on the NMR time scale up to 100 °C.

Introduction

There is currently a certain optimism that transition metal cluster chemistry could lead to a new era in homogeneous hydrocarbon catalysis.[2] The reactivity of metal-to-metal bonds and the synthesis of new cluster compounds are clearly two topics requiring study if such aspirations are to be realized. Bimetallic compounds containing metal-to-metal multiple bonds[3] will surely occupy a unique position in this field of chemistry. They are the smallest examples of unsaturated metal cluster compounds and provide building blocks for the systematic synthesis of polynuclear compounds. Furthermore, the organometallic reaction schemes[4] of mononuclear complexes may be extended to dinuclear systems.

We have previously shown that an extensive coordination chemistry surrounds metal-to-metal triple bonds in the chemistry of molybdenum[5-10] and tungsten.[11-20] Others have shown[21] that acetylenes, but *not* olefins,[22] add across metal-to-metal triple bonds, although the same products can be obtained directly by reaction of the acetylenes with $Cp_2Mo_2(CO)_6$ without isolating the presumed $Cp_2Mo_2(CO)_4$ intermediate.[23] In this paper we describe the addition of allenes to the M–M triple bonds in $Cp_2M_2(CO)_4$ (M = Mo and W) and the properties of the products, including a full structural characterization of the prototypal compound, $Cp_2Mo_2(CO)_4(C_3H_4)$. A preliminary report of some of this work has appeared.[24]

Results and Discussion

Syntheses. Addition of allene (1 equiv) to hydrocarbon solutions of $Cp_2M_2(CO)_4$, where M = Mo or W, leads to deep red solutions and to the formation of microcrystalline, orange- or tan-colored precipitates, the latter being formed in ca. 10% yield based on molybdenum or tungsten. Deep red crystals of the compound $Cp_2M_2(CO)_4(C_3H_4)$ were the only products isolated from solution. NMR tube experiments showed that reaction 1 is both rapid and irreversible.

$$Cp_2M_2(CO)_4 + CH_2=C=CH_2$$
$$\rightarrow Cp_2M_2(CO)_4(C_3H_4) \quad (1)$$
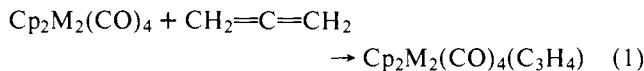
The preparation of two substituted allenic derivatives $Cp_2Mo_2(CO)_4(allene')$, where allene' = 1-methylallene (1,2-butadiene) or 1,3-dimethylallene (2,3-pentadiene), has also been achieved but more forcing conditions were required, namely, sealed tube techniques and elevated temperatures, 60–80 °C. No reaction between 1,1-dimethylallene and $Cp_2Mo_2(CO)_4$ has been observed under analogous conditions. Thus, for the addition of allenes to the metal-to-metal triple bond in $Cp_2Mo_2(CO)_4$ we observe the reactivity order

$$CH_2=C=CH_2 > MeCH=C=CH_2$$
$$> MeCH=C=CHMe > Me_2C=C=CH_2$$
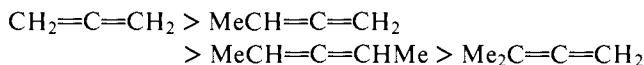
This suggests that steric factors are important, although whether this is primarily a kinetic or thermodynamic effect is uncertain.

We have found that when allene is added to a hydrocarbon solution containing both $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ the red, crystalline product showed only homodinuclear ions in the mass spectrometer. The absence of heterodinuclear ions (Mo–W containing) leads us to believe that the formation of

