A Crystallographic Study of the Metal-to-Metal Bond in Tetraallyldimolybdenum[1]

F. A. Cotton* and J. R. Pipal

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received December 30, 1970

Abstract: A crystallographic study has been carried out to elucidate the molecular structure of tetraallyldimolybdenum. It is found to be crystallographically isomorphous with the analogous chromium compound and to have a qualitatively similar structure. The molybdenum atoms are separated by 2.183 (2) Å. Two of the allyl groups are located so that they bridge the two metal atoms symmetrically; the planes of these allyl groups are parallel to the Mo–Mo line. Each of the other two allyl groups is bonded to a single metal atom in such a way that the six Mo–C distances are nearly identical, lying in the range 2.28–2.35 Å. The molecule has as its sole element of virtual (not crystallographic) symmetry a plane perpendicular to the Mo–Mo line. The C–C distances (average 1.37 Å) found when H atoms are included in refinement (but not themselves refined) are significantly shorter than those obtained (average 1.41 Å) when H atoms are omitted. The Mo–Mo distance is compared with Mo–Mo distances in related molecules and with the Cr–Cr distance in the analogous $Cr_2(C_3H_5)_4$ molecule. Crystallographic data are as follows: space group $P42_1c$; unit cell $a = b = 18.472$ (10), $c = 7.688$ (6) Å; $V = 2623.09$ Å^3; D_{calcd} for $Z = 8$, 1.804 g cm^{-3}. Diffractometer data (1209 independent reflections above background) were used to refine the structure anisotropically to final $R_1 = 0.067$, $R_2 = 0.049$; the esd of an observation of unit weight was 1.023.

In recent years the existence and wide occurrence of strong, short multiple metal-to-metal bonds has been recognized and verified.[2–7] In particular, metal atoms in formal oxidation states which provide d^4 configurations on the individual metal atoms form the strongest bonds, namely quadruple ones. This was first recognized for various species containing Re^{III}, such as $Re_2X_8^{2-}$ ($X = Cl$,[3] Br[4]), $Re_2Cl_6(PEt_3)_2$,[5] $Re_2(O_2CR)_4Cl_2$,[6] and $Re_2(O_2CR)_2I_4$.[7] For molybdenum, the acetate $Mo_2(O_2CCH_3)_4$ was shown by Lawton and Mason[8] to have a very short bond, of length 2.11 Å. An Mo–Mo distance nearly as short is found in the $Mo_2Cl_8^{4-}$ ion as observed in several crystalline salts.[9] For $Cr_2(O_2CCH_3)_4(H_2O)_2$ it has recently been shown[10] that there is a Cr–Cr distance, *viz.*, 2.36 Å, short enough to imply the existence of a quadruple interaction in this compound also.

In the light of these results, we were fascinated by the reports[11,12] that in tetraallydichromium, $Cr_2(C_3H_5)_4$, the Cr–Cr distance is only about 1.97 Å, since this is some 0.3 Å shorter than that in the hydrated acetate. Since the bond in the dichromium(II) group thus appears to be so drastically shortened when allyl groups are present rather than acetate groups, we were intrigued by the question of what would happen to the M–M distance in the dimolybdenum(II) group upon making a similar exchange of ligands. Any significant shortening would result in an Mo–Mo distance under 2.0 Å, an intriguing if unlikely possibility.

The compound $Mo_2(C_3H_5)_4$ had already been mentioned in the literature,[13] and with the kind assistance of Professor Wilke we obtained a copy of the thesis[14] giving details of its preparation and characterization. The procedure described in the thesis (summarized later in the Experimental Section of this paper) was employed to obtain a pure sample of $Mo_2(C_3H_5)_4$, and crystals of the substance suitable for crystallographic structure work were prepared. This paper reports the results of a three-dimensional X-ray crystallographic study of the structure of the substance.

Experimental Section

Tetraallyldimolybdenum(II) was prepared according to the method of Oberkirch.[14] It is an extremely air- and moisture-sensitive compound, and all operations were necessarily carried out in an atmosphere of high-purity argon. Pentane and ether were dried by refluxing over a Na–K melt. Allyl chloride (Matheson) was distilled using a 0.5-m Vigreux column. The first 15 ml was discarded and only that fraction boiling at 44.5–45.5° accepted. Molybdenum pentachloride was obtained from the Climax Molybdenum Co., and a freshly opened bottle was used. A solution of allylmagnesium chloride was prepared and standardized according to usual procedures.[15]

The reaction was carried out in a 1000-ml three-necked flask equipped with a 500-ml dropping funnel and gas inlet. The first flask was connected to another 1000-ml flask by means of a V-shaped transfer tube and a schlenk filter. The entire apparatus was evacuated and flamed several times prior to use. By means of a syringe, 508 ml (0.25 mol) of the Grignard reagent was added to the flask. Molybdenum pentachloride (12.4 g) and 450 ml of ether were placed in a 500-ml flask and stirred for 0.5 hr at room temperature. The orange-brown solution was then added to the dropping funnel using a V-shaped transfer tube. Not all the $MoCl_5$ had dissolved, and as a result approximately 1 g was lost.

