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Preparation and Structures of the Homologous Quadruply Bonded Tris(cyclooctatetraene)dimolybdenum and -ditungsten

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The methods of preparation and the crystal and molecular structures of $Mo_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$ are reported. The crystalline compounds, which are air-stable for periods of several days, can be prepared by reaction of the metal tetrahalides with $K_2C_8H_8$ in tetrahydrofuran. The Mo and W compounds, crystallizing in the space group $I\bar{4}$, are isomorphous with each other but not with $Cr_2(C_8H_8)_3$. The unit cell dimensions at 21 ± 1 °C for $Mo_2(C_8H_8)_3$ are $a = 15.815$ (2) Å, $c = 15.014$ (2) Å, and $V = 3755$ (1) Å^3 and for $W_2(C_8H_8)_3$ are $a = 15.820$ (3) Å, $c = 15.041$ (3) Å, and $V = 3764$ (2) Å^3, with $Z = 8$. Both structures were determined by X-ray crystallography at 21 ± 1 °C and that of $W_2(C_8H_8)_3$ has also been determined by neutron diffraction at 110 K, where the cell dimensions are $a = 15.664$ (3) and $c = 14.980$ (3) Å. Each of these compounds has a molecular structure, essentially the same as that for the chromium homologue, in which the pair of closely bonded metal atoms (W–W = 2.375 (1) Å and Mo–Mo = 2.302 (2) Å) lies over one sharply folded ring which has all of its carbon atoms bonded to one or both metal atoms. Each metal atom also has attached to it a η^4-C_8H_8 ring. The M–M bonds can be construed as quadruple.

Introduction

Although the ability of transition metals to form compounds containing multiple M–M bonds (double,[2] triple,[3] and quadruple[4]) was recognized only recently, considerable progress has already been made[5] in exploring this new phase of transition-metal chemistry. One aspect of this development that has caused some consternation has been the apparent reluctance of the element tungsten to form quadruple bonds, even though (a) it forms triple bonds easily and abundantly,[6] (b) molybdenum forms both triple and quadruple bonds in abundance,[5] and (c) rhenium forms numerous quadruple[5] and some triple bonds.[7] Indeed the only documented cases of W–W quadruple bonds,[8] prior to the present work occur in $W_2(CH_3)_8^{4-}$ and the mixed-ligand ions $[W_2Cl_{8-x}(CH_3)_x]^{4-}$. In fact, the series $[Cr_2(CH_3)_8]^{4-}$, $[Mo_2(CH_3)_8]^{4-}$, and $[W_2(CH_3)_8]^{4-}$ represents the only proven set of three homologous quadruply bonded species aside from the one we are reporting here.[24]

The existence of several compounds with the formula $M_2(C_8H_8)_3$ (M = Ti, V, Cr, Mo, W) was first announced a number of years ago.[9] However, except for $Ti_2(C_8H_8)_3$ no preparative methods nor any identifying physical or chemical properties were revealed nor has there subsequently been any published account, however terse, of the methods of preparation of these substances. The structure of $Ti_2(C_8H_8)_3$, in which there is no M–M bond, was reported[10] in 1966. It was with the report last year by Brauer and Krüger,[11] of the structure of $Cr_2(C_8H_8)_3$ which indicates the presence of a quadruple Cr–Cr bond, that we became interested in the structures of $Mo_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$. It was obvious, as Brauer and Krüger themselves stated, that the molybdenum and tungsten compounds are likely to have similar molecular structures. Our keen, long-standing[6,8,12] interest in the question of the stability of quadruple W–W bonds led us to examine the preparation and structure of $W_2(C_8H_8)_3$ and, in order to have a complete homologous series, the molybdenum compound.

Procedure

All reactions were done under nitrogen and solvents were carefully dried and degassed.

Preparation of $Mo_2(C_8H_8)_3$. Molybdenum(IV) chloride was prepared according to a published method.[13] A mixture of $MoCl_4$ (1.5 g, 6.3 mmol) and 12.5 mmol of $K_2C_8H_8$ in tetrahydrofuran was stirred for 24 h at room temperature, giving a brown solution. After filtration the solution was taken to dryness under vacuum and the brown-black residue then recrystallized from toluene, to give 0.9 g (35% yield) of black crystalline product.

Preparation of $W_2(C_8H_8)_3$. Tungsten(IV) chloride was prepared by reaction of WCl_6 with $W(CO)_6$ in refluxing chlorobenzene. It was collected by filtration, dried under vacuum, and used without further purification. The reaction of WCl_4 (2.0 g, 6.1 mmol) with $K_2C_8H_8$ (12.4 mmol) in tetrahydrofuran gave a green solution, which was filtered after 24 h. After solvent removal and recrystallization from hot toluene, green-black crystals, mp >360 °C, were obtained (0.4 g; 20% yield based on WCl_4).

Determination of the X-ray Crystal Structure of $W_2(C_8H_8)_3$. A crystal was ground to a sphere of radius 0.229 mm and was sealed in a thin-walled glass capillary under nitrogen. The crystal was examined on a Syntex $P\bar{1}$ automated diffractometer using Mo Kα radiation (λ 0.710 73 Å) with a graphite-crystal monochromator. A body-centered tetragonal cell was indicated and the cell parameters derived from the setting angles for 15 reflections are the following:

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Table I. Data Pertaining to the Neutron Diffraction Study of $W_2(C_8H_8)_3$

space group	$I\bar{4}$
cell dimensions, 110 K	
a, Å	15.664 (3)
c, Å	14.980 (3)
Z, molecules/unit cell	8
μ, cm^{-1}	2.06
range of transmission coefficients	0.55–0.77
refined isotropic extinction coefficient g	0.48 (6) × 10^4
refined scale factor	0.933 (7)
standard deviation of an observation of unit weight	1.156
no. of independent data	1739
no. of variables	437
$R(F_o)$	0.122
$R(F_o^2)$	0.136
$R_w(F_o^2)$	0.142

$a = 15.820$ (3), $c = 15.041$ (3) Å; $V = 3764$ (2) Å^3; $d_{calcd} = 2.40$ g cm^{-3} for $Z = 8$ and a molecular weight of 680.16.

Intensity data were collected at 21 ± 1 °C using θ–2θ scans with variable scan rates of 4.0–24.0°/min and a scan range from 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0°. A total of 3047 unique reflections in the range $0 < 2\theta \leq 60°$ were collected, of which 2063 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure.[14] A spherical absorption correction ($\mu = 129.5$ cm^{-1}) was applied to the data. The range of calculated transmission factors is from 0.0260 to 0.0905. The systematic absences and the subsequent least-squares refinement revealed the space group to be $I\bar{4}$.

