in the experiment with $^{18}O_2$. The infrared spectra of complex II and its isotopic derivatives are given in Figures 1 and 2 and Table I. In the far-infrared region, a medium band at 343 cm^{-1} is the only one that is not affected by the change of $P(C_6H_5)_3$ to $P(C_6D_5)_3$ and C_6H_6 to C_6D_6. It is shifted to 337 cm^{-1} by incorporation of ^{18}O, and therefore this band may be assigned to the Rh–CO_2 bond stretching mode.

$P(C_6D_5)_3$. Pentadeuteriobromobenzene was prepared by bromination of hexadeuteriobenzene. Ether solution of C_6D_5MgBr, prepared from Mg and C_6D_5Br, was placed in a flask and an ether solution of PCl_3 was added slowly. After vigorous reaction had ended, unreacted reagent was decomposed by 100 ml of HCl. $P(C_6D_5)_3$ was crystallized from the ether layer; yield 40.3% for C_6D_5Br.

Analysis of Carbon Dioxide. In a helium flow 39.25 mg of complex II was pyrolyzed in a quartz tube at 500° for 20 min, and the generated gas was trapped on KOH. The CO_2 content was 4.86 wt %; the calculated value was 3.76 wt % for $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3C_6H_6$. Carbon dioxide was also detected by an F & M Model 80 pyrolyzer gas chromatograph.

Infrared Spectra. Infrared spectra were recorded with a Hitachi Perkin-Elmer Model 225 infrared spectrometer. The wave number calibration was made by the use of known absorption lines of CO, CO_2, and water vapor. Infrared absorptions were observed in the form of Nujol and hexachlorobutadiene mulls.

Molecular Weight Determination. The molecular weight of complex II was determined on a Mechrolab vapor-pressure osmometer. Bibenzyl was used as the reference compound. The observed molecular weight of complex II measured in a benzene solution was 1057; the calculated value for $Rh_2(CO)_2(CO_2)(P(C_6H_5)_3)_3C_6H_6$ is 1171.

Nmr. Nmr spectra were recorded with a Varian HA-100 spectrometer in CD_2Cl_2, C_6D_6, or $CDCl_3$ solutions. Integration of the phenyl protons of $P(C_6H_5)_3$ and methyl protons of the coordinated solvent molecules determined the numbers incorporated in the molecule.

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Stereochemically Nonrigid Organometallic Molecules. XXI.[1] The Crystal and Molecular Structures of Tris(cyclopentadienyl)nitrosylmolybdenum[2]

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Abstract: The crystal and molecular structures of tris(cyclopentadienyl)nitrosylmolybdenum, $(C_5H_5)_3MoNO$, have been determined from 2288 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the monoclinic space group $B2_1/a$ with eight molecules in a unit cell of dimensions $a = 15.425 \pm 0.006$ Å, $b = 7.423 \pm 0.004$ Å, $c = 24.050 \pm 0.007$ Å, and $\beta = 103° 40' \pm 3'$ ($\rho_{obsd} = 1.60$ g cm^{-3}; $\rho_{calcd} = 1.59$ g cm^{-3}). The structure, including hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional unweighted R factor of 3.5%. The principal features of the structure are the following. (1) There is an essentially linear (179.2°) Mo–N–O group, with Mo–N = 1.751 (3) Å and N–O = 1.207 (4) Å. The short Mo–N and relatively long N–O distances indicate very strong metal–ligand π bonding. (2) One of the C_5H_5 rings is an exemplary σ or *monohapto* cyclopentadienyl ring. The Mo–C distance is 2.291 (3) Å and the C–C distances (in Å) listed in order from the bound carbon atom around the ring are 1.468 (5), 1.349 (5), 1.442 (6), 1.344 (5), 1.468 (5). (3) The other two rings have almost identical relationships to the metal atom. No simple distinction (such as *pentahapto vs. trihapto*) can be made between them. Around each one, the Mo–C distances go in the following order, where pairs of corresponding bonds to the two rings are listed together: 2.599 (4), 2.682 (5); 2.588 (5), 2.609 (5); 2.343 (5), 2.347 (4); 2.338 (5), 2.324 (3); 2.422 (5), 2.444 (4). These two rings have very different orientations relative to the h^1-C_5H_5 ring, however, and this is most important in considering how to interpret the low-temperature pmr spectrum which has been reported for this fluxional molecule.

In a previous paper in this series,[4] the preparation and a study of the temperature dependence of the proton magnetic resonance spectrum of the molecule $(C_5H_5)_3MoNO$ were described. At room temperature, there is only one narrow line for all 15 protons, but in the temperature range 0 to −50° one ring becomes distinguishable as a *monohapto*[5] cyclopentadienyl group while the other two remain nmr equivalent. Between −60 and −110°, further complexities appear in the spectrum, notably a separation of the resonance due to ten protons into two equally intense resonances separated by ~1 ppm. As noted in the initial report,[4] there are at least two structural

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[1] Part XX: F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, **91**, 1339 (1969).

[2] This work was supported in part by the National Science Foundation under Grant No. GP-7034X.

[3] Fellow of the Council for Scientific and Humanistic Development, Central University of Venezuela, Caracas, Venezuela.

[4] Part XVIII: F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, **90**, 6232 (1968).

[5] *Cf.* F. A. Cotton, *ibid.*, **90**, 6230 (1968), for an explanation of this notation.

hypotheses which could explain the observations in the lower temperature range and no obvious way of distinguishing between them on the basis of the pmr data alone.

Therefore, an X-ray crystallographic study was undertaken. Bearing in mind the differences which might exist between molecular structures in solution and in the crystal, it was, nevertheless, hoped that the crystallographic results would provide a clue as to the correct interpretation of the pmr data. This paper describes the crystallographic study and discusses the bearing of the results on the interpretation of the fluxional character of the molecule in solution.

