Stereochemically Nonrigid Organometallic Molecules. XVI. The Crystal and Molecular Structure of *p*-Methyl-π-benzyl-π-cyclopentadienyldicarbonylmolybdenum[1,2]

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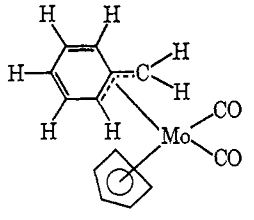
Abstract: The crystal and molecular structures of the fluxional molecule, *p*-methyl-π-benzyl-π-cyclopentadienyldicarbonylmolybdenum, $(p\text{-}CH_3C_6H_4CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$, have been determined by single-crystal X-ray diffraction techniques. The principal crystallographic data are as follows: space group $P2_1/c$; unit cell dimensions, a = 6.334 Å, b = 17.179 Å, c = 12.861 Å, β = 106.98°; Z = 4. Using 1990 independent reflections collected manually on a General Electric diffractometer, the structure was solved using Patterson and Fourier methods and refined by least squares to final unweighted and weighted residuals of 0.050 and 0.072, respectively. All hydrogen atoms of the $CH_3C_6H_4CH_2$ group were located and were refined isotropically. The heavier atoms were refined anisotropically. The gross features of the structure are essentially those postulated for the analogous benzyl compound by King and Fronzaglia. The C_5H_5 ring is, of course, "sandwich-bonded" to the metal atom, and the Mo–C–O groups are normal. The $p\text{-}CH_3C_6H_4CH_2$ group is bonded, somewhat unsymmetrically, through the CH_2 carbon atom, the ring carbon to which CH_2 is attached, and one carbon atom *ortho* to that, thus giving a π-allyl complex. The formation of this π-allyl complex would require some interference with the π-electron delocalization in the ring, and, in fact, there is a marked alternation of bond lengths, the three longer ones lying in the range 1.42–1.43 Å while the shorter ones have lengths of 1.33 and 1.36 Å. Some of the implications of this structure with regard to the rearrangement pathway that is responsible for the fluxional character of the molecule are discussed.

In 1966 King and Fronzaglia[4] reported the first benzyl complex of a transition metal, $(C_6H_5CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$, in which three carbon atoms of the benzyl moiety were presumed to form an allyl group, attached to the metal atom as indicated in I. The benzyl group so bound to a metal is a benzolog of the allyl group in π-allylmetal complexes. Just as remarkable as the π-allyl type of structure is the fluxional character[5] of the molecule; King and Fronzaglia discussed several possible rearrangement pathways to account for the observed averaging of nmr resonances.



I

The compound $[(C_6H_5)_3C]_2Ni$ has been reported by Wilke and Schatt,[6] and King[7] has suggested that this too may be a π-benzyl complex.

Our interest in this type of fluxional organometallic molecule has led us to prepare and study the *p*-methyl analog of King and Fronzaglia's compound. Chemical and nmr studies[8] will be reported later. In order to have an unequivocal structural basis for discussing the fluxional behavior of the molecule, and also to ascertain how, in detail, the aromatic ring is modified so as to enable the π-allyl system to become established, an X-ray crystallographic investigation of the structure of $(CH_3C_6H_4CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$ has been carried out. This paper presents the results of that investigation.

Procedure

Deep red, monoclinic prisms of $(CH_3C_6H_4CH_2)(C_5H_5)(CO)_2Mo$ were grown from a solution in a mixture of pentane and methylene chloride at 0° using material kindly provided by Mr. T. J. Marks. Operating in a glove box filled with nitrogen, a crystal of dimensions 0.419 × 0.073 × 0.127 mm was placed in a thin-walled Lindemann glass capillary. Weissenberg films of the $0kl$, $1kl$, and $2kl$ levels and a precession film of $h0l$ showed the crystals to be monoclinic with systematic absences on $0k0$ for $k = 2n + 1$ and on $h0l$ for $l = 2n + 1$ conforming to the space group $P2_1/c$ (No. 14). The unit cell dimensions were measured and the data collected at 21 ± 1° using Ni-filtered Cu Kα radiation (λ 1.5418 Å). The angle β, measured on films from a calibrated precession camera, was found to be 106.98 ± 0.05°. The unit cell lengths were measured using a General Electric manually operated counter diffractometer. Observed values were plotted against the function $^1/_2[(\cos^2\theta)/(\sin\theta) + (\cos^2\theta)/\theta]$ and extrapolated[9] to θ = 90.0°, giving the following results: a = 6.334 ± 0.003 Å, b = 17.179 ± 0.001 Å, and c = 12.861 ± 0.002 Å. (Uncertainties represent esti-

