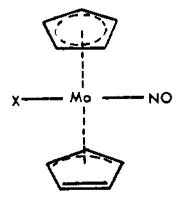
Highly Unsymmetrical Cyclopentadienylmetal Groups. The Structure of Bis(cyclopentadienyl)methylnitrosylmolybdenum[1]

F. A. Cotton*[2a] and G. A. Rusholme[2b]

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received June 1, 1971

Abstract: Bis(cyclopentadienyl)nitrosylmethylmolybdenum crystallizes in the monoclinic space group $P2_1$ (No. 4) with $a = 7.044$ (6) Å, $b = 11.26$ (1) Å, $c = 13.60$ (1) Å, $\beta = 94.60$ (2)°, and $Z = 4$. A complete three-dimensional single crystal X-ray analysis, based on 2475 independent reflections collected in two stages on a General Electric XRD-5 manual and General Electric XRD-6 automatic diffractometers, has been completed. The two independent molecules are approximate mirror images of each other and their structures are very similar to that of tricyclopentadienylnitrosylmolybdenum. The principal structural features are (1) linear Mo–N–O systems, 178 (1) and 178 (2)°, with short Mo–N bond distances, 1.75 (1) and 1.76 (1) Å, and elongated N–O distances, 1.23 (1) and 1.21 (1) Å, indicative of substantial back donation from the metal to the ligand. (2) The two *polyhapto*cyclopentadienyl groups per independent molecule exhibit asymmetric bonding to the metal atom with two relatively short, one intermediate, and two long Mo–C bond distances. The mean values of these short, medium, and long distances are 2.346, 2.443, and 2.604 Å, respectively. (3) The (h^1-C_5H_5) ring of $(C_5H_5)_3MoNO$ is here replaced by CH_3. The two independent M–CH_3 bond lengths are 2.20 (2) and 2.20 (1) Å which are markedly shorter than other reported Mo–C σ bonds, for reasons which are not obvious. The significance of the structure reported here is that it verifies the unusual, skew *polyhapto*cyclopentadienylmolybdenum structure found in $(C_5H_5)_3MoNO$ and, in conjunction with nmr work reported elsewhere, confirms previously stated views as to the dynamical processes responsible for the complex temperature dependence of the pmr spectra of $(C_5H_5)_3MoNO$.

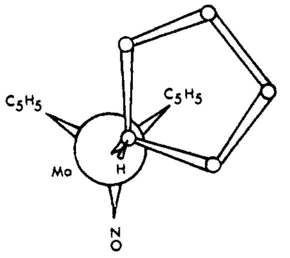
Compounds of the type $(C_5H_5)_2Mo(NO)X$, where X is a univalent group, were first prepared by King[3] who reported those with X = I and CH_3. Each compound at room temperature was found to have only a single, sharp pmr line for the ten cyclopentadienyl protons, and this line was said to remain sharp down to −55° for the iodo compound. King proposed that the molecules are fluxional ones, with the instantaneous structure I, and went on to postulate a combination of interchange of the two modes of ring-to-metal bonding and rapid rotation ("ring whizzing") of the π-allylic (trihapto) ring to explain the pmr equivalence of the ten protons.[4]



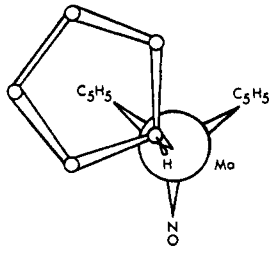
(I)

Later, the compound $(C_5H_5)_3Mo(NO)$ was reported[5] and shown to be a fluxional one in which all 15 protons are nmr equivalent at room temperature. It was further shown that in the temperature range from about 0 to about −50° one of the rings loses its time-average equivalence to the other two and displays the characteristic spectrum of a *monohapto*cyclopentadienyl ring. Finally, between about −50 and −110° the resonance due to the ten protons of the other two rings was observed to broaden and separate into two separate signals of equal intensity which then became sharp. While these observations are not intrinsically incompatible with King's postulate, they do not actually substantiate it and can be explained in an entirely different manner.

An X-ray crystallographic study[6] of $(C_5H_5)_3MoNO$ showed that while it does contain one h^1-C_5H_5 ring, the other two are substantially equivalent to each other in their relationship to the metal atom and by no means distinguishable as h^3-C_5H_5 and h^5-C_5H_5 types. The appearance of separate nmr signals for these two rings at lower temperatures can be attributed to the slowness of hindered rotation of the h^1-C_5H_5 ring about the Mo–C bond with the preferred rotamers being (as in the crystal) IIa and IIb. It has also been demonstrated[7] that neither $(C_5H_5)_2Mo(NO)I$ nor $(C_5H_5)_2Mo(NO)$-CH_3 shows any broadening of the cyclopentadienyl proton resonance line down to −110°. If in $(C_5H_5)_3$-MoNO, the broadening and then complete separation of the signal due to the two non-(h^1-C_5H_5) rings had been attributable to a slowing of (h^3-C_5H_5)/(h^5-C_5H_5) interchange, it would be difficult to understand the complete absence of any broadening down to −110°



(IIa)



(IIb)

---

[1] Work supported by the National Science Foundation, under Grant No. GP 7034X.