---

(1) Supported in part by the National Science Foundation, under Grant No. GP 7034X.

(2) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

(3) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(4) F. A. Cotton, B. G. DeBoer, and M. Jeremic, *ibid.*, **9**, 2143 (1970).

(5) F. A. Cotton and B. M. Foxman, *ibid.*, 7, 2135 (1968).

(6) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *ibid.*, 7, 1570 (1968).

(7) W. K. Bratton and F. A. Cotton, *ibid.*, **8**, 1299 (1969).

(8) D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, **87**, 921 (1965).

(9) J. B. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969); **9**, 346 (1970).

(10) F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *J. Amer. Chem. Soc.*, **92**, 2926 (1970).

(11) G. Albrecht and D. Stock, *Z. Chem.*, 7, 321 (1967).

(12) T. Aoki, A. Furusaki, Y. Tomiie, K. Ono, and K. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 545 (1969).

(13) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Kerm, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, W. Walter, and H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966).

(14) W. Oberkirch, Dissertation, Technische Hochschule, Aachen, 1963.

(15) O. Grummitt, E. P. Budewitz, and C. C. Chudd, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 749.

The $MoCl_5$ solution was added slowly to the Grignard reagent over a period of 4 hr at room temperature. A green color developed with the first drop of $MoCl_5$ and rapidly became an intensely dark green. Stirring was done with a magnetically activated stirring bar. Copious amounts of $MgCl_2$ precipitated. Two hours after the $MoCl_5$ had been added, the contents of the first flask were filtered into the second. The ether was removed by a pot-to-pot distillation, and the residue was stored under vacuum at −20°.

The residue was dissolved in the minimum amount of pentane and cooled to −80°. This was repeated on the precipitate obtained after removing the mother liquor with a syringe. The second time the cooling was done more slowly with the hope of getting good crystals, but this was not a success. The solid was therefore dissolved in ether and the solution was filtered, cooled to −80° over 5.5 hr, and left for another 3.5 hr. The mother liquor was then removed with a syringe, leaving behind approximately 0.3 g of very dark green acicular crystals, which were stored under vacuum at −20°. A pmr spectrum was obtained on a sample dissolved in dry, air-free benzene and was identical with that reported by Oberkirch in his thesis. The spectrum is extremely complex, and no attempt has been made to interpret it.

The acicular crystals were mounted in 0.2 mm glass capillaries in a glove box equipped with a BASF catalytic oxygen scavenger which kept the oxygen content at 1 ppm or lower. The crystals were relatively soft and easily cleavable. In almost every case, the crystals mounted were fragments cut from the center sections of large needles.

Several of the crystals mounted were found to be suitable for X-ray study. One was examined in detail by means of Laue, rotation, and Weissenberg photographs and found to have Laue tetragonal (4/*mmm*) point symmetry and to have systematic absences on $h00$ for $h = 2n + 1$ and hhl for $l = 2n + 1$. These absences uniquely define the space group as $P\bar{4}2_1c$ (no. 114, D_{2d}^4). Cell constants, measured on films, are $a = b = 18.48$ Å and $c = 7.67$ Å. These are just slightly larger than those for the Cr analog which has the same space group. Thus, it seemed probable that the two compounds are isomorphous. A slightly chipped parallelpiped (0.107 × 0.113 × 0.416 mm) was used to collect intensity data. It was mounted on a eucentric goniometer head with the crystal *c* (*c**) axis tilted about 2° away brom the ϕ axis of the head to minimize multiple reflection. Data were taken with Mo Kα radiation on a General Electric XRD-6 automated diffractometer with Datex control. Eight reflections were centered and used to generate[16] a unique data set of 1783 reflections out to $\sin\theta/\lambda = 0.64$ ($2\theta = 55°$). A standard θ–2θ scan technique was employed, with the scan range extending from 1.0° below $2\theta(K\alpha_1)$ to 1.0° above $2\theta(K\alpha_2)$. The scan rate was 2°/min. Stationary background counts of 10 sec were taken at each end of the scan. Instrument stability and decomposition were monitered by measuring a set of four reflections, widely separated in reciprocal space, after every 75 reflections.