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[1] Part XV: F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, **90**, 5412 (1968).

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[3] National Institutes of Health Predoctoral Fellow.

[4] R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[5] For discussion and references pertaining to fluxional organometallic molecules in general, see F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[6] G. Wilke and H. Schatt, *Angew. Chem. Intern. Ed. Engl.*, **5**, 582 (1966).

[7] R. B. King in "Annual Surveys of Organometallic Chemistry," Vol. 3, D. Seyferth and R. B. King, Ed., Elsevier Publishing Co., Amsterdam, 1967, p 403.

[8] T. J. Marks, unpublished work.

[9] A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (London), **57**, 126 (1965); J. B. Nelson and D. P. Riley, *ibid.*, **57**, 160 (1945).

mates of precision.) Because of the instability of the compound, the density was not measured. The calculated density for $Z = 4$ is 1.607 g/cc.

The crystal was aligned on the diffractometer so that its a^* axis was coincident with the ϕ axis of the goniometer. The intensities of 2278 independent reflections (index sets hkl and $h\bar{k}\bar{l}$) within the sphere $(\sin \theta/\lambda) \leq 0.588$ were measured with a scintillation counter; the pulse height discriminator was set to accept 95% of the Cu Kα peak with the window centered on the Cu Kα peak. A moving-crystal-moving-counter scan technique was employed with a scan range (in 2θ) of 2.66° to conform with the mosaic spread of the crystal. The scan rate was 4°/min.

The integrated intensities (I) were obtained from the total counts (P) of a coupled $\theta/2\theta$ scan from $2\theta_{\text{calcd}} - 1.33°$ to $2\theta_{\text{calcd}} + 1.33°$ and from stationary background measurements (B_1, B_2) of 20-sec duration each at the limits of the scan; it was assumed that $I = P - B_1 - B_2$. Of 25 strong reflections which exceeded the linear response range of the counter, 18 could be measured at lower current (5 mA) and were scaled using 19 medium intensity reflections measured under both sets of conditions. The nonlinearity of the counter for strong reflections was then plotted from these 18 reflections, and from this curve intensities were assigned to the remaining seven very strong reflections. Three reflections differing in ϕ, X, and 2θ which were checked at frequent intervals exhibited a maximum variation of ±4%, which was random with time; thus, there was no evidence for significant crystal decomposition.

The intensities were converted[10] to relative values of $|F_o|^2$ and $|F_o|$, rejecting 286 reflections for which $I \leq 0$ or $I < 3(P + B_1 + B_2)^{1/2}$ (see Table I). Of the remaining 1992 reflections, the 100 and 020 reflections were eventually suspected of suffering seriously from extinction and were rejected.

Table I. Distribution of Intensities as a Function of Statistical Reliability

Rejected data		Accepted data	
Range[a]	No.	Range[a]	No.
$I \leqslant 0$	66	$3 < I/\Delta I \leqslant 4$	56
$0 < I/\Delta I \leqslant 1$	53	$4 < I/\Delta I \leqslant 6$	106
$I < I/\Delta I \leqslant 2$	98	$6 < I/\Delta I \leqslant 10$	164
$2 < I/\Delta I \leqslant 3$	69	$10 < I/\Delta I \leqslant 20$	341
Total	286	$20 < I/\Delta I \leqslant 50$	719
		$50 < I/\Delta I \leqslant 100$	433
		$I > 100$	177
		Total	1992

[a] $\Delta I = (P + B_1 + B_2)^{1/2}$.

