# X-ray and Neutron Diffraction Studies of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] at 163 K

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The structure of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] (**1**) has been determined by X-ray diffraction at 163(3) K [$a$ = 6.969(2) Å, $b$ = 12.651(2) Å, $c$ = 7.954(2) Å, $\beta$ = 103.36(2)°, monoclinic, $P2_1/m$ (No. 11), $Z$ = 2] and neutron diffraction at 163.0(5) K [$a$ = 6.968(2) Å, $b$ = 12.658(3) Å, $c$ = 7.953(2) Å, $\beta$ = 103.34(2)°]. Refinements in space group $P2_1/m$ against both data sets improved the description of the structure obtained by refinements in $P2_1$ in this and an earlier study. The structure exhibits orientational disorder in the C$_5$Me$_5$ group, yet relatively accurate geometric parameters have been obtained, with esd's from the neutron diffraction study of 0.007 Å for Mo–H, 0.010 Å for C–H, and 0.003 Å (average) for all other bond lengths. The molecule adopts a "four-legged piano stool" geometry with the hydride ligand approximately *trans* to one of the Cp* ring carbons [Mo–H(1) = 1.789(7) Å]. Comparison of the title complex with related d$^4$ CpMo(CO)$_3$L complexes (L = formally anionic, monodentate, $\eta^1$ ligand) suggests that the conformation of these complexes is determined primarily by steric interactions between the ligand, L, and the Cp or Cp* ring, rather than by electronic effects of either Cp/Cp* or L.

## Introduction

Transition metal hydrides are involved in the key steps of numerous catalytic cycles, and the systematic study of the structure and reactivity of metal hydrides is fundamentally important in organometallic chemistry. The diversity of reactivity patterns exhibited by transition metal hydrides is exemplified by [MoH($\eta$-C$_5$H$_5$)(CO)$_3$]. This molybdenum hydride is one of several metal carbonyl hydrides that have been shown to undergo cleavage of the M–H bond to deliver hydrogen as a proton (H$^+$), as a hydrogen atom (H$^\bullet$), or as a hydride (H$^-$) in reactions with many different substrates.[1] While there have been numerous structural studies of cyclopentadienyl (Cp = C$_5$H$_5$) complexes which adopt a "four-legged piano stool" geometry, there are still relatively few reported structures which contain the pentamethylcyclopentadienyl (Cp* = C$_5$Me$_5$) ligand, and all have been published only since 1986.[2,3] In reference to the surge in activity in this area, Kubas, Hoff, and co-workers have pointed out[4] that

the synthesis of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] (**1**) was first described over 20 years ago,[5] but the chemistry of this and related Cp* complexes was only recently "rediscovered". To our knowledge, however, this structure is the only one of the type Cp*MoL$_3$L' to be reported.

The structure of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$], determined by X-ray diffraction at room temperature, was reported in 1986 by Leoni, Pasquali, and co-workers.[2] Our interest in the structure was to undertake a more accurate study at low temperature and assess the feasibility of conducting an experimental charge density study of this compound.[6] In the course of our investigation it became apparent that the previously reported structure involved an incorrectly assigned space group, with a resultant inaccurate molecular geometry. The results presented herein provide an accurate determination of the geometry of **1**, including one of only three reports of a terminal Mo–H distance characterized by neutron diffraction.[7]

## Experimental Section

**Preparation of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$].** The title compound was prepared according to the method of Asdar *et al.*[8] Yellow crystals suitable for diffraction studies were grown by slow cooling of a methanol solution of **1** from room temperature to –5 °C. The crystalline material is air-sensitive and was handled accordingly. As a precaution,[2,4] crystals were kept in the dark until required for data collection. However, extensive X-ray data collection time during which the crystals were exposed to light, albeit while maintained at 163(3) K, provided no evidence for light-induced decomposition.

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(4) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870.
(5) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.
(6) The extent of the disorder present in this structure even at 163 K precludes an accurate charge density study of this compound.
(7) (a) [MoH$_2$($\eta$-C$_5$H$_5$)$_2$]: Schultz, A. J.; Stearley, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 3303. (b) The structure of the Cp analogue of **1** has also been studied by neutron diffraction. [MoH($\eta$-C$_5$H$_5$)(CO)$_3$]: Cameron, R. P., Jr.; Stevens, E. D.; Sweany, R. L.; Koetzle, T. F. *Acta Crystallogr., Sect. B*, in press.
(8) Asdar, A.; Tudoret, M.-J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353.