Upon completion of the data taking process, 35 strong reflections were carefully centered and used to determine accurate cell constants. The results of a least-squares refinement are $a = b = 18.472$ (10) Å, $c = 7.688$ (6) Å, and $V = 2623.09$ Å^3. The density calculated assuming $Z = 8$ is 1.804 g cm^{-3}. Because of the highly reactive nature of this compound, the density was not measured experimentally. The final unit cell dimensions differed negligibly from those used to compute diffractometer settings.

The measured data were converted to observed structure factors (F_o) by means of DIFDAR, a data reduction program written by Dr. Alan Parkes. Standard deviations (in dekacounts) were assigned to the integrated net intensity measurements (I) according to the formula

$$\sigma(I) = [(CNT + k^2B)/10.0 + 0.000I^2]^{1/2}$$

where CNT is the intensity measured during the scan, B is the sum of the two background measurements ($B_1 + B_2 + 0.90$), k is a correction factor for variable scan width, and I is equal to $CNT - kB + 0.45$. The quantities 0.45 and 0.90 arise because the scalar readings are in dekacounts; they represent, respectively, the mean value and twice the mean value of counts between 0.1 and 1.0 dekacount which are not actually recorded. A reflection was considered to be observed and subsequently used in the refinement if $I/\sigma(I) \geqslant 2.0$. A total of 1209 reflections was accepted as nonzero. Structure factors computed for the rejected reflections after refinement was complete were all satisfactorily small. The check reflections showed a very slight decrease over time, indicating a small amount of decomposition (about 3%). A program was written to correct the data for this and produce a data deck suitable for our least-squares program.[17]

Since the tetraallyldimolybdenum(II) appeared to be isomorphous with its chromium analog, we did not calculate a Patterson function, but proceeded immediately to four cycles of least-squares refinement using the Cr atom positions given in the paper by Aoki, *et al.*[12] The form factors used for neutral Mo and subsequently C are those of Cromer and Waber.[18] An anomalous dispersion correction was applied to the Mo atoms using values of Δf and $\Delta f'$ from Cromer.[19] Allowing only the scale factor and then also the positional and isotropic thermal parameters of the two molybdenum atoms to refine, a conventional residual, $R_1 = (\Sigma||F_o| - |F||/\Sigma|F_o|)$, of 0.165, was reached. The addition of all 12 carbons as given by Aoki, *et al.*[12] (without further refinement), reduced R_1 to 0.127. Three cycles of isotropic followed by three of anisotropic refinement for all 14 heavy atoms reduced R_1 to 0.0698. At this point the metal–metal bond length was 2.187 Å. A difference Fourier map[20] phased on the heavy atoms was calculated in the hope of locating the hydrogen atoms (which constitute 11.4% of the total electron density). The map proved to be too noisy to permit us to determine any of the hydrogen atom positions. The largest peak has a maximum density of 1.15 e/Å^3 and was located on the $\bar{4}$ axis at $z = 0.32$.

In the hope of reducing the noise in the difference electron density map, several small corrections were undertaken. The first was an absorption calculation[21] which gave minimum and maximum transmission factors of 0.812 and 0.833, which differ by only 2.5%. Since the measurements of the eight crystal faces have at least this much error and probably more, the absorption correction was considered insignificant and omitted.

Another effect, for which the calculated corrections were large enough that these had to be applied, stems from the use of a zirconium filter. The wavelength of the absorption edge of Zr (0.6888 Å) is close enough to the Mo Kα wavelength that when backgrounds were counted on the low-angle side of reflections which occur at low angles, the filter absorbs and the measured backgrounds are diminished. Thus, when a plot of $k(B_2 - B_1)/(CNT - 2k(B_2 + 0.45) + 0.45)$ *vs.* 2θ was made for reflections with $(CNT - 2k(B_2 + 0.45)) \geqslant 1000$ dekacounts, a distinct 2θ dependence was observed which could be approximated as a straight line with slope -5.18×10^{-3} and intercept 0.201. If we define $R = k(B_2 - B_1)/(CNT - 2k(B_2 + 0.45) + 0.45)$, $I = CNT - kB + 0.45$, and $I' = CNT - 2k(B_2 + 0.45) + 0.45$, then $I' = I/(1 + R)$. I' is the more appropriate value to use for the intensity since it is corrected for the systematic error introduced by the filter below a 2θ value characteristic for a given λ and filter. Instead of calculating R separately from B_1 and B_2 for each reflection, it was calculated from the above-mentioned graph as a function of 2θ and the necessary correction applied to all data. The values of R ran from 0.185 at the lowest angles to 0.0 at the highest ones.