The molybdenum atom was found in a three-dimensional Patterson map. Using signs given by the molybdenum atom, a three-dimensional Fourier map was computed from which the coordinates of the carbon and oxygen atoms were obtained. After several cycles of isotropic least-squares refinement,[10e,11a] absorption corrections were applied. The faces of the crystal had been carefully identified and measured, and absorption corrections for the monoclinic prism were calculated[10d] using $\mu = 83.38$ cm^{-1}. Anomalous dispersion corrections were introduced,[11b] and refinement was changed to anisotropic using thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The experimental weighting scheme used was that of Doedens and Ibers[12] with $p = 0.045$.

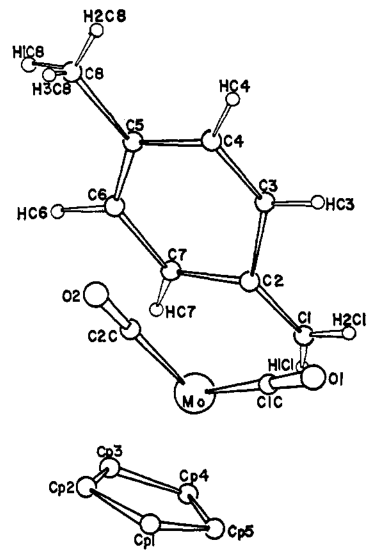

Figure 1. A projection of the molecule on the a^*c plane after rotation by 20° about the a^* axis. This figure defines the atom numbering scheme used in Tables II–VI.

At $R_1 = (\Sigma||F_o| - |F_o||)/\Sigma|F_o| = 0.091$, a difference Fourier map was computed and all of the hydrogen atoms on the p-$CH_3C_6H_4CH_2$ ligand were unambiguously located, but the C_5H_5 hydrogen atoms could not be located either in this difference Fourier map or in the final one. The hydrogen atoms were refined isotropically while refinement of the other atoms was continued anisotropically. The refinement was considered complete when in one cycle no thermal or positional parameter changed by as much as its estimated standard deviation. After this final cycle of refinement, R_1 was 0.050 and $R_2 = \{\Sigma[|F_o| - |F_o|]^2/\Sigma w|F_o|^2\}^{1/2}$ was 0.072. In the final electron density difference map, the standard deviation in the electron density[13] was 0.17 e/Å.^{3} The highest peak in the difference map contained 0.27 e/Å.^{3}

Results

The final atomic positional and thermal parameters are given in Table II. The anisotropic thermal parameters are listed in Table III. A list of calculated struc-

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(10) Computer programs used in this study were: (a) D. P. Shoemaker, MIXG2, calculates diffractometer settings; DISTAN, calculates orthogonal cell coordinates, intra- and intermolecular contacts and angles; (b) R. C. Elder, PDATA2, corrects MIXG2 output for ϕ_0 and scan width and prints diffractometer setting in convenient format; PUBTAB, prepares compact tabulation of structure factors; (c) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, MIFR-2A, 1962 Fourier summation for Patterson or Fourier maps; (d) W. C. Hamilton, GONO9, used for the absorption correction; (e) C. T. Prewitt, SFLS5, 1967, least-squares refinement of parameters minimizing $\Sigma(w||F_o| - |F_c||^2)$; (f) D. L. Weaver, WOFF2, calculates average Δ^2 *vs.* average F_o for weighting; (g) J. S. Wood, MGEOM, calculates intramolecular bond lengths and angles and standard deviations and best least-squares planes; (h) M. J. Bennett, PMMO, data reduction and σ calculation.

(11) (a) Scattering factors for Mo, O, and C were from D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965); scattering factors for H are from R. Mason and G. B. Robertson, "Advances in Structural Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Divsion, John Wiley and Sons, Inc., New York, N. Y., 1966, p 57; (b) "International Tables for Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.2B.

(12) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(13) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949).