**Table I.** X-ray and Neutron Data Collection and Refinement Parameters for 1

| | neutron | X-ray |
|---|---|---|
| | *Crystal Sample* | |
| faces [dist from origin, mm] | (011) [2.28]; (0$\bar{1}$1) [1.10]; ($\bar{1}5\bar{1}$) [1.23]; ($\bar{1}$00)[1.44]; ($0\bar{1}0$) [0.0]; (100) [0.0]; ($0\bar{1}\bar{1}$) [0.0] | |
| $V$ (mm$^3$) | 4.01 | |
| abs cor | analytical | empirical |
| abs coeff,$^a$ $\mu$ (cm$^{-1}$) | 1.89 | 9.52 |
| transm coeff | 0.723–0.822 | 0.569–0.686 |
| | *Crystal Data* | |
| crystal system | monoclinic | monoclinic |
| space group | $P2_1/m$ (No. 11) | $P2_1/m$ (No. 11) |
| $a^b$ (Å) | 6.968(2) | 6.969(2) |
| $b^b$ (Å) | 12.658(3) | 12.651(2) |
| $c^b$ (Å) | 7.953(2) | 7.954(2) |
| $\beta^b$ (deg) | 103.34(2) | 103.36(2) |
| cell vol (Å$^3$) | 682.61(3) | 682.27(14) |
| calcd density (g·cm$^{-3}$) | 1.538 | 1.539 |
| | *Diffraction Measurements* | |
| $T$ (K) | 163.0(5) | 163(3) |
| wavelength, $\lambda$ (Å) | 1.0462(1) | 0.71073 |
| $(\sin\theta)/\lambda$ limit (Å$^{-1}$) | 0.89 | 0.65 |
| scan type | $\omega$–$2\theta$ step scans (variable no. of steps) | $\omega$–$2\theta$ |
| no. of observns | | |
| total | 3126 | 5916 |
| independent ($R_{int}$) | 2735 (0.066) | 1652 (0.016) |
| used in refinement ($n$) | 2241 ($F^2 > 0$) | 1634 ($F > 2.0\sigma(F)$) |
| | *Refinement$^c$* | |
| no. of variables ($v$) | 170 | 91 |
| extinction param (g$^d$) | 0.4(1) | n/a |
| largest extinction factor | 1.10 for refln (020) | |
| indices of fit$^e$ | | |
| $R(F^2)$, $R(F)$ | 0.124 | 0.031 |
| $R_w(F^2)$, $R_w(F)$ | 0.108 | 0.047 |
| $S(F^2)$, $S(F)$ | 1.164 | 2.56 |

$^a$ Evaluated from mass absorption coefficients ($\mu/\rho$) taken from ref 9 for non-hydrogen atoms; determined by Koetzle and McMullan[10] for hydrogen atoms for the neutron diffraction study. $^b$ Determined from least-squares fits of $\sin^2\theta$ values for 32 reflections with $0.40 < (\sin\theta)/\lambda < 0.52$ Å$^{-1}$ for the neutron diffraction study and for 50 reflections with $0.40 < (\sin\theta)/\lambda < 0.57$ Å$^{-1}$ for X-ray diffraction study. $^c$ Neutron data reduction was performed with locally written programs, and the least-squares refinement, with the program UPALS.[11] X-ray data reduction and least-squares refinements were conducted using the SHELXTL[12] suite of programs. Neutron scattering lengths were taken from ref 13; X-ray scattering factors were taken from ref 14. $^d$ Isotropic g × 10$^3$ for type I crystal with Lorentzian mosaic distribution, according to the formalism of Becker and Coppens.[15] $^e$ Neutron: $R(F^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$; $R_w(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma(wF_o^2)^2]^{1/2}$; $S(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/(n - v)]^{1/2}$. X-ray: $R(F) = \Sigma|F_o = F_c|/\Sigma F_o$; $R_w(F) = [\Sigma w|F_o - F_c|^2/\Sigma(wF_o)^2]^{1/2}$; $S(F) = [\Sigma w|F_o - F_c|^2/(n - v)]^{1/2}$.

**X-ray Diffraction Study.** A crystal of dimensions 0.50 × 0.50 × 0.25 mm was coated with hydrocarbon oil, mounted on short glass fiber, and transferred directly to a Siemens R3m/V diffractometer, where it was cooled rapidly by the nitrogen stream of a modified Enraf-Nonius low-temperature device. Despite the air-sensitive nature of the crystal, this method of mounting proved adequate to prevent decomposition during more than 2 weeks of data collection and examination of the crystal. An initial attempt to collect data at 120 K was unsuccessful: the $\omega$-scan profiles of some reflections broadened into bimodal distributions, thus preventing accurate intensity measurements. When the crystal was warmed to 163 K, these profiles coalesced again into Gaussian shapes with scan widths suitable for recording meaningful intensity data throughout the reciprocal lattice. These observations suggest that 1 undergoes a reversible phase transition in the temperature range ca. 120–150 K; an exact transition temperature was not established.

Details of the data collection are given in Table I. Solution by direct methods yielded a structure in accord with the description by Leoni *et*

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(10) Koetzle, T. F.; McMullan, R. K. Research Memo. C-4, Brookhaven National Laboratory, Upton, NY, 1980.

(11) Lundgren, J.-O., Crystallographic Computer Programs. Report UUIC-B13-4-05; Institute of Chemistry, University of Uppsala: Uppsala, Sweden, 1982; modified, Brookhaven National Laboratory, 1983.

(12) Sheldrick, G. *SHELXTL* 4.2; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1991.

(13) Koester, L.; Yelon, W. B. In *Neutron Diffraction Newsletter*; Lehmann, M. S., Ed.; International Union of Crystallography (Commission for Neutron Diffraction): Chester, U.K., 1983.

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV. Present distributor: Kluwer Academic Publishers, Dordecht, The Netherlands.

*al.*[2] in the space group $P2_1$. The positions of all non-hydrogen atoms were located by successive difference Fourier syntheses and refined using anisotropic displacement parameters. However, large and seemingly irregular atomic displacement parameters prompted the refinement of the structure in the centrosymmetric space group $P2_1/m$. Further discussion of the structure and comparison of the refinements in the two space groups are included below.

