

References and Notes

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- (4) Complex II is purified by column chromatography on grade no. 1 alumina eluting with isoctane. The red-purple solid is isolated by simply removing the solvent at room temperature by rotary evaporation. As II is light sensitive in solution all manipulations should be carried out in darkened rooms.
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- (8) The compound IV has been reported in erratic, low yields by the photolysis of $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeMo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$: R. C. Job and M. D. Curtis, *Inorg. Chem.*, **12**, 2510 (1973).
- (9) The compound we obtain has the ir spectroscopic features reported⁸ for IV and the uv-visible spectrum is similar to I. The synthesis of IV by heating III has been independently studied, and an X-ray structure confirms its formulation as an analog to I: R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, following paper.
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Synthesis, Reactivity, and Molecular Structure of Cyclopentadienylmolybdenum Dicarbonyl Dimer. The Molybdenum-Molybdenum Triple Bond

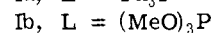
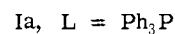
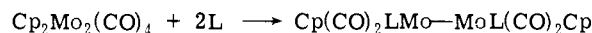
Sir:

We wish to report the thermal conversion of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ to the triply bonded $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ as well as the molecular structure and reactivity of the latter. In an attempt to prepare diolefin complexes of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, we have refluxed the hexacarbonyl dimer in various olefins and observed the formation of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ analogous to the recently reported $\text{Cp}_2\text{Cr}_2(\text{CO})_4$.¹

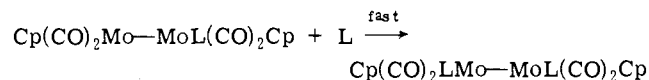
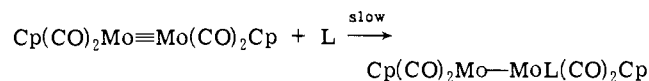
In refluxing 1-octene or toluene, the thermal decomposition of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ to $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is erratic, with yields varying from about 0 to 90%. This observation, coupled with the results of Ginley and Wrighton² which suggest a Mo-Mo bond scission in the photolytic formation of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ from $\text{Cp}_4\text{Mo}_2(\text{CO})_6$, raises the possibility that the thermal reaction also proceeds via a free radical pathway.

Only recently has any precedent been reported for such a mechanism in organometallic reactions. Byers and Brown³ have observed that carbonyl substitution reactions of $\text{HRe}(\text{CO})_5$ proceed via a radical chain path and that in the absence of added chain initiators the reactions are very erratic. Similarly, Osborne et al. and Lappert and Lednor have shown that oxidative additions of low valent complexes may proceed via radical pathways.^{4,5}

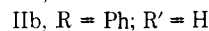
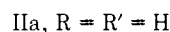
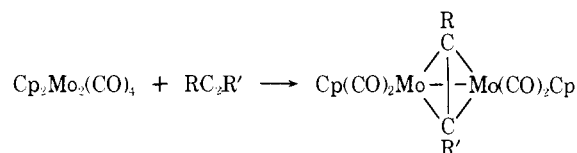
$\text{Cp}_2\text{Mo}_2(\text{CO})_4$, prepared as described above, has physical properties identical with those reported earlier.^{6,7} The chemical properties of the tetracarbonyl dimer are remarkably different from those of the permethylated analog, $(\text{C}_5\text{Me}_5)_2\text{Mo}_2(\text{CO})_4$, as reported by King et al.^{8,9} These authors were unable to find any addition reactions involving the $\text{Mo}\equiv\text{Mo}$ triple bond that did not completely cleave the dimer. In contrast, $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ readily adds soft nucleophiles, e.g., phosphines and phosphites, to give addition products in which the metal-metal π -bonds have been displaced:



Compounds Ia and Ib are identical with those prepared by CO displacement from $\text{Cp}_2\text{Mo}_2(\text{CO})_6$.^{10,11} No mono-substitution is observed when a molar equivalent of ligand is allowed to react with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. The observed products are equimolar mixtures of disubstituted Ia or Ib and unreacted tetracarbonyl dimer. This behavior is in keeping with the maintenance of the 18-electron count around each molybdenum.

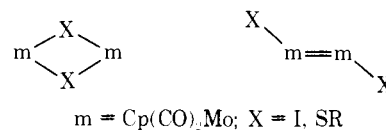


$\text{Cp}_2\text{Mo}_2(\text{CO})_4$ also reacts with acetylenes to give addition products, $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RC}_2\text{R}')$. On the basis of their ir and NMR spectra, these complexes are assigned a tetrahedrane structure.



Both IIa and IIb are red crystalline solids and melt at 147–149 and 134–136°, respectively. IIa has carbonyl stretches at 2000, 1920, and 1850 cm^{-1} and its NMR spectrum shows two singlets at τ 4.67 (Cp) and 5.17 (H). The corresponding data for IIb are: 2000, 1930, and 1850 cm^{-1} ; 2.96 (Ph), τ 4.65 (H), and 4.78 (Cp).

Unlike the permethylated analog $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ reacts with I_2 to give the violet, dimeric iodide, $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{I}_2$, III, mp 129–130°. This complex shows carbonyl bands at 1950 sh, 1940, and 1860 cm^{-1} , and the NMR consists of a singlet at τ 5.18. In solution, the iodide decomposes by a second-order process to give $\text{CpMo}(\text{CO})_3\text{I}$ among other products. Possibly related compounds are formed when $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is allowed to react with organic disulfides. These compounds may be formulated with no formal Mo-Mo bond, or a double bond, depending on whether or not the structure is bridged.