[2] (a) Address correspondence to Department of Chemistry, Texas A and M University, College Station, Texas 77843; (b) NATO Fellow, 1970–1972.

[3] R. B. King, *Inorg. Chem.*, 7, 90 (1968).

[4] The second postulate is superfluous.

[5] F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, 90, 6232 (1968).

[6] J. L. Calderon, F A. Cotton, and P. Legzdins, *ibid.*, 91, 2528 (1969)

[7] J. L. Calderon and F. A. Cotton, *J. Organometal. Chem.*, 30, 377 (1971).

in either of the other two compounds, especially $(C_5H_5)_2Mo(NO)CH_3$. Thus, it seemed very likely indeed that the $(C_5H_5)_2Mo$ portion of the three $(C_5H_5)_2$-$Mo(NO)X$ molecules has the same structure in each case and that this is not an $(h^3\text{-}C_5H_5)(h^5\text{-}C_5H_5)Mo$ arrangement.

In order to verify this conclusion and to examine more closely the structural arrangement which does prevail in these $(C_5H_5)_2Mo$ moieties, the present X-ray crystallographic investigation of $(C_5H_5)_2Mo(NO)CH_3$ was undertaken. The two non-$(h^1\text{-}C_5H_5)$ rings in $(C_5H_5)_3MoNO$ were each found to have a highly unsymmetrical relationship to the molybdenum atom, such that the ten Mo–C distances range from 2.32 to 2.68 Å.

Experimental Section

A sample of $(C_5H_5)_2Mo(NO)CH_3$ was kindly supplied by Mr. J L. Calderon. A crystallographic sample with dimensions 0.24 × 0.46 × 0.04 mm along *a*, *b*, and *c*, respectively, was cleaved from the brown, plate-like crystalline product and mounted in a sealed glass capillary to avoid air decomposition.

Optical examination and a reciprocal lattice symmetry of C_{2h} indicated that the crystals belonged to the monoclinic system. The systematic absences $\{0k0\} = 2n + 1$ observed in Weissenberg and precession photographs showed that the space group was either $P2_1/m$ or $P2_1$ (No. 11 and No. 4, respectively). The unit cell dimensions were obtained from least-squares analysis of accurately measured angular settings of 26 high-angle reflections. These were made with a General Electric four-circle diffractometer using Mo Kα radiation; they are $a = 7.044\ (6)$ Å, $b = 11.26\ (1)$ Å, $c = 13.60\ (1)$ Å, and $\beta = 94.60\ (2)°$. The uncertainties are estimates of precision.

The observed density at 24° measured by flotation in aqueous zinc nitrate solution was 1.68 (2) g cm^{-3}, which is identical with the calculated value of 1.68 g cm^{-3} for four molecules of bis(cyclopentadienyl)nitrosylmethylmolybdenum (mol wt 271.2) per unit cell.

The crystal was aligned on a General Electric XRD-5 manual diffractometer so that *b* was coincident with the ϕ axis of the diffractometer. Mo Kα radiation filtered by 0.04-mm niobium foil was used to measure 2023 independent reflections (index sets $\bar{h}kl$ and hkl) within the sphere $2\theta \leq 50°$. Intensities were measured by a scintillation counter with the pulse-height discriminator set to accept 95% of the Mo Kα peak with the window centered on the Mo Kα peak. The distances from the crystal to the source and from the crystal to the 2° circular screening aperture were 5.73 and 7.05 in., respectively. A moving crystal-moving counter scan technique was employed with a scan range of 2.66° to conform with the mosaic spread of the crystal and the take-off angle of 2°. The scan rate was 4°/min. Stationary background counts of 10 sec were taken at each extreme of the θ–2θ range. From the readings, the low-angle background counts being corrected for K edge absorption by the filter, the intensity, *I*, assuming a linear change in background between the two limits of the scan, is given by $I = P - [(B_1 + B_2)T_P/2T_B]$; *P* is the scanned count, B_1 and B_2 are the stationary background counts, and T_P and T_B are the counting times of the scan and background, respectively.

Periodic checks of six reference reflections indicated an overall decline in intensity of ~8%. The decline was greatest during the initial stages of data correction, while only statistical variation was observed toward its conclusion. Plots of reference intensity *vs.* time had the same form for all reference reflections. The data were scaled to the intensities at the initiation of data collection by fitting linear portions to the mean of these plots.