Table II. Final Atomic Positional Parameters[a]

Atom	x	y	z	$B^b \times 10^4$
Mo	0.04613 (7)	0.72131 (2)	0.46461 (3)	2.7
C1	0.2671 (12)	0.7519 (4)	0.3600 (5)	4.0
C2	0.1171 (10)	0.8153 (3)	0.3448 (4)	3.5
C3	0.1791 (10)	0.8925 (4)	0.3839 (5)	4.0
C4	0.0329 (11)	0.9498 (3)	0.3712 (5)	4.4
C5	−0.1975 (11)	0.9369 (3)	0.3230 (5)	4.2
C6	−0.2639 (10)	0.8634 (3)	0.2892 (4)	3.8
C7	−0.1117 (10)	0.8013 (3)	0.2996 (4)	3.4
C8	−0.3589 (18)	1.0030 (5)	0.3089 (11)	6.6
Cp1	−0.0129 (14)	0.6121 (4)	0.5552 (5)	5.2
Cp2	−0.2191 (13)	0.6329 (4)	0.4883 (8)	5.8
Cp3	−0.2194 (15)	0.6245 (4)	0.3824 (7)	6.7
Cp4	−0.0208 (19)	0.5981 (4)	0.3782 (7)	6.9
Cp5	0.1132 (16)	0.5905 (4)	0.4874 (8)	5.9
C1C	0.3031 (10)	0.7596 (3)	0.5751 (4)	3.7
C2C	−0.0746 (9)	0.8039 (3)	0.5370 (4)	3.5
O1	0.4513 (8)	0.7839 (3)	0.6423 (4)	5.8
O2	−0.1372 (9)	0.8521 (2)	0.5824 (4)	5.6
H1C1	0.226 (8)	0.707 (3)	0.306 (4)	3.5 (9)
H2C1	0.395 (13)	0.763 (4)	0.389 (6)	5.3 (1.4)
HC3	0.332 (12)	0.903 (4)	0.418 (6)	6.7 (1.6)
HC4	0.103 (11)	1.002 (4)	0.401 (6)	6.2 (1.4)
HC6	−0.426 (10)	0.852 (3)	0.260 (5)	4.5 (1.1)
HC7	−0.166 (11)	0.756 (4)	0.268 (6)	4.6 (1.3)
H1C8	−0.510 (17)	0.996 (5)	0.248 (8)	9.3 (2.5)
H2C8	−0.304 (15)	1.052 (6)	0.301 (8)	8.8 (2.5)
H3C8	−0.393 (19)	1.015 (6)	0.357 (9)	9.6 (3.5)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed. [b] Or equivalent B.

Table III. Anisotropic Thermal Parameters ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	229.8 (1.6)	18.2 (2)	41.5 (3)	0.2 (3)	24.8 (5)	1.3 (1)
C1	271 (21)	38 (2)	70 (5)	9 (6)	74 (8)	11 (3)
C2	292 (18)	30 (2)	46 (3)	−5 (5)	42 (6)	11 (2)
C3	283 (20)	32 (2)	66 (4)	−21 (5)	33 (7)	9 (2)
C4	390 (23)	24 (2)	75 (5)	−23 (5)	44 (8)	8 (2)
C5	347 (20)	28 (2)	72 (4)	13 (5)	56 (7)	15 (2)
C6	287 (19)	32 (2)	50 (3)	−6 (5)	19 (6)	9 (2)
C7	288 (18)	26 (2)	44 (3)	−8 (5)	19 (6)	4 (2)
C8	482 (37)	31 (3)	151 (11)	40 (8)	89 (17)	23 (5)
Cp1	603 (34)	21 (2)	82 (5)	−28 (6)	95 (11)	5 (3)
Cp2	409 (27)	26 (2)	141 (8)	−25 (6)	77 (12)	4 (3)
Cp3	525 (34)	30 (3)	115 (7)	−45 (7)	−27 (13)	5 (3)
Cp4	873 (51)	29 (2)	99 (6)	−63 (9)	176 (15)	−19 (3)
Cp5	381 (31)	23 (2)	159 (10)	22 (7)	94 (14)	7 (3)
C1C	293 (19)	30 (2)	49 (4)	1 (5)	23 (7)	8 (2)
C2C	301 (19)	22 (3)	63 (4)	−8 (4)	55 (7)	3 (2)
O1	314 (16)	60 (2)	75 (4)	−32 (5)	−22 (6)	6 (2)
O2	578 (21)	28 (2)	105 (4)	0 (4)	15 (8)	−12 (2)

ture factors and observed structure amplitudes has been deposited with the ASIS–NAPS.[14]