A secondary extinction correction was also applied, since examination of F_o/F_c for reflections with high intensities indicated that the effect was significant for a limited number of reflections. This correction was applied to all reflections with measured intensities in excess of 4000 dekacounts.

Continued refinement using the corrected data led, in two cycles, to the awkward problem of the temperature parameters for C(31) and C(42) becoming nonpositive definite. This prompted us to reconsider the choice, which had been quite arbitrarily made, of the handedness of the molecule in this acentric space group. Since both real and imaginary parts of the anomalous dispersion correction had been applied to the atomic form factor for molybdenum, an incorrect choice could lead to such a difficulty. Upon changing to the other enantiomorph, refinement proceeded smoothly through three cycles to convergence, all atoms having positive definite temperature parameters and R_1 reaching the value 0.0696.

A new difference Fourier map as well as a Fourier map employing observed amplitudes and calculated phases were now computed.

---

[16] Diffractometer settings were calculated using PICK-2 (J. A. Ibers).

[17] C. T. Prewitt, SFLS5, "A Full-Matrix Crystallographic Program for the IBM, 360" (modified by B. M. Foxman and subsequently M. D. Laprade), 1966. This program minimizes $\Sigma w||F_o| - |F_c||^2$, where $w = 1/\sigma^2(F)$.

[18] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[19] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[20] All Fourier maps were calculated with a modified version of FORDAP II by A. Zalkin.

[21] Using K. Knox's version of ABSCOR.

Table I. Positional and Anisotropic Thermal Parameters[a]

Atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[c]
Mo_1	0.20782 (8)	0.05528 (7)	−0.17270 (18)	3.03 (7)	2.26 (7)	1.76 (6)	−0.27 (6)	0.09 (6)	0.03 (6)	2.35
Mo_2	0.28550 (8)	−0.03267 (8)	−0.13844 (19)	2.43 (7)	2.94 (7)	2.53 (7)	0.10 (5)	0.10 (7)	−0.26 (6)	2.63
C_{11}	0.3738 (11)	0.0354 (12)	−0.0251 (37)	4.0 (11)	3.6 (10)	14.1 (22)	0.3 (9)	−0.5 (15)	−1.5 (14)	7.20
C_{12}	0.3361 (12)	0.0906 (11)	−0.0970 (44)	5.4 (13)	2.5 (10)	15.9 (25)	−1.4 (9)	−0.3 (16)	−3.1 (15)	7.96
C_{13}	0.2829 (13)	0.1399 (12)	−0.0688 (29)	5.5 (12)	6.6 (13)	6.0 (12)	−1.5 (11)	−0.0 (11)	−3.8 (11)	6.00
C_{21}	0.1985 (11)	0.1049 (11)	−0.4453 (21)	5.9 (13)	5.8 (11)	1.7 (8)	−2.3 (10)	−0.8 (9)	2.0 (8)	4.50
C_{22}	0.1569 (11)	0.0440 (12)	−0.4458 (26)	4.9 (11)	5.2 (12)	4.5 (11)	−2.2 (10)	−1.2 (9)	3.2 (10)	4.88
C_{23}	0.1017 (9)	0.0358 (11)	−0.3232 (24)	3.2 (9)	6.9 (12)	2.8 (8)	−1.4 (9)	−0.4 (8)	0.6 (10)	4.31
C_{31}	0.1442 (10)	0.0265 (10)	0.0615 (21)	4.7 (10)	4.4 (10)	2.3 (8)	3.6 (9)	0.1 (7)	0.4 (7)	3.81
C_{32}	0.2082 (12)	−0.0054 (10)	0.1227 (23)	7.8 (13)	4.6 (10)	3.3 (9)	2.1 (10)	1.1 (11)	1.0 (9)	5.20
C_{33}	0.2313 (11)	−0.0746 (10)	0.0981 (23)	5.9 (11)	4.8 (10)	2.1 (8)	0.8 (9)	0.5 (8)	−0.5 (9)	4.26
C_{41}	0.2617 (14)	−0.1473 (11)	−0.2592 (30)	8.6 (16)	4.2 (11)	5.2 (13)	−0.9 (10)	−1.4 (11)	−1.0 (10)	6.02
C_{42}	0.2871 (12)	−0.1039 (11)	−0.3916 (27)	4.9 (10)	4.7 (10)	3.5 (10)	1.6 (10)	0.7 (10)	−1.3 (9)	4.37
C_{43}	0.3493 (11)	−0.0672 (11)	−0.3791 (27)	5.9 (12)	6.5 (12)	4.2 (11)	−0.2 (10)	4.6 (10)	−0.8 (10)	5.56