The corrected intensities were used to calculate structure factor amplitudes on a relative scale using the equation $|F_o| = (I/Lp)^{1/2}$, where Lp = Lorentz–polarization factor. Their estimated standard deviations, $\sigma_F = [\sigma_I^2 + (0.02I)^2]^{1/2}(4ILP)^{-1/2}$, were also computed; $\sigma_I = [P + (T_P/2T_B)^2(B_1 + B_2)]^{1/2}$. The 202 reflections for which $F_o^2/\sigma(F_o^2) < 1.0$ were rejected from further consideration.

By consideration of the vectors within the three-dimensional Patterson synthesis, it was possible to reject the centrosymmetric space group, $P2_1/m$. The two independent metal positions for the space group $P2_1$ were located from the Patterson synthesis and two cycles of least-squares analysis on these positions gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.182$ and $R_2 = \Sigma w_F||F_o| - |F_c||^2/\Sigma w_F|F_o|^2 = 0.283$ where the weights were $w_F = \sigma_F^{-2}$. The coordinates of the remaining 26 nonhydrogen atoms were determined from an observed Fourier synthesis phased on these metal parameters. Three further cycles of refinement of all atom parameters reduced the residuals to $R_1 = 0.075$ and $R_2 = 0.070$. All atoms were then assigned anisotropic thermal parameters and three cycles of refinement of all parameters resulted in convergence with $R_1 = 0.056$ and $R_2 = 0.057$. However, as the errors in the parameters were still large, high angle data $50° < 2\theta < 65°$ plus 22 interdata shell-scaling reflections were collected on a General Electric XRD-6 automatic diffractometer with Mo Kα radiation filtered through 0.05-mm Zr foil. These data were collected from the same crystal as had been used on the manual diffractometer after a check had shown that no significant crystal decomposition had occurred. A similar mode of data collection was employed with the principal difference that the scan range was now variable, being equal to 2° plus the $\alpha_1\alpha_2$ splitting at the relevant $2\theta_{hkl}$ value. The scan rate was 2°/min and each background was counted for 20 sec. Variation of five low-angle reference reflections during data collection was random with time. After correction for geometric effects in the same manner as before, it was found that there had been sporadic malfunctioning of the scaling circuit. It was therefore necessary to apply strict rejection criteria to these data. Reflections were accepted if: (1) $|B_1 - B_2| < 3(B_1 + B_2)^{1/2}$; (2) at least two independent measurements of F_o^2 which differed by less than $3\sigma(F_o^2)$ were obtained; (3) $F_o^2 > 3\sigma(F_o^2)$. The two independent data sets, containing a total of 2475 unique reflections, were scaled together using the mean value of the factors between common reflections. Two further cycles of refinement in which all parameters including individual scale factors for each data set and unit weighting for all data were varied indicated a dependence between $w_F\Delta^2$ and F_o. Therefore, prior to the final four cycles of least-squares refinement an empirical weighting scheme $\sigma = [1.70 + 0.3077(F_o - 33.0)]^{1/2}$ if $F_o > 33.0$, $\sigma = (1.70)^{1/2}$ if $33.0 > F_o > 18.0$, and $\sigma = [1.70 - 0.3381(F_o - 18.0)]^{1/2}$ if $F_o < 18.0$ was used thereby removing this dependence and reducing the standard deviation of an observation of unit weight to 0.98. The final residuals were $R_1 = 0.062$ and $R_2 = 0.068$. The two independent scale factors which had been used for each data set were equal within 1σ and all parameter shifts were less than 0.1σ. No absorption correction was applied to the data ($\mu = 11.65$ cm^{-1}). The final difference Fourier synthesis had no maxima greater than 0.6 e/Å^3 except for four maxima of approximately 1.2 e/Å^3 immediately adjacent to the metal positions.

All cycles of least-squares refinement were of full-matrix type. Atomic scattering factors[8] were corrected for the real and imaginary parts of anomalous dispersion.[9]

Computer programs employed were: PICK2 (J. A. Ibers), for refining cell constants and generating angular settings for data collection; DIFDAR (A. S. Parkes) and REDUCE (B. G. DeBoer, J. G. Norman, Jr.), for data reduction; FORDAP (A. Zalkin), for Patterson and Fourier synthesis; SFIX (local version of C. T. Prewitt's SFLS-5), for least-squares analysis based on the minimization of the function $D = w_F(|F_o| - |F_c|)^2$; MGEOM (J. S. Wood), for least-squares planes; STAN1 (B. G. DeBoer), for molecular geometry; and ORTEP (C. K. Johnson), for illustrations.