The molecular structure is displayed in Figure 1. This view is derived from a projection on the a^*c plane after rotation by 20° about the a^* axis. Figure 1 defines the numbering scheme used in Tables II–VI. Table IV lists intramolecular distances and Table V gives bond angles. The best least-squares planes for the two rings are defined by the equations in Table VI, where the deviations of individual atoms from these mean planes are also given.

Discussion

The gross features of the molecular structure are as anticipated by King and Fronzaglia and represented schematically in I. The packing of the molecules involves no abnormal contacts except perhaps the following two: (1) HC7 and O1 between molecules at (x, y, z) and $(x, {}^1/_2 - y, {}^1/_2 + z)$, 2.58 Å: (2) HC4 and O2 between molecules at (x, y, z) and $(\bar{x}, \bar{y}, \bar{z})$, 2.52 Å.

The $(\pi\text{-}C_5H_5)Mo(CO)_2$ portion of the molecule is quite comparable to the corresponding portions of other molecules such as $(\pi\text{-}C_5H_5)Mo(CO)_3C_3F_7$.[15] As shown in Table VI, the C_5H_5 ring does not deviate significantly from planarity. The MoC_5 group approximately defines a pentagonal pyramid, but there are deviations from this idealized geometry as the C–C and Mo–C bond lengths as well as the C–C–C bond angles listed in Tables IV and V show. Our inability to locate the hydrogen atoms of C_5H_5 although all others showed up quite clearly together with the great magnitude of the temperature parameters of the cyclopentadienyl carbon atoms lead us to believe that here, as in the majority of molecules containing $(\pi\text{-}C_5H_5)M$ groups, there is considerable librational motion and/or rotational disorder in the C_5H_5 ring.[16] Consequently, no effort will be made to rationalize the variations in C–C bond lengths and C–C–C angles. It does seem quite clear, however, that, as in $(\pi\text{-}C_5H_5)Mo(CO)_3C_3F_7$, the C_5H_5 ring is tipped, in the sense that a perpendicular from Mo to the mean ring plane does not strike the ring at its center. Thus Cp1 and Cp5 are closest (2.29, 2.30 Å) to Mo; Cp3 is farthest (2.38 Å) with Cp2 and Cp4 at intermediate distances (2.35, 2.37 Å). The Mo–C–O groups are nearly, though not precisely, linear and the mean Mo–C (1.953 Å) and C–O (1.15 Å) distances are within the expected ranges.

We turn now to the structural details of the $p\text{-}CH_3\text{-}C_6H_4CH_2$ moiety and its relationship to the metal atom. The allyl group bound to Mo is formed by C1, C2, and C7. The molybdenum atom is significantly closer to the exocyclic end (C1) of the allyl group. Never-

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(14) This table has been deposited as Document No. NAPS-00032 with the ASIS National Auxiliary Publication Service, ℅ CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

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

(16) A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.*, **5**, 892 (1966).

Table IV. Intramolecular Distances (Å)