**Neutron Diffraction Study.** A crystal of volume 4.01 mm$^3$ was mounted on a hollow aluminum pin, sealed in an aluminum canister under a helium atmosphere, and placed in a closed-cycle helium refrigerator (Air Products DISPLEX Model CS-202). This in turn was mounted on the H6M four-circle diffractometer at the High Flux Beam Reactor, Brookhaven National Laboratory. Diffraction data obtained at 163 K confirmed the space group extinction conditions and unit-cell parameters determined from the 163 K X-ray data (Table I). The intensity data were recorded[16] by $\omega$-$2\theta$ step scans for one quadrant of reciprocal space, using a Be(002) monochromated neutron beam of wavelength 1.0462(1) Å (based on a prior calibration for a KBr crystal, $a_0$ = 6.6000 Å, at 298 K). A 70-step scan of fixed width, $\Delta 2\theta$ = 2.8°, was used in the range $4 \leq 2\theta \leq 55°$. Scan widths were calculated according to $\Delta 2\theta = 1.582(1 + 1.702 \tan\theta)°$ for $55 \leq 2\theta \leq 111.5°$, using variable step sizes and 60–90 steps per scan. Counting times were determined by monitoring the incident beam; no significant crystal or instrument instability was observed on the basis of the intensities of two reflections remeasured every 50 reflections. Initial refinement models were based on the non-hydrogen atomic coordinates from the 163 K X-ray diffraction study. Refinements were conducted in both $P2_1$ and $P2_1/m$ space groups. Hydrogen atom positions were

(15) Becker, P. J.; Coppens, P. *Acta Crystallogr.* **1974**, *A30*, 129.

(16) McMullan, R. K.; Andrews, L. C.; Guthy, J.; Koetzle, T. F.; Reidinger, F.; Thomas, R.; Williams, G. J. B. NEXDAS, Neutron and X-ray Data Acquisition System. Unpublished work.
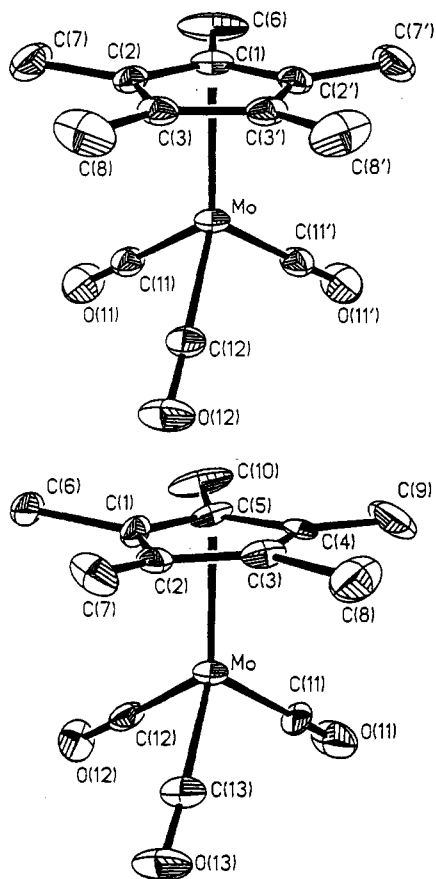
**Figure 1.** Comparison of the geometric and atomic displacement parameters (shown at 30% probability) for [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] from refinement of the 163 K X-ray diffraction data in (a, top) space group $P2_1/m$ and (b, bottom) space group $P2_1$. (Hydrogen atoms are omitted). In Figure 1a the mirror plane of the $P2_1/m$ space group relates primed and unprimed atomic sites, passes through C(6), C(1), and Mo, and relates C(12) and O(12) in the sites of disorder, one of which is shown here. Figure 1b shows the molecule in the same perspective, indicating the degree of pseudosymmetry attained by refinement.

located by difference Fourier syntheses, and initial refinements were conducted by differential Fourier synthesis.[17] The refinement models in both space groups invoke statistical disorder of a similar nature involving mirror symmetry which is imposed in $P2_1/m$ and is approximately attained in $P2_1$. Convergence was reached at $R(F^2) = 0.124$, $R_w(F^2) = 0.108$, and $S(F^2) = 1.164$, for 2734 data ($F^2 > 0$) and 170 variables using full-matrix least-squares refinement of the $P2_1/m$ model. However, satisfactory convergence could not be achieved for least-squares refinements in space group $P2_1$ ($R(F^2) > 0.15$).