Results[10]

The molecular structure and atom numbering system are shown in Figure 1, a projection on the (100) plane. Figure 2 shows the molecular packing viewed along the *b* axis. Figure 3 shows each of the four cyclopentadienyl rings with the C–C and Mo–C distances recorded to facilitate comparisons. Final atomic positional and thermal parameters, with standard deviations derived from the inverse matrix of the final least-squares refinement cycle, are given in Table I. Inter-

---

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

(9) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(10) A table of the observed and final calculated structure amplitudes (in electrons), multiplied by 10, for $(C_6H_5)_2MoNOCH_3$ 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 check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Table I. Final Positional and Thermal Parameters[a,b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo1	0.6835 (1)	0.0	0.36625 (6)	2.90 (3)	3.42 (4)	2.92 (3)	0.41 (3)	0.35 (3)	0.34 (3)
C1	0.465 (4)	0.027 (2)	0.520 (2)	14 (2)	5 (1)	6.9 (9)	−1 (1)	8 (1)	−1.3 (8)
C2	0.674 (4)	0.065 (2)	0.537 (1)	13 (2)	11 (2)	1.7 (5)	5 (1)	−0.1 (7)	−0.0 (7)
C3	0.700 (3)	0.155 (2)	0.482 (1)	8 (1)	9 (1)	5.5 (8)	−2.2 (9)	1.7 (8)	−4.7 (9)
C4	0.534 (3)	0.175 (1)	0.421 (1)	9 (1)	3.9 (6)	4.3 (6)	1.1 (7)	1.2 (7)	−0.7 (5)
C5	0.400 (2)	0.100 (2)	0.452 (1)	5.7 (8)	7 (1)	5.9 (8)	1.3 (7)	1.9 (6)	−2.5 (8)
C6	0.391 (3)	−0.130 (2)	0.320 (1)	5.2 (8)	11 (2)	6.5 (9)	−3.1 (9)	1.7 (7)	−5 (1)
C7	0.563 (3)	−0.196 (1)	0.311 (1)	13 (2)	3.4 (7)	6.8 (9)	−0.2 (8)	3 (1)	−0.2 (6)
C8	0.665 (2)	−0.142 (1)	0.240 (1)	6.2 (7)	3.8 (6)	4.7 (6)	0.0 (5)	2.2 (6)	0.1 (5)
C9	0.562 (3)	−0.044 (1)	0.2056 (9)	7.8 (9)	5.9 (6)	3.3 (5)	−1.3 (6)	−0.0 (5)	−0.7 (5)
C10	0.396 (3)	−0.034 (2)	0.254 (2)	6.2 (9)	8 (1)	8 (1)	2.6 (8)	−4.2 (8)	−4.5 (9)
C11	0.890 (2)	−0.119 (2)	0.447 (1)	5.0 (7)	8 (1)	6.2 (8)	1.7 (7)	0.6 (6)	2.8 (7)
N1	0.876 (1)	0.067 (1)	0.3140 (8)	3.3 (4)	4.7 (5)	5.5 (5)	0.1 (4)	0.4 (4)	0.9 (4)
O1	1.009 (1)	0.112 (1)	0.2740 (9)	4.2 (4)	7.5 (7)	8.1 (6)	−0.2 (4)	1.8 (4)	2.9(5)
Mo2	0.8407 (1)	−0.5778 (1)	0.10336 (6)	2.47 (3)	2.71 (3)	2.67 (3)	0.34 (3)	0.33 (2)	0.28 (3)
C21	0.934 (2)	−0.583 (2)	0.2796 (7)	6.0 (6)	5.4 (6)	2.0 (3)	−1.1 (7)	0.5 (4)	0.3 (5)
C22	1.116 (2)	−0.597 (1)	0.2447 (8)	5.5 (6)	5.4 (8)	3.1 (4)	0.1 (5)	−0.5 (4)	−1.2 (5)
C23	1.146 (2)	−0.493 (2)	0.1906 (9)	6.2 (7)	5.2 (7)	4.2 (5)	0.1 (7)	1.4 (5)	−2.2 (6)
C24	0.988 (2)	−0.418 (1)	0.1932 (9)	5.9 (7)	3.2 (6)	3.7 (5)	−1.9 (4)	−0.2 (5)	−0.4 (4)
C25	0.862 (2)	−0.473 (1)	0.2501 (9)	6.5 (7)	5.3 (8)	3.0 (4)	0.7 (6)	0.8 (5)	−1.2 (5)
C26	1.080 (2)	−0.742 (1)	0.0471 (9)	3.1 (5)	5.1 (7)	4.6 (6)	0.9 (4)	−0.2 (4)	−0.7 (5)
C27	0.880 (2)	−0.770 (1)	0.0252 (8)	5.0 (6)	3.1 (5)	3.2 (4)	−0.1 (4)	0.4 (4)	−0.2 (4)
C28	0.807 (2)	−0.685 (1)	−0.0431 (8)	4.3 (5)	5.1 (6)	2.5 (4)	−0.1 (5)	−0.7 (4)	−1.1 (4)
C29	0.956 (2)	−0.601 (1)	−0.0540 (8)	4.6 (5)	3.2 (6)	3.2 (4)	0.3 (4)	0.9 (4)	−0.6 (3)
C30	1.121 (2)	−0.640 (1)	0.0010 (8)	3.8 (5)	4.4 (6)	3.5 (5)	−0.6 (4)	0.0 (4)	−0.0 (4)
C31	0.620 (1)	−0.690 (1)	0.1617 (9)	2.0 (4)	5.7 (7)	4.8 (5)	−0.8 (5)	0.4 (4)	1.5 (5)
N2	0.651 (1)	−0.486 (1)	0.0590 (6)	3.2 (3)	4.3 (5)	3.4 (3)	0.1 (4)	0.4 (3)	0.8 (4)
O2	0.518 (1)	−0.422 (1)	0.0308 (8)	4.9 (4)	6.0 (5)	7.6 (6)	2.4 (4)	0.7 (4)	1.4 (5)