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

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	0.000 00 (0)	0.245 87 (7)	0.000 00 (0)	0.007 55 (5)	0.0107 (1)	0.007 46 (6)	0.0024 (1)	0.006 21 (9)	0.0014 (1)
Mo2	0.077 71 (6)	0.253 36 (7)	−0.274 60 (6)	0.008 50 (5)	0.0100 (1)	0.007 15 (5)	−0.0010 (1)	0.007 94 (8)	−0.0012 (1)
O1	0.0679 (6)	0.5510 (8)	0.2087 (6)	0.0157 (7)	0.019 (1)	0.0135 (7)	−0.008 (2)	0.011 (1)	−0.018 (1)
O2	0.3011 (7)	0.2458 (8)	0.1061 (9)	0.0088 (6)	0.031 (2)	0.0122 (8)	0.007 (2)	0.000 (1)	−0.005 (2)
O3	−0.0358 (8)	−0.0090 (13)	−0.5087 (7)	0.0217 (10)	0.050 (2)	0.0133 (8)	−0.021 (3)	0.016 (1)	−0.025 (2)
O4	0.1731 (8)	−0.0967 (8)	−0.1376 (7)	0.0209 (8)	0.016 (1)	0.0141 (7)	0.010 (2)	0.014 (1)	−0.002 (2)
C1	0.0487 (7)	0.4461 (10)	0.1361 (7)	0.0113 (7)	0.015 (1)	0.0082 (6)	0.005 (2)	0.013 (1)	−0.004 (2)
C2	0.1949 (12)	0.2448 (10)	0.0570 (13)	0.0133 (11)	0.014 (2)	0.0148 (13)	0.008 (2)	0.004 (2)	0.006 (2)
C3	0.0060 (10)	0.0930 (11)	−0.4135 (9)	0.0178 (10)	0.014 (1)	0.0150 (9)	−0.010 (2)	0.019 (1)	−0.015 (2)
C4	0.1386 (7)	0.0247 (10)	−0.1662 (8)	0.0078 (6)	0.015 (1)	0.0093 (7)	0.006 (1)	0.008 (1)	−0.005 (2)
C5	−0.1577 (10)	0.1722 (17)	0.0969 (10)	0.0136 (9)	0.030 (2)	0.0121 (10)	−0.010 (3)	0.014 (1)	−0.007 (3)
C6	−0.1939 (10)	0.0995 (12)	−0.0470 (13)	0.0100 (9)	0.019 (2)	0.0236 (17)	−0.014 (2)	0.003 (2)	0.008 (3)
C7	−0.1242 (9)	−0.0092 (13)	−0.0628 (9)	0.0183 (9)	0.017 (1)	0.0162 (9)	−0.001 (2)	0.023 (1)	0.013 (2)
C8	−0.0196 (12)	−0.0442 (15)	0.0492 (10)	0.0284 (14)	0.024 (2)	0.0168 (10)	−0.011 (3)	0.032 (2)	−0.001 (3)
C9	−0.0359 (12)	0.0542 (13)	0.1590 (8)	0.0273 (15)	0.023 (2)	0.0089 (8)	0.004 (3)	0.020 (2)	0.012 (2)
C10	0.2896 (8)	0.3622 (13)	−0.2295 (10)	0.0106 (7)	0.022 (2)	0.0182 (11)	−0.004 (2)	0.019 (1)	0.000 (3)
C11	0.1983 (10)	0.5025 (12)	−0.1963 (11)	0.0181 (9)	0.018 (1)	0.0254 (12)	−0.026 (2)	0.028 (2)	−0.031 (2)
C12	0.1065 (9)	0.5416 (9)	−0.3382 (9)	0.0162 (9)	0.009 (1)	0.0144 (8)	0.004 (2)	0.018 (1)	0.011 (2)
C13	0.1253 (8)	0.4316 (11)	−0.4417 (9)	0.0156 (8)	0.016 (2)	0.0193 (9)	−0.005 (2)	0.027 (1)	0.000 (2)
C14	0.2327 (7)	0.3428 (12)	−0.3750 (10)	0.0161 (6)	0.016 (2)	0.0318 (11)	−0.009 (2)	0.041 (1)	−0.003 (2)
C15	−0.0794 (10)	0.4905 (13)	−0.1099 (11)	0.0145 (9)	0.019 (2)	0.0195 (12)	−0.002 (2)	0.018 (2)	−0.011 (3)
C16	−0.0736 (8)	0.3516 (10)	−0.2033 (8)	0.0078 (6)	0.015 (1)	0.0090 (8)	0.004 (2)	0.005 (1)	0.006 (2)
C17	−0.1359 (10)	0.2650 (11)	−0.3293 (8)	0.0115 (9)	0.025 (2)	0.0041 (6)	−0.006 (2)	−0.001 (1)	−0.004 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Numbers in parentheses are estimated standard deviations in the last significant digits.

the $Cp_2M_2(CO)_4$(allene) compounds proceeds via direct addition of allene to the dinuclear compounds and does not involve mononuclear intermediates. The detailed mechanism of the addition is unknown.

Physical Properties. $Cp_2M_2(CO)_4(C_3H_4)$, where M = Mo and W, and $Cp_2Mo_2(CO)_4$(allene′), where allene′ = Me-CH=C=CH₂ and MeCH=C=CHMe, are red, crystalline compounds which are only sparingly soluble in alkane solvents but appreciably soluble in the aromatic solvents 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 more rapidly decomposed.

All compounds show molecular ions $Cp_2M_2(CO)_4$(allene)$^+$ as well as ions formed by the pairwise loss of carbonyl ligands in the mass spectrometer. The absence of the ions Cp_2M_2(allene)(CO)$_x^+$, where x = 1 or 3, was quite striking. The Cp_2M_2(allene)$^+$ type ions were by far the most intense ones; strong signals due to doubly charged ions, Cp_2M_2(allene)$^{2+}$, were also observed.