Atoms	Distance	Atoms	Distance
C1–C2	1.421 (9)	Mo–C1C	1.936 (6)
C2–C7	1.416 (8)	Mo–C2C	1.970 (6)
C2–C3	1.432 (8)	Mo–C1	2.269 (7)
C4–C5	1.426 (9)	Mo–C2	2.364 (5)
C6–C7	1.419 (8)	Mo–C7	2.480 (6)
C3–C4	1.328 (9)	Mo–C3	3.309 (6)
C5–C6	1.361 (8)	Mo–C6	3.510 (7)
C5–C8	1.502 (12)	Mo–Cp1	2.296 (6)
		Mo–Cp2	2.349 (8)
Cp1–Cp2	1.385 (11)	Mo–Cp3	2.382 (8)
Cp2–Cp3	1.386 (13)	Mo–Cp4	2.371 (8)
Cp3–Cp4	1.354 (14)	Mo–Cp5	2.290 (7)
Cp4–Cp5	1.419 (14)		
Cp5–Cp1	1.394 (12)	C1–H1C1	1.03 (5)
		C1–H2C1	0.81 (8)
C1C–O1	1.153 (8)	C3–HC3	0.95 (7)
C2C–O2	1.149 (7)	C4–HC4	1.02 (7)
		C6–HC6	1.01 (6)
C1–C1C	2.712 (9)	C7–HC7	0.90 (7)
C2–C1C	3.007 (8)	C8–H1C8	1.06 (10)
C2–C2C	3.062 (7)	C8–H2C8	0.93 (11)
C7–C2C	2.994 (9)	C8–H3C8	0.75 (11)
C1C–H1C1	3.47 (5)		
C1C–H2C1	2.62 (7)		
C2C–HC7	3.44 (6)		
Cp4–H1C1	2.76 (9)		
Cp4–HC7	3.07 (10)		
Cp3–HC7	2.76 (10)		

Table V. Bond Angles (Degrees)

Atoms	Angle	Atoms	Angle
C1–C2–C7	119.2 (5)	H1C1–C1–H2C1	121 (6)
C1–C2–C3	123.9 (5)	H1C1–C1–C2	117 (3)
C7–C2–C3	116.4 (5)	H2C1–C1–C2	114 (5)
C2–C3–C4	122.2 (5)	HC3–C3–C2	118 (4)
C3–C4–C5	121.8 (6)	HC3–C3–C4	120 (4)
C4–C5–C6	117.7 (6)	HC4–C4–C3	113 (4)
C4–C5–C8	120.6 (7)	HC4–C4–C5	125 (4)
C6–C5–C8	121.7 (6)	HC6–C6–C5	119 (3)
C5–C6–C7	122.0 (5)	HC6–C6–C7	119 (3)
C6–C7–C2	119.7 (5)	HC6–C7–C2	123 (4)
		HC7–C7–C6	117 (4)
Cp1–Cp2–Cp3	108.5 (7)	H1C8–C8–H2C8	108 (8)
Cp2–Cp3–Cp4	110.1 (7)	H2C8–C8–H3C8	92 (11)
Cp3–Cp4–Cp5	106.6 (7)	H1C8–C8–H3C8	103 (10)
Cp4–Cp5–Cp1	107.9 (9)	H1C8–C8–C5	116 (5)
Cp5–Cp1–Cp2	106.8 (6)	H2C8–C8–C5	116 (6)
		H3C8–C8–C5	117 (8)
Mo–C1C–O1	177.6 (5)		
Mo–C2C–O2	177.3 (5)		
C1C–Mo–C2C	76.6 (2)		

Table VI. Molecular Planes

1. Plane through the cyclopentadienyl ring atoms $-0.329x - 0.944y + 0.010z + 9.151 = 0$ Distance of atoms from plane (Å)			
Cp1	0.0008		
Cp2	0.0015		
Cp3	−0.0038		
Cp4	0.0051		
Cp5	−0.0037		
Mo	−2.009		
2. Plane through C2, C3, C4, C5, C6, C7 $-0.375x - 0.222y + 0.900z - 0.937 = 0$ Distance of atoms from plane (Å)			
C2	−0.022	C1	0.053
C3	0.024	C8	−0.056
C4	−0.006	HC7	−0.080
C5	−0.011	H1C1	−0.392
C6	0.005	H2C1	0.027
C7	0.010	HC3	0.029
		HC4	0.020
		HC6	0.072