[a] Standard deviations occurring in the last significant figure are given in parentheses. [b] Anisotropic temperature factors are of the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] B's are isotropic thermal parameters equivalent to the anisotropic tensors. All B_{ij} and B values are in Å^2.

Table II. Molecular Dimensions

Atoms		Atoms	
	A. Interatomic Distances, A		
Mo(1)–Mo(2)	2.183 (2)	Mo(2)–C(32)	2.51 (2)
Mo(1)–C(11)	3.29 (2)	Mo(2)–C(33)	2.22 (2)
Mo(1)–C(12)	2.52 (2)	Mo(2)–C(41)	2.35 (2)
Mo(1)–C(13)	2.24 (2)	Mo(2)–C(42)	2.35 (2)
Mo(1)–C(21)	2.29 (2)	Mo(2)–C(43)	2.28 (2)
Mo(1)–C(22)	2.31 (2)	C(11)–C(12)	1.35 (3)
Mo(1)–C(23)	2.30 (2)	C(12)–C(13)	1.36 (3)
Mo(1)–C(31)	2.22 (2)	C(21)–C(22)	1.36 (3)
Mo(1)–C(32)	2.53 (2)	C(22)–C(23)	1.40 (3)
Mo(1)–C(33)	3.21 (2)	C(31)–C(32)	1.40 (3)
Mo(2)–C(11)	2.24 (2)	C(32)–C(33)	1.36 (3)
Mo(2)–C(12)	2.48 (2)	C(41)–C(42)	1.38 (3)
Mo(2)–C(13)	3.23 (2)	C(42)–C(43)	1.34 (3)
Mo(2)–C(31)	3.22 (2)	C–C (av)	1.37
	B. Angles, Deg		
C(11)–C(12)–C(13)	144 (3)	C(31)–C(32)–C(33)	128 (2)
C(21)–C(22)–C(23)	120 (2)	C(41)–C(42)–C(43)	122 (2)

Unfortunately, the difference map still had a noise level comparable to the expected magnitudes of hydrogen atoms. The highest peak was still the one on the $\bar{4}$ axis (1.15 e/Å^3). Neither map showed any indication of neglected or misplaced heavy atoms nor any suggestion of disorder. The full map gave evidence of considerable thermal motion in the allyl groups, particularly at C(12).

Since the hydrogen atoms provide a significant fraction of the total electron density (11.4%), it was deemed wise to include them, at calculated positions, in the final cycles of refinement. All C–H distances were taken as 1.0 Å. The directions of the C–H bonds on the terminal carbon atoms were taken as 120 and 240° to the C–C bond. The C–H direction at the center carbon atom was taken as the direction of a line bisecting the C–C–C angle. On this basis, positional parameters were computed for the hydrogen atoms; these were held fixed in all subsequent cycles of refinement. In each cycle, each hydrogen atom was assigned a fixed isotropic thermal parameter 1.0 Å^2 greater than the value of the equivalent isotropic thermal parameter of the carbon atom to which it is attached.[22]

After several cycles of refinement including the hydrogen atoms in the way just explained, the residual dropped very slightly (to 0.0680) and some small but significant shifts occurred in the carbon atom positions. Analysis of the data at this point showed that there was a definite dependence of $w(|F_o| - |F_c|)^2$ on $\lambda^{-1} \sin \theta$. The estimated standard deviation of an observation of unit weight was 2.48, meaning the $\sigma(F)$'s were too small. Standard deviations were changed to $\sigma(F) = 0.356(\sin \theta/\lambda) + 0.24$ if $\sin \theta/\lambda \leqslant 0.37$ and $\sigma(F) = 0.720(\sin \theta/\lambda) - 2.30$ for $\sin \theta/\lambda > 0.37$. Several cycles of refinement now reduced R_1 to 0.067, and R_2 to 0.049. The estimated standard deviation of an observation of unit weight was now 1.023 and $w(|F_o| - |F_c|)^2$ was essentially independent of $\lambda^{-1} \sin \theta$ and F_o. All bond lengths and angles appeared reasonable, except for the angle C(11)–C(12)–C(13), which will be discussed later. A final difference Fourier map was similar to those discussed earlier and had a standard deviation 0.22 e/Å^3. During the final cycle no parameter shifted by more than one-fifth of its estimated standard deviation. A table of the observed and the final calculated structure factors is available.[23]