In the infrared spectra several bands were observed in the region 2000–1800 cm^{-1} which must be due to ν_{str}(CO) and ν_{str}(C=C) of the allenic moiety. However, in the absence of a detailed ^{13}C-labeling study an unequivocal assignment is not possible. IR data are recorded in the Experimental Section.

The nature of the tan compounds which accompany the formation of the allene adducts in reaction 1 (M = Mo and W) is uncertain. These compounds are virtually insoluble in all common spectroscopic solvents. They do not appear to be formed by reaction of allene with $Cp_2M_2(CO)_4$(allene), but, rather, competitively upon reaction of allene with $Cp_2M_2(CO)_4$. Elemental analyses are consistent with empirical formulas for 1:1 adducts, i.e., $Cp_2M_2(CO)_4(C_3H_4)$. These compounds are essentially nonvolatile, although at 300 °C, ions corresponding to $Cp_2M_2(C_3H_4)^+$ and $Cp_2M_2(C_3H_4)(CO)_2^+$, together with weaker ions of m/e considerably greater than $CpM_2(C_3H_4)(CO)_4^+$, were observed in the mass spectrometer. It has been shown by comparison with an authentic sample that the molybdenum compound is not $Cp_2Mo_2(CO)_4$-(MeC≡CH). IR data are given in the Experimental Section.
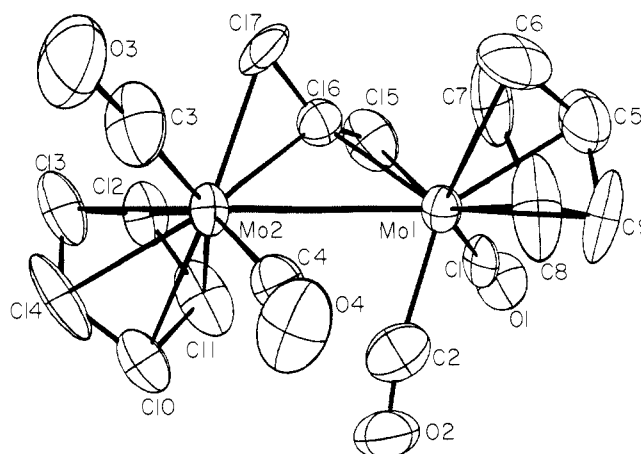

Figure 1. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_3H_4)$. Atoms are represented by their ellipsoids of thermal vibration, scaled to enclose 50% of the electron density.

Molecular Structure of $Cp_2Mo_2(CO)_4(C_3H_4)$. In order to show in detail how the allene ligand is attached to the $Cp_2Mo_2(CO)_4$ unit in these molecules we have employed x-ray crystallography to determine the molecular structure of the prototype molecule, i.e., the one containing unsubstituted allene itself. This structure determination also provides the most direct possible proof that the C_3H_4 moiety retains its identity as $H_2C=C=CH_2$ and does not rearrange, e.g., to form methylacetylene.

The molecular structure is shown in Figure 1. The positional and thermal parameters of the atoms, numbered as in Figure 1, are listed in Table I. Bond distances are listed in Table II and bond angles in Table III. While the molecule is not subject to any crystallographic symmetry element, it has essentially C_2 symmetry, with the C_2 axis passing through C(16), the central carbon atom of the allene, and the midpoint of the Mo–Mo bond.

The bonding of the allene to the metal atoms can be regarded, at least qualitatively, as a combination of two more or less independent ethylene–metal bonds sharing a common

Table II. Bond Lengths (Å) in Cp₂Mo₂(CO)₄(C₃H₄)[a]

Mo(1)–Mo(2)	3.117 (1)	Mo(2)–C(13)	2.35 (1)
Mo(1)–C(1)	2.03 (1)	Mo(2)–C(14)	2.33 (1)
Mo(1)–C(2)	2.03 (1)	C(1)–O(1)	1.07 (1)
Mo(1)–C(4)	3.09 (2)	C(2)–O(2)	1.11 (2)
Mo(1)–C(15)	2.23 (2)	C(3)–O(3)	1.22 (1)
Mo(1)–C(16)	2.11 (1)	C(4)–O(4)	1.02 (1)
Mo(1)–C(5)	2.24 (1)	C(5)–C(6)	1.49 (2)
Mo(1)–C(6)	2.32 (1)	C(6)–C(7)	1.18 (2)
Mo(1)–C(7)	2.38 (2)	C(7)–C(8)	1.36 (2)
Mo(1)–C(8)	2.33 (2)	C(8)–C(9)	1.39 (2)
Mo(1)–C(9)	2.23 (2)	C(9)–C(5)	1.59 (2)
Mo(2)–C(2)	3.17 (1)	C(10)–C(11)	1.58 (2)
Mo(2)–C(3)	1.85 (1)	(C(11)–C(12)	1.50 (2)
Mo(2)–C(4)	2.08 (1)	C(12)–C(13)	1.41 (2)
Mo(2)–C(16)	2.13 (1)	C(13)–C(14)	1.35 (2)
Mo(2)–C(17)	2.23 (2)	C(14)–C(10)	1.40 (2)
Mo(2)–C(10)	2.38 (1)	C(15)–C(16)	1.44 (2)
Mo(2)–C(11)	2.34 (1)	C(16)–C(17)	1.41 (1)
Mo(2)–C(12)	2.38 (1)		