The positional parameters for the two tungsten atoms were derived from a three-dimensional Patterson map and least-squares refinement, including thermal parameters, gave the following residuals:

$$R_1 = \Sigma||F_o| - |F_c||/|F_o| = 0.11$$

$$R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2} = 0.14$$

The positional parameters of the remaining atoms, except for H, were obtained from difference electron density maps. Isotropic and subsequent anisotropic refinement to convergence gave values of $R_1 = 0.043$ and $R_2 = 0.055$. Refinement of the enantiomorphic structure with inverted atomic coordinates lowered the residuals to $R_1 = 0.038$ and $R_2 = 0.048$, and this was clearly the correct enantiomer for this crystal. The error in an observation of unit weight was 0.968. An extinction correction was not found to be significant. Tables of observed and calculated structure factor amplitudes are available as supplementary material.

Determination of the X-ray Structure of $Mo_2(C_8H_8)_3$. An essentially tetrahedral crystal, with faces subsequently identified as 101, 01$\bar{1}$, 0$\bar{1}\bar{1}$, and $\bar{1}$01, was selected, glued to a glass fiber and examined at 21 ± 1 °C on a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation. It was found to be isomorphous with the tungsten compound, space group $I\bar{4}$, with $a = 15.815$ (2) Å, $c = 15.014$ (2) Å, and $V = 3755$ (1) Å^3. Data were measured in the range $0 < 2\theta \leq 60°$ affording 2753 reflections with $I > 3\sigma(I)$. The positional coordinates derived for $W_2(COT)_3$ were used for initial refinement. Final least-squares refinement with all atoms having anisotropic thermal parameters gave residuals $R_1 = 0.0322$ and $R_2 = 0.0461$ with the esd of an observation of unit weight = 1.12. Refinement of the enantiomorphic structure (inverted coordinates) gave $R_1 = 0.0308$ and $R_2 = 0.0438$ with the error in an observation of unit weight equal to 1.07, indicating that, once again, the second enantiomer is the correct one.

Neutron Structure of $W_2(C_8H_8)_3$. A crystal weighing 16.4 mg and having approximate dimensions of 3.1 × 2.4 × 1.3 mm was sealed in a lead glass capillary. With the crystal mounted in a general orientation and cooled to 110 K with a nitrogen cold stream,[15,16] all data were collected on an automated diffractometer at the Cp-5 reactor at Argonne National Laboratory. The cell dimensions (see Table I) used in the structural solution were obtained at Texas A&M University from refinement of the angular settings of reflections on an X-ray diffractometer (Mo Kα X-radiation) with the crystal cooled to 110 K.

The neutron data in one octant were measured to $(\sin\theta)/\lambda = 0.62$ Å^{-1} using the θ–2θ step-scan mode in a manner previously described.[17] A set of F_o^2 values, where F_o is the observed structure factor amplitude, was obtained by applying Lorentz and absorption corrections to the data. Comparison of the linear absorption coefficients of $W_2(C_8H_8)_3$ with respect to neutrons (λ 1.142 (1) Å, $\mu = 2.06$ cm^{-1}) and X-rays (Mo Kα, $\mu = 129.5$ cm^{-1}) emphasizes one important advantage of neutron diffraction in studying heavy-atom organometallic crystal structures. The variance of F_o^2 was calculated from standard counting statistics with an added factor of $(0.05F_o^2)^2$ based on the 5% maximum variation of two reference reflections which were measured periodically throughout the data collection.

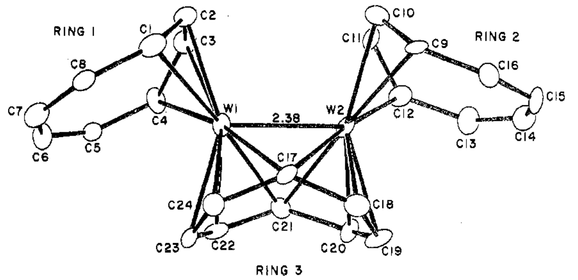


Figure 1. A perspective view based on neutron diffraction data of the $W_2(C_8H_8)_3$ molecule showing the atom labeling scheme. The hydrogen atoms, each of which bears the same number as the carbon atom to which it is bonded, have been omitted for clarity.

Solution and Refinement of the Structure. The initial positions of the nonhydrogen atoms used in the least-squares refinements[18] were obtained from the X-ray structural solution. The initial positions of the 24 hydrogen atoms were calculated from the refined coordinates of the carbon atoms and idealized sp^2 hybridized geometry about each carbon atom. In the final stages of refinement, the data were corrected for secondary extinction[19] and all atoms were treated with anisotropic thermal parameters. However, three of the hydrogen atom thermal parameters became nonpositive definite, and they were reassigned isotropic thermal parameters. When one considers that there are 50 independent atoms in the neutron structure such that the ratio of observations to variables is only 4:1, problems of this type are expected. The final discrepancy indices are given in Table I. A scaled difference Fourier map based on the final refined parameters was featureless. The structure factors are available as supplementary materials.

Results

The atomic positional and thermal vibration parameters are given in Tables II, III, and IV for the $Mo_2(C_8H_8)_3$ X-ray structure, the $W_2(C_8H_8)_3$ X-ray structure, and the $W_2(C_8H_8)_3$ neutron structure, respectively. Figure 1 shows the heavy-atom skeleton of the $W_2(C_8H_8)_3$ molecule and defines the numbering scheme used throughout for both this compound and, mutatis mutandis, for $Mo_2(C_8H_8)_3$. The hydrogen atom positional parameters listed in Table IV bear the same identifying numbers as the carbon atoms to which they are bonded.

Table V lists a number of pertinent internuclear distances and angles. The entire $W_2(C_8H_8)_3$ molecule, including hydrogen atoms, is shown in a stereoview in Figure 2. It is clear from Table V that the X-ray and neutron results for $W_2(C_8H_8)_3$ are in good agreement with each other and also with the X-ray results for $Mo_2(C_8H_8)_3$. Table VI describes several planes in the $Mo_2(C_8H_8)_3$ molecule, chosen to correspond to those previously defined by Brauer and Krüger[11] for $Cr_2(C_8H_8)_3$.

Discussion

The molecular structures of $Mo_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$ are homologous to that of $Cr_2(C_8H_8)_3$ although they crystallize in different crystal classes. In that respect, the present results are not surprising. However, the fact that we have here a complete triad of isostructural molecules with M–M multiple bonds is novel and important. The importance of these compounds is enhanced by their being easy to prepare and having considerable thermal and chemical stability.

