

Molecular Structure of Dicyclopentadienyltetracarbonyldimolybdenum($Mo\equiv Mo$). Semibridging Carbonyls as Four-Electron Donors in Complexes with Metal–Metal Multiple Bonds

Robert J. Klingler, William M. Butler, and M. David Curtis*

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109. Received December 12, 1977

Abstract: The molecular structure of dicyclopentadienyltetracarbonyldimolybdenum has been determined by single-crystal x-ray diffraction analysis. The crystals are orthorhombic, space group $Pbcm$ with $a = 6.485$ (2), $b = 18.564$ (2), $c = 11.639$ (2) Å, and $Z = 4$. Based on 871 reflections with $F_o^2 > 3\sigma(F_o^2)$, the structural data were refined by full-matrix least-squares methods to R indexes of $R = 0.043$ and $R_w = 0.054$. The short molybdenum–molybdenum bond distance, 2.448 (1) Å, is consistent with a triple bond between the Mo atoms. The carbonyls form an unusual asymmetric bridge. A bonding model which is consistent with the observed structure and chemical reactivity of the molecule is suggested. In the model, the carbon monoxide ligands are considered to be four-electron donors. The bonding implications of the linear Cp–Mo–Mo–Cp axis are discussed. It is suggested that the “metal–metal π bonds” are somewhat delocalized over all the heavy atoms of the molecule. Such delocalization represents the first example of a carbon–carbon π system conjugating with a metal–metal π system.

Interest in the structural characterization of metal–metal multiple bonds has been growing at a profound rate. Bonds of order four are quite prevalent while double and triple bonds are less abundant.^{1,2} We have observed the formation of cyclopentadienylmolybdenum dicarbonyl dimer (I) by thermal decarbonylation of cyclopentadienylmolybdenum tricarbonyl dimer.³ On the basis of the effective atomic number rule, this compound is predicted to have a $Mo\equiv Mo$ triple bond. Unlike other compounds of chromium⁴ and molybdenum with triple bonds,⁵ the chemistry of I is extremely rich.^{3,6} Some of the reaction types are characteristic of acetylenes, while others are more specific to this metal system. Therefore, a crystallographic investigation was undertaken to determine if the unique reactivity of I had any structural basis.

Experimental Section

Crystals suitable for x-ray analysis were grown by slow evaporation of methylene chloride solution. The dark brown crystals are air stable. A crystal measuring $0.21 \times 0.14 \times 0.13$ mm was chosen. The crystal belongs to the orthorhombic system. The observed systematic extinctions, $0kl$ ($k = 2n$) and $h0l$ ($l = 2n$), are consistent with the space group $Pbcm$. Lattice constants were calculated by least-squares refinement on the setting angles of 12 reflections with 2θ greater than 35° . The cell parameters are $a = 6.485$ (2), $b = 18.564$ (2), $c = 11.639$ (2) Å, $V = 1401.2$ (5) Å³. The calculated density with $Z = 4$ is 2.06 g/cm³, which compares to the observed density of 2.04 g/cm³ measured by flotation in a mixture of carbon tetrachloride and methylene bromide.

Intensity data were collected by the θ - 2θ scan method using molybdenum $K\alpha$ radiation with a Syntex PI automatic diffractometer equipped with a graphite crystal monochromator. The scan range of $\pm 0.9^\circ$ was applied symmetrically to the calculated $Mo\ K\alpha_1$ - $K\alpha_2$ doublet. The scan rate varied between the limits 1.5 to 15 deg/min and was inversely proportional to the peak count rate. The counting rate was corrected for coincidence loss according to

$$A = [1 - (1 - 4\tau I_0)^{1/2}] / 2\tau$$

where A = corrected count rate, I_0 = observed count rate, and τ = dead time of the detector. The integrated intensities and their standard deviations were computed according to the following equations:

$$I = D(A - B/C)$$

$$\sigma(I) = D(A + B/C^2)^{1/2}$$

where D = scan rate, B = sum of left and right backgrounds, and C = background to scan time ratio. Three standard reflections were checked after every 50 reflections and the variation was less than 3%.

The data set was collected out to $2\theta = 60^\circ$, giving 2388 unique reflections of which 871 with $I > 3\sigma(I)$ were used for the structure determination. The integrated intensities were corrected for Lorentz and polarization effects. An absorption correction was applied,⁷ based on a linear absorption coefficient of 17.50 cm⁻¹.