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

Table III. Bond Angles in Cp₂Mo₂(CO)₄(C₃H₄)[a]

Mo(2)–Mo(1)–C(1)	119.5 (3)	Mo(1)–C(1)–O(1)	176 (1)
–C(2)	76.7 (6)	Mo(1)–C(2)–O(2)	171 (2)
Mo(2)–Mo(1)–C(4)	39.2 (4)		
–C(15)	73.7 (4)	Mo(2)–C(3)–O(3)	176 (1)
–C(16)	43.0 (2)	Mo(2)–C(4)–O(4)	164 (1)
–C(5)	143.1 (4)		
		C(15)–C(16)–C(17)	146 (1)
–C(6)	108.0 (5)		
–C(7)	94.0 (3)	C(5)–C(6)–C(7)	114 (1)
–C(8)	105.8 (4)	C(6)–C(7)–C(8)	116 (2)
–C(9)	140.6 (4)	C(7)–C(8)–C(9)	105 (2)
Mo(1)–Mo(2)–C(2)	37.6 (3)	C(8)–C(9)–C(5)	107 (1)
Mo(1)–Mo(2)–C(3)	118.8 (4)		
		C(9)–C(5)–C(6)	96 (1)
–C(4)	69.7 (3)		
–C(16)	42.5 (2)	C(10)–C(11)–C(12)	103 (1)
–C(17)	70.7 (3)	C(11)–C(12)–C(13)	112 (1)
–C(10)	110.6 (4)	C(12)–C(13)–C(14)	104 (1)
–C(11)	89.9 (4)	C(13)–C(14)–C(10)	120 (1)
–C(12)	110.4 (3)	C(14)–C(10)–C(11)	101 (1)
–C(13)	144.9 (3)		
–C(14)	144.9 (5)		

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

carbon atom, C(16). Thus C(15) and C(16) constitute the ethylene bound to Mo(1) and C(16) and C(17) the ethylene bound to Mo(2). The two metal–olefin groupings are nearly orthogonal. The bonding is slightly distorted from ideal olefin–metal bonding because the Mo(1)–C(15) and Mo(2)–C(17) distances, 2.23 (2) and 2.23 (2) Å, are about 0.1 Å longer than the Mo(1)–C(16) and Mo(2)–C(16) distances, 2.11 (1) and 2.13 (1) Å. This is the first example of an allene bounded to two metal atoms which are themselves bonded to each other.[25]

The structure here differs in two important respects from the recently reported structures of Cp₂Mo₂(CO)₄(RCCR) compounds with R = H[26] and Et.[27] In the latter, the Mo–Mo bonds are much shorter (~2.98 Å) than that found here, 3.117 (1) Å, presumably because of the requirement for formation of bonds to the two π components of the same C–C triple bond, whereas in the present case optimum overlap with the pairs of π electrons can be obtained without such a close approach. In this molecule we do not find a unique CO ligand in a semi-bridging position, as is the case with the acetylene compounds, presumably because the longer Mo–Mo distance here introduces less crowding. However, as Figure 1 shows, two of the CO groups, C(2)–O(2) and C(4)–O(4), are somewhat bent (171 and 164°) in directions implying some repulsive interaction of their oxygen atoms with the cyclopentadienyl groups on the other metal atoms. The one rather short metal to carbonyl carbon (Mo(2)–C(3)) bond (1.85 (1) Å) is presumably the result of intramolecular interactions.