## Results and Discussion

The more accurate and precise molecular parameters are obtained from the centrosymmetric ($P2_1m$) refinements with approximately half the number of variable parameters that are required to define the structure in space group $P2_1$. For the 163 K X-ray data, refinements in space groups $P2_1/m$ and $P2_1$ converged at identical fit indices ($R(F) = 0.031$); however the molecular geometry derived without mirror constraint shows unreasonably large variations among chemically equivalent bond lengths. Thus, for example, Cp*-ring C–C bond lengths in the $P2_1$ model differ as much as 0.184(22) Å, as compared to variations of 0.009(7) Å in the $P2_1/m$ model. Bond lengths of the carbonyl ligands likewise show similar differences on comparison. The derived atomic displacement parameters ($U_{ij}$'s), depicted in
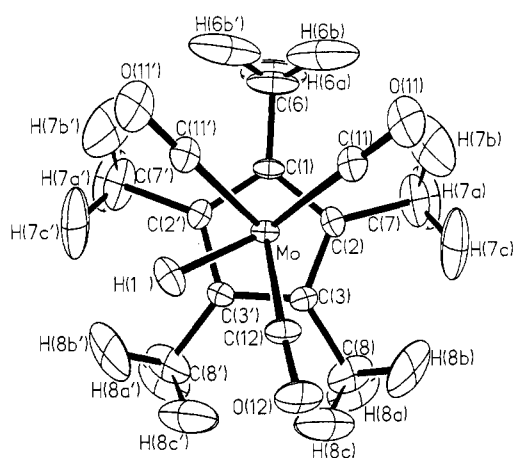
(17) McMullan, R. K. DIFSYN, a differential Fourier synthesis refinement program. Unpublished work, 1979. Cruickshank, D. W. J. *Acta Crystallogr.* **1950**, *3*, 10.



**Figure 2.** Molecular structure of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] at 163 K, as determined by neutron diffraction, shown with 25% probability ellipsoids. Rotational disorder of the Cp* ring is evident and is described here at a reduced probability level because of the large $U_{ij}$ displacements of the ligand atoms, particularly within the methyl groups. Atoms H(1), C(12), and O(12), which are disordered about the mirror plane, are shown in one of their two equivalent positions.

Figures 1 and 2, provide additional strong criteria for assessing the physical validity of the refinement models. In the $P2_1/m$ model, the $U_{ij}$ parameters of Cp* atoms show the pattern expected for rigid-body rotational displacements normal to the axis through the ring center and the Mo atom. The same also appears true for the Mo(CO)$_3$ group, which has fewer observable $U_{ij}$ values. By contrast, the $P2_1$ model yields $U_{ij}$ parameters less consistent with coupled atomic displacements of rigid groups; rather, the principal axes of the ellipsoids associated with a number of atoms are more or less randomly oriented within the groups, as shown in Figure 1b. Further evidence supporting the choice of the $P2_1/m$ space group comes from an attempt to determine the absolute structure in the $P2_1$ refinement. Refinement of the Rodgers' $\eta$ parameter[18] yielded a value of –0.05(17), indicating a racemic mixture of the two possible enantiomeric forms.

The neutron diffraction results confirm the above observations and the choice of $P2_1/m$ as the correct symmetry of the structure. Refinements in $P2_1$ against the neutron data, in fact, failed to converge without severe dampening of the atomic parameters, and the results are of uncertain value. Thus, the discussion of the structure will be based on the $P2_1/m$ refinement results, taking those of the neutron study which provide more complete information on the structural geometry. Results obtained from the X-ray and neutron studies are identical for most atoms within experimental error.

The molecular geometry and atomic numbering scheme of **1** are shown in Figure 2, atomic coordinates are given in Table II, and selected bond lengths and angles are listed in Table III. As previously noted, the molecular geometry conforms to the "four-legged piano stool" description with the four "legs" comprising three carbonyl ligands and the hydride ligand. A crystallographic mirror plane (at $y = 0.25$) passes through atoms Mo(1), C(1), C(6), and H(6a) and bisects the C(3)–C(3') bond of the C$_5$ ring. Since the molecules of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] (Figure 2) do not themselves possess mirror symmetry, imposing the crystallographic mirror plane requires statistical disorder of both the hydride ligand and one carbonyl ligand (C(12)–O(12)). The positions of these atoms are well resolved by the data, and the geometry of the ligands is precisely defined. In addition, the Cp* ring exhibits rotational disorder which results in large displacement parameters for the atoms of the methyl groups. Thus the accuracy and precision of the geometries associated with the methyl groups are somewhat less than those of the rest of the molecule.

(18) Rodgers, D. *Acta Crystallogr.* **1981**, *A37*, 734.

**Table II.** Coordinates[a] ($\times 10^4$) and Anisotropic Displacement[a,b] Parameters ($\times 10^3$) for 1 from the Neutron Diffraction Study