Structure Determination

The positions of the two unique molybdenum atoms were determined from a three-dimensional Patterson function. After one cycle of least-squares refinement on the positional parameters and the scale factor, the discrepancy indexes

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

and

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

were $R_1 = 0.354$ and $R_2 = 0.417$. The function minimized was $w(|F_o| - |F_c|)^2$. The weight factor, w , was calculated according to the expression $w = 4F^2 / (\sigma^2(I) + P^2I^2)$ with $P = 0.04$. A difference Fourier revealed the positions of all nonhydrogen atoms. Full-matrix least-squares refinement proceeded normally to yield discrepancy indexes of $R_1 = 0.051$ and $R_2 = 0.064$.⁸

Unusually large thermal parameters for the carbon atoms of the carbonyl groups suggested the possibility of disorder. A difference Fourier confirmed the existence of two equally populated carbon positions 0.8 Å apart. This disorder may be interpreted as a superposition of the structures A and B in which the carbonyls “exchange”

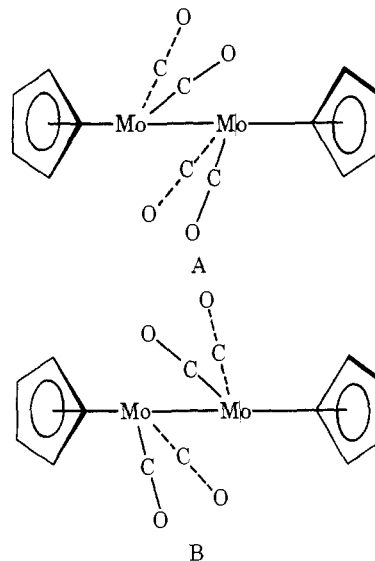
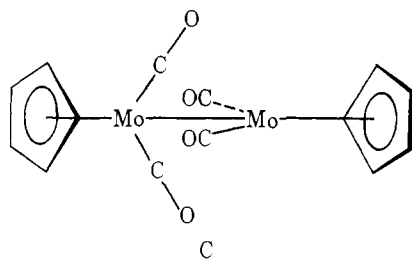


Table I. Fractional Atomic Coordinates^{a,b}

	X	Y	Z
Mo1	0.1954 (2)	0.1860 (1)	0.2500 (0)
Mo2	0.3373 (1)	0.0639 (1)	0.2500 (0)
O1	-0.0258 (11)	0.0802 (4)	0.4435 (8)
O2	0.5645 (11)	0.1693 (4)	0.4403 (7)
C1	0.0585 (28)	0.1161 (10)	0.3741 (18)
C1	0.1018 (28)	0.0764 (10)	0.3815 (20)
C2	0.4815 (23)	0.1305 (8)	0.3664 (19)
C2	0.4322 (26)	0.1721 (11)	0.3772 (23)
C3	0.2847 (30)	-0.0573 (8)	0.2500 (0)
C4	0.2521 (33)	0.3073 (8)	0.2500 (0)
C5	0.3925 (35)	-0.0437 (9)	0.3395 (14)
C6	0.1416 (37)	0.2946 (8)	0.3364 (12)
C7	0.5802 (23)	-0.0195 (6)	0.3062 (13)
C8	-0.0461 (23)	0.2695 (7)	0.3093 (19)
H1	0.180 (21)	-0.022 (9)	0.250 (0)
H2	0.351 (16)	-0.042 (6)	0.408 (11)
H3	0.639 (15)	-0.014 (6)	0.363 (10)
H4	0.427 (20)	0.329 (7)	0.250 (0)
H5	0.170 (14)	0.314 (5)	0.399 (11)
H6	-0.076 (16)	0.278 (7)	0.360 (12)

^a Estimated standard deviations of the least significant figure(s) are given in parentheses in this and all subsequent tables. ^b Structures A and B differ in the position of the carbonyl atoms C1 and C2. Half atoms were placed at the two positions listed for each atom.

molybdenums. The position of the oxygen does not differ measurably in the two structures. The other possibility, a superposition of structure C with a structure in which the carbonyls again "exchange" molybdenums, was ruled out on the basis of the solid-state IR spectrum.



The average C-Mo-C angle for structure A is 86.1°. In structure C the average C-Mo-C angle is 135.4°. The calculated value for this angle, based on the ratio of the intensity of the asymmetric to the symmetric stretch, is 81.4°.