NMR Studies. ¹H, ¹³C, and ¹³C[H] NMR spectra were recorded in benzene-d_6, toluene-d_8, and CD₂Cl₂ for the compounds Cp₂M₂(CO)₄(C₃H₄), where M = Mo and W, and Cp₂Mo₂(CO)₄(allene′), where allene′ = MeCH=C=CH₂ and MeCH=C=CHMe. These spectra were essentially invariant with temperature in the range 100 to −90 °C. The spectra were unchanged by the addition of allene indicating that exchange between free and coordinated allene must be slow on the NMR time scale. Indeed Cp₂Mo₂(CO)₄(C₃H₄) did not react with either CO or PPh₃, which indicates that the allene does not dissociate from the Mo₂ moiety, nor is it readily displaceable. Complete NMR data are recorded in the Experimental Section. The following discussion is confined to matters relating to solution stereochemistry, dynamical solution behavior, and bonding properties in these compounds.

Cp₂M₂(CO)₄(C₃H₄) Compounds (M = Mo, W). The ¹H NMR spectra of the Cp₂M₂(CO)₄(C₃H₄) compounds are very similar; that of the molybdenum compound is shown in Figure

2. The allenic protons appear as two sets of triplets and can be assigned to a so-called deceptively simple AA′BB′ multiplet,[28] consistent with the adoption of a solution structure having C_2 molecular structure, as shown in Figure 3. The ¹³C and ¹³C[¹H] spectra are also consistent with a structure having C_2 molecular symmetry. For M = Mo the terminal allenic carbon atoms are equivalent and shifted upfield (δ 36 ppm) relative to free allene (δ 74 ppm). In the ¹H-undecoupled spectrum the terminal allenic signal becomes four equally intense lines, assignable to the X portion of an X₂AA′BB′ spectrum with $J_{AX} \approx J_{BX} \approx 160$ Hz, indicative of approximately sp² hybridization at these terminal carbon atoms.[29] The appearance of two carbonyl resonances, of equal intensity, indicates that the two types of carbonyl ligands (see Figure 3) are not interconverted readily. Thus, the NMR data suggest that the compounds Cp₂M₂(CO)₄(C₃H₄) adopt a solution structure with the same symmetry as that found in the solid state. It is also apparent that enantiomerization does not occur rapidly on the NMR time scale, since this requires H_A, H_B site exchange as indicated in eq 2.

(2)
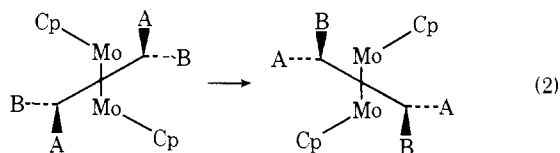
Cp₂Mo₂(CO)₄(MeCH=C=CHMe). Coordination of racemic 1,3-dimethylallene to a Cp₂Mo₂(CO)₄ moiety having C_2 molecular symmetry could lead to the formation of the three dl pairs of enantiomers[30] shown in Figure 4. ¹H and ¹³C NMR spectra indicate the presence of only one pair of enantiomers, which on the basis of steric considerations we assign to I in Figure 4.

Cp₂Mo₂(CO)₄(MeCH=C=CH₂). Coordination of 1-methylallene to Cp₂Mo₂(CO)₄ could lead to the formation of the two dl pairs of enantiomers shown in Figure 5. NMR data indicate that only one pair exists in solution at a detectable concentration. On the basis of steric considerations we suggest that this corresponds to the I enantioners shown in Figure 5. This 1-substituted allene effectively labels the ends of the molecule. The observation of two cyclopentadienyl resonances with relative intensities of 1:1 and four carbonyl resonances
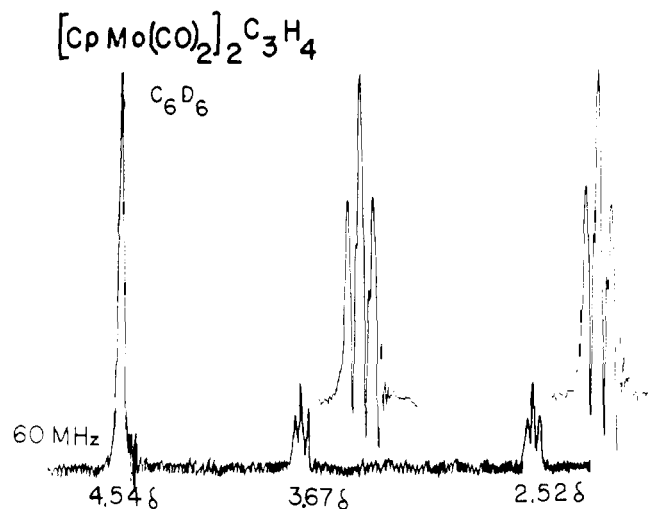
Figure 2. ¹H NMR spectrum of Cp₂Mo₂(CO)₄(C₃H₄), recorded at 60 MHz in benzene-d_6 at 35 °C. Insets show the allenic proton resonances at higher spectrum amplitude and at scale expansion. The spectrum remains unchanged at 100 °C.
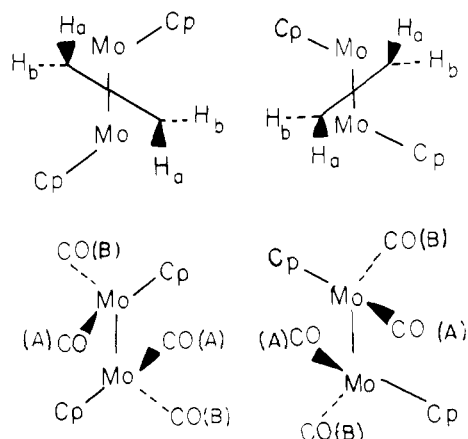