Results

The fractional coordinates and anisotropic thermal parameters are given in Table I. The structure is depicted in Figure 1, where the numbering scheme for the atoms is also shown. Table II gives interatomic distances and angles.[24] The molecule consists of discrete dimeric units as expected. Two of the allyl ligands are essentially bridging the metals, and two are terminal. Intermolecular contacts were calculated with ORTEP[25] and none was found to be abnormally short. The shortest carbon–carbon contact was 3.696 Å, the shortest carbon–hydrogen contact 2.878 Å, and the shortest hydrogen–hydrogen contact 2.485 Å.

Discussion

A discussion of the structure of $Mo_2(C_3H_5)_4$ naturally centers around two main points: (1) the structure itself and a comparison with the homologous chromium compound and (2) the relationship of this compound to other dinuclear molybdenum(II) species.

The molecular structures of $Mo_2(C_3H_5)_4$ and $Cr_2(C_3H_5)_4$ are qualitatively identical, and thus their crystals are isostructural. The latter fact was actually assumed as a working hypothesis to expedite the solution and refinement of the $Mo_2(C_3H_5)_4$ structure. Since the structure in question is so novel, indeed unique, its verification in a compound homologous to $Cr_2(C_3H_5)_4$,

---

(22) The scattering factors for the hydrogen atoms were taken from R. Mason and G. B. Robertson, "Advances in Structural Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Wiley, New York, N. Y., 1966, p 57.

(23) The table of observed and final calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(24) These were calculated with DTEMP, a distance and angle program written by Dr. M. D. Laprade.

(25) C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations."

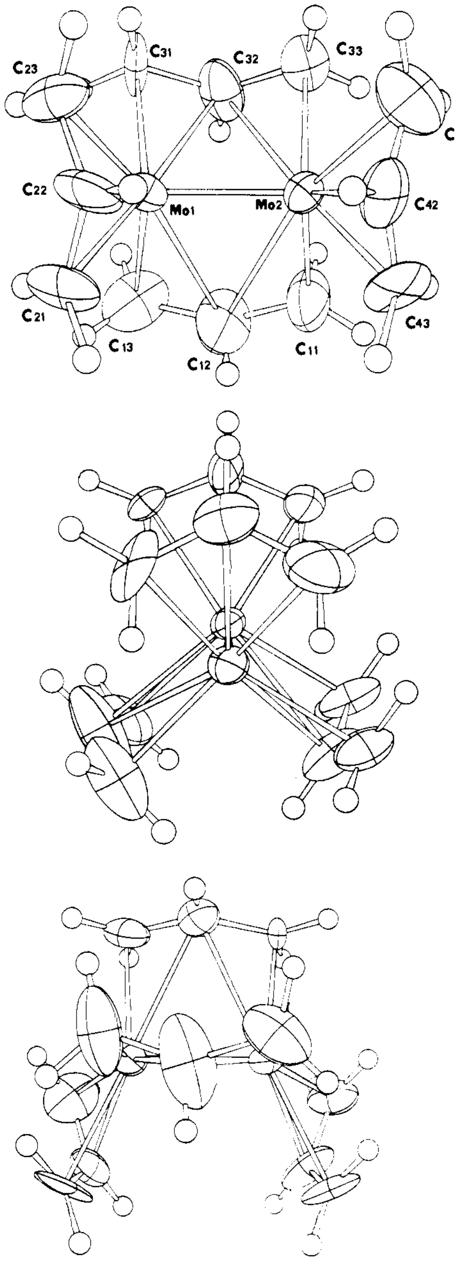

Figure 1. Three views of the $Mo_2(C_3H_5)_4$ molecule. The atom numbering scheme is given in the upper view. Atoms other than hydrogen atoms are represented by thermal vibration ellipsoid contours at the 50% probability level, while the hydrogen atoms are depicted as spheres of radius 0.1 Å.

where it was first found, is in itself of interest. The structure of the chromium compound was based on a somewhat restricted set (656 independent reflections) of photographically recorded data and refined to a final conventional (1.0, unit weighted) *R* factor of 0.112; the estimated deviations in the positional parameters of the carbon atoms were high (0.06 Å) and reported C–C distances covered a rather large range, 1.31–1.57 Å. Although the possibility of gross error in the chromium structure appeared slight, a confirmation investigation, leading to more precise parameters, seemed desirable.