$$I(a)/I(s) = \tan^2(\theta/2)$$

An analogous chromium compound has its carbonyls positioned as in A.¹⁰

Close investigation showed that the disorder was limited to the

Table II. Anisotropic Thermal Parameters^{a,b}

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	5.22 (5)	2.01 (3)	10.30 (10)	0.38 (3)	0.0 (0)	0.0 (0)
Mo2	5.12 (5)	2.10 (3)	9.82 (10)	0.47 (3)	0.0 (0)	0.0 (0)
O1	7.02 (35)	6.08 (41)	10.93 (69)	0.07 (29)	4.20 (42)	0.80 (45)
O2	6.43 (34)	5.61 (37)	8.32 (54)	0.14 (28)	-1.29 (35)	-0.61 (36)
C1	5.2 (8)	2.2 (7)	4.5 (12)	0.8 (6)	0.7 (9)	0.2 (9)
C1	5.4 (8)	3.6 (7)	6.1 (12)	0.9 (6)	0.2 (9)	0.3 (8)
C2	4.3 (6)	3.0 (7)	5.5 (11)	0.4 (5)	-0.7 (7)	-0.8 (8)
C2	4.1 (7)	4.3 (9)	8.8 (17)	0.1 (7)	0.3 (9)	-1.2 (10)
C3	6.9 (9)	2.3 (5)	20.6 (35)	-0.0 (5)	0.0 (0)	0.0 (0)
C4	9.1 (12)	2.4 (5)	17.1 (25)	-0.4 (6)	0.0 (0)	0.0 (0)
C5	15.6 (16)	7.3 (8)	6.4 (12)	5.4 (9)	2.3 (11)	0.6 (7)
C6	18.4 (17)	6.8 (7)	4.7 (9)	6.0 (9)	-1.7 (10)	-1.9 (6)
C7	9.8 (7)	4.2 (4)	14.3 (19)	2.9 (5)	-7.0 (9)	-3.9 (6)
C8	10.0 (9)	5.0 (5)	18.4 (22)	3.2 (5)	8.4 (11)	4.9 (7)

^a All values multiplied by 10^4 . The form of the anisotropic thermal parameter is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.
^b The isotropic temperature factor assigned to the hydrogen atoms was 4.5.

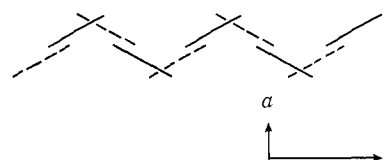
carbonyls. The rings are not disordered. First, a difference map based on the molybdenums and the disordered carbonyls produced a regular pentagon with only five distinct maxima. Second, least-squares refinement on ten evenly spaced half-carbons caused them to regroup, producing a regular pentagon of five full carbons. Third, a difference map based on all nonhydrogen atoms revealed five hydrogens at reasonable bonding distances from the cyclopentadienyl carbons.

The hydrogens were entered at a bond length of 1.0 Å and they refined to an average value of 0.87 (12) Å. The final discrepancy factors are $R_1 = 0.043$ and $R_2 = 0.054$. A listing of the calculated and observed structure factors is available.⁹

Description of the Structure

The important interatomic distances and angles are presented in Tables I-III. Figure 1 depicts the structure and the numbering scheme. The space group requires a mirror plane which contains the molybdenum-molybdenum axis and bisects the carbonyls. However, the structure has refined to C_{2h} symmetry within experimental error. The pairs of carbonyl groups related by the pseudo-center of inversion are nearly coplanar with the metal-metal bond. These two planes form an angle of 95.0° to each other (see Figure 2).

The molecules are arranged into infinite chains. The chains lie in the mirror planes of the space group. The members of the chain alternate between $Z = 1/4$ and $Z = 3/4$.



where

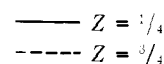


Figure 3 depicts the packing of these chains. The c axis is perpendicular to the Mo-Mo bond axis. On the average, the a axis is perpendicular and the b axis is parallel to the Mo-Mo bond axis.

This compound readily forms large needles from methylene chloride solution. In the crystal used for the structure determination, the long spindle axis of the needle was parallel to the b axis of the unit cell. Therefore, it may be possible to obtain spectral measurements both perpendicular and parallel to the Mo-Mo bond axis.

There are no significant intermolecular interactions, the shortest being a 3.13-Å O...O contact (see Figure 3).

Discussion

The Mo-Mo Bond. The Mo-Mo bond length, 2.448 Å, though 0.8 Å shorter than the single bond length in $Cp_2Mo_2(CO)_6$,¹¹ is significantly (0.23-0.28 Å) longer than those observed in the two other compounds which contain molybdenum triple bonds: 2.167 Å in $Mo_2(CH_2SiMe_3)_6$ ¹² and 2.214 Å in $Mo_2(NEt_2)_6$.^{2,13} It has already been noted that

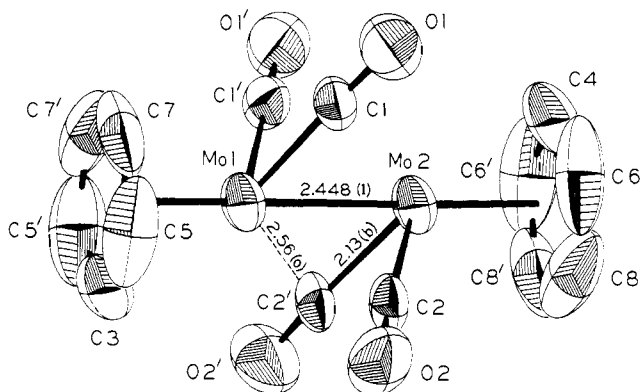


Figure 1. The molecular structure of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. The vibrational ellipsoids are drawn at the 50% probability level. (a) Number is the average (std dev = ± 0.05) of four independent $\text{M} \cdots \text{C}$ distances. (b) Number is the average (std dev = ± 0.05) of four independent $\text{M}-\text{C}$ distances.