Figure 3. Schematic view of Cp₂Mo₂(CO)₄(C₃H₄) viewed perpendicular to the Mo-Mo axis from above (top) and from below (bottom) the C₃Mo₂ core showing the symmetry related allenic protons (top) and carbonyl ligands (bottom).

Figure 4. Schematic representations of the three pairs of enantiomers for Cp₂Mo₂(CO)₄(MeCH=C=CHMe).
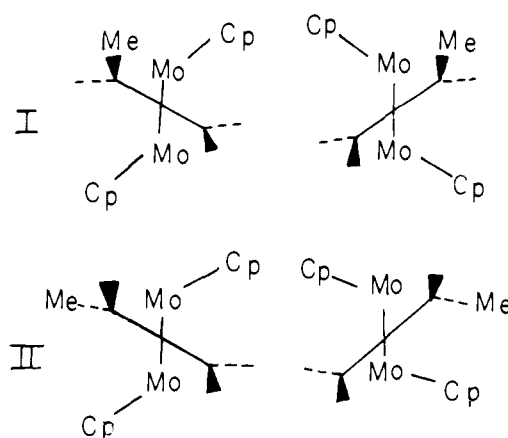
Figure 5. Schematic representation of the two pairs of enantiomers for Cp₂Mo₂(CO)₄(MeCH=C=CH₂).

ca. 27% ¹³CO by the reaction sequence

$$Cp_2Mo_2(CO)_6 \xrightarrow{\Delta} Cp_2Mo_2(CO)_4 \xrightarrow{+2^{13}CO}$$

$$Cp_2Mo_2(*CO)_6 \xrightarrow{\Delta} Cp_2Mo_2(*CO)_4$$

with relative intensities of 1:1:1:1 clearly shows that both enantiomerization, reaction 2, and CO site exchange must be processes with $\Delta G^{\ddagger} > 20$ kcal mol⁻¹.

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 and vacuum line procedures.[31] Solvents (benzene, toluene, and pentane) were dried and freed from molecular oxygen by distillation from Na-K amalgams (25% Na-75% K by weight), benzophenone, and phenyl ether. Samples of Cp₂M₂(CO)₄ (M = Mo and W) and their allene adducts were stored and handled in a Vacuum Atmospheres Co. Dri-Lab System.

Materials. Cp₂Mo₂(CO)₆ was synthesized by the well-established route.[32] Cp₂W₂(CO)₆ was synthesized by a published procedure[33] in which Cp₂W₂(CO)₃(CH₂C₆H₅) is pyrolyzed. The compounds Cp₂M₂(CO)₄ were prepared by thermolysis using a N₂ flushing system.[21] Allene was purchased from Matheson; 1,2-butadiene and 3-methyl-1,2-butadiene were purchased from Chemical Samples Co. ¹³CO (90%) was purchased from Prochem Ltd. The ¹³CO-labeled compounds Cp₂Mo₂(*CO)₄(allene), where allene = CH₂=C=CH₂, MeCH=C=CH₂, and MeCH=C=CHMe, were prepared by the addition of the allene to Cp₂Mo₂(*CO)₄. The latter was enriched to

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 spectrophotometer. ¹H NMR spectra were obtained from Varian 60- and 100-MHz spectrometers equipped with variable temperature probes. ¹³C NMR spectra were recorded on a Varian XL-100 spectrometer in the FT mode. Mass spectra were obtained using an AEI-MS9 mass spectrometer by the method of direct insertion (100-300 °C).