| atom | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|---|---|---|-----|-----|-----|-----|-----|-----|
| Mo | 9982(3) | 2500 | 8122(3) | 23(1) | 44(1) | 25(1) | 0 | 6(1) | 0 |
| C(1) | 6581(3) | 2500 | 6979(3) | 23(1) | 63(2) | 24(1) | 0 | 4(1) | 0 |
| C(2) | 7051(2) | 1589(1) | 8060(2) | 30(1) | 37(1) | 52(1) | -5(1) | 17(1) | -9(1) |
| C(3) | 7800(2) | 1937(1) | 9780(2) | 31(1) | 48(1) | 33(1) | 3(1) | 14(1) | 13(1) |
| C(6) | 5584(5) | 2500 | 5115(4) | 32(2) | 174(5) | 30(2) | 0 | 5(1) | 0 |
| H(6a) | 4016(11) | 2500 | 4914(9) | 43(4) | 293(15) | 52(4) | 0 | -6(3) | 0 |
| H(6b) | 5958(11) | 1830(8) | 4465(7) | 129(5) | 311(15) | 52(3) | 23(6) | -2(3) | -78(5) |
| C(7) | 6621(5) | 474(2) | 7511(7) | 56(2) | 51(2) | 162(3) | -18(1) | 47(2) | -45(2) |
| H(7a) | 5150(9) | 265(5) | 7516(11) | 75(4) | 71(4) | 256(9) | -43(3) | 64(5) | -56(5) |
| H(7b) | 6793(15) | 319(7) | 6257(14) | 178(9) | 130(8) | 211(9) | -68(7) | 103(8) | -129(8) |
| H(7c) | 7549(13) | -57(6) | 8368(17) | 105(6) | 41(3) | 318(15) | -1(4) | 29(7) | -18(6) |
| C(8) | 8301(4) | 1263(4) | 11368(5) | 58(2) | 128(3) | 77(2) | 25(2) | 34(2) | 69(2) |
| H(8a) | 7041(9) | 1166(7) | 11910(8) | 97(4) | 182(7) | 116(4) | 36(4) | 66(4) | 92(5) |
| H(8b) | 8769(13) | 499(7) | 11084(13) | 133(7) | 126(6) | 179(9) | 62(6) | 61(6) | 113(7) |
| H(8c) | 9424(13) | 1594(9) | 12322(8) | 120(6) | 218(11) | 63(3) | -6(6) | -3(4) | 66(5) |
| C(11) | 10925(3) | 1490(2) | 6597(2) | 37(1) | 43(1) | 58(1) | 0(1) | 23(1) | -9(1) |
| O(11) | 11465(4) | 903(2) | 5719(4) | 70(2) | 62(2) | 111(2) | -5(1) | 53(2) | -37(2) |
| C(12) | 12401(5) | 2227(3) | 9882(4) | 27(1) | 64(4) | 30(1) | 3(2) | 5(1) | 9(2) |
| O(12) | 13744(6) | 2018(5) | 10934(6) | 30(2) | 106(5) | 50(2) | 6(2) | -3(2) | 25(3) |
| H(1) | 11371(12) | 3635(7) | 9032(11) | 60(5) | 50(5) | 71(5) | -21(4) | 17(4) | -15(4) |

[a] Estimated standard deviations in the last significant digit are given in parentheses. [b] The anisotropic temperature factor has the form $T = \exp(-2\pi^2 \Sigma_i \Sigma_j h_i h_j a_i^* a_j^* U_{ij})$.

**Table III.** Selected Interatomic Distances[a] (Å) and Angles[a] (deg) for 1 from the Neutron Diffraction Study[b]

| | | | |
|---|---|---|---|
| Mo–C(1) | 2.335(3) | Mo–C(2) | 2.336(2) |
| Mo–C(3) | 2.342(2) | Mo–C(11) | 1.976(2) |
| Mo–C(12) | 1.957(4) | Mo–H(1) | 1.789(7) |
| C(1)–C(2) | 1.430(2) | C(1)–C(6) | 1.484(4) |
| C(2)–C(3) | 1.417(3) | C(2)–C(7) | 1.488(3) |
| C(3)–C(3') | 1.424(4) | C(3)–C(8) | 1.497(3) |
| C(6)–H(6a) | 1.067(9) | C(6)–H(6b) | 1.056(9) |
| C(7)–H(7a) | 1.059(7) | C(7)–H(7b) | 1.051(11) |
| C(7)–H(7c) | 1.064(13) | C(8)–H(8a) | 1.071(6) |
| C(8)–H(8b) | 1.062(12) | C(8)–H(8c) | 1.043(10) |
| C(11)–O(11) | 1.142(3) | C(12)–O(12) | 1.133(5) |

| | | | |
|---|---|---|---|
| C(11)–Mo–C(12) | 88.3(1) | C(11)–Mo–C(11') | 80.6(1) |
| C(11')–Mo–C(12) | 101.5(1) | H(1)–Mo–C(11) | 122.8(3) |
| H(1)–Mo–C(11') | 60.2(3) | H(1)–Mo–C(12) | 63.7(3) |
| Mo–C(11)–O(11) | 179.7(2) | Mo–C(12)–O(12) | 175.8(4) |
| C(2)–C(1)–C(2') | 107.4(2) | C(1)–C(2)–C(3) | 108.2(2) |
| C(2)–C(3)–C(3') | 108.1(1) | C(2)–C(1)–C(6) | 126.1(1) |
| C(1)–C(2)–C(7) | 125.9(3) | C(3)–C(2)–C(7) | 125.6(3) |
| C(2)–C(3)–C(8) | 126.8(3) | C(3')–C(3)–C(8) | 124.7(2) |
| C–C–H$_{av}$ | 111.8(8) | H–C–H$_{av}$ | 107.1(6) |

[a] Estimated standard deviations in the least significant digit are given in parentheses. They are derived from the variances and covariances of the refined positional parameters, except for averaged dimensions for which esd's are derived from the distribution of observed values, using the formula $\Sigma_{i=1}^{n}(d_i - \bar{d})^2/n(n-1)$. [b] Atoms in positions related by mirror symmetry to those of the unique atomic positions are indicated with a prime.

The Mo–C(O) distances lie within the typical range observed for Mo(CO)$_m$L$_n$ complexes.[19] Mo–C(ring) distances are 0.02–0.03 Å shorter than the mean distance reported by Orpen et al.[19] in a survey of 78 such distances from relatively accurate structure determinations of MoCp*L$_n$ complexes. However, this difference is insignificant if one bears in mind that the standard deviation of the distribution of Mo–C(ring) distances examined[19] is 0.047 Å.