Experimental Procedure

Tris(cyclopentadienyl)nitrosylmolybdenum was prepared by the reaction of 4.45 g (5 mmoles) of $[C_5H_5Mo(NO)I_2]_2$ (prepared from iodine and $C_5H_5Mo(CO)_2NO$ by the published procedure[6]) and 5.38 g (20 mmoles) of thallium cyclopentadienide in 125 ml of THF under nitrogen. Initially the solution was green, but upon stirring for ~18 hr it became reddish purple and a yellow precipitate of thallium(I) iodide formed. The precipitate was removed by suction filtration under nitrogen, and the solvent was evaporated under vacuum to yield the crude product in ~65% yield (2.0 g). A portion of this product was chromatographed (eluted with dichloromethane) on a column of neutral alumina (activity grade 1), and the eluate was evaporated under a stream of nitrogen to yield red crystals of analytically pure $(C_5H_5)_3MoNO$.

Anal. Calcd for $C_{15}H_{15}MoNO$: Mo, 29.87; C, 56.09; H, 4.71; N, 4.36. Found: Mo, 29.6; C, 55.9; H, 4.70; N, 4.39. The analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

The compound is air stable, melts at 79.5–80.5° (uncorrected), and dissolves in polar organic solvents such as dichloromethane, chloroform, and tetrahydrofuran to yield moderately air-stable solutions. It is only sparingly soluble in nonpolar organic solvents. Its infrared spectrum (Nujol mull) exhibits a strong ν(NO) frequency at 1610 cm^{-1}, and its room-temperature proton nmr spectrum (CS_2) shows only one peak at τ 4.2.

Diamond-shaped single crystals suitable for X-ray work were obtained by slow evaporation of dichloromethane–pentane solutions of the compound. One such crystal of approximate dimensions 0.3 × 0.3 × 0.1 mm was mounted on the end of a glass fiber for use during the subsequent work.

Preliminary Weissenberg ($0kl$ and $1kl$ levels) and precession ($hk0$, $hk1$, $h0l$, and $h1l$ levels) photographs indicated the crystals to be monoclinic. Moreover, the observed systematic absences, hkl for $h + l \neq 2n$, $h0l$ for $h \neq 2n$ ($l \neq 2n$), and $0k0$ for $k \neq 2n$ indicated the probable space group $B2_1/a$ having the following equipoints $(0, 0, 0;\ ^1/_2, 0, ^1/_2)\ x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ ^1/_2 + x, ^1/_2 - y, z;\ ^1/_2 - x, ^1/_2 + y, \bar{z}$. The following unit cell dimensions were obtained, at 22°, by a method described elsewhere[7] using Cu Kα radiation ($\lambda(K_{\alpha_1})$ 1.5404 Å, $\lambda(K_{\alpha_2})$ 1.5443 Å): $a = 15.425 \pm 0.006$ Å, $b = 7.423 \pm 0.004$ Å, $c = 24.050 \pm 0.007$ Å, and $\beta = 102° 40' \pm 3'$. The angle β was derived from precession photograph measurements, and its uncertainty represents the estimated precision of these measurements. The density was determined by flotation in aqueous zinc nitrate solutions as 1.60 ± 0.01 g cm^{-3}, and this agrees well with the calculated density of 1.59 g cm^{-3} for a formula weight of 321.2, $Z = 8$, and a unit cell volume of 2678 $Å^3$. With $Z = 8$ in the space group $B2_1/a$, there are no crystallographic symmetry elements imposed on the molecule.

Intensity data were collected on a General Electric XRD-5 manual diffractometer with the crystal so aligned that its a^* axis coincided with the ϕ axis of the instrument.[8] The crystal was placed 5.73 in. from the source, while the distance from the crystal to the detector with a circular aperture of 2° was 7.05 in. The integrated intensities of 2523 independent reflections within the sphere $\theta \leq 70°$ were measured using nickel-filtered Cu Kα radiation.

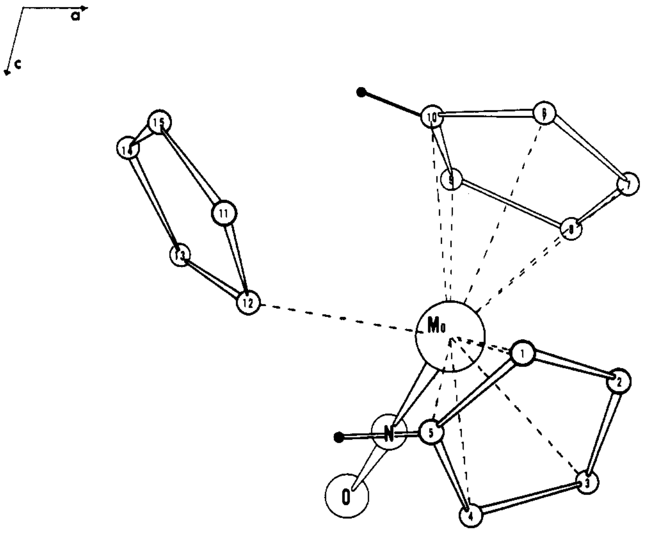

Figure 1. A projection of the molecule on the (010) plane. The atom numbering scheme is indicated. Two hydrogen atoms are shown as small, filled circles.

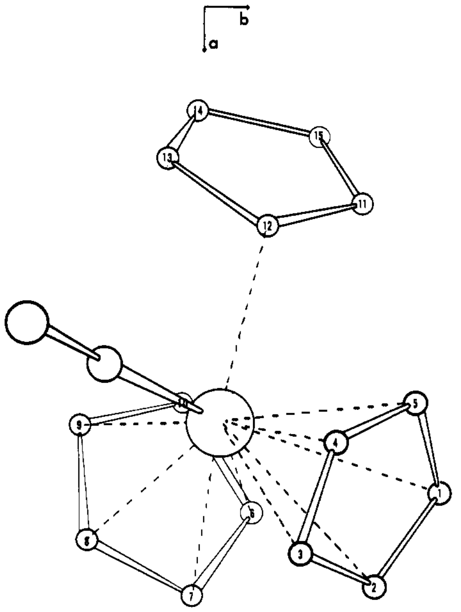

Figure 2. A projection of the molecule on the (001) plane.