Table V allows a ready comparison of the results obtained for $W_2(C_8H_8)_3$ by X-ray and neutron diffraction. In no case does the difference between the two values for any parameter exceed twice the sum of their esd's and for most the differences

Table II. Positional and Thermal Parameters for $Mo_2(C_8H_8)_3$ Obtained by X-ray Diffraction[a,b]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.08841 (2)	0.19606 (2)	0.29089 (3)	0.00217 (1)	0.00205 (1)	0.00213 (1)	−0.00003 (2)	−0.00049 (2)	0.00033 (3)
Mo(2)	0.18416 (2)	0.11555 (2)	0.21251 (3)	0.00228 (1)	0.00211 (1)	0.00224 (1)	−0.00001 (2)	−0.00044 (3)	0.00025 (3)
C(1)	−0.0574 (3)	0.1822 (3)	0.2763 (4)	0.0022 (1)	0.0030 (2)	0.0046 (2)	−0.0008 (3)	−0.0007 (4)	0.0004 (4)
C(2)	−0.0227 (3)	0.2240 (3)	0.2006 (3)	0.0028 (2)	0.0031 (2)	0.0031 (2)	0.0010 (3)	−0.0019 (3)	0.0002 (3)
C(3)	0.0324 (3)	0.2946 (3)	0.1980 (4)	0.0033 (2)	0.0028 (2)	0.0036 (2)	0.0011 (3)	0.0002 (3)	0.0023 (3)
C(4)	0.0667 (3)	0.3422 (3)	0.2692 (4)	0.0032 (2)	0.0023 (2)	0.0048 (3)	−0.0003 (3)	0.0008 (4)	0.0011 (3)
C(5)	0.0329 (4)	0.3751 (3)	0.3514 (4)	0.0036 (2)	0.0026 (2)	0.0041 (2)	0.0004 (3)	−0.0001 (4)	−0.0015 (4)
C(6)	−0.0313 (4)	0.3536 (4)	0.4051 (4)	0.0033 (2)	0.0040 (2)	0.0038 (2)	0.0011 (4)	0.0002 (4)	−0.0014 (4)
C(7)	−0.0847 (3)	0.2788 (4)	0.4093 (4)	0.0028 (2)	0.0042 (2)	0.0041 (2)	0.0011 (4)	0.0020 (4)	0.0002 (4)
C(8)	−0.0908 (3)	0.2098 (3)	0.3584 (4)	0.0024 (2)	0.0032 (2)	0.0044 (2)	−0.0004 (3)	0.0009 (4)	0.0013 (4)
C(9)	0.1421 (4)	0.0107 (4)	0.1103 (4)	0.0050 (3)	0.0037 (2)	0.0027 (2)	−0.0000 (4)	−0.0021 (4)	−0.0016 (4)
C(10)	0.1255 (4)	0.0944 (4)	0.0784 (3)	0.0040 (2)	0.0048 (2)	0.0023 (2)	0.0015 (4)	−0.0019 (3)	−0.0017 (4)
C(11)	0.1788 (4)	0.1647 (4)	0.0726 (4)	0.0057 (3)	0.0034 (2)	0.0025 (2)	0.0028 (4)	0.0010 (4)	0.0011 (3)
C(12)	0.2656 (4)	0.1729 (4)	0.0970 (4)	0.0043 (2)	0.0034 (2)	0.0040 (2)	−0.0001 (4)	0.0026 (4)	0.0017 (4)
C(13)	0.3402 (4)	0.1210 (4)	0.0808 (4)	0.0045 (3)	0.0045 (3)	0.0043 (3)	0.0007 (5)	0.0025 (5)	0.0007 (5)
C(14)	0.3525 (4)	0.0362 (4)	0.0658 (5)	0.0047 (3)	0.0042 (2)	0.0050 (3)	0.0019 (4)	0.0027 (5)	−0.0000 (5)
C(15)	0.2961 (5)	−0.0351 (4)	0.0735 (4)	0.0068 (3)	0.0031 (2)	0.0036 (2)	0.0028 (4)	0.0007 (5)	0.0007 (4)
C(16)	0.2133 (5)	−0.0445 (4)	0.0989 (4)	0.0054 (3)	0.0032 (2)	0.0033 (2)	0.0013 (4)	−0.0012 (5)	−0.0013 (4)
C(17)	0.1165 (3)	0.0467 (3)	0.3433 (3)	0.0030 (2)	0.0030 (2)	0.0029 (2)	−0.0005 (3)	0.0009 (3)	0.0012 (3)
C(18)	0.1992 (3)	0.0166 (3)	0.3217 (4)	0.0033 (2)	0.0027 (2)	0.0036 (2)	0.0010 (3)	−0.0006 (4)	0.0010 (3)
C(19)	0.2773 (3)	0.0592 (4)	0.3176 (4)	0.0029 (2)	0.0040 (2)	0.0028 (2)	0.0022 (3)	−0.0007 (3)	0.0003 (3)
C(20)	0.2942 (3)	0.1452 (4)	0.3043 (4)	0.0023 (2)	0.0042 (2)	0.0037 (2)	0.0007 (3)	−0.0009 (3)	−0.0010 (4)
C(21)	0.2416 (3)	0.2189 (3)	0.3196 (4)	0.0027 (2)	0.0030 (2)	0.0041 (2)	−0.0009 (3)	−0.0016 (3)	−0.0017 (3)
C(22)	0.1851 (4)	0.2350 (3)	0.3936 (4)	0.0036 (2)	0.0031 (2)	0.0031 (2)	0.0003 (3)	−0.0021 (3)	−0.0013 (3)
C(23)	0.1271 (4)	0.1824 (4)	0.4392 (3)	0.0042 (2)	0.0042 (2)	0.0024 (2)	0.0027 (4)	−0.0016 (3)	−0.0004 (4)
C(24)	0.0879 (4)	0.1067 (4)	0.4094 (3)	0.0038 (2)	0.0034 (2)	0.0025 (2)	0.0016 (3)	−0.0000 (3)	0.0016 (3)