It is particularly interesting to compare the geometry of 1 with that of [MoH($\eta$-C$_5$H$_5$)(CO)$_3$] (2), which was characterized recently by a neutron diffraction study at 103 K.[7b] While both structures are readily described by a "piano-stool" geometry, the orientation of the cyclopentadienyl ligand relative to the other ligands differs in the two cases. 2 adopts an approximate $C_s$ molecular symmetry, the Mo–H bond being eclipsed with a Cp

C–H bond (dihedral angle H(1)–Mo–CEN–C(6) = 2.9°; CEN = centroid of C$_5$ ring); in 1 the C$_5$ ring is rotated 27.0° (dihedral angle H(1)–Mo–CEN–C(3') = –24.1°) relative to the orientation in 2. This is perhaps a consequence of the greater steric requirements of the Cp* ligand. The hydrido and carbonyl ligands in 1 are thus oriented so as to adopt a staggered configuration with respect to the exocyclic C–C bonds. The requirement of staggering four ligands with respect to five exocyclic C–C bonds results in the enlargement of one of the interligand angles (C(11)–Mo–C(12) = 88.3(1)°) relative to that in 2 (79.7(1)°). As a consequence, the other angles between adjacent carbonyl and hydrido ligands are slightly smaller than those observed in 2. It should be noted that sum of the four interligand (carbonyl–carbonyl and carbonyl–hydride) angles differs little between the two complexes (292.8(4)° in 1 and 291.6(2)° in 2).

The structure of [MoH($\eta$-C$_5$Me$_5$)(CO)$_2$(CNBu$^t$)][3j] (3) also invites comparison with 1 (and 2). The geometry of 3 is similar to 1 as shown in Figure 3. In 3, the adopted configuration places the hydride and both carbonyl ligands in an orientation staggered with respect to the exocyclic C–C bonds of the C$_5$Me$_5$ group. The isocyanide group, however, lies in an almost eclipsed orientation (C(3)–Mo–CEN–C(12) = 5.6°). This differs from the configuration of 2, in which only one carbonyl group is staggered with respect to the C–H bonds of the C$_5$H$_5$ group, while the hydride and two carbonyl groups lie in an eclipsed orientation. A comparison of the coordination geometries of 1–3 is given in Table IV.

Extended Hückel calculations by Hoffmann and co-workers[20] on [Mo(Me)(C$_5$H$_5$)(CO)$_3$] comparing configurations with the methyl group either eclipsed or staggered with respect to a Cp C–H bond show the former to be favored by 0.4 kcal/mol, with a small barrier to ring rotation. The geometry of 2 is consistent with this finding (hydride eclipsed), and it appears from examination of 1 and 3 that the C$_5$Me$_5$ ligand promotes a preference for the other orientation (hydride staggered). In an attempt to understand the origin of preferences for these two conformations we examined the conformations of all neutral (i.e. d$^4$) Cp'M(CO)$_3$L complexes (M = Cr, Mo, W; Cp' = Cp, Cp*; L = monodentate, formally anionic, $\eta^1$ ligand) available in the Cambridge Structural Database[21] (March 1992 version). The

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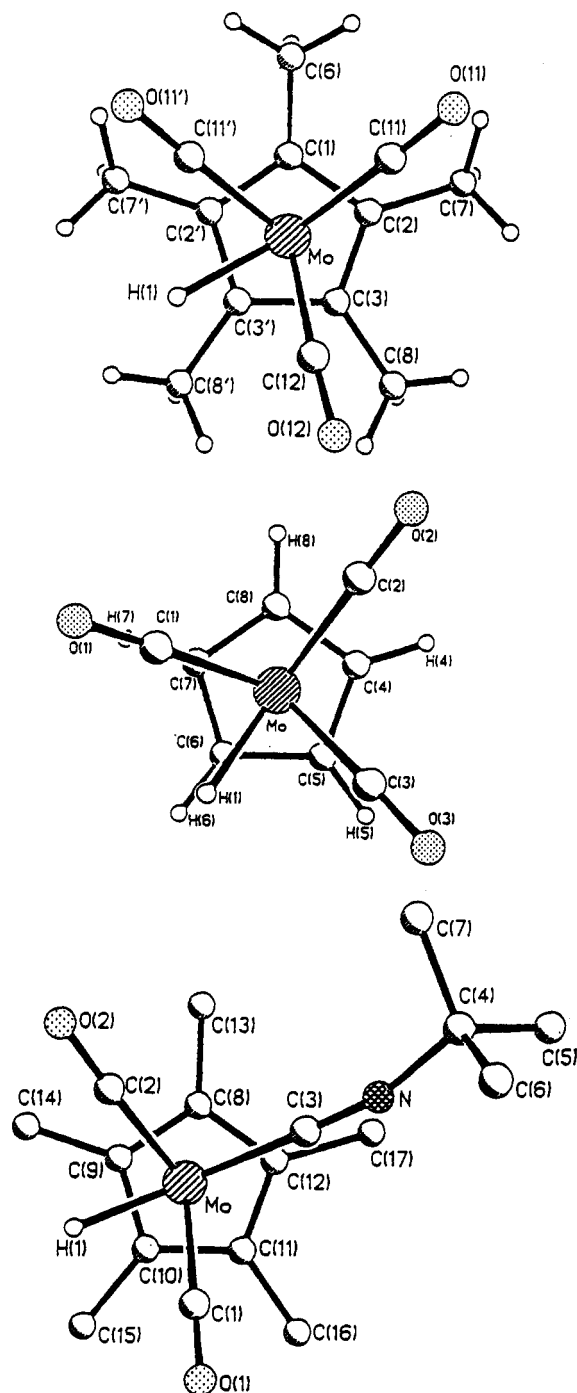
**Figure 3.** Comparison (from top to bottom) of the geometries of [MoH-($\eta$-C$_5$Me$_5$)(CO)$_3$] (1), [MoH($\eta$-C$_5$H$_5$)(CO)$_3$] (2), and [MoH($\eta$-C$_5$Me$_5$)-(CO)$_2$(CNBu$^t$)] (3).