The intensities were measured using a scintillation counter with a pulse height discriminator set to accept 95% of the Cu Kα peak. The data were collected using a θ/2θ scan technique at a 2θ scan rate of 4°/min. The peak counts, P, were obtained from a 2θ scan of 2.66° from $2\theta_{calcd} - 1.33°$ to $2\theta_{calcd} + 1.33°$. Stationary background counts, B_1, B_2, of 20 sec were taken at each of the limits of the scan. From these readings the intensity, I, assuming a linear change in background, or its equivalent, between the two limits of the scan, is given by $I = P - (B_1 + B_2)$. Several strong reflections which exceeded the linear response range of the counter were remeasured with a lower current and were scaled to the other data by using medium intensity reflections measured with both current settings. One reflection (111) which exceeded the linear response range of the counter at even the lowest possible current setting was rejected from further consideration. Periodic checks of eight standard reflections showed a variation in intensity (±1%) having no 2θ dependence, which is consistent with fluctuations in the electronic circuits rather than with crystal decomposition.

Statistically insignificant reflections (234) were rejected using the criteria: (1) $I \leq 0$; (2) $I < 3(P + B_1 + B_2)^{1/2}$. The remaining

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(6) R. B. King, *Inorg. Chem.*, **6**, 30 (1967).

(7) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

(8) For this experiment, the conditions for multiple diffraction were maximized: W. A. Zachariasen, *Acta Cryst.*, **18**, 705 (1965). Since agreement between observed and calculated structure factors was later found to be very good, the effects are probably small in this case.

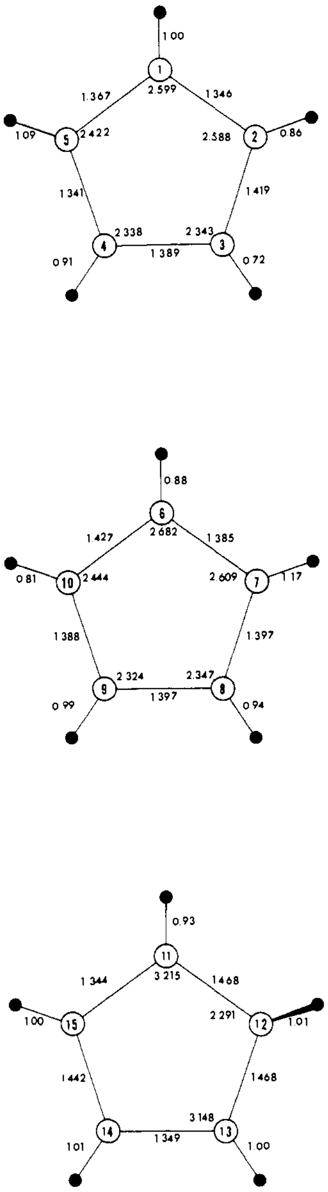

Figure 3. Diagrams of the three cyclopentadienyl rings showing the C–C, C–H, and (inside) Mo–C distances.

2288 reflections were corrected for Lorentz and polarization effects and a set of $|F_0|^2$ and $|F_0|$ values (on a relative scale) was thus obtained.

Appreciable variations in the intensities of the $h00$ reflections were observed as a function of crystal orientation; φ scans of several of these reflections evidenced variations of ±20%. Consequently, absorption corrections ($\mu = 83.0\ \text{cm}^{-1}$), based on the equations of the crystal faces, were applied to the data for the final stages of refinement.

Table I. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	Isotropic B, Å^2 [b]
Mo	0.35464 (2)	0.01715 (3)	0.15295 (1)	2.875
C_1	0.4089 (4)	0.3495 (6)	0.1594 (2)	6.83
C_2	0.4832 (3)	0.2488 (7)	0.1724 (2)	6.23
C_3	0.4853 (3)	0.1375 (6)	0.2190 (2)	5.96
C_4	0.3983 (4)	0.1914 (7)	0.2353 (2)	6.23
C_5	0.3565 (3)	0.3111 (6)	0.1969 (3)	6.78
C_6	0.3867 (3)	0.0646 (6)	0.0487 (2)	5.77
C_7	0.4577 (3)	−0.0288 (6)	0.0814 (2)	5.96
C_8	0.4254 (3)	−0.1848 (5)	0.1023 (2)	4.88
C_9	0.3339 (2)	−0.1943 (5)	0.0800 (2)	4.37
C_{10}	0.3084 (3)	−0.0356 (6)	0.0504 (2)	4.80
C_{11}	0.1774 (2)	0.2351 (5)	0.0957 (2)	4.43
C_{12}	0.2072 (2)	0.0923 (4)	0.1377 (1)	3.57
C_{13}	0.1494 (2)	−0.0601 (5)	0.1152 (2)	4.20
C_{14}	0.0956 (3)	−0.0136 (5)	0.0652 (2)	4.80
C_{15}	0.1131 (2)	0.1715 (6)	0.0531 (2)	5.01
N	0.3269 (2)	−0.1534 (4)	0.1962 (1)	3.68
O	0.3068 (2)	−0.2714 (3)	0.2255 (1)	5.35
H_1	0.399 (3)	0.429 (7)	0.125 (2)	8.1 (1.1)
H_2	0.527 (4)	0.251 (7)	0.156 (2)	9.2 (1.4)
H_3	0.512 (4)	0.092 (8)	0.237 (2)	8.7 (1.3)
H_4	0.386 (4)	0.145 (8)	0.268 (2)	9.3 (1.3)
H_5	0.294 (4)	0.376 (8)	0.198 (2)	9.9 (1.4)
H_6	0.391 (3)	0.164 (8)	0.029 (2)	8.4 (1.2)
H_7	0.532 (5)	0.013 (6)	0.098 (3)	9.9 (1.6)
H_8	0.462 (3)	−0.277 (5)	0.121 (2)	5.8 (0.8)
H_9	0.294 (3)	−0.292 (5)	0.086 (2)	6.3 (0.8)
H_{10}	0.257 (4)	−0.007 (5)	0.039 (2)	6.4 (1.0)
H_{11}	0.201 (3)	0.351 (6)	0.101 (2)	7.2 (0.9)
H_{12}	0.210 (2)	0.120 (4)	0.179 (1)	4.7 (0.6)
H_{13}	0.153 (2)	−0.180 (5)	0.135 (1)	4.8 (0.6)
H_{14}	0.048 (3)	−0.093 (5)	0.042 (2)	5.6 (0.7)
H_{15}	0.083 (3)	0.235 (5)	0.018 (2)	6.4 (0.8)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed. [b] The equivalent isotropic thermal parameters given for atoms other than hydrogens were calculated by VIBELL from the anisotropic temperature factors listed in Table II.