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

Table III. Positional and Thermal Parameters for $W_2(C_8H_8)_3$ Obtained by X-ray Diffraction[a,b]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	−0.08754 (4)	−0.19716 (4)	−0.29060 (5)	0.00257 (2)	0.00245 (2)	0.00239 (2)	0.00029 (4)	−0.00037 (6)	0.00020 (6)
W(2)	−0.18618 (4)	−0.11413 (4)	−0.20970 (6)	0.00272 (2)	0.00253 (2)	0.00249 (2)	0.00037 (4)	−0.00041 (6)	−0.00003 (6)
C(1)	0.057 (1)	−0.181 (1)	−0.277 (1)	0.0031 (7)	0.0030 (7)	0.0041 (10)	−0.000 (1)	−0.001 (1)	−0.001 (1)
C(2)	0.024 (1)	−0.222 (1)	−0.204 (1)	0.0022 (5)	0.0039 (7)	0.0034 (7)	0.002 (1)	−0.000 (1)	−0.002 (2)
C(3)	−0.030 (1)	−0.297 (1)	−0.197 (1)	0.0033 (6)	0.0029 (6)	0.0032 (9)	−0.001 (1)	0.001 (1)	−0.000 (1)
C(4)	−0.063 (1)	−0.344 (1)	−0.268 (1)	0.0042 (8)	0.0024 (6)	0.0041 (8)	0.000 (1)	0.001 (1)	0.004 (1)
C(5)	−0.031 (1)	−0.377 (1)	−0.350 (2)	0.0040 (9)	0.0022 (7)	0.0063 (13)	0.001 (1)	−0.000 (2)	−0.001 (2)
C(6)	0.036 (2)	−0.354 (1)	−0.405 (1)	0.0059 (11)	0.0033 (8)	0.0042 (9)	0.001 (2)	0.004 (2)	−0.004 (1)
C(7)	0.087 (1)	−0.280 (1)	−0.408 (2)	0.0042 (8)	0.0040 (8)	0.0041 (10)	0.003 (1)	−0.002 (2)	0.001 (2)
C(8)	0.096 (1)	−0.211 (1)	−0.357 (2)	0.0038 (9)	0.0028 (7)	0.0064 (12)	0.000 (1)	−0.001 (2)	0.004 (2)
C(9)	−0.145 (2)	−0.008 (1)	−0.108 (1)	0.0058 (11)	0.0037 (8)	0.0035 (8)	−0.000 (2)	−0.000 (2)	−0.003 (1)
C(10)	−0.128 (1)	−0.091 (1)	−0.075 (1)	0.0056 (10)	0.0045 (9)	0.0022 (7)	0.004 (2)	−0.003 (1)	−0.001 (1)
C(11)	−0.178 (2)	−0.161 (2)	−0.069 (1)	0.0068 (11)	0.0060 (11)	0.0011 (6)	0.005 (2)	−0.001 (2)	−0.001 (1)
C(12)	−0.268 (1)	−0.170 (2)	−0.093 (2)	0.0048 (10)	0.0045 (9)	0.0038 (9)	−0.001 (2)	0.002 (2)	0.002 (2)
C(13)	−0.343 (2)	−0.115 (2)	−0.076 (1)	0.0050 (10)	0.0060 (12)	0.0028 (8)	−0.001 (2)	−0.001 (2)	0.001 (2)
C(14)	−0.350 (2)	−0.032 (1)	−0.063 (1)	0.0065 (12)	0.0040 (9)	0.0034 (9)	0.003 (2)	0.002 (2)	−0.002 (2)
C(15)	−0.300 (2)	0.035 (1)	−0.075 (2)	0.0100 (16)	0.0037 (8)	0.0035 (10)	0.006 (2)	0.001 (2)	0.001 (2)
C(16)	−0.213 (2)	0.047 (1)	−0.096 (1)	0.0059 (11)	0.0037 (8)	0.0025 (7)	0.003 (2)	−0.001 (2)	−0.002 (1)
C(17)	−0.114 (1)	−0.054 (1)	−0.335 (1)	0.0033 (7)	0.0031 (7)	0.0029 (8)	−0.001 (1)	−0.001 (1)	−0.001 (1)
C(18)	−0.197 (1)	−0.016 (1)	−0.317 (1)	0.0047 (9)	0.0040 (8)	0.0035 (8)	0.001 (2)	−0.001 (2)	0.004 (1)
C(19)	−0.279 (1)	−0.059 (1)	−0.313 (1)	0.0030 (7)	0.0043 (8)	0.0025 (7)	0.001 (1)	−0.001 (1)	0.003 (1)
C(20)	−0.292 (1)	−0.147 (1)	−0.300 (2)	0.0034 (7)	0.0048 (9)	0.0043 (10)	0.002 (1)	0.000 (2)	−0.000 (2)
C(21)	−0.235 (1)	−0.217 (1)	−0.314 (1)	0.0023 (6)	0.0028 (7)	0.0054 (11)	−0.001 (1)	−0.002 (1)	0.002 (1)
C(22)	−0.183 (1)	−0.237 (1)	−0.391 (1)	0.0044 (8)	0.0031 (7)	0.0031 (8)	−0.000 (1)	−0.003 (1)	−0.002 (1)
C(23)	−0.127 (2)	−0.187 (2)	−0.438 (1)	0.0051 (10)	0.0059 (11)	0.0029 (9)	0.001 (2)	−0.002 (2)	0.001 (2)
C(24)	−0.090 (1)	−0.110 (1)	−0.405 (1)	0.0036 (8)	0.0059 (10)	0.0014 (6)	−0.000 (2)	−0.001 (1)	0.004 (1)

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

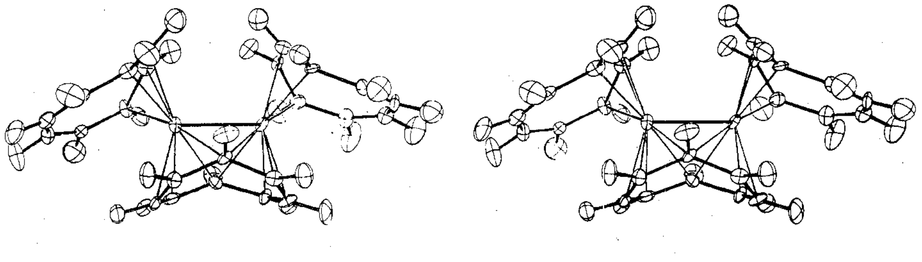


Figure 2. A stereoscopic view based on the neutron diffraction data of the $W_2(C_8H_8)_3$ molecule. The thermal ellipsoids are scaled to 50% probability.