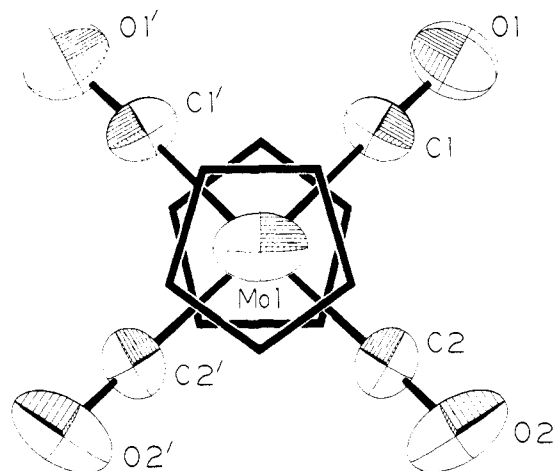


Figure 2. View of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ looking down the metal-metal axis.

there is not a strict correlation between bond order and bond length.² Coordination number, oxidation state, and type of bridging ligands have a drastic effect on bond length. Part of the observed lengthening of the $\text{Mo} \equiv \text{Mo}$ bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is undoubtedly due to the lower oxidation state. While the radius of Mo^+ is expected to be larger than that of Mo^{3+} , it would be incorrect to attribute all of the difference to changes in oxidation state. Dahl has shown coordination number to be the most significant factor in metal-carbon bond lengths.¹⁴ Indeed, examples can be found to extend this conclusion to include metal-metal bonds. The $\text{Mo}-\text{Mo}$ bond length in $\text{Mo}_2(\text{CO})_{10}^{2-}$, 3.12 Å,¹⁵ is 0.14 Å shorter than that in $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, 3.24 Å.¹¹ This is the opposite of what is expected on the basis of oxidation state.

It is difficult to deduce the effect of coordination numbers on the $\text{Mo} \equiv \text{Mo}$ bond lengths in the three structures owing to vast differences in steric requirements of the ligands. A comparison of the triple bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ to the single bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ is more meaningful owing to the similarity in the ligands. The difference between the effective metal radii may be estimated from the average metal-ring distances for the two compounds. The average metal-carbon (Cp) distance in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is only 0.08 Å shorter than the corresponding distance in $\text{Cp}_2\text{Mo}_2(\text{CO})_6$. Therefore, the 0.80-Å decrease in metal-metal bond length in going from the single bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ to the triple bond in compound $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is predominantly due to an increase in metal-metal bond multiplicity. The effect of the bridging carbonyls on the molybdenum-molybdenum triple bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ will be considered in the following section.

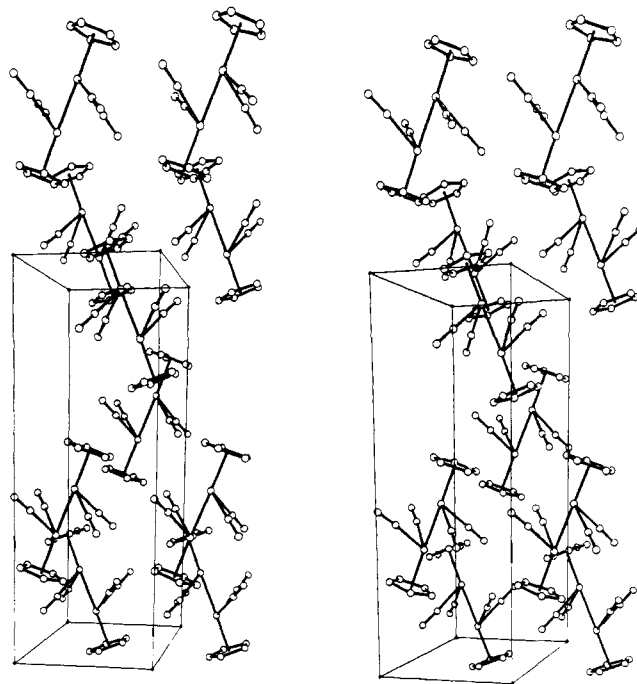


Figure 3. Packing diagram for $\text{Cp}_2\text{Mo}_2(\text{CO})_4$.