Solution and Refinement of the Structure

A three-dimensional Patterson map revealed the position of the molybdenum atom, and the rest of the structure was solved by conventional least-squares and Fourier calculations. For atoms other than hydrogen, the scattering factors used during this analysis were those of Cromer and Waber,[9] while the form factors used for hydrogen were those experimentally determined for H atoms in biphenyl by Mason and Robertson.[10] Anomalous dispersion corrections for Mo ($\Delta f' = -0.54$ e, $\Delta f'' = 2.89$), applied to F_c,[11] were taken from a standard source.[12] The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed structure amplitude, $|F_c|$ is the calculated structure amplitude, and $w = [\sigma(F)]^{-2}$.

Three cycles of full-matrix least-squares refinement of scale factor and positional and isotropic thermal parameters for all atoms, excluding hydrogens, led to a discrepancy index of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.095$. The weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, using unit weights was 0.121. At this point absorption corrections and an experimental weighting scheme similar to that of Doedens and Ibers[13] were introduced. A difference Fourier map using only the low-angle data ($\sin\theta/\lambda \leq 0.40$) revealed all 15 hydrogen atoms. Two

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(9) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(10) R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, p 57.

(11) C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163.

(12) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(13) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). Our weighting scheme differs only in that $p = 0.045$.

Table II. Anisotropic Temperature Factors $(\times 10^4)^b$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	27.4 (2)	127.5 (8)	15.2 (1)	0 (0)	4.7 (1)	0 (0)
C_1	88 (4)	175 (8)	33 (1)	−34 (4)	−9 (2)	8 (2)
C_2	50 (2)	381 (13)	28 (1)	−62 (5)	14 (1)	−29 (3)
C_3	54 (2)	226 (9)	29 (1)	−6 (3)	−15 (1)	−6 (2)
C_4	81 (3)	316 (11)	22 (1)	−74 (5)	18 (1)	−36 (2)
C_5	50 (2)	228 (9)	48 (2)	−13 (4)	7 (2)	−55 (3)
C_6	76 (3)	212 (8)	30 (1)	−2 (4)	24 (1)	2 (2)
C_7	49 (2)	242 (9)	40 (1)	−6 (3)	22 (1)	−19 (3)
C_8	47 (2)	207 (8)	28 (1)	18 (3)	14 (1)	−16 (2)
C_9	47 (2)	192 (7)	22 (1)	−14 (3)	12 (1)	−20 (2)
C_{10}	49 (2)	273 (9)	19 (1)	17 (3)	8 (1)	−9 (2)
C_{11}	36 (2)	202 (7)	26 (1)	15 (3)	8 (1)	7 (2)
C_{12}	27 (1)	199 (6)	18 (1)	0 (2)	5 (1)	−2 (1)
C_{13}	35 (2)	245 (7)	19 (1)	−13 (3)	7 (1)	−1 (2)
C_{14}	34 (2)	306 (10)	20 (1)	−16 (3)	3 (1)	−4 (2)
C_{15}	37 (2)	324 (10)	20 (1)	12 (3)	4 (1)	15 (2)
N	34 (1)	170 (5)	19 (1)	5 (2)	6 (1)	3 (1)
O	66 (2)	218 (5)	26 (1)	−5 (2)	17 (1)	25 (1)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed.

Table III. Root-Mean-Square Amplitudes of Vibrations (Å) and Their Direction Cosines[a]

Atom	Minor axis	Medium axis	Major axis
Mo	0.177 (0.996, 0.019, 0.086)	0.189 (−0.023, 0.999, 0.044)	0.206 (−0.085, −0.046, 0.995)
C_1	0.206 (0.320, 0.940, 0.116)	0.259 (0.495, −0.270, 0.826)	0.387 (0.808, −0.207, −0.552)
C_2	0.196 (0.896, 0.434, 0.094)	0.255 (−0.268, 0.361, 0.893)	0.364 (−0.354, 0.825, −0.440)
C_3	0.186 (0.691, 0.196, 0.696)	0.253 (−0.167, 0.978, −0.110)	0.358 (−0.703, −0.040, 0.710)
C_4	0.199 (0.207, 0.641, 0.739)	0.239 (0.775, 0.354, −0.524)	0.373 (−0.598, 0.681, −0.423)
C_5	0.195 (0.217, 0.856, 0.470)	0.243 (0.963, −0.267, 0.040)	0.401 (−0.159, −0.444, 0.882)
C_6	0.232 (0.676, 0.438, −0.592)	0.245 (−0.331, 0.899, 0.287)	0.324 (0.658, 0.001, 0.753)
C_7	0.205 (0.949, −0.187, −0.256)	0.251 (0.250, 0.937, 0.243)	0.348 (0.195, −0.295, 0.936)
C_8	0.185 (0.724, −0.613, −0.317)	0.255 (0.690, 0.654, 0.310)	0.293 (0.018, −0.443, 0.896)
C_9	0.199 (−0.205, 0.739, 0.642)	0.219 (0.931, 0.350, −0.104)	0.281 (0.302, −0.577, 0.759)
C_{10}	0.210 (−0.635, 0.393, 0.665)	0.236 (0.687, −0.106, 0.719)	0.287 (0.352, 0.914, −0.203)
C_{11}	0.192 (0.922, −0.374, 0.096)	0.238 (0.383, 0.856, −0.346)	0.272 (0.047, 0.356, 0.933)
C_{12}	0.174 (0.996, −0.015, 0.092)	0.222 (−0.085, 0.253, 0.964)	0.236 (0.038, 0.967, −0.250)
C_{13}	0.193 (0.973, 0.227, −0.037)	0.229 (0.026, 0.053, 0.998)	0.265 (−0.229, 0.972, −0.046)
C_{14}	0.192 (0.893, 0.186, 0.411)	0.241 (−0.417, −0.007, 0.909)	0.295 (−0.172, 0.983, −0.071)
C_{15}	0.201 (0.864, −0.195, 0.463)	0.233 (−0.501, −0.252, 0.828)	0.308 (0.045, 0.948, 0.315)
N	0.194 (0.968, −0.234, 0.091)	0.217 (0.251, 0.913, −0.321)	0.234 (−0.008, 0.334, 0.943)
O	0.195 (0.424, 0.688, −0.589)	0.272 (0.833, −0.551, −0.044)	0.302 (0.355, 0.472, 0.807)