Table IV. Positional and Thermal Vibration Parameters for $W_2(C_8H_8)_3$ Obtained by Neutron Diffraction

Positional Parameters[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W(1)	−0.0854 (7)	−0.1953 (6)	−0.2889 (7)	H(1)	0.0821 (13)	−0.1172 (12)	−0.2556 (13)
W(2)	−0.1873 (6)	−0.1133 (7)	−0.2087 (7)	H(2)	0.0306 (12)	−0.1880 (13)	−0.1363 (13)
C(1)	0.0596 (5)	−0.1810 (5)	−0.2755 (6)	H(3)	−0.0608 (12)	−0.3092 (11)	−0.1326 (12)
C(2)	0.0244 (5)	−0.2238 (5)	−0.1998 (5)	H(4)	−0.1186 (11)	−0.3790 (12)	−0.2481 (11)
C(3)	−0.0290 (5)	−0.2956 (5)	−0.1974 (5)	H(5)	−0.0691 (14)	−0.4299 (14)	−0.3738 (15)
C(4)	−0.0644 (5)	−0.3426 (5)	−0.2695 (5)	H(6)	0.0423 (12)	−0.3979 (12)	−0.4638 (13)
C(5)	−0.0300 (5)	−0.3766 (5)	−0.3517 (5)	H(7)	0.1308 (11)	−0.2743 (13)	−0.4708 (14)
C(6)	0.0346 (5)	−0.3537 (5)	−0.4079 (6)	H(8)	0.1375 (13)	−0.1607 (13)	−0.3906 (13)
C(7)	0.0894 (5)	−0.2788 (5)	−0.4124 (6)	H(9)	−0.0885 (12)	0.0263 (12)	−0.1257 (11)
C(8)	0.0947 (5)	−0.2083 (5)	−0.3597 (5)	H(10)	−0.0613 (12)	−0.1030 (11)	−0.0613 (13)
C(9)	−0.1475 (5)	−0.0072 (5)	−0.1099 (5)	H(11)	−0.1497 (10)	−0.2224 (10)	−0.0571 (12)
C(10)	−0.1281 (6)	−0.0919 (6)	−0.0735 (5)	H(12)	−0.2880 (12)	−0.2370 (11)	−0.1041 (13)
C(11)	−0.1810 (5)	−0.1632 (5)	−0.0677 (6)	H(13)	−0.4045 (11)	−0.1564 (13)	−0.0784 (18)
C(12)	−0.2686 (5)	−0.1700 (6)	−0.0952 (5)	H(14)	−0.4196 (12)	−0.0188 (13)	−0.0464 (15)
C(13)	−0.3442 (5)	−0.1190 (5)	−0.0758 (6)	H(15)	−0.3357 (13)	0.0983 (12)	−0.0623 (14)
C(14)	−0.3559 (6)	−0.0340 (6)	−0.0590 (6)	H(16)	−0.2034 (13)	0.1116 (12)	−0.1123 (14)
C(15)	−0.3033 (5)	0.0395 (5)	−0.0692 (6)	H(17)	−0.0647 (9)	−0.0047 (11)	−0.3199 (12)
C(16)	−0.2195 (5)	0.0478 (6)	−0.0957 (5)	H(18)	−0.2044 (11)	0.0492 (10)	−0.3038 (12)
C(17)	−0.1161 (5)	−0.0502 (5)	−0.3354 (5)	H(19)	−0.3315 (13)	−0.0161 (11)	−0.2989 (13)
C(18)	−0.1998 (5)	−0.0163 (5)	−0.3171 (5)	H(20)	−0.3591 (11)	−0.1620 (11)	−0.2746 (11)
C(19)	−0.2794 (5)	−0.0585 (5)	−0.3144 (6)	H(21)	−0.2625 (11)	−0.2758 (11)	−0.2845 (12)
C(20)	−0.2957 (5)	−0.1468 (5)	−0.2996 (5)	H(22)	−0.1869 (10)	−0.3032 (12)	−0.4151 (11)
C(21)	−0.2364 (5)	−0.2192 (5)	−0.3131 (6)	H(23)	−0.0915 (11)	−0.2142 (11)	−0.4889 (11)
C(22)	−0.1852 (5)	−0.2374 (6)	−0.3902 (6)	H(24)	−0.0286 (10)	−0.0912 (10)	−0.4384 (12)
C(23)	−0.1275 (5)	−0.1831 (5)	−0.4372 (5)				
C(24)	−0.0882 (5)	−0.1076 (5)	−0.4070 (5)				

Isotropic Thermal Parameters ($Å^2$)[b]

atom	β, $Å^2$	atom	β, $Å^2$	atom	β, $Å^2$
H(5)	3.7 (4)	H(15)	3.2 (3)	H(20)	2.5 (3)