analysis, presented in Table V, focuses on whether the M–L bond is eclipsed or staggered with respect to a C–H (Cp) or an exocyclic C–C (Cp*) bond. A variety of compounds have been structurally characterized with the general formula CpM(CO)$_3$L, but no additional Cp* analogues were found. The data show that while the majority of the Cp complexes adopt the eclipsed conformation analogous to that of 2, there are a number of examples which are better described as staggered (cf. 1 and 3), or at least adopting an intermediate conformation. As both $\sigma$- and $\pi$-donor ligands, L, can lead to each possible conformation, it appears that electronic factors do not play a dominant role in deciding which conformation is adopted. However, one can perhaps argue that, in general, the more sterically demanding ligands adopt a more staggered conformation. This is consistent with the fact that the two Cp* complexes (1 and 3) yield staggered conformations. Exceptions

to this rule are CpMo(CO)$_3$($\overline{\text{CHCH(CHCMe}_2)\text{C(CN)}_2\text{C(CN}_2)}$-$\overline{\text{CH}_2}$), which has a bulky ligand, yet, has a torsion angle of only 5.0°, and CpMo(CO)$_3$(S(O)OH), which has a relatively compact ligand yet has a torsion angle of 21.0°.

Hoffmann and co-workers also observe that CpMo(CO)$_3$L complexes typically exhibit tilting of the Cp ring by several degrees. However, in neither 1 nor 2 does the C$_5$ ring tilt[22] more than 0.8°, though some ring slippage, attributed to packing forces,[7b] is noted in 2. The Mo–C(ring) distances vary by no more than 0.007(4) Å in 1, for which no unusually short intermolecular contacts are observed.

In addition to the steric differences between the Cp* and Cp ligands in 1 and 2, electronic differences should be expected due to the ability of Cp* to act as a stronger donor ligand. Such differences are not apparent from comparison of distances associated with the carbonyl ligands. However, the Mo–H distance in 1 is significantly longer (by 0.069(7) Å) than that of 2. Such a difference might be attributed to the fact that Cp* ligands have a stronger trans influence than Cp ligands. There has been one other report of a terminal Mo–H distance characterized by neutron diffraction. The reported distance of 1.685(3) Å in [MoH$_2$(C$_5$H$_5$)$_2$][7a] is shorter (by 0.104(7) Å) than that observed in 1 and (by 0.035(5) Å) than that observed in 2. It is unclear why this distance is so much shorter, although slightly larger anisotropic displacement parameters, and thus greater librational shortening of the Mo–H bond length, in the dihydride structure (determined at room temperature) may in part account for the observed difference. Bond distance comparisons with 3 are less meaningful, as the structure of 3 was determined by X-ray diffraction in addition to being determined a higher temperature (293 K).

**Conclusions**

The structure of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] has been characterized by X-ray and neutron diffraction at 163 K, yielding an accurate description of the geometry of this compound and correcting a previous structure determination in which the space group was misassigned. Comparison with related d$^4$ CpMo-(CO)$_3$L complexes suggests that the conformation of these complexes is determined primarily by steric interactions between the ligand, L, and the Cp or Cp* ring, rather than by electronic effects of either Cp/Cp* or L.

(22) The tilt angle referred to is the angle between the line joining the ring centroid to Mo and the normal to the mean plane of the five ring carbon atoms.
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**Table IV.** Comparison of Coordination Geometries[a] of [MoH($\eta$-C$_5$Me$_5$)(CO)$_3$] (**1**),[b] [MoH($\eta$-C$_5$H$_5$)(CO)$_3$][7b] (**2**), and [MoH($\eta$-C$_5$Me$_5$)(CO)$_2$(CNBu$^t$)][4j] (**3**)