theless, the two C–C distances in the allyl group are identical within the experimental uncertainties. It is possible that the tipping of the allyl group is mainly caused by intramolecular steric factors. Since this is the first X-ray study of a (π-allyl)molybdenum complex, comparisons can be made only with structures containing other metal atoms. As expected, the Mo–C distances are longer than palladium–, iron–, or nickel–allyl distances. The carbon-carbon distances (1.421 and 1.416 Å) are longer than those in any of the three compounds $(C_3H_5)_2Pd_2Cl_2$[17] (1.357 and 1.395 Å), $(C_3H_5)_2Pd_2(CH_3CO_2)_2$[18] (1.34, 1.37, 1.42, and 1.33 Å), and $[(CH_3)_4C_8H_4]Fe_2(CO)_5$[19] (1.36, 1.40, 1.35, and 1.37 Å) but are comparable with those in $Ni[(CH_2)_2CCH_3]_2$[20] (1.417 and 1.410 Å). As these bonds are affected by the extent of overlap with the metal, not only the metal size and coordination number but the nature of the other ligands coordinated to the metal must be taken into account.

The entire $CH_3C_6H_4CH_2$ moiety is approximately planar. The CH_2 carbon atom is slightly out of plane toward the Mo atom (by ~0.05 Å) while the CH_3 carbon atom is a comparable distance out of plane in the opposite direction. Although the uncertainties in the positions of the hydrogen atoms are great enough to discourage any attempt at detailed discussion, it may be noted that one of the methylene hydrogen atoms appears to lie considerably out of plane (~0.4 Å) away from the Mo atom and, largely because of this fact, the C–C and two C–H bonds involving C1 appear to define a very flat pyramid.

The four-carbon chain, C3–C4–C5–C6, which together with C2 and C7 constitutes the ring, has dimensions which approach those of a *cis*-1,3-butadiene group. Thus, usual values[21] for the double and single C–C bonds in such a group are 1.34 and 1.47 Å. In the C3–C4–C5–C6 chain of this molecule, the "double bonds" have lengths of 1.33 and 1.36 Å, while the "single-bond" (C4–C5) length is 1.43 Å. Thus, it would appear that the formation of the allyl system, C1–C2–C7, and its attachment to the molybdenum atom has resulted in some localization of the π-electron structure of the remainder of the ring. It is possible that this might have consequences in the chemical reactivity of this part of the molecule and studies along this line are in progress.[8]

It is interesting to compare the present structural result with the views of Davison and Rode[22] concerning the isomeric forms of King's[23] allyl complex $(\pi\text{-}C_5H_5)Mo(CO)_2C_3H_5$. Davison and Rode's work showed

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(17) A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).

(18) M. Churchill and R. Mason, *Nature*, **204**, 777 (1964).

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(20) H. Dietrich and R. Uttech, *Naturwissenshaften*, **50**, 613 (1963).

(21) *Cf.* "Tables of Interatomic Distances," Special Publication No. 18 (and Supplement, 1956–1959), L. E. Sutton, Ed., The Chemical Society, London, 1958, 1965, where average values are given. For a recent specific example of an endocyclic 1,3-butadiene group (with distances of 1.35, 1.45, 1.35 Å), see I. L. Karle, J. Karle, and J. A. Estlin, *Acta Cryst.*, **23**, 494 (1967).

(22) A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967).

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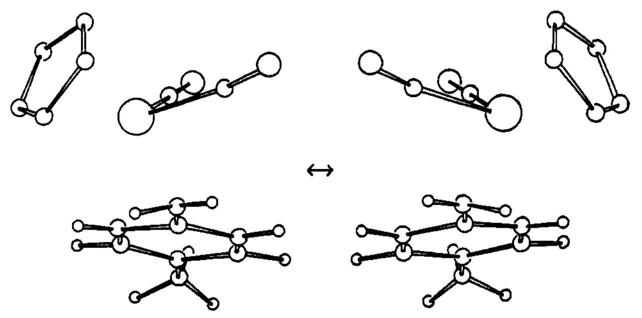

Figure 2. A view of the stylized molecule in its enantiomorphous forms to illustrate the rotation of the Mo(π-C$_5$H$_5$)(CO)$_2$ group which must accompany movement of the Mo atom relative to the benzyl moiety as these enantiomorphs are interconverted.

that two isomers which exist in solution in equilibrium most likely differ in a conformational sense, with interconversion of the conformers taking place by internal rotation. The structure we have found for $(CH_3C_6H_4CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$ corresponds to their structure A, which they felt was most likely the predominant one. Of course, the presence of the ring in the π-benzyl molecules creates a very strong steric preference for Davison and Rode's configuration A; the infrared spectrum[8] of $(CH_3C_6H_4CH_2)(\pi\text{-}C_5H_5)(CO)_2Mo$ gives no indication of the presence of more than one isomer in hexane solution and we presume that this is the isomer found by us in the crystal.