[a] Direction cosines are referred to the orthogonal axis system *a*, *b*, *c**.

further cycles of refinement of all parameters for the 33 atoms resulted in $R_1 = 0.078$ and $R_2 = 0.111$. Atoms other than hydrogen atoms were next assigned anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and four final cycles of refinement of positional and thermal parameters for all atoms resulted in convergence with $R_1 = 0.035$ and $R_2 = 0.047$. A Hamilton R factor test[14] validated both the anisotropic model and the model including the hydrogen atoms at the 99.5% confidence level.

During the last cycle of refinement, no parameter shifted more than one-fifth of its estimated standard

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(14) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

Table IV. Intramolecular Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
A. Bond Distances			
Mo–C_1	2.599 (4)	C_1–C_2	1.346 (7)
Mo–C_2	2.588 (5)	C_2–C_3	1.419 (7)
Mo–C_3	2.343 (5)	C_3–C_4	1.389 (7)
Mo–C_4	2.338 (5)	C_4–C_5	1.341 (7)
Mo–C_5	2.422 (5)	C_5–C_1	1.367 (8)
Mo–C_6	2.682 (5)	C_6–C_7	1.385 (7)
Mo–C_7	2.609 (5)	C_7–C_8	1.397 (6)
Mo–C_8	2.347 (4)	C_8–C_9	1.397 (5)
Mo–C_9	2.324 (3)	C_9–C_{10}	1.388 (5)
Mo–C_{10}	2.444 (4)	C_{10}–C_6	1.427 (7)
Mo–C_{12}	2.291 (3)	C_{11}–C_{12}	1.468 (5)
Mo–N	1.751 (3)	C_{12}–C_{13}	1.468 (5)
N–O	1.207 (4)	C_{13}–C_{14}	1.349 (5)
		C_{14}–C_{15}	1.442 (6)
		C_{15}–C_{11}	1.344 (5)
C_1–H_1	1.00 (5)	C_9–H_9	0.99 (4)
C_2–H_2	0.86 (5)	C_{10}–H_{10}	0.81 (6)
C_3–H_3	0.72 (6)	C_{11}–H_{11}	0.93 (5)
C_4–H_4	0.91 (5)	C_{12}–H_{12}	1.01 (3)
C_5–H_5	1.09 (6)	C_{13}–H_{13}	1.00 (3)
C_6–H_6	0.88 (5)	C_{14}–H_{14}	1.01 (4)
C_7–H_7	1.17 (7)	C_{15}–H_{15}	1.00 (4)
C_8–H_8	0.94 (4)		
B. Selected Nonbonded Contacts			
C_1–C_6	3.357	H_1–H_6	3.02
C_2–C_6	3.314	H_2–H_6	3.35
C_2–C_7	2.969	H_2–H_7	2.26
C_3–C_7	3.487	H_3–H_7	3.47
C_4–C_{12}	3.421	H_4–H_{12}	3.07
C_5–C_{11}	3.306	H_5–H_{11}	2.46
C_5–C_{12}	2.920	H_5–H_{12}	2.28
C_9–C_{12}	3.385	H_9–H_{13}	2.80
C_9–C_{13}	3.296	H_{10}–H_{11}	3.26
C_{10}–C_{11}	3.205	H_{10}–H_{13}	3.34
C_{10}–C_{12}	3.030	H_{10}–H_{14}	3.31
C_{10}–C_{13}	3.186	H_{10}–H_{15}	3.18
C_{10}–C_{14}	3.381		
C_{10}–C_{15}	3.395		
C_3–N	3.107		
C_4–N	2.862		
C_{12}–N	2.752		
C_{13}–N	3.071		

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed. Atoms weighted with the inverse standard deviations in their positional parameters.

deviation. A final difference Fourier map computed at this point showed a peak of 0.54 e/Å^3 in the vicinity of the molybdenum atom, and all other peaks were less than 0.36 e/Å^3. The final standard deviation of an observation of unit weight was 0.91, thereby suggesting that the use of a smaller p factor might have been preferable. The chosen weighting scheme satisfied Cruickshank's criterion[15] as $\Sigma w[|F_o| - |F_c|]^2$ was substantially the same in different ranges of both $|F_o|$ and sin θ/λ. A comparison of the observed and final calculated structure amplitudes indicated that six strong low-angle reflections (sin $\theta/\lambda \leq 0.1$) apparently suffer from extinction, but these had been rejected during final refinement at the 3.5σ confidence level (omitting a total of 16 rejected reflections, $R_1 = 0.031$).

The following programs for the IBM 360 computer were used in this structure analysis and interpretation: (1) D. P. Shoemaker, MIT X-Ray Goniometer Package, MIXG-2, 1962; (2) R. C. Elder, convenient listing of diffractometer settings, PDATH2; (3) M. J. Bennett, general Data Reduction Program, PMMO; (4) a modified version of A. Zalkin, Fourier analysis program, FORDAP; (5) W. C. Hamilton, absorption correction program, GONO9; (6) a modified version of C. T. Prewitt, Full-Matrix Crystallographic Least Squares Program, SFLS5, 1966; (7) J. S. Wood, Molecular Geometry with Estimated Standard Deviations, MGEOM, 1964; (8) D. P. Shoemaker, crystallographic bond distance, bond angle, and dihedral angle program, DISTAN, 1963; (9) D. P. Shoemaker and R. C. Srivastava, program for analysis of anisotropic temperature factors, VIBELL, 1963; (10) R. C. Elder, data presentation program, PUBTAB.