As far as we are aware, only in these two isostructural molecules has the symmetrical bridging allyl group been found. It is interesting that its dimensions do not differ significantly from those of the well-known type of h^3-C_3H_5 group, further discussion of which is given later. It may be noted that a highly unsymmetrical type of bridging allyl has been observed in the compounds $[Pt(acac)(C_3H_5)]_2$[26] and $[PtCl(C_3H_5)]_4$.[27] In these cases there is a Pt–C σ bond to one of the terminal carbon atoms, while the remaining two carbon atoms constitute an olefin which is μ bonded to the other platinum atom.

The two molecules $Cr_2(C_3H_5)_4$ and $Mo_2(C_3H_5)_4$ are *strictly* stoichiometrically analogous molecules containing metal atoms of different transition series in which there are very strong, multiple metal-to-metal bonds. This is the first such pair for which structural data are available, and thus it affords the opportunity to make a type of comparison never before possible.[28] Heretofore, the nearest approaches to such a pair have always involved some difference, as for example in oxidation state and charge (*viz.*, $Mo_2Cl_8^{4-}$ or $Tc_2Cl_8^{3-}$ *vs.* $Re_2Cl_8^{2-}$) or in the presence of additional ligands (*viz.*, $Cr_2(O_2CCH_3)_4(H_2O)_2$ *vs.* $Mo_2(O_2CCH_3)_4$) whose effect on the structural parameters is uncertain. In the case of end groups, it is actually very likely, *a priori*, that their presence has a decided effect on the M–M bonding, so a comparison of the M–M distances in $Cr_2(O_2CCH_3)_4(H_2O)_2$ and $Mo_2(O_2CCH_3)_4$ cannot lead straightforwardly to a meaningful comparison of the relative propensities of Cr^{II} and Mo^{II} to form multiple M–M bonds under strictly analogous circumstances.

The attempt to compare the M–M distances in a pair such as $Cr(O_2CCH_3)_4(H_2O)_2$ (Cr–Cr = 2.36 Å) and $Mo_2(O_2CCH_3)_4$ (Mo–Mo = 2.11 Å) leads to ambiguities not easily resolved. The distances show quite clearly that the Mo–Mo bond is far stronger than the Cr–Cr bond, even though both are quadruple in character. However, it is difficult to decide, if not actually meaningless to ask, whether the water molecules are attached to the chromium atoms because the Cr–Cr interaction is relatively weak or whether the weakness of the Cr–Cr interaction makes possible the attachment of the water molecules. From a practical point of view it must simply be said that under the circumstances, a fair comparison of the intrinsic M–M bonding tendencies of the two metal atoms cannot be made using these two stoichiometrically different molecules.

In the $M_2(C_3H_5)_4$ molecules, however, the M–M distances seem to suggest rather directly that the two metals have closely similar tendencies to form multiple M–M bonds. Thus, the difference between the Mo–Mo and Cr–Cr distances is 0.21 Å, while the difference between the ring planes in $(h^5\text{-}C_5H_5)_2Ru$ and $(h^5\text{-}C_5H_5)_2Fe$, which ought to provide some rough but useful measure of the difference in diameters of divalent first and second transition series elements, is about 0.36 Å. Again, the M–C distances in $Cr(CO)_6$ and $Mo(CO)_6$ differ by 0.14, which would suggest that bonds of comparable strength between pairs of the metal atoms might differ by ~0.3 Å. In conclusion, then, it would appear that in the M_2-

---

(26) W. S. McDonald, B. E. Mann, G. Raper, B. L. Shaw, and G. Shaw, *Chem. Commun.*, 1254 (1969).

(27) G. Raper and W. S. McDonald, *ibid.*, 655 (1970).

(28) There are, of course, several cases of strict stoichiometric analogs among molecules with essentially single bonds. Since this paper was submitted, the structures of $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ were published: L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970). The Cr–Cr and Mo–Mo single bond lengths, 2.97 and 3.12 Å, respectively, differ by about the same amount as do the quadruple bond lengths in the $M_2(C_3H_5)_4$ molecules.