Tetracyanoethylene and HCl also form addition products with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$, but these are not yet adequately characterized. The chemistry and fluxional behavior of these adducts are currently under study.

The structure of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ has been determined by X-ray diffraction methods.¹² The compound crystallizes in the orthorhombic system: $a = 6.485$ (2), $b = 18.465$ (2), $c = 11.639$ (3) Å; $V = 1401.2$ (5) Å³; $Z = 4$; ρ (obsd) = 2.04, ρ (calcd) = 2.06 g cm^{-3} . While the systematic extinctions are compatible with several space groups, the structure has been refined in $Pbcm$ (no. 57, D_{2h}^{11}). The data set consisted of 2388 unique reflections collected by automated diffractometer out to $2\theta = 60^\circ$. Reflections (871) with $F > 3\sigma(F)$ were used in the refinement and the current discrepancy indices are $R_1 = 0.043$ and $R_2 = 0.054$.¹²

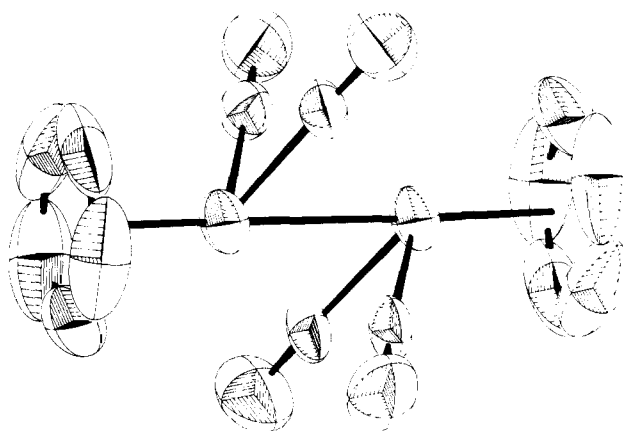


Figure 1. ORTEP II drawing of the molecular structure of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. The thermal ellipsoids are drawn at 50% contours.

The molecule lies on a mirror plane which contains the Mo–Mo axis and bisects the Cp rings. Although only C_s symmetry is required, the structure has refined to C_{2h} symmetry within experimental error. The carbonyl groups are disordered, but we have been able to interpret the disorder in terms of a superposition of the structure shown in Figure 1 and a nearly equivalent structure in which the carbonyls “exchange” molybdenums.

The Mo–Mo bond length, 2.448 (1) Å, is ca. 0.8 Å shorter than the Mo–Mo bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, 3.235 (1) Å,¹³ thus confirming the triple bond formulation. The Cr≡Cr distance, 2.280 (2) Å, in $(\text{C}_5\text{Me}_5)\text{Cr}_2(\text{CO})_4$ is 1.00 Å shorter than the Cr–Cr bond in $\text{Cp}_2\text{Cr}_2(\text{CO})_6$.¹⁴ However, the bond in the latter compound is anomalously long due to steric crowding.

The carbonyl groups lie over the Mo–Mo bond, and probably interact with it. The “short” Mo–C distances average 2.130 ± 0.050 Å and the “long” Mo–C average distance is 2.554 ± 0.050 Å. The carbonyls thus form a “class I” asymmetric bridging system in Cotton and Troup’s classification.¹⁵ The average Mo–C–O bond angle is $175.9 \pm 1.2^\circ$, and the average Mo–Mo–C(carbonyl) angle is $67.4 \pm 1.1^\circ$.

One of the more striking features of this structure is the near linearity of the Cp–Mo–Mo–Cp axis. The structures of $\text{Cp}_2\text{M}_2(\text{CO})_6$ (M = Cr, Mo, W)^{13,16} show pronounced M–M–Cp angles. This angle is opened to 159° in $(\text{C}_5\text{Me}_5)_2\text{Cr}_2(\text{CO})_4$.¹⁴ The opening of this angle and the position of the carbonyls over the Cr≡Cr bond in the latter compound were ascribed to the nonbonded interactions involving the bulky C_5Me_5 ligand. However, it is clear from the present structure that these bonding features are *not* dictated by nonbonding interactions, and the cause of these unusual structural features must be sought in terms of the electronic influence of the metal–metal triple bond.

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- The structure determination will be reported in detail later. $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$; $R_2 = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}}{2}$; $w = 4F^2 / (\sigma^2(h) + (0.04)^2 F^2)$. The dimensions of the data crystal were $0.21 \times 0.14 \times 0.13$ mm. Following absorption and 1/LP corrections, the structure was solved by standard heavy atom procedures and refined using the full-matrix algorithm on F .
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Transition Metal Catalyzed Rearrangement of 11,12-Dimethyl[4.4.2]propella-2,4,11-triene as a Route to Stable Cyclooctatetraene Bond Shift Isomers. Implications for [1,5]-Sigmatropic Migration within the Metal Coordination Sphere

Sir:

Although monosubstitution of the [4.4.2]propella-2,4,11-triene system at C_2 and C_{11} leads to striking regioselectivity¹ during $\text{Mo}(\text{CO})_6$ -promoted skeletal rearrangement to 1,2-annulated cyclooctatetraenes,² further practical exploitation of remaining mechanistic questions is not easily accommodated by these compounds. Qualitative ranking of several possible isomerization schemes has proven possible, but there is yet no insight into the level of metal coordination which becomes available. Working toward this last goal, we here report on the behavior of the title compound (**1**)³ when subjected to the action of $\text{Mo}(\text{CO})_6$ in refluxing benzene (Scheme I). The selection of **1** was predicated upon

Scheme I