Results

A table of the observed and final calculated structure amplitudes (in electrons), multiplied by 10, for $(C_5H_5)_3$MoNO has been deposited with the ASIS National Auxiliary Publications Service.[16] The molecular structure and atom numbering system are shown in Figure 1, a projection on the (010) plane. Figure 2 shows a projection on the (001) plane which will be of value in later discussions. Figure 3 shows each of the three cyclopentadienyl rings with the C–C, C–H, and Mo–C distances recorded to facilitate comparisons. Final atomic positional and thermal parameters are given in Table I with the listed standard deviations being derived from the inverse matrix of the final least-squares refinement cycle. The hydrogen atoms are labeled according to the carbon atoms to which they are bonded (*i.e.*, H_1 is bonded to C_1). Anisotropic temperature factors and the root-mean-square amplitudes of vibration with their direction cosines are listed in Tables II and III, respectively. Intramolecular distances and bond angles are given in Tables IV and V, while Table VI gives the equations for planes through the cyclopentadienyl rings and the distances of pertinent atoms from these mean planes.

Discussion

Few compounds containing three C_5H_5 residues per metal atom have been reported.[17] Those formed by the lanthanide metals are thought to be basically ionic in nature, but no detailed structural investigation has been reported. Those of the actinides have properties suggesting that they may be more covalent in nature, and one of them, $(C_5H_5)_3$UCl, has been studied by X-ray diffraction.[18] However, because of the overwhelming contribution of the uranium atom to the scattering, virtually nothing was learned about how the C_5H_5 groups are attached to the metal atom.

The crystal structure of $(C_5H_5)_3$MoNO consists of a closely packed array of monomeric molecular units, with normal van der Waals contacts between the units. The shape of the molecule does not appear to be attributable in any significant particular to intermolecular forces.

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(15) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, p 113.

(16) For this table, order NAPS Document No. NAPS-00297 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001, remitting $1.00 for microfiche or $3.00 for photocopies. Make checks or money orders payable to: ASIS–NAPS.

(17) *Cf.* J. M. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).

(18) C. H. Wong, T.-M. Yen, and T.-Y. Lee, *Acta Cryst.*, **18**, 340 (1965).

Table V. Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
C_1-Mo-C_2	30.1 (2)	C_5-C_1-C_2	109.1 (5)
C_2-Mo-C_3	33.0 (2)	C_1-C_2-C_3	106.9 (4)
C_3-Mo-C_4	34.5 (2)	C_2-C_3-C_4	106.4 (4)
C_4-Mo-C_5	32.7 (2)	C_3-C_4-C_5	108.0 (5)
C_5-Mo-C_1	31.4 (2)	C_4-C_5-C_1	109.2 (5)
C_6-Mo-C_7	30.3 (2)	C_{10}-C_6-C_7	107.0 (4)
C_7-Mo-C_8	32.2 (2)	C_6-C_7-C_8	108.6 (4)
C_8-Mo-C_9	34.8 (1)	C_7-C_8-C_9	108.3 (4)
C_9-Mo-C_{10}	33.7 (1)	C_8-C_9-C_{10}	107.7 (3)
C_{10}-Mo-C_6	31.9 (1)	C_9-C_{10}-C_6	108.0 (4)
C_{12}-Mo-N	84.7 (1)	C_{15}-C_{11}-C_{12}	109.8 (3)
Mo-N-O	179.2 (2)	C_{11}-C_{12}-C_{13}	103.2 (3)
Mo-C_{12}-C_{11}	115.9 (2)	C_{12}-C_{13}-C_{14}	109.7 (3)
Mo-C_{12}-C_{13}	111.9 (2)	C_{13}-C_{14}-C_{15}	108.5 (3)
		C_{14}-C_{15}-C_{11}	108.7 (3)
C_5-C_1-H_1	131 (3)	C_8-C_9-H_9	127 (2)
H_1-C_1-C_2	120 (3)	H_9-C_9-C_{10}	125 (2)
C_1-C_2-H_2	127 (3)	C_9-C_{10}-H_{10}	123 (4)
H_2-C_2-C_3	126 (4)	H_{10}-C_{10}-C_6	128 (3)
C_2-C_3-H_3	123 (5)	C_{15}-C_{11}-H_{11}	129 (3)
H_3-C_3-C_4	126 (5)	H_{11}-C_{11}-C_{12}	121 (3)
C_3-C_4-H_4	119 (4)	C_{11}-C_{12}-H_{12}	118 (2)
H_4-C_4-C_5	133 (4)	H_{12}-C_{12}-C_{13}	114 (2)
C_4-C_5-H_5	125 (3)	C_{12}-C_{13}-H_{13}	123 (2)
H_5-C_5-C_1	126 (3)	H_{13}-C_{13}-C_{14}	127 (2)
C_{10}-C_6-H_6	128 (3)	C_{13}-C_{14}-H_{14}	125 (2)
H_6-C_6-C_7	125 (3)	H_{14}-C_{14}-C_{15}	126 (2)
C_6-C_7-H_7	131 (2)	C_{14}-C_{15}-H_{15}	123 (2)
H_7-C_7-C_8	120 (3)	H_{15}-C_{15}-C_{11}	128 (2)
C_7-C_8-H_8	123 (2)		
H_8-C_8-C_9			

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed.

The molecular structure itself exhibits many interesting and a few very singular and arresting features. We shall begin by examining how each of the four ligand groups is related to the metal atom and then discuss the manner in which the ligand groups interact with each other in this very crowded molecule. One of the C_5H_5 groups is very simply related to the metal, namely through a simple two-center, two-electron bond. The NO group is strongly but not anomalously bound, while the remaining two C_5H_5 groups enjoy a curious and, we think, unprecedented form of interaction with the metal.