Table III. Selected Bond Lengths and Angles.^a

bond	<i>d</i> , Å	bond	<i>d</i> , Å
Mol-Mo2	2.4477 (12)	Cl-O1	1.18 (2)
Mol-C1	2.14 (2)	Cl-O1	1.10 (2)
Mol-C1	2.14 (2)	C2-O2	1.13 (2)
Mo2-C2	2.06 (2)	C2-O2	1.24 (2)
Mo2-C2	2.17 (2)	C3-C5	1.28 (2)
Mol-C2	2.52 (2)	C5-C7	1.35 (2)
Mol-C2	2.62 (2)	C7-C7	1.31 (3)
Mo2-C1	2.51 (2)	C4-C6	1.26 (2)
Mo2-C1	2.57 (2)	C6-C8	1.34 (2)
Mol-C3	2.28 (2)	C8-C8	1.38 (4)
Mol-C5	2.28 (1)	C3-H1	0.95 (12)
Mol-C7	2.30 (1)	C5-H2	0.83 (12)
Mo2-C4	2.28 (2)	C7-H3	0.77 (12)
Mo2-C6	2.28 (1)	C4-H4	1.21 (12)
Mo2-C8	2.31 (1)	C6-H5	0.83 (12)
		C8-H6	0.64 (12)
Bond Angles			
C1-Mol-Mo2	66.0 (5)		
C1-Mol-Mo2	67.6 (5)		
C2-Mo2-Mol	67.3 (4)		
C2-Mo2-Mol	68.7 (5)		
C1-Mol-C1'	85.1 (10)		
C1-Mol-C1'	87.1 (11)		
C2-Mo2-C2'	82.3 (10)		
C2-Mo2-C2'	89.5 (10)		
Mol-C1-O1	176.3 (16)		
Mol-C1-O1	174.5 (16)		
Mo2-C2-O2	175.3 (16)		
Mo2-C2-O2	177.4 (14)		

^a The values for both structures A and B have been listed.

The Carbonyls. The carbonyls are bent back over the metal-metal bond forming an asymmetric bridge. The average "short" $\text{Mo}-\text{C}$ distance is 2.13 (5) Å and the average "long" $\text{Mo}-\text{C}$ distance is 2.56 (5) Å. Asymmetric carbonyl bridging is also observed in $(\text{C}_5\text{Me}_5)\text{Cr}_2(\text{CO})_4$ ^{10a} and $\text{Cp}_2\text{Cr}(\text{CO})_4$.^{10b} The $\text{M}-\text{M}-\text{C}$ angle decreases from 76.0° in $(\text{C}_2\text{Me}_5)_2\text{-Cr}_2(\text{CO})_4$ and 73.6° in $\text{Cp}_2\text{Cr}_2(\text{CO})_4$ to 67.4 (1.1)° in $(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$. The acute angle must be due to a bonding interaction. This is in accord with the IR spectrum, in which

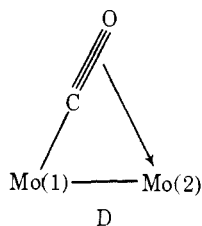
Table IV. Listing of the M-C-O Angle θ vs. the Bridge Asymmetry $(D_2 - D_1)/D_1$ (See Figure 4)

compd	$(D_2 - D_1)/D_1$	θ	ref
$Fe_3(CO)_9(PPhMe_2)_3$	0.0	141	17
$Cp_2Rh_2Fe_2(CO)_8$	0.0	136	18
$Fe_3(CO)_{11}PPh_3$	0.05	139	19
$GeMe_2Mn_2(CO)_5$	0.06	134	20
$Fe_3(CO)_{11}PPh_3^a$	0.10	143	19
$Fe_3(CO)_{12}^a$	0.11	148	21
$Cp_2Rh_2Fe_2(CO)_8$	0.22	152	18
$Ru_4(CO)_{13}$	0.24	150	22
$[Fe(py)_6][Fe_4(CO)_{13}]$	0.25	155	23
$Fe_2(CO)_7$ dipy	0.32	161	24
$(C_{12}H_{16})Fe_2(CO)_6$	0.33	162	25
$Fe_3(CO)_8(SC_4H_8)_2$	0.45	167	26
$Cp_2Mo_2(CO)_6^a$	0.61	173	11
$Cp_2Mo_2(CO)_5(CN)$	0.62	172	11
$Cp_2Cr_2(CO)_6$	0.72	172	11
$Tc_2(CO)_{10}$	0.76	178	27
$Mn_2(CO)_{10}$	0.83	177	28
$Mn_2(CO)_5$ (diphos) $_2$	0.04	174	16
$Cp_2Mo_2(CO)_4^a$	0.20	176	this work
$Cp_2V_2(CO)_5$	0.24	169	29
$(C_5Me_5)_2Cr_2(CO)_4^a$	0.39	173	10a
$Cp_2Cr_2(CO)_4^a$	0.29	171	10b

^a Represents an average over similar carbonyls in the structure.

the observed frequencies of 1900 and 1850 cm^{-1} are much too low for normal terminal carbonyls.

These bridging carbonyls are highly unusual in that the M-C-O angle of 175.9 (1.2) $^\circ$ has remained remarkably close to 180 $^\circ$. This angle usually decreases rather quickly as the carbonyls bend over and begin to bridge. A possible bonding mode for the CO groups has them bound to one molybdenum in a normal terminal fashion and also donating electron density from the CO π bonds to the second molybdenum. This novel



bonding mode, in which carbon monoxide acts as a four-electron donor, has been observed once before.¹⁶ The existence of two types of bridging carbonyl is dramatically displayed by comparing the M-C-O angle with the degree of bridge asymmetry (see Figure 4 and Table IV). The solid circles represent "normal" bridging carbonyls. The entire range from the totally symmetric bridge in $Co_2(CO)_8$ to the essentially terminal carbonyls in $Cp_2Mo_2(CO)_6$ and $Mn_2(CO)_{10}$ is represented. The M-C-O angle is essentially linear, $\approx 180^\circ$ for the terminal structures, and smoothly decreases to $\approx 136^\circ$ in the structures with symmetric carbonyl bridges.