Anisotropic Thermal Parameters ($\times 10^4$)[c]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	10 (4)	7 (4)	18 (5)	−3 (3)	4 (3)	−2 (3)	H(1)	40 (9)	20 (8)	40 (9)	−14 (7)	0 (7)	−8 (7)
W(2)	1 (4)	23 (5)	19 (4)	0 (3)	2 (3)	−1 (4)	H(2)	31 (8)	38 (9)	33 (9)	3 (7)	7 (7)	4 (8)
C(1)	14 (3)	12 (3)	22 (4)	−4 (3)	−2 (3)	8 (3)	H(3)	34 (8)	22 (7)	34 (9)	−6 (7)	9 (7)	5 (6)
C(2)	14 (3)	15 (3)	16 (4)	1 (3)	−2 (3)	3 (3)	H(4)	26 (7)	31 (8)	25 (7)	−8 (7)	3 (6)	−9 (6)
C(3)	19 (3)	9 (3)	20 (4)	−2 (3)	1 (3)	3 (3)	H(6)	38 (9)	28 (8)	42 (10)	−5 (7)	24 (8)	−13 (7)
C(4)	20 (4)	6 (3)	20 (3)	−4 (3)	6 (3)	−3 (3)	H(7)	15 (7)	45 (10)	41 (10)	3 (7)	8 (7)	0 (8)
C(5)	13 (3)	17 (3)	15 (3)	3 (3)	−2 (3)	−2 (3)	H(8)	34 (9)	39 (9)	35 (9)	−17 (8)	3 (7)	3 (8)
C(6)	17 (4)	19 (4)	20 (4)	2 (3)	6 (3)	0 (3)	H(9)	33 (9)	27 (7)	25 (8)	5 (7)	−3 (6)	−2 (6)
C(7)	15 (3)	13 (3)	23 (4)	1 (3)	0 (3)	5 (3)	H(10)	29 (9)	28 (8)	35 (8)	3 (7)	0 (7)	−3 (7)
C(8)	9 (3)	17 (3)	20 (3)	0 (3)	−2 (3)	0 (3)	H(11)	16 (6)	16 (7)	38 (8)	−1 (6)	2 (6)	9 (6)
C(9)	14 (4)	12 (3)	16 (3)	3 (3)	−9 (3)	−2 (3)	H(12)	40 (9)	16 (7)	39 (9)	−11 (6)	7 (8)	3 (6)
C(10)	21 (4)	25 (4)	13 (3)	4 (3)	−4 (3)	−3 (3)	H(13)	9 (7)	31 (8)	95 (17)	−8 (6)	10 (8)	−12 (10)
C(11)	10 (3)	12 (3)	20 (3)	3 (3)	2 (3)	0 (3)	H(14)	17 (8)	33 (9)	71 (14)	−6 (7)	9 (8)	−4 (9)
C(12)	20 (4)	21 (4)	17 (4)	4 (3)	−1 (3)	4 (3)	H(16)	34 (9)	21 (8)	48 (11)	−5 (7)	0 (8)	2 (7)
C(13)	19 (4)	16 (3)	25 (4)	0 (3)	7 (3)	3 (3)	H(17)	11 (6)	27 (7)	35 (8)	−12 (6)	−8 (6)	2 (6)
C(14)	24 (5)	22 (4)	26 (4)	7 (3)	−2 (3)	−2 (3)	H(18)	31 (8)	16 (7)	33 (8)	2 (6)	8 (6)	−1 (6)
C(15)	17 (3)	15 (3)	23 (4)	9 (3)	4 (3)	−4 (3)	H(19)	33 (9)	18 (7)	46 (10)	10 (7)	2 (7)	−15 (7)
C(16)	16 (3)	19 (4)	15 (3)	2 (3)	3 (3)	−3 (3)	H(21)	28 (8)	20 (8)	35 (8)	−7 (7)	−1 (7)	−10 (7)
C(17)	4 (3)	13 (3)	18 (4)	−2 (3)	−1 (2)	0 (2)	H(22)	17 (7)	37 (9)	28 (8)	8 (6)	−3 (6)	−3 (7)
C(18)	17 (4)	12 (4)	17 (3)	−4 (3)	−1 (3)	2 (3)	H(23)	29 (8)	28 (7)	18 (7)	12 (6)	4 (6)	1 (6)
C(19)	7 (3)	19 (4)	21 (3)	−3 (3)	−5 (3)	6 (3)	H(24)	22 (7)	21 (7)	31 (8)	0 (5)	16 (7)	3 (6)
C(20)	7 (3)	12 (3)	27 (4)	0 (2)	−2 (3)	−6 (3)							
C(21)	16 (3)	14 (4)	17 (3)	0 (3)	−1 (3)	−6 (3)							
C(22)	13 (3)	21 (4)	18 (3)	2 (3)	−6 (3)	2 (3)							
C(23)	15 (3)	20 (3)	13 (3)	11 (3)	1 (3)	3 (3)							
C(24)	13 (3)	14 (3)	16 (3)	−2 (3)	3 (3)	2 (3)							

[a] *x*, *y*, and *z* are fractional coordinates. [b] Isotropic temperature factors of the form $\exp(-B \sin^2 \theta/\lambda^2)$. [c] Anisotropic thermal parameters of the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

are about equal to the sum of the esd's. However, the esd's obtained by X-ray diffraction were large enough to make many potentially interesting comparisons of distances and angles meaningless. Therefore, the neutron diffraction study was performed in order to confirm the W–W distance and to determine accurately the C–C distances. The added precision afforded by the neutron results allows us to make more meaningful comparisons with the $Mo_2(C_8H_8)_3$ and $Cr_2(C_8H_8)_3$ structures as well as to make internal comparisons.

These molecules contain two types of metal to C_8H_8 attachment. Two of the C_8H_8 rings are attached in the well-known 1–4-η fashion. The pattern of C–C distances, given in Table VII, and the bending of these rings are entirely typical for such moieties. Each of these rings is bent, across C(1)–C(4) and C(9)–C(12), to form two planes, and the dihedral angles are 145.6 and 148.9° for $Mo_2(C_8H_8)_3$. In $Cr_2(C_8H_8)_3$ the corresponding dihedral angles were equal with a value of 150.6°. In the free diene portions of these rings

Table V. Bond Distances and Angles[a,b]