Preparation of Cp₂Mo₂(CO)₄(H₂C=C=CH₂). Cp₂Mo₂(CO)₄ (0.50 g, 1.16 mmol) was dissolved in toluene (40 mL). H₂C=C=CH₂ (2.0 mmol) was condensed into the flask, and the mixture magnetically stirred for 2 h. A red solution and an orange precipitate resulted. The toluene solution was centrifuged to remove the orange precipitate, and the red solution was reduced in volume to about 2 mL. Pentane was added and red crystals (0.382 g, 0.81 mmol, 70% yield) were filtered off and dried in vacuo. Anal. Calcd for Cp₂Mo₂(CO)₄(C₃H₄): C, 43.06; H, 2.98. Found: C, 42.97; H, 3.08. IR 1995 w, 1960 m, 1915 s, 1860 s, 1830 m, cm⁻¹. Orange powder from precipitate isolated was 0.102 g, 0.22 mmol, 18% yield. Anal. Calcd for Cp₂Mo₂(CO)₄(C₃H₄): C, 43.06; H, 2.98. Found: C, 42.34; H, 3.00. IR 1945 m, 1920 w, 1900 s, 1840 s, 1720 cm⁻¹ s.

¹H NMR (benzene-d_6): free H₂C=C=CH₂ δ 4.55 (s); Cp₂Mo₂(CO)₄H₂C=C=CH₂ (red compound) δ 4.54 (Cp, s), 3.67 (t, J = 4.0 Hz), 2.52 (t, J = 4.0 Hz). ¹³C NMR data (benzene-d_6):

decoupled, free $H_2C=C=CH_2$ 73.67 ($H_2C=$), 212.58 ($=C=$); $Cp_2Mo_2(CO)_4(H_2C=C=CH_2)$ 233.48 (CO), 237.16 (CO), 93.09 (Cp), 36.66 ($H_2C=$), 196.96 ppm ($=C=$).

$^{13}C^{1}H$ undecoupled $Cp_2Mo_2(CO)_4H_2C=C=CH_2$: Cp, $J_{^{13}C-H}$ = 177 Hz; and H_2C, $J_{^{13}C-H}$ = 160 and 170 Hz.

Mass Spectrum of ($Cp_2Mo_2(CO)_4(CH_2=C=CH_2)$): m/e 474 ($Cp_2Mo_2(CO)_4H_2C=C=CH_2^+$), 418 ($Cp_2Mo_2(CO)_2(H_2C=C=CH_2)^+$), 362 ($Cp_2Mo_2(H_2C=C=CH_2)^+$), 322 ($Cp_2Mo_2^+$).

Preparation of $Cp_2W_2(CO)_4(H_2C=C=CH_2)$. This was prepared in the same way as $Cp_2Mo_2(CO)_4(H_2C=C=CH_2)$. Instead of an orange precipitate, a tan, insoluble compound was obtained along with a red, soluble compound. Red compound: Anal. Calcd for $Cp_2W_2(CO)_4(C_3H_4)$: C, 31.41; H, 2.18; Found: C, 31.41; H, 2.11. IR 1943 m, 1906 s, 1848 s, 1820 m. Tan compound: Anal. Calcd for $Cp_2W_2(CO)_4(C_3H_4)$: C, 31.41; H, 2.18. Found: C, 29.90; H, 2.11. IR 1930 s, 1907 m, 1884 s, 1821 s, 1691 cm^{-1} s.

^1H NMR (benzene-d_6) δ 4.57 (Cp), 4.46 (t, J = 3.5 Hz), 2.82 (t, J = 3.5 Hz). ^{13}C NMR (benzene-d_6) 91.76 (Cp), 31.58 ppm ($H_2C=$).

Preparation of $Cp_2Mo_2(CO)_4(Me(H)C=C=CH_2)$. This was prepared in the same manner as $Cp_2Mo_2(CO)_4(H_2C=C=CH_2)$. No insoluble compound was formed. Again, red crystals were obtained but by an addition of pentane to a concentrated toluene solution. IR 1944 s, 1921 s, 1905 sh, 1877 w, 1848 m, 1837 cm^{-1} m. ^1H NMR (benzene-d_6) free $Me(H)C=C=CH_2$ δ 5.03 (multiplet=CH); 4.64 ($=CH_2$, multiplet), 1.52 (Me quintet, J_{HH} = 4 Hz); $Cp_2Mo_2(CO)_4$-$Me(H)C=C=CH_2$ δ 4.57 and 4.52 (1:1) (Cp), 3.49 and 2.33 ($=CH_2$), 3.08 ($=CH$), 1.74 (Me doublet, ^2J = 7.5 Hz).

^{13}C NMR (benzene-d_6) 239.58 (CO), 237.03 (CO), 233.69 (CO), 232.96 (CO), 93.29 (Cp), 92.96 (Cp), 196.77 ($=C=$), 56.23 ($MeHC=$), 35.10 ($H_2C=$), 27.24 ppm (Me).