However, $Mn_2(CO)_5(Ph_2PCH_2CH_2PPh_2)_2$ (open square \square), $Cp_2Mo_2(CO)_4$ (solid square \blacksquare), $Cp_2V_2(CO)_5$ (open triangle \triangle), $(C_5Me_5)_2Cr_2(CO)_4$ (solid triangle \blacktriangle), and $Cp_2Cr_2(CO)_4$ (open circle \circ), which are proposed to exhibit the new carbonyl bonding mode depicted in D, do not fall on the smooth curve. In these cases the M-C-O angle is essentially independent of the degree of asymmetry of the bridge. This is of course what would be expected of the bonding mode depicted in D. The M-C-O axis should not bend as the interaction with the second metal increases because both the carbon and the oxygen are bonding to the second metal. In the case of the "normal" carbonyls, only the carbon has a substantial

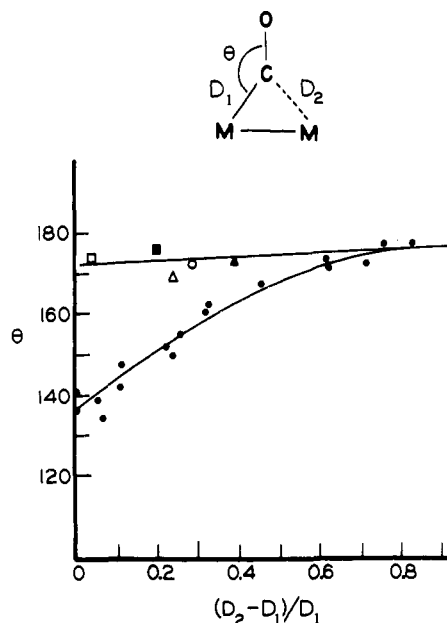


Figure 4. Plot of the M-C-O angle θ vs. the bridge asymmetry $(D_2 - D_1)/D_1$.

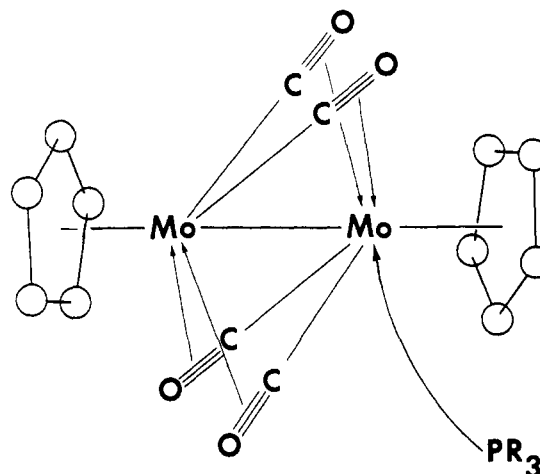


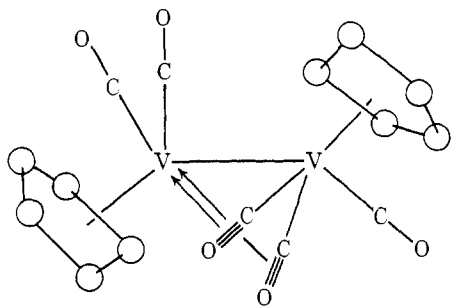
Figure 5. Nucleophilic displacement of the Mo-Mo π bonds by nucleophiles.

bonding interaction with the second metal. Extended Hückel calculations are consistent with this interpretation. These demonstrate that the overlap population between the oxygen and Mo(2) is almost as large as the overlap population between the carbon and Mo(2). Large metal-oxygen overlaps are not observed in "normal" bridging carbonyls.

Finally, the spatial distribution of the carbonyls is consistent with this bonding mode. The two planes of carbonyls are approximately 90 $^\circ$ apart (Figure 2), allowing each carbonyl on Mo(1), for example, to donate electrons to separate $d\pi$ orbitals on Mo(2). Structure C, on the other hand, would have both carbonyls on Mo(1) donating electrons into only one $d\pi$ orbital on Mo(2). Such an arrangement is considered less likely.