	$Mo_2(C_8H_8)_3$ X-ray	$W_2(C_8H_8)_3$ X-ray	$W_2(C_8H_8)_3$ neutron
	A. Bond Distances, Å		
M(1)-M(2)	2.302 (1)	2.375 (1)	2.37 (1)
M(1)–C(1)	2.327 (5)	2.31 (2)	2.29 (1)
M(1)–C(2)	2.264 (5)	2.23 (2)	2.22 (1)
M(1)–C(3)	2.271 (5)	2.31 (2)	2.26 (1)
M(1)–C(4)	2.359 (6)	2.38 (2)	2.35 (1)
C(1)–C(2)	1.425 (8)	1.38 (3)	1.43 (1)
C(2)–C(3)	1.416 (8)	1.46 (3)	1.40 (1)
C(3)–C(4)	1.416 (9)	1.41 (3)	1.42 (1)
C(4)–C(5)	1.441 (8)	1.43 (3)	1.45 (1)
C(5)–C(6)	1.340 (9)	1.40 (3)	1.37 (1)
C(6)–C(7)	1.455 (9)	1.43 (3)	1.46 (1)
C(7)–C(8)	1.336 (9)	1.33 (4)	1.36 (1)
C(8)–C(1)	1.410 (8)	1.44 (3)	1.44 (1)
M(2)–C(9)	2.355 (5)	2.37 (2)	2.31 (1)
M(2)–C(10)	2.241 (5)	2.27 (2)	2.25 (1)
M(2)–C(11)	2.242 (6)	2.24 (2)	2.26 (1)
M(2)–C(12)	2.343 (6)	2.35 (2)	2.30 (1)
C(9)–C(10)	1.432 (9)	1.43 (4)	1.47 (1)
C(10)–C(11)	1.398 (10)	1.37 (4)	1.39 (1)
C(11)–C(12)	1.427 (10)	1.47 (4)	1.44 (1)
C(12)–C(13)	1.459 (9)	1.50 (4)	1.46 (1)
C(13)–C(14)	1.372 (9)	1.34 (4)	1.37 (1)
C(14)–C(15)	1.443 (10)	1.34 (4)	1.42 (1)
C(15)–C(16)	1.373 (11)	1.43 (4)	1.38 (1)
C(16)–C(9)	1.435 (10)	1.39 (4)	1.44 (1)
M(1)–C(17)	2.530 (6)	2.40 (2)	2.43 (1)
M(1)–C(21)	2.487 (5)	2.38 (2)	2.42 (1)
M(1)–C(22)	2.258 (5)	2.22 (2)	2.28 (1)
M(1)–C(23)	2.319 (5)	2.30 (2)	2.33 (1)
M(1)–C(24)	2.272 (5)	2.21 (2)	2.24 (1)
M(2)–C(17)	2.488 (5)	2.41 (2)	2.41 (1)
M(2)–C(21)	2.465 (5)	2.40 (2)	2.41 (1)
M(2)–C(18)	2.279 (5)	2.25 (2)	2.23 (1)
M(2)–C(19)	2.335 (5)	2.31 (2)	2.31 (1)
M(2)–C(20)	2.269 (5)	2.20 (2)	2.24 (1)
C(17)–C(18)	1.430 (8)	1.48 (3)	1.44 (1)
C(18)–C(19)	1.408 (8)	1.46 (3)	1.41 (1)
C(19)–C(20)	1.400 (9)	1.42 (3)	1.42 (1)
C(20)–C(21)	1.450 (8)	1.45 (3)	1.48 (1)
C(21)–C(22)	1.444 (9)	1.45 (3)	1.44 (1)
C(22)–C(23)	1.414 (9)	1.38 (4)	1.43 (1)
C(23)–C(24)	1.421 (9)	1.44 (4)	1.41 (1)
C(24)–C(17)	1.446 (8)	1.43 (3)	1.47 (1)
	B. C–C–C Angles, deg		
C(1)–C(2)–C(3)	128.7 (5)	131 (2)	128.8 (7)
C(2)–C(3)–C(4)	129.3 (5)	126 (2)	129.0 (7)
C(3)–C(4)–C(5)	134.1 (5)	136 (2)	134.0 (7)
C(4)–C(5)–C(6)	134.8 (6)	134 (2)	134.8 (7)
C(5)–C(6)–C(7)	132.2 (6)	131 (2)	132.7 (7)
C(6)–C(7)–C(8)	132.9 (6)	136 (2)	131.5 (7)
C(7)–C(8)–C(1)	136.5 (5)	135 (2)	136.7 (7)
C(8)–C(1)–C(2)	134.3 (5)	132 (2)	134.6 (7)
C(9)–C(10)–C(11)	130.2 (6)	130 (2)	128.7 (7)
C(10)–C(11)–C(12)	129.5 (5)	129 (2)	127.5 (7)
C(11)–C(12)–C(13)	133.2 (7)	131 (2)	132.7 (7)
C(12)–C(13)–C(14)	133.8 (7)	132 (3)	132.8 (8)
C(13)–C(14)–C(15)	131.5 (7)	135 (3)	133.6 (8)
C(14)–C(15)–C(16)	134.2 (6)	135 (2)	131.2 (7)
C(15)–C(16)–C(9)	135.7 (6)	134 (2)	137.2 (8)
C(16)–C(9)–C(10)	131.8 (7)	133 (3)	130.7 (8)
C(17)–C(18)–C(19)	130.8 (5)	128 (2)	129.6 (7)
C(18)–C(19)–C(20)	129.7 (5)	127 (2)	128.1 (7)
C(19)–C(20)–C(21)	130.4 (5)	130 (2)	127.7 (7)
C(20)–C(21)–C(22)	128.0 (6)	130 (2)	127.8 (7)
C(21)–C(22)–C(23)	131.9 (5)	130 (2)	129.2 (7)
C(22)–C(23)–C(24)	128.5 (5)	125 (2)	128.3 (7)
C(23)–C(24)–C(17)	129.3 (5)	132 (2)	128.3 (6)
C(24)–C(17)–C(18)	131.3 (5)	130 (2)	129.5 (6)

[a] Figures in parentheses are esd's occurring in the least significant digit of the preceding parameter. [b] C–H distances, Å, each with an esd of 0.02 Å, are as follows, in the order C(1)–H(1) to C(24)–H(24): (Ring 1) 1.10, 1.11, 1.11, 1.07, 1.09, 1.09, 1.09, 1.11; (Ring 2) 1.09, 1.08, 1.06, 1.10, 1.11, 1.04, 1.06, 1.06; (Ring 3) 1.10, 1.05, 1.08, 1.09, 1.07, 1.10, 1.07, 1.08.

Table VI. Selected Planes for $Mo_2(C_8H_8)_3$

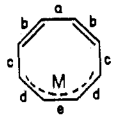
plane no.	equations of best planes
1	$-0.7898x + 0.6127y - 0.0277z + 2.3693 = 0$
2	$0.2724x - 0.2789y - 0.92097z - 0.9600 = 0$
3	$-0.6819x + 0.4938y - 0.5396z - 0.2315 = 0$
4	$-0.2048x + 0.0673y - 0.9765z - 2.1086 = 0$
5	$0.0337x + 0.0337y - 0.9879z - 4.7045 = 0$
6	$-0.7600x + 0.5327y - 0.3722z - 2.4454 = 0$
7	$-0.2233x + 0.0368y - 0.9741z - 5.4015 = 0$
8	$-0.6514x + 0.3997y - 0.6449z - 4.2141 = 0$
plane no.	**deviations (Å) of atoms from their best planes**
1	C(1), −0.001 (5); C(2), 0.002 (5); C(3), −0.002 (5); C(4), 0.001 (5); Mo(1),[a] −1.695 (0)
2	C(9), 0.000 (5); C(10), 0.000 (5); C(11), 0.000 (6); C(12), 0.000 (6); Mo(2),[a] −1.695
3	C(1), 0.036 (5); C(4), 0.003 (5); C(5), −0.041 (6); C(6), 0.049 (6); C(7), 0.007 (6); C(8), −0.055 (5)
4	C(9), 0.043 (5); C(12), 0.010 (6); C(13), −0.049 (7); C(14), 0.041 (7); C(15), 0.035 (6); C(16), −0.080 (6)
5	C(18), 0.000 (5); C(19), 0.000 (5), C(20), 0.000 (5); Mo(2),[a] 1.374 (0)
6	C(22), 0.000 (6); C(23), 0.000 (6); C(24), 0.000 (6); Mo(1),[a] 1.409 (0)
7	C(17), −0.003 (5); C(18), 0.003 (5); C(20), −0.003 (5); C(21), 0.002 (6); Mo(2),[a] 1.711 (0)
8	C(17), −0.014 (5); C(24), 0.019 (6); C(21), 0.015 (6); C(22), −0.019 (6); Mo(1),[a] 1.726 (0)

Dihedral Angles (deg) between Planes

∠1,3 = 148.9	∠5,6 = 74.8	∠6,8 = 18.5
∠2,4 = 145.6	∠5,7 = 18.3	∠7,8 = 38.0

[a] This atom was not included in plane calculation.