[a] Numbers in parentheses are esd's in the last figure quoted for all tables. [b] The form of the temperature factor expression is $\exp[-\frac{1}{4}\cdot(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

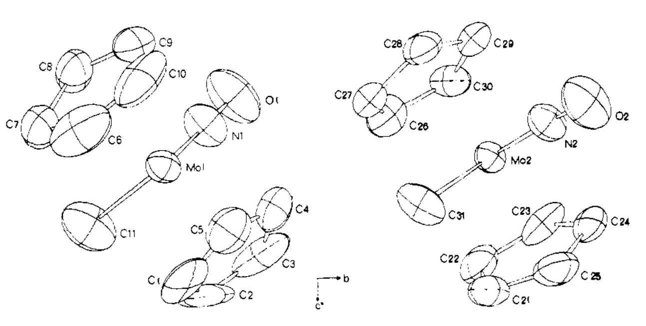


Figure 1. A projection of the two molecules constituting the asymmetric unit on the (100) plane. The numbering scheme is defined.

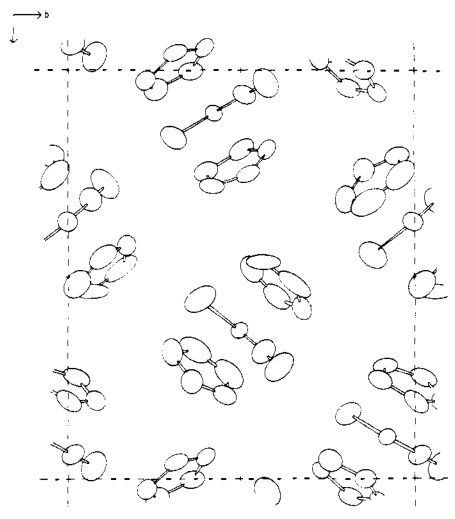


Figure 2. An [100] projection showing the packing.

atomic distances and angles are given in Table II. Table III gives the best weighted least-squares plane

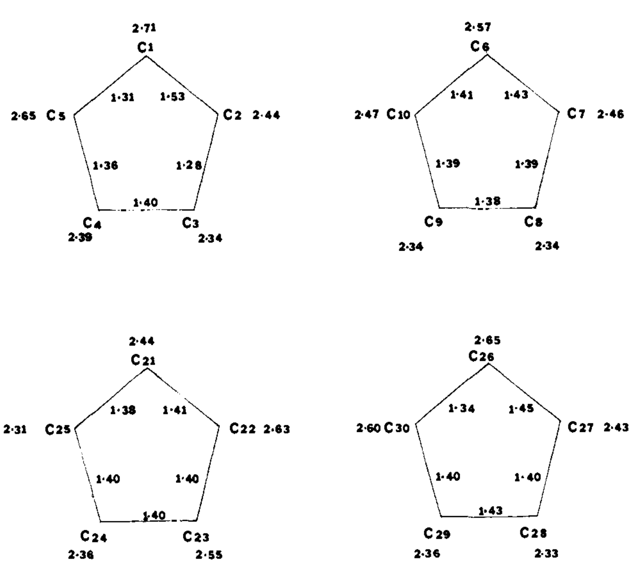


Figure 3. The four crystallographically independent C_5H_5 rings. Numbers indicate the C–C and Mo–C distances, in ångströms.

for each cyclopentadienyl ring together with the distances of pertinent atoms from these planes. Table IV compares the Mo–C distances here determined with those reported for tris(cyclopentadienyl)nitrosylmolybdenum.