The chemistry of $Cp_2Mo_2(CO)_4$ is also consistent with the bonding mode proposed for the carbonyls. Numerous soft nucleophiles readily displace the Mo-Mo π bonds and the stereochemistry of the observed products is consistent with the backside displacement of the bridging carbonyls as depicted in Figure 5.^{3,6}

The unusual structure of $Cp_2V_2(CO)_5$ may be explained in similar terms if it is assumed that $Cp_2V_2(CO)_5$ is the intermediate adduct formed by addition of 1 equiv of carbon monoxide to the vanadium-vanadium triple bond in the hy-



pothetical $\text{Cp}_2\text{V}_2(\text{CO})_4$ molecule. The bridging carbonyls on the $\text{V}(\text{CO})_3$ unit are unusual in that the V-C-O angle, open triangle in Figure 4, is much too large for the symmetry of the V(1)-C-V(2) bridge system. Therefore, the carbonyl binding mode depicted in D is strongly implicated for these carbonyls. The two carbonyls on the $\text{V}(\text{CO})_2$ unit have presumably been displaced by the fifth CO and are observed to be "normal" terminal carbonyls.²⁹ It is interesting to note that $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ reacts with 1 equiv of cyanide ion to yield $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{CN})]^-$, the structure of which is currently under investigation.

The carbonyl bonding depicted in D is expected to increase the metal-metal bond length. Instead of attempting to assign a fractional bond order³⁰ between one and three, it is felt that it is much more realistic to think of the molybdenum-molybdenum bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ as a triple bond which has been lengthened slightly by a bonding interaction with the bridging carbonyls. It should be noted that "normal" bridging carbonyls typically have the effect of decreasing metal-metal bond lengths.³²⁻³⁸

The carbonyl bonding mode depicted in structure D may be a very important factor in the unusual chemistry of this compound. By donating more than two electrons, the carbonyls effectively stabilize a highly reactive, electrophilic center, but are bound weakly enough to be easily displaced by an incoming nucleophile.

The Cp-Mo-Mo-Cp Axis. One of the most striking features of this structure is the near linearity of the Cp-Mo-Mo-Cp axis which contrasts to the bent axes found in all other CpMMcP structures.^{10,11} The strong implication is that there is an electronic factor which favors the linear configuration in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. It is postulated that the nature of the electronic factor favoring the linear configuration lies in the interaction of the rings with the same orbitals used to form the metal-metal π bonds. As discussed more fully in ref 10b, the interaction of the Cp-ring e_1 orbitals with the back lobes of the metal-metal π bond will populate molecular orbitals with a metal-metal π^* component when the CpMMcP axis is linear. As the CpMMcP axis is bent, molecular orbitals having a σ^* component become populated. Apparently, when the metal is molybdenum, the energy matching between ring and metal orbitals is such that the linear configuration has the lowest energy. Hence, the Cp rings may be thought of as conjugated with the M-M π system.

It is probable that the linear CpMoMoCp axis in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ persists in solution. The cyclopentadienyl signal in the NMR spectrum of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ remains a sharp singlet from -90 to 90 °C. In contrast, cis and trans conformations of the cyclopentadienyl ligands have been observed in the low-temperature NMR spectra of $\text{Cp}_2\text{M}_2(\text{CO})_6$ (M = Cr, Mo, W), which are known to have a bent CpMMcP axis.¹¹

Any detailed description of the conjugated system must also include the carbonyls. It has already been pointed out that the carbonyl π system is involved in the metal-metal π system. These considerations imply that the "metal-metal π bonds" in this compound are actually delocalized over all the heavy atoms in the molecule. This may prove to be true for a large

number of metal-metal multiply bonded systems. Two recent reports suggest that the low-frequency IR absorptions normally assigned to metal-metal stretching modes have substantial contributions from the ligands.^{39,40}

The structure and chemistry of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ are unique. Further investigations of this and related compounds are currently in progress in our laboratories.

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Supplementary Material Available: Listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Cluster Condensation Reactions. Synthesis and Structure of Pentascandium Octachloride (Sc_5Cl_8). An Infinite Chain Structure Derived by Cluster Condensation

Kenneth R. Poepelmeier and John D. Corbett*

Contribution from the Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011. Received December 30, 1977