The h^1-C_5H_5 Ring. The only previously reported structure of a molecule containing a *monohapto*- or σ-bonded cyclopentadienyl ring is that of $(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_5H_5)$ in which the standard deviations were relatively large, thus obscuring details.[19] The present work affords the first opportunity to examine this structural situation in accurate detail. As shown in Figure 3, the variation in C–C bond lengths is quite marked and in excellent agreement with the expected occurrence of double bonds in the 2 and 4 positions. It is also noteworthy that the angle formed by the bonds to the non-olefinic carbon atom is only 103° while the other four angles are ~109°. Also, no carbon atom deviates from the mean plane by more than 0.013 Å. All of these features are very similar to (though much more accurately established than) the structural features of cyclopentadiene itself.[20]

The mean of the values of the three accurately measured angles between bonds to the carbon atom (C_{12}) which is attached to the Mo atom is 110.3°. This carbon atom may therefore be considered as approximately sp^3 hybridized. The bond it forms to the molybdenum atom is 2.29 Å in length. A single-bond radius for Mo in this compound may therefore be taken as $2.29 - 0.77 = 1.52$ Å. This is about 0.1 Å shorter than the molybdenum radius which is obtained in (dien)Mo$(CO)_3$[21] and $(h^5\text{-}C_5H_5)(CO)_3MoC_2H_5$,[22] namely ~ 1.61 Å. However, the formal oxidation states of Mo in these two compounds are 0 and +1, respectively, whereas in $(C_5H_5)_3$MoNO it is +3 if we treat NO as a neutral ligand (as we propose to do; *vide infra*). Therefore a smaller radius is not unexpected.

The MoNO Group. The Mo–N–O group does not deviate from linearity by any chemically or electronically significant amount. There is a very small deviation (0.8°) which appears to be real (*i.e.*, statistically significant, esd ≈ 0.2°), but nonbonded repulsions could easily be responsible for this. In short, this particular MNO group may be added to the relatively short list of truly linear ones found in structures determined with high accuracy.[23]

The Mo–N distance is a very short one (1.751 Å) as may be seen by comparison with the Mo–N and Mo–C distances[21] (2.32 and 1.95 Å, respectively) in dienMo$(CO)_3$. It was estimated[21] that in dienMo$(CO)_3$, where the carbonyl groups must be engaged in considerable π bonding

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(19) M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(20) G. Liebling and R. E. Marsh, *Acta Cryst.*, **19**, 202 (1965).

(21) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965). dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$.

(22) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

(23) A list of others, with references, will be found in a paper by A. T. McPhail and G. A. Sim, *J. Chem. Soc.*, 1858 (1968).

Table VI. Best Weighted Least-Squares Planes[a]

Atoms	Plane	L	M	N	D
C_1–C_5	1	0.3505	0.7150	0.6050	6.0364
C_6–C_{10}	2	−0.3133	0.4772	0.8211	−0.5986
C_{11}–C_{15}	3	−0.8127	0.3017	0.4984	−0.1795

Distances of Atoms from Planes, Å					
Atoms	Plane 1	Atoms	Plane 2	Atoms	Plane 3
C_1	−0.003	C_6	−0.022	C_{11}	0.011
C_2	0.024	C_7	−0.013	C_{12}	−0.011
C_3	−0.033	C_8	0.028	C_{13}	0.013
C_4	0.038	C_9	−0.030	C_{14}	−0.008
C_5	−0.027	C_{10}	0.037	C_{15}	−0.005
Mo	−2.140	Mo	2.145	Mo	−1.784

Dihedral angle between planes 1 and 2 is 43.3°

[a] The equations of the planes are $LX + MY + NZ = D$, where L, M, and N are the direction cosines referred to the orthogonal axis system a, b, c^*, and $X = ax$, $Y = by$, and $Z = cz$.

with the metal atom, probably attaining or closely approaching double-bond character, the Mo to C bonds are about 0.36 Å shorter than Mo–C single bonds. For the Mo atom in $(C_5H_5)_3MoNO$ we have already estimated a single-bond radius of 1.52 Å. Adding to this a single-bond radius of 0.64 Å for sp-hybridized nitrogen, we obtain as an estimated single-bond length for Mo–N in this compound 2.26 Å. The observed distance is some 0.51 Å shorter than this, which indicates that there is a very large amount of Mo-to-N π bonding arising out of back-donation from Mo to N *via* π orbitals.

If this is indeed the case, the N-to-O π bond order should be appreciably reduced, and therefore the N–O distance ought to be relatively long. Exactly this is observed. The N–O distance here is 1.207 (4) Å, whereas in other structures[23] in which linear MNO groups have been structurally characterized with high accuracy the distances tend to be smaller,[24] as indicated by the following examples, where the reported NO distances are presented with their reported esd's in parentheses: $[(C_6H_5)_3P]_2Mn(CO)_2NO$, 1.18 (1) Å; $Fe(CN)_5NO]^{2-}$, 1.13 (2) Å; $[C_5H_5Cr(NO)SC_6H_5]_2$, 1.19 (1) Å.

Clearly, all of the structural data lead to the conclusion that there is a very strongly bound NO group of the type which is often *formally* described[25] as coordinated NO^+. We propose here, however, that this *formalism* should *not* (as it generally has done) serve as a basis for figuring the oxidation states of metal atoms. Regardless of whether one makes the formal assumption of an initial transfer of one electron to the metal so as to create an NO^+ group which is then postulated to coordinate in the same manner as the isoelectronic CO group, the actual electron distribution in the MNO group must be such that a state of approximate electroneutrality exists. Indeed, it is likely that there may be some net accumulation of negative charge in the NO group.

Specifically, in the present molecule, we treat the NO group as a neutral ligand. If the three C_5H_5 groups are regarded as anionic, or tending to be so, the formal oxidation state of the molybdenum atom is III.

The Two *polyhapto*-C_5H_5 Groups. It is strikingly evident from Figure 3 that there is no major difference between these two rings insofar as their structural relationship to the metal atom is concerned. It is also obvious that the observed relationship is not one which can be either described or explained in a simple way. In this paper we shall be concerned mainly with presenting the observations. An attempt to interpret the observations will be deferred until structural data for some related molecules become available. The most prominent structural features of the $(C_5H_5)_2Mo$ portion of the molecule will now be stated.

(1) All five carbon atoms in each of these rings are close enough to the Mo atom that a bonding interaction must be assumed to exist, and yet the strengths of the bonds must vary considerably since the distances span a considerable range. In each ring there are two adjacent carbon atoms at distances of 2.32–2.35 Å from the Mo atom. These distances are in the range of distances reported for compounds having conventional $(h^5\text{-}C_5H_5)Mo$ moieties. Data were recently summarized by Churchill and Fennessey[26] and from their tabulation the range is 2.26 to 2.40 Å with a mean of 2.34 Å (values uncorrected for libration are being considered here). In each ring there is then one carbon atom lying 2.43 ± 0.01 Å from Mo; this must be nearly as strongly bonded as the two closest ones. Finally, each ring has two adjacent carbon atoms which are 2.59–2.68 Å; the bonding of these to the Mo atom must be considerably weaker, but still, at these distances an appreciable bonding interaction must exist.