Discussion

The two crystallographically independent molecules of $(C_5H_5)_2Mo(NO)CH_3$, Figure 1, pack as monomeric molecular units as shown in Figure 2 with no abnormal intermolecular contacts. In fact, there are only three contacts less than 3.5 Å; O_2–C_{27} 3.33 (2) Å, O_1–C_{21} 3.48 (2) Å, and O_1–C_{22} 3.40 (2) Å, which are comparable to the sum of the van der Waals radii, 3.4 Å. Pre-

Table II

Atoms	Distance	Atoms	Distance
	Intramolecular Bond Distances (Å)		
Mo1–C1	2.71 (2)	Mo2–C21	2.43 (1)
Mo1–C2	2.44 (1)	Mo2–C22	2.63 (1)
Mo1–C3	2.34 (1)	Mo2–C23	2.55 (1)
Mo1–C4	2.39 (2)	Mo2–C24	2.36 (1)
Mo1–C5	2.65 (2)	Mo2–C25	2.31 (1)
Mo1–C6	2.57 (2)	Mo2–C26	2.65 (1)
Mo1–C7	2.46 (2)	Mo2–C27	2.43 (1)
Mo1–C8	2.34 (1)	Mo2–C28	2.33 (1)
Mo1–C9	2.34 (1)	Mo2–C29	2.36 (1)
Mo1–C10	2.47 (1)	Mo2–C30	2.60 (1)
Mo2–C11	2.20 (2)	Mo2–C31	2.20 (1)
Mo1–N1	1.75 (1)	Mo2–N2	1.76 (1)
N1–O1	1.23 (1)	N2–O2	1.21 (1)
C1–C2	1.53 (4)	C21–C22	1.41 (2)
C1–C5	1.31 (2)	C21–C25	1.38 (2)
C2–C3	1.28 (3)	C22–C23	1.40 (2)
C3–C4	1.40 (3)	C23–C24	1.40 (2)
C4–C5	1.36 (2)	C24–C25	1.37 (2)
C6–C7	1.43 (3)	C26–C27	1.45 (2)
C6–C10	1.41 (2)	C26–C30	1.34 (2)
C7–C8	1.39 (2)	C27–C28	1.40 (2)
C8–C9	1.38 (2)	C28–C29	1.43 (2)
C9–C10	1.39 (3)	C29–C30	1.40 (2)
	Inter- and Intramolecular Nonbonded Contacts Less Than 3.5 Å		
C1–C6	3.26 (2)	O1–C21[a]	3.48 (2)
C2–C11	2.90 (3)	O1–C22[a]	3.40 (2)
C2–N1	3.45 (2)	C21–C31	2.89 (2)
C3–C11	3.41 (3)	C22–C26	3.14 (2)
C3–N1	2.86 (2)	C22–C30	3.36 (2)
C4–C10	3.36 (2)	C23–C26	3.42 (2)
C4–N1	3.16 (2)	C23–C30	3.06 (2)
C5–C6	3.16 (3)	C24–N2	2.97 (1)
C5–C10	3.08 (2)	C25–C31	3.16 (2)
C7–C11	2.96 (3)	C25–N2	2.89 (2)
C8–C11	3.12 (2)	C27–C31	2.86 (2)
C8–N1	2.91 (2)	C27–O2[a]	3.33 (2)
C9–N1	2.85 (2)	C28–C31	3.17 (2)
C9–O2[a]	3.50 (2)	C28–N2	2.90 (2)
C10–O1	3.21 (2)	C29–N2	3.03 (1)
C11–N1	2.76 (2)	C31–N2	2.71 (2)
	Principal Bond Angles (Deg)		
Atoms	Angle	Atoms	Angle
C11–Mo1–N1	87.9 (5)	C31–Mo2–N2	85.5 (5)
C2–C1–C5	102 (2)	C22–C21–C25	109 (1)
C1–C2–C3	109 (2)	C21–C22–C23	105 (1)
C2–C3–C4	109 (2)	C22–C23–C24	110 (1)
C3–C4–C5	107 (2)	C23–C24–C25	107 (1)
C4–C5–C1	116 (2)	C24–C25–C21	109 (1)
C7–C6–C10	107 (1)	C27–C26–C30	109 (1)
C6–C7–C8	108 (2)	C26–C27–C28	107 (1)
C7–C8–C9	108 (1)	C27–C28–C29	106 (1)
C8–C9–C10	110 (1)	C28–C29–C30	109 (1)
C9–C10–C6	108 (2)	C29–C30–C26	108 (1)
Mo1–N1–O1	178 (2)	Mo2–N2–O2	178 (1)

[a] Intermolecular contacts.

sumably, therefore, packing forces have only minor effects upon the gross geometry of the two independent molecules and are not the cause of the asymmetric cyclopentadienyl bonding to be discussed below.

As can be seen from Figure 1, the two discrete molecules, molecules 1 and 2 being defined as those which contain Mo1 and Mo2, respectively, are approximately mirror images of each other which possibly accounts for the smallness of the differences between the intensities of Friedel pairs. By calculation the inequality of a Friedel pair is found to be of the order of one standard deviation in F_o^2, and consequently it was not possible within the accuracy of this analysis to establish the absolute configuration of this system by either the Friedel pairs that were measured or by least-squares analysis of both configurations. Refinement in either enantiomorph converged to the same *R* values without significant structural differences.