Abstract: Single crystals of the phase pentascandium octachloride, Sc_5Cl_8 , are obtained in several weeks by chemical transport from 940 to 960 °C in a sealed tantalum container starting with powdered metal and ScCl_3 . The role the lower valent gas-phase species $\text{ScCl}_2(\text{g})$ plays in the formation of Sc_5Cl_8 at high temperature is discussed in terms of the postulated transport reaction $\text{Sc}_5\text{Cl}_8(\text{s}) + 2\text{ScCl}_3(\text{g}) = 7\text{ScCl}_2(\text{g})$. The structure of the green-hued, black crystals has been determined with full-matrix least-squares refinement of all atoms with anisotropic thermal parameters. This phase crystallizes in the monoclinic space group $C2/m$ with $a = 17.78$ (2), $b = 3.523$ (8), and $c = 12.04$ (1) Å, $\beta = 130.10$ (6)°, and $Z = 2$; final residuals were $R = 0.115$ and $R_w = 0.136$ for 486 independent reflections with $2\theta \leq 50^\circ$ and $I > 3\sigma(I)$. Structurally Sc_5Cl_8 contains separate infinite chains of metal octahedra which share trans edges as in Gd_2Cl_3 ; the common edges contain the shortest Sc-Sc bond yet observed, 3.021 (7) Å. A second, parallel chain consists of edge-shared octahedra of chloride about isolated scandium(III) atoms. The connectivity description $[\text{Sc}(\text{Cl})_{4/3}(\text{Cl})_{2/3}]_\infty[\text{Sc}_4\text{Cl}_4(\text{Cl})_{2/3}(\text{Cl})_{4/3}]_\infty$ is well approximated by $(\text{ScCl}_2^+)_\infty(\text{Sc}_4\text{Cl}_6^-)_\infty$, the latter emphasizing the anionic nature of the metal chain. The structure can be considered as arising from the formal condensation of M_6X_{12} clusters such as are found in $\text{Sc}_7\text{Cl}_{12}$. The anionic character of the metal chain allows the metal atoms therein to be formally more reduced than in Gd_2Cl_3 , an effect which is reflected in the relative shortening of the bonds in Sc_5Cl_8 . The sums of metal-metal bond orders in four structurally diverse scandium chlorides as well as in Gd_2Cl_3 are found to be a smooth function of the number of delocalized electrons therein. Important in the variety of scandium chloride structures found with small changes in composition is the varied role halogen atoms serve in connectivity together with the ability of scandium to generate isolated cations and thence strongly metal-metal bonded anionic arrays.

Introduction

Evidence that any rare-earth metal, yttrium, or scandium would reduce its corresponding trihalide to compositions with $X:M < 2.0$ has until very recently been limited to the single example of the unusual gadolinium compound Gd_2Cl_3 ^{1,2} where a remarkable infinite metal chain consisting of edge-shared octahedra is formed. Later McCollum and co-workers³ were able to reduce scandium trichloride and tribromide to the composition Sc_2X_3 with scandium foil at elevated temperatures when proper attention was paid to avoiding blockage of the metal surface by product, a condition which also allows the preparation of the monochloride ScCl which contains double metal layers.⁴ Recent applications of the technique of chemical transport along a temperature gradient above 880 °C have now allowed kinetic accessibility to several additional scandium phases in the composition range $2.0 > \text{Cl:Sc} > 1.0$. Among these are $\text{Sc}_7\text{Cl}_{10}$,⁵ with infinite metal chains composed of double octahedra, $\text{Sc}_7\text{Cl}_{12}$,⁶ which contains discrete six-atom metal clusters, and the compound of interest in this work, Sc_5Cl_8 . The chemistry of very reduced rare-earth metal halides ($X:M < 2$) has also recently been broadened substantially by Simon and coworkers,⁷ who have reported the formation of monochlorides for $M = \text{Gd}, \text{Tb}, \text{Er},$ and Lu together with Tb_2Cl_3 which is isostructural with Gd_2Cl_3 . This paper reports on the synthesis, single-crystal x-ray structure, and electron paramagnetic resonance behavior of Sc_5Cl_8 and relates these results both in terms of architecture and electronic states to those of other polyscandium structures. The formation of

Sc_5Cl_8 and other transported compositions is considered in terms of transport by the high-temperature species $\text{ScCl}_2(\text{g})$.

Experimental Section

Synthesis. All preparation and analyses of materials were as described in an earlier publication.⁴ The best metal available (99.998 atomic % purity) was used and as such had impurity levels in atomic parts per million as follows: H, 401; C, 105; O, 118; F, 14; Fe, 50; Ni, 20; Cu, <20; Ta, 260; W, 160; Gd, <7; La, 6.4; Ho, <4; other rare earths and other metals, <1 each. Typically ca. 0.25–0.50 g of ScCl_3 was placed in one end of a 12 cm, 9 mm o.d. tantalum tube along with two $0.4 \times 4 \times 110$ mm metal strips and the tube welded under a He atmosphere (0.8–0.9 atm). Typical reaction gradients were $T_1 \rightarrow T_2$ (850 \rightarrow 1000 to 1050 °C) and the time of the reaction ranged from 4 to 6 weeks. The temperatures were monitored by thermocouples attached to the outside of the evacuated fused silica jacket in which the tantalum reaction tube had been sealed. The transported phases were identified by powder x-ray diffraction and in addition microprobe analysis was performed on new phases in order to estimate their composition and to ensure absence of other metallic elements. In all cases the products were found condensed in the hotter regions of the reaction tube away from the cold end where the ScCl_3 had been originally placed.

Specifically, in one particular reaction where the gradient was $T_1 \rightarrow T_2$ (850 \rightarrow 1010 °C) three distinct phases were found in separate bands of crystallites loosely attached on both the metal strips and container walls and ordered in increasing degree of reduction. The most oxidized phase $\text{Sc}_7\text{Cl}_{12}$ (as previously identified from a single-crystal diffraction study⁶) was found in the coolest region of the tube followed by a band of $\text{ScCl}_{1.58 \pm 0.04}$ (Sc_5Cl_8) and finally in the middle