Preparation of $Cp_2Mo_2(CO)_4Me(H)C=C=C(H)Me$. Cp_2-$Mo_2(CO)_4$ (0.2604 g, 0.60 mmol) was dissolved in toluene (10 mL) and syringed into a Carius tube (25 mL volume). $Me(H)C=C=C(H)Me$ (1 mL, large excess) was added to the tube before sealing. This tube was heated to 80 °C for 1 day. The tube was opened and solvent stripped to reduce the volume of solution. Pentane was added and red crystals (0.203 g, 0.40 mmol, 67% yield) were filtered off and dried.

Anal. Calcd: C, 45.43; H, 3.62. Found: C, 45.69; H, 3.62. IR 1950 m, 1900 s, 2866 s, 1830 cm^{-1} m. ^1H NMR free $Me(H)C=C=C(H)Me$ δ 5.08 (H) broad, 1.62 (Me) broad. Cp_2Mo_2-$(CO)_4(Me(H)C=C=C(H)Me)$ 4.58 (Cp), 3.02 (H quartet, ^2J = 6.5 Hz), 1.71 (Me doublet, ^2J = 6.5 Hz). ^{13}C NMR (benzene-d_6) 232.89 (CO), 239.32 (CO), 93.06 (Cp), 195.88 ($=C=$); 54.88 ($Me(H)C=$), 25.55 ppm (Me).

X-Ray Structural Characterization of $Cp_2Mo_2(CO)_4C_3H_4$. Data Collection. A deep red crystal of $Cp_2Mo_2(CO)_4$(allene) measuring 0.32 × 0.15 × 0.16 mm was sealed in a glass capillary and placed on a Syntex PĪ automated diffractometer. Preliminary investigations showed that the crystal was probably monoclinic and that it was a single crystal of good quality. ω scans showed that several intense reflections had widths at half-height of less than 0.25°. Using 15 strong reflections in the range 20° < 2θ(Mo Kα) < 30°, selected to give varied crystal orientations, the unit cell parameters were found to be a = 10.932 (2) Å, b = 7.776 (2) Å, c = 10.015 (1) Å, $β$ = 107.82 (2)°, V = 8.10.6 Å^3. The volume is indicative of the presence of two molecules in the unit cell. The procedures preliminary to data collection have been described previously.[34]

All data were collected using Mo Kα radiation monochromatized in the incident beam with a graphite crystal. A total of 2041 unique reflections with 0 < 2θ(Mo Kα) ≤ 55° were collected at 23 ± 2 °C using the θ–2θ scan technique with variable scan rates from 4.0 to 24.0° per minute depending on the intensities of the reflections, and a scan range of 1.0° above and below the Kα$_2$ and Kα$_1$ peaks, respectively. Background measurements were made at both limits of each scan, with equal time intervals for background and peak counting. Intensities of three standard reflections measured every 50 reflections showed no significant variation during data collection. Lorentz and polarization corrections were applied.[35] The Mo Kα linear absorption coefficient for this crystal is 15.3 cm^{-1}. Absorption corrections were omitted since it was found that the maximum relative error in F arising from neglect of absorption effects is <6%. A careful examination of the intensity data established the crystal symmetry as no higher than monoclinic, and systematic absences for $h0l$, $h + l = 2n + 1$, indicated the probable space groups to be either of the nonstandard pair, $P2/n$

or Pn. Structure solution was attempted in space group $P2/n$, but without success. Therefore, the space group was taken to be Pn and this choice was validated by the successful structure solution and refinement to be described next.[36]

Solution and Refinement[35] of the Structure. A three-dimensional Patterson map revealed the positions of the molybdenum atoms. With the x and z coordinates of Mo(1) fixed, the remaining heavy atom coordinates were refined by least squares to give discrepancy factors of

$$R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.226$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.336$$

The function $\Sigma w(|F_o| - |F_c|)^{1/2}$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. All structure factor calculations and least-squares refinements were executed using only those 1276 reflections for which $F_o^2 > 3\sigma(F_o)^2$. Atomic scattering factors were those of Cromer and Waber.[37] Anomalous dispersion effects were included in the scattering factors of molybdenum.[38]

After refining both molybdenum positions, subsequent difference Fourier maps revealed the approximate positions of all remaining nonhydrogen atoms. The structure was refined to convergence by full-matrix least squares to give final discrepancy factors of R_1 = 0.030 and R_2 = 0.046.

The error in an observation of unit weight was 1.16. With anisotropic thermal parameters for each atom, but x and z for Mo(1) fixed to specify the origin, the final data/parameter ratio is 6.2. A final difference Fourier map was devoid of significant features. Changing the enantiomorphic specification resulted in no significant change in atomic coordinates or discrepancy factors, so the original structure was retained.

Supplementary Material Available. A table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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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) Å^3, 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