The geometries of the two molecules, aside from their being enantiomorphous, exhibit no differences in dimensions greater than the expected maximum error except for the usual spread of C–C bond lengths within the cyclopentadienyl groups. Each cyclopentadienyl group is unsymmetrically bonded to a Mo atom with Mo–C bond lengths ranging from 2.34 to 2.71 Å for molecule 1 and from 2.31 to 2.65 Å for molecule 2. In all four cases there are two relatively short Mo–C bond lengths of approximately 2.35 Å, which is within the range of Mo–C bond lengths found within compounds such as $Mo(C_5H_5)_2H_2$,[11] $Mo(C_5H_5)_2S_2C_6H_3CH_3$,[12] $Mo(C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$,[13] and others, where approximate pentagonal-pyramidal MoC_5 geometry exists. The asymmetry of the bonding is such that the remaining three Mo–C distances in each cyclopentadienyl group are greater than this value, one being approximately 2.44 Å while the other two are approximately 2.61 Å. The pattern of C–Mo distances in each of the four crystallographically independent C_5H_5–Mo groups in this structure is essentially the same as that found for each of the two non-(h^1-C_5H_5–Mo) groups in $(C_5H_5)_3MoNO$; the comparison is shown in detail in Table IV.

Each cyclopentadienyl ring is planar within experimental error, no deviation from planarity exceeding 0.038 Å. The mean C–C distance is 1.39 Å from which the mean deviation is ±0.03 Å. However, it is evident that, for some obscure reason C2 is badly misplaced. If the C2–C1 and C2–C3 distances are excluded, the mean C–C distance and the mean deviation therefrom are 1.39 ± 0.02 Å. This is in excellent agreement with values of C–C distance in normal h^5-C_5H_5 rings in other compounds. Within each molecule the rings have an approximately staggered relative orientation, as in $(C_5H_5)_3MoNO$ and various $(h^5\text{-}C_5H_5)_2MoX_2$ molecules.

The angles between the perpendiculars to mean planes of the rings within molecule 1 and 2 are 41 (2) and 44 (2)°, respectively. Both values are comparable to those found in $(C_5H_5)_3MONO$ and $(h^5\text{-}C_5H_5)_2MoS_2C_6H_3CH_3$ which exhibit dihedral angles of 43.3 and ~46°, respectively, although larger than that found in $(h^5\text{-}C_5H_5)_2MoH_2$, 34 (1)°. The perpendicular distances of the Mo atom to the mean plane of the C_5H_5 rings within molecules 1 and 2 are 2.18, 2.11, 2.13, and 2.14 Å, the mean value of which, 2.14 Å, is equivalent to those found within $(C_5H_5)_3MoNO$, 2.140 and 2.145 Å, but slightly greater than that found in regular $Mo(h^5\text{-}C_5H_5)$ pentagonal-pyramidal coordination, *e.g.*, $(h^5\text{-}C_5H_5)_2Mo(p\text{-}CH_3C_6H_4CH_2)$, 2.09 Å.

The nitrosyl groups within each molecule have Mo–N–O angles of 178 (2) and 178 (1)°, neither of which is significantly different from linearity. The Mo–N, 1.75 (1) and 1.76 (1) Å, N–O, 1.23 (1) and 1.21 (1) Å, bond lengths are equivalent and equal to the values 1.751 (3) and 1.207 (4) Å obtained for the linear Mo–N–O system of $(C_5H_5)_3MoNO$.

---

(11) M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).

(12) J. R. Knox and C. K. Prout, *Chem. Commun.*, 1277 (1967).

(13) F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 90, 5418 (1968).

Table III. Weighted Least-Squares Planes[a]

Plane		Equation	Dihedral angle, deg
I	C_1–C_5	$-0.3176x + 0.6526y + 0.6880z = 4.193$	41 (2)
II	C_6–C_{10}	$0.4208x + 0.5626y + 0.7116z = 3.282$	
III	C_{21}–C_{25}	$0.3637x + 0.4315y + 0.8256z = 2.594$	44 (2)
IV	C_{26}–C_{30}	$-0.3256x + 0.5418y + 0.7760z = -6.456$	

Distances of Atoms from Planes, Å

Atoms	Plane I	Atoms	Plane II	Atoms	Plane III	Atoms	Plane IV
C1	−0.006	C6	−0.011	C21	−0.014	C26	−0.020
C2	−0.027	C7	0.005	C22	0.006	C27	0.031
C3	0.038	C8	0.001	C23	0.002	C28	−0.030
C4	−0.024	C9	−0.006	C24	−0.010	C29	0.019
C5	0.019	C10	0.012	C25	0.016	C30	0.000
Mo1	−2.180	Mo1	2.109	Mo2	−2.132	Mo2	2.137

[a] The orthogonal coordinates (x, y, z) are directed along the crystal axes a, b, and c^*, respectively, and are in A. The weight given to each atom i in forming the plane is $w_i = [a\sigma_{x_i}b\sigma_{y_i}c\sigma_{z_i}]^{-2/3}$.