Table III. Dimensions of *Pentahapto*allyl Groups in Various Compounds

Compound	Ref	Type of data	C–C(av), Å	Esd of C–C,[a] Å	C–C–C[b] angle, deg	H atoms included in refinement
$Mo_2(C_3H_5)_4$	*c*	Diff	1.41	0.03		No
$Mo_2(C_3H_5)_4$	*c*	Diff	1.37	0.03	128 (123)[i]	Yes
$[PdCl(C_3H_5)_2]$	*d*	Film	1.36	0.045	129	No
$[PdCl(C_3H_5)_2]$	*e*	Film	1.376	0.015	120	Yes
$[PdCl(C_4H_8)]_2$	*f*	Diff	1.36	0.03	112	No
$[PdCl(C_7H_{13})]_2$	*g*	Diff	1.41	0.0	118	No
$[PdBr(C_7H_{11})]_2$	*h*	Diff	1.40	0.03	*j*	No

[a] The average value of the esd of an individual C–C distance. [b] The average of all allyl C–C–C angles in the molecule. [c] Present work. [d] W. E. Oberhausli and L. F. Dahl, *J. Organometal. Chem.*, **3**, 43 (1965). [e] A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965). [f] R. Mason and A. G. Wheeler, *J. Chem. Soc.*, 2549 (1968). [g] R. Mason and A. G. Wheeler, *ibid.*, 2543 (1968). [h] B. T. Kilbourn, R. H. B. Mars, and P. G. Owston, *Chem. Commun.*, 1438 (1968). [i] The lower value, in parentheses, is obtained if the anomalously high angle of 144° is omitted in computing the average. [j] Not comparable to others since it is in a ring.

$(C_3H_5)_4$ molecules chromium and molybdenum exhibit quite comparable abilities to engage in multiple M–M bonding, though chromium may be slightly the inferior.

The Mo–Mo distance in $Mo_2(C_3H_5)_4$, 2.18 Å, is somewhat longer than the Mo–Mo distances found in $Mo_2(O_2CCH_3)_4$ and $Mo_2Cl_8^{-4}$, namely, 2.11[8] and 2.14 Å,[9] respectively. Nevertheless, it seems reasonable to believe that an Mo–Mo bond of essentially similar character exists in all three species. Because of the low symmetry and relatively complex structure of $Mo_2(C_3H_5)_4$, it is not possible to set forth a qualitatively simple scheme for quadruple bonding as has been done in the other cases, but, nevertheless, a strong quadruple bond may be presumed to exist.

In conclusion, a few words may be said concerning the dimensions of the allyl groups in this molecule. Each of the four is symmetrical within the uncertainties; no pair of C–C distances differs by more than 0.04 Å, while each individual distance has an esd of 0.03 Å. The mean of the eight C–C distances is 1.37 Å. In attempting to compare this with results for other h^3-allyl species, two problems arise. First, despite the fact that a considerable number of h^3-allyl)–metal complexes have been examined crystallographically, only a few structures have been refined to a level of accuracy comparable to the present one—which is not itself particularly accurate. In Table III the present results and a few from the literature which are reasonably similar in accuracy are listed. It will be seen that two sets of mean C–C distances are reported, one centering around 1.37 and the other around 1.41 Å. We find that when the $Mo_2(C_3H_5)_4$ structure is refined with hydrogen atoms entirely omitted, the mean C–C distance comes out at 1.41 Å, whereas when H atoms are included in the refinement (though not themselves refined), the mean C–C distance is reduced to 1.37 Å. Unfortunately, the literature results cannot be categorized in this simple way, as Table III shows, although the uncertainties are sufficiently large that the possibility of such a correlation cannot be considered entirely closed. It would be interesting if the influence of including H atoms on the C–C distances could be investigated independently in another case, and it would also be valuable to have some further structural results on $(h^3\text{-}C_3H_5)M$ systems with lower esd's for general comparison purposes.

The C–C–C angles in the allyl groups seem quite reasonable except for the C(11)–C(12)–C(13) angle which comes out as 144 (3)°. We do not believe that this result should be taken literally because of the high thermal vibration amplitude also found for C(12). Examination of the literature shows that the problem of large thermal vibrations has rather consistently been troublesome in structural studies of (h^3-allyl)metal compounds. A particularly interesting comparison is that between the values of the angle found in $[PdCl(C_3H_5)]_2$ using data at 25[29] and −140°,[30] the apparent value of the angle changes from 128.6 ± 3.3° at 25° to 119.8 ± 0.9° at −140°.

Acknowledgment. We thank the National Science Foundation for funds used to purchase the diffractometer. We benefited from the help and advice of Dr. B. G. DeBoer and Mr. James Smart.

(29) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, **3**, 43 (1965).

(30) A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965).