Finally, it remains to point out the implications of this structure with respect to the fluxional nature of the molecule. Even the simplest and shortest excursion by the metal atom which has the potentiality of producing the observed averaging in the nmr spectrum requires that simultaneously there be a considerable reorientation of the other ligands, π-C$_5$H$_5$ and the two CO groups. As Figure 2 shows, this set of ligands must rotate by about 150° in order to give a new conformation which is exactly the mirror image of the old one. Thus, at best, the pathway of the rearrangement accounting for the fluxional nature of the molecule will not be simple and, of course, there are more complicated trajectories for the metal atom relative to the benzyl moiety which are not, as yet, ruled out by any experimental data.

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The Molecular Configuration of $[H_2NFe(CO)_3]_2$ and Its Identity with the Previously Reported $[HNFe(CO)_3]_2$. The Influence of Bridged Ligands on the Basic Geometry of an Organometallic Complex Containing a Strong Metal–Metal Bond

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Abstract: An X-ray analysis of di-μ-amido-bis(tricarbonyliron), $[H_2NFe(CO)_3]_2$, has been carried out in order to assess the stereochemical consequence of replacement of a second-row nonmetallic bridging atom with a first-row atom in a ligand-bridged binuclear organometallic complex containing a strong metal–metal interaction. This diamagnetic complex, initially formulated and widely accepted as $[HNFe(CO)_3]_2$ with a presumed bridging diimido group, has been conclusively shown from the X-ray work and mass spectrometric analysis to possess a di-μ-amido structure. The two Fe(CO)$_3$ moieties are symmetrically linked to each other by two bridging amido groups and a "bent" iron–iron bond such that the resulting idealized molecular configuration of C$_{2v}$-2mm symmetry possesses a nonplanar Fe$_2$N$_2$ fragment with a sharply acute bridging Fe–N–Fe angle of 74.4° (esd, 0.5°) and Fe–Fe and Fe–N distances of 2.402 (6) and 1.98 (1) Å, respectively. A detailed comparison of its $[NFe(CO)_3]_2$ framework with those of $[C_2H_5SFe(CO)_3]_2$ and other electronically and structurally analogous sulfur-, nitrogen-, and phosphorus-bridged complexes is made. Despite sterically predictable variations in the X–Fe–X angles of the X$_2$Fe$_2$ system (X = N, S) in these homologous complexes, there is near-constancy of the Fe–Fe distances and Fe–X–Fe angles for a given X-bridged ligand. The considerably shorter Fe–Fe distances in the nitrogen-bridged dimers (2.37–2.40 Å) compared to the sulfur-bridged dimers (2.51–2.55 Å) are found to be primarily a consequence of the much smaller Fe–X distances (1.94–2.02 *vs.* 2.23–2.27 Å) counterbalanced to some extent by the somewhat larger Fe–X–Fe angles (72–75 *vs.* 67–70°). Crystals of $[H_2NFe(CO)_3]_2$ contain four dimeric molecules in an orthorhombic cell of symmetry Pna2$_1$ and of cell lengths a = 13.60 Å, b = 6.81 Å, c = 11.77 Å. A least-squares refinement of the structure resulted in a final unweighted discrepancy index of R_1 = 6.5% for the 472 independent nonzero reflections collected photographically.

The structural investigation of $[H_2NFe(CO)_3]_2$ was motivated in large part by the desire to assess the "size effect" of different bridging atoms on the molecular geometry of an organometallic ligand-bridged dimer containing a metal–metal bond.

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