Table VII. Average C–C Distances, A, of Different Types in the $M_2(C_8H_8)_3$ Molecules[a]



	no. averaged	$Cr_2(C_8H_8)_3$ X-ray	$Mo_2(C_8H_8)_3$ X-ray	$W_2(C_8H_8)_3$ neutron
a	2	1.405 (8)	1.449 (7)	1.44 (2)
b	4	1.349 (15)	1.355 (10)	1.370 (5)
c	4	1.428 (7)	1.436 (10)	1.448 (5)
d	4	1.394 (11)	1.425 (5)	1.440 (9)
e	2	1.403 (5)	1.407 (9)	1.395 (7)

[a] The estimated standard deviations for the average bond distances are the larger of the values calculated according to $[\Sigma_n(l_i - \bar{l})^2/n(n-1)]^{1/2}$ and $[\Sigma_n\sigma^2(l_i)/n^2]^{1/2}$.

there is an alternation of distances that corresponds well with the alternation of three single and two double bonds. In the "bound diene" portions the three C–C distances are nearly the same with the central one perhaps the shortest. This is quite common in (1–4-η-butadiene)metal moieties.[20]

The third C_8H_8 ring serves to tie the two (η^4-C_8H_8)M units together. It donates all eight of its π electrons to the metal atoms and, though the bonding is evidently complex in its details, we may conclude from the symmetry of the situation that four π electrons are donated to each metal atom.

The average of the 24 crystallographically independent C–H distances, as given by the neutron diffraction study of $W_2(C_8H_8)_3$, is 1.084 (4) Å. It is interesting the compare this with the mean C–H distance found in the X-ray study of $Cr_2(C_8H_8)_3$, which is 0.94 (10) Å. Although the very large esd for the latter means that it is not statistically different from the neutron value, it is typical of the values given by X-ray studies and reflects the fact that the centroid of the electron

Table VIII. Metal–Metal Distances, Å, in Two Complete Triads of Quadruply Bonded Compounds

	$M_2(C_8H_8)_3$	$[M_2(CH_3)_8]^{4-}$ [a]
Cr	2.214 (1)[b]	1.980 (5)
Mo	2.302 (2)	2.147 (3)
W	2.375 (1)	2.264 (1)

[a] See ref 8b and 23 for sources. [b] From ref 11.

density of the hydrogen atom does not coincide with the position of the proton (which is what the neutron experiment locates) but instead lies about 0.1 Å closer to the carbon atom.

Since these molecules are diamagnetic, it may be assumed that the formal bond order for the M–M bond must in each case be 2 or 4. In each case the M–M distance is far less than would be expected for double bonds. For chromium there is no double bond known but in $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$ there is a triple bond (and also 18-electron configurations on the metal atoms, as in the present case) and the Cr–Cr distance is 2.276 (2) Å.[21] The comparison of the distance of 2.214 (1) Å in $Cr_2(C_8H_8)_3$ with this would support the assignment of bond order 4 in preference to 2. In a similar way, the Mo–Mo distance of 2.302 (2) Å in $Mo_2(C_8H_8)_3$ is shorter than the triple-bond distance of 2.448 (1) Å in the 18-electron compound $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$.[22] There are no examples of double or triple bonds between tungsten atoms having 18-electron configurations, but in the various $Re_3Cl_9L_3$ type compounds, where the metal atoms have 18-electron configurations, the R═Re distances are in the range 2.45–2.50 Å. These comparisons support the view that the $M_2(C_8H_8)_3$ molecules with M = Cr, Mo, and W contain quadruple bonds.

Bond lengths and bond orders are not simply related in these systems with multiple metal–metal bonds and one source of difficulty in making valid comparisons is the effect of total (formal) electron population of the metal atoms. For that reason we have been careful in the foregoing comparisons to use molecules in which there are 18-electron configurations throughout. There is evidently a consistent tendency for bonds to be shorter when the formal electron population is lower. Thus, for the Mo_2X_6 (X = NR_2, CH_2SiMe_3, for example) species where the formal population is 12, the bonds are very much shorter, viz., 2.16–2.23 Å, than in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$. Other similar examples could be cited.

With the triad of $M_2(C_8H_8)_3$ molecules now complete, we can examine the change in metal–metal distance for a complete set of isostructural molecules as we proceed from the first to the third transition series. In only one other case, namely, for the series $[M_2(CH_3)_8]^{4-}$, has this been possible.[8b,23] The distances in the two series are listed in Table VIII. It should be noted that the $[M_2(CH_3)_8]^{4-}$ ions have metal atoms with formal electron populations of 16, while the $M_2(C_8H_8)_3$ species have populations of 18. In accord with this, all of the former have shorter M–M bonds, by 0.23, 0.15, and 0.11 Å for the Cr_2, Mo_2, and W_2 compounds, respectively. Clearly, the two sets of distances do not increase with increasing atomic number in a parallel fashion. In the $M_2(C_8H_8)_3$ series the total increase, from the Cr_2 to the W_2 compound, 0.16 Å, is only about half of that, 0.28 Å, in the $[M_2(CH_3)_8]^{4-}$ series. At the present time we do not understand these bonds well enough to be able to account for these differences in behavior.

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Registry No. $Mo_2(C_8H_8)_3$, 66719-22-0; $W_2(C_8H_8)_3$, 66719-23-1.

Supplementary Material Available: Tables of the observed and calculated structure factors for both of the X-ray structures and the neutron structure (30 pages). Ordering information is given on any current masthead page.

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(15) We wish to thank our collaborators, Drs. C. E. and J. Strouse, for designing and assembling the low-temperature apparatus at the CP-5 reactor. The apparatus is a modified version of a similar system designed for an X-ray diffractomer.[16]

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(24) Since this paper was written, another complete series of compounds, $M_2(mhp)_4$, mhp = 6-methyl-2-hydroxypyridine anion, M = Cr, Mo, W, which also have good thermal and chemical stability, has been obtained and characterized. A full report on these compounds is available: F. A. Cotton, P. E. Fanwick, R. H. Niswander, and J. C. Sekutowski, *J. Am. Chem. Soc.*, in press.