(2) The rings are in an eclipsed relationship to each other, and the dihedral angle between their mean planes is 43.3°. There are only two other compounds of known structure in which two cyclopentadienyl rings are each bonded through five carbon atoms to a molybdenum atom, in each of which a conventional $(h^5\text{-}C_5H_5)Mo$ relationship is found. In one of them, $(C_5H_5)_2MoH_2$,[27] the rings are eclipsed and the angle between the ring planes is 34 ± 1°. In the other, $(C_5H_5)_2MoS_2C_6H_3CH_3$,[28] the rings are staggered and the angle between their planes is ~46°.

The factors which determine the relative stabilities of staggered and eclipsed rotational conformations of the rings, even in a symmetrical case such as ferrocene, have

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(24) It was shown in ref 21 that for CO groups bond length is relatively insensitive to bond order when the latter is in the range of 2–3. Thus even small increases in CO and presumably NO distances in MCO and MNO systems are indicative of substantial decreases in CO or NO π bonding.

(25) *Cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, pp 747–752.

(26) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 6, 1213 (1967).

(27) M. Gerlock and R. Mason, *J. Chem. Soc.*, 296 (1965).

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

never been identified. Approximate molecular orbital treatments do not disclose any inherent difference in energy between staggered and eclipsed configurations; consideration of nonbonded repulsions would then lead us to expect slightly greater stability for the staggered form. Contrary to this expectation, the ferrocene molecule in the gas phase is reported[29] to have the eclipsed configuration. In view of the general ignorance of rotational energy dependence even in relatively simple situations, it is impossible to offer any explanation of the eclipsed configuration here. Some of the nonbonded contacts (especially $C_2 \cdots C_7$, $H_2 \cdots H_7$) between the two *polyhapto* rings are quite short and would be somewhat lengthened by rotation to a staggered configuration. The preference for an eclipsed configuration is therefore especially surprising here. It may be noted though that the nmr equivalence within each set of protons in these rings, even at −110°, shows that the barrier to rotation, namely, the energy difference between staggered and eclipsed configurations, is not greater than ~10 kcal/mole (unless one assumes that the rings rotate in a concerted fashion so as to preserve the eclipsed relationship between them).

The angle between the mean ring planes (43.3°) is consistent with the analysis of Ballhausen and Dahl,[30] although their treatment can be used in only a loose manner, if at all, in the present case because of the great distortion from a pentagonal pyramidal MoC_5 geometry.

(3) The rings are slightly but definitely puckered. In view of the various severe intramolecular nonbonded contacts, it is impossible to say with any certainty how much of this is due to bonding forces and how much to nonbonded repulsions.

Interpretation of the Pmr Spectrum. As we have already noted in the introductory section, the pmr spectrum of this molecule at moderately low temperature in solution shows the presence of an h^1-C_5H_5 ring, while the protons of the other two rings remain indistinguishable. However, at lower temperatures (*ca.* −100°) each of the other rings gives a separate signal, while the h^1-C_5H_5 ring gives a more complex spectrum consistent with the notion that its two edges lie in different environments. These observations can be accounted for if the instantaneous structure at low temperature in solution is the same as, or very similar to, that which we have found in the crystal.

It is clear from Figures 1 and 2 that the two edges of the h^1-C_5H_5 ring lie in significantly different relationships to the remainder of the group of ligands. H_{11} and H_{15} project upward and away from the other three ligand groups whereas H_{13} and H_{14}, especially H_{13}, are close to the NO group. Thus the gradual evolution of the XAA′BB′ spectrum which the h^1-C_5H_5 ring gives at about −50° into an XABCD spectrum at about −110° could be attributed solely to the slowing of rotation about the Mo–C_{12} bond, with the h^1 ring settling into a rotational configuration similar to that found in the crystal. It is not *necessary* to assume that the other two rings are chemically different from each other.

Conversely, as the h^1-C_5H_5 ring settles into a rotational orientation like that seen in the crystal, a difference, which could easily be large, must arise between the degrees of intramolecular shielding felt by the protons in each of the other two rings. Since each set of five protons continues to give a single line down to the lowest temperature of observation, we assume that internal rotation of each ring continues to be rapid. However, as indicated in Figure 1 by the two protons shown as small filled circles, protons on each of the rings will make their closest approach to the h^1-C_5H_5 ring in very different regions. Thus, protons from the C_6–C_{10} ring pass over the π cloud of the butadiene region of the h^1-C_5H_5 ring while protons of the C_1–C_5 ring are at all times much farther from this butadiene moiety, and at the point of closest approach they lie approximately in the nodal plane of the butadiene π system. Environmental differences of this sort have been reported to cause chemical shift differences of the order of 1 ppm in other compounds. Examples are provided by the methylene protons in the cycloheptatriene complexes $C_7H_8M(CO)_3$, M = Cr, Mo, W.[31]

In summary then, the kind of structure we have found for $(C_5H_5)_3MoNO$ in the crystal, in which two of the rings have essentially the same relationship to the metal atom and differ only in their orientation relative to the h^1-C_5H_5 and NO groups, *can* account for all of the complex changes which occur in the pmr spectrum of this molecule at lower temperatures in solution. It is not *necessary* to assume that the three rings are each bonded differently to the metal. At the same time, it should be stressed that there is no evidence to show that the molecular structure found in the crystal *is in fact* retained in solution. In our report[4] on the pmr spectrum of the molecule, it was pointed out that while the assumption of an instantaneous structure with three differently bonded rings, *e.g.*, $(h^1$-$C_5H_5)(h^3$-$C_5H_5)(h^5$-$C_5H_5)MoNO$, seemed natural it was not in fact *demanded* by the pmr results. The study reported here shows that there is a real and not merely hypothetical alternative to such a structure.

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[29] R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).

[30] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

[31] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).