Table IV. Comparison of Molybdenum to Carbon Distances in $(C_5H_5)_2Mo(NO)CH_3$ and $(C_5H_5)_2Mo(NO)(h^1\text{-}C_5H_5)$

	$(C_5H_5)_2Mo(NO)CH_3$ (±0.02 Å) Molecule 1	Molecule 2		Average		$(C_5H_5)_2Mo(NO)C_5H_5$ (±0.005 Å)
a	2.34	2.31	2.33	2.34	2.34	2.34
a′	2.34	2.33				2.32
b	2.39	2.36	2.36			2.34
b′	2.34	2.36				2.35
c	2.44	2.44		2.44	2.43	2.42
c′	2.46	2.43				2.44
d	2.65	2.55	2.57	2.61	2.62	2.59
d′	2.47	2.60				2.61
e	2.71	2.63	2.64			2.60
e′	2.57	2.65				2.68
Perpendicular Distance of Metal Atoms from Least-Squares Planes						
Planes of C_5H_5 Rings						
	2.180	2.132		2.139	2.143	2.145
	2.109	2.137				2.140
Dihedral Angle between C_5H_5 Planes						
	41°	44°				43.3°

The only surprising feature in the present structure is the shortness of the Mo–CH_3 bonds, 2.20 (1) and 2.20 (2) Å, in the two molecules. This is unexpectedly short when compared to the length of the Mo–C σ bond in $(C_5H_5)_3MoNO$, 2.291 (3) Å. Moreover, the latter is itself short in comparison to Mo–C σ bond lengths in a number of other compounds. Churchill has recently summarized pertinent data.[14] For example, $(h^5\text{-}C_5H_5)Mo(CO)_3$–R bond lengths are 2.40 (2) Å for R = CH_2CH_3, 2.36 (2) Å for CH_2CO_2H, and 2.38 (1) Å for CH_3. Churchill concludes from these and other data that "the covalent radius of molybdenum is 1.61–1.62 Å both in seven-coordination [as in $(h^5\text{-}C_5H_5)Mo(CO)_3R$ complexes, where $h^5\text{-}C_5H_5$ is regarded as formal tridentate six-electron donor ligand] and in octahedral six-coordination." He notes that the Mo–$(h^1\text{-}C_5H_5)$ distance in $(C_5H_5)_3MoNO$ is considerably shorter than those discussed above but points out that "the molybdenum atom (here) is in a higher formal oxidation state than ... in $(h^5\text{-}C_5H_5)Mo(CO)_3R$ species and is in a considerably different coordination environment." One could take exception to this statement as it pertains to oxidation state. If the usual conventions are followed, all C_5H_5 and R groups are considered as uninegative and the linear MNO group is presumed to contain NO^+, and there is no formal difference in oxidation states. We are, in any event, inclined to regard the question of oxidation state as a moot one in such highly covalent molecules. We do suggest that it would be desirable to know if, *in general*, M–$(h^1\text{-}C_5H_5)$ bonds are intrinsically likely to be appreciably (*i.e.*, ~0.1 Å) longer than M–CH_3 bonds (and presumably, other M–C_nH_{2n+1} bonds) or whether unique steric or electronic factors are at work in the $(C_5H_5)_2Mo(NO)R$ molecules.

The main purpose of this investigation, which was to find out if the very skew ring-to-metal geometry found for two of the rings in $(C_5H_5)_2Mo(NO)(h^1\text{-}C_5H_5)$ would be characteristic of $(C_5H_5)_2Mo(NO)R$ molecules generally, has been accomplished. As Table IV demonstrates very clearly the structural characteristics of the $(C_5H_5)_2Mo$ portions of $(C_5H_5)_2Mo(NO)(h^1\text{-}C_5H_5)$ and $(C_5H_5)_2Mo(NO)CH_3$ are virtually identical. The two rings in the $(C_5H_5)_2Mo$ moiety have identical, albeit peculiar, geometrical relationships to the metal atom. The notion of a $(h^5\text{-}C_5H_5)(h^3\text{-}C_5H_5)Mo$ arrangement, with rapid interconversion of the two ring types thus again fails of support, and it now seems very safe indeed to reject it as a possibility for any $(C_5H_5)_2Mo(NO)R$ molecule.

Another useful result of the present investigation is to increase greatly the pool of data on the geometry of the highly skew *polyhapto*cyclopentadienylmetal moieties. Structure parameters are now known for six crystallographically independent C_5H_5M moieties of this kind. With this degree of replication it is possible to adjudge the atypicality of certain individual Mo–C distances (such as those among the set of long bonds which are >2.70 or <2.50 Å) and thereby select a reliable set of characteristic structure parameters which may later be of use in theoretical discussions.

---

(14) M. R. Churchill in "Perspectives in Coordination Chemistry," Vol. III, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1970, p 91.