| 1 | | 2 | | 3 | |
|---|---|---|---|---|---|
| H(1)–Mo–C(11′) | 60.2(3) | H(1)–Mo–C(1) | 64.4(2) | H(1)–Mo–C(2) | 67(1) |
| H(1)–Mo–C(12) | 63.7(3) | H(1)–Mo–C(3) | 66.0(2) | H(1)–Mo–C(1) | 69(1) |
| C(11)–Mo–C(11′) | 80.6(1) | C(1)–Mo–C(2) | 81.5(1) | C(3)–Mo–C(2) | 81.4(2) |
| C(11)–Mo–C(12) | 88.3(1) | C(2)–Mo–C(3) | 79.7(1) | C(3)–Mo–C(1) | 83.8(2) |
| H(1)–Mo–C(11) | 122.8(3) | H(1)–Mo–C(2) | 122.7(2) | H(1)–Mo–C(3) | 130(1) |
| C(11′)–Mo–C(12) | 101.5(1) | C(1)–Mo–C(3) | 102.6(1) | C(2)–Mo–C(1) | 104.4(2) |
| Mo–CEN[c] | 2.00 | Mo–CEN | 2.01 | Mo–CEN | 2.00 |
| CEN–Mo–H(1) | 112.2 | CEN–Mo–H(1) | 114.6 | CEN–Mo–H(1) | 111.6 |
| CEN–Mo–C(11′) | 124.3 | CEN–Mo–C(1) | 126.6 | CEN–Mo–C(2) | 124.6 |
| CEN–Mo–C(11) | 124.3 | CEN–Mo–C(2) | 122.7 | CEN–Mo–C(3) | 118.7 |
| CEN–Mo–C(12) | 125.2 | CEN–Mo–C(3) | 126.6 | CEN–Mo–C(1) | 127.4 |
| H(1)–Mo–CEN–C(3′) | –24.1 | H(1)–Mo–CEN–C(6) | 2.9 | H(1)–Mo–CEN–C(10) | –30.3 |
| C(11′)–Mo–CEN–C(3′) | –92.4 | C(1)–Mo–CEN–C(6) | –72.5 | C(2)–Mo–CEN–C(10) | –106.0 |
| C(11)–Mo–CEN–C(3′) | 164.6 | C(2)–Mo–CEN–C(6) | –177.4 | C(3)–Mo–CEN–C(10) | 149.7 |
| C(12)–Mo–CEN–C(3′) | 48.5 | C(3)–Mo–CEN–C(6) | 80.3 | C(1)–Mo–CEN–C(10) | 45.3 |

[a] Distances (Å) and angles (deg) are from the neutron diffraction studies of **1** and **2** and an X-ray diffraction study of **3**. Estimated standard deviations in the least significant digit are given in parentheses. The notation used to designate atoms is that of the original papers. [b] Atoms in positions related by mirror symmetry to those of the unique atomic positions are indicated by a prime. [c] Designates the centroid of the C$_5$ ring.

**Table V.** Coordination Geometries of Mononuclear Cp′M(CO)$_3$L Complexes (M = Cr, Mo, W; Cp′ = $\eta$-C$_5$H$_5$, $\eta$-C$_5$Me$_5$)

| complex | M | L | tors[a] | E/I/S[b] | REFCODE[c] | ref |
|---|---|---|---|---|---|---|
| CpMo(CO)$_3$Br | Mo | $\pi$-donor | 1.2 | E | SENCUJ | 23 |
| CpW(CO)$_3$Cl | W | $\pi$-donor | 1.7 | E | BACFAM | 24 |
| CpMo(CO)$_3$Cl | Mo | $\pi$-donor | 2.5 | E | CPDMOC01 | 24 |
| CpMo(CO)$_3$H | Mo | $\sigma$-donor | 2.9 | E | | 7b |
| CpMo(CO)$_3$(C$_3$F$_7$) | Mo | $\sigma$-donor | 3.1 | E | CPFPMO10 | 25 |
| CpW(CO)$_3$(OC(O)Me) | W | $\pi$-donor | 3.2 | E | FOLVEH | 26 |
| CpW(CO)$_3$($\overline{C}$C(Ph)CF$_2$$\overline{C}$(CN)$_2$) | W | $\sigma$-donor | 3.2 | E | GEDMIL | 27 |
| CpW(CO)$_3$(SC(S)NMe$_2$) | W | $\pi$-donor | 3.7 | E | CIXKAV | 28 |
| CpMo(CO)$_3$($\overline{C}$HCH(CHCMe$_2$)C(CN)$_2$C(CN$_2$)$\overline{C}$H$_2$) | Mo | $\sigma$-donor | 5.0 | E | JACRUB10 | 29 |
| CpW(CO)$_3$(CH$_2$S(O)Ph) | W | $\sigma$-donor | 5.9 | E | VARGIE | 30 |
| CpW(CO)$_3$(CH$_2$CO$_2$Et)[d] | W | $\sigma$-donor | 6.3 | E | DASYUR | 31 |
| CpW(CO)$_3$($\overline{C}$C(Ph)C(CN)$_2$$\overline{C}$(CN)$_2$) | W | $\sigma$-donor | 10.0 | I | BEDGAS | 32 |
| CpMo(CO)$_3$(CH$_2$CO$_2$H) | Mo | $\sigma$-donor | 11.9 | I | CPCMMO10 | 33 |
| CpW(CO)$_3$(S–C$_7$H$_4$NS) | W | $\pi$-donor | 16.9 | I | FERPUN | 34 |
| CpMo(CO)$_3$($\overline{P}$(Ph)NPCl$_2$NPCl$_2$N) | Mo | $\sigma$-donor | 18.9 | I | FAWZUY | 35 |
| CpMo(CO)$_3$CH$_2$Ph | Mo | $\sigma$-donor | 19.4 | I | FIGCUT | 36 |
| CpCr(CO)$_3$($\overline{P}$(Ph)NPCl$_2$NPCl$_2$N) | Cr | $\sigma$-donor | 20.8 | S | FAWZOS | 35 |
| CpMo(CO)$_3$(S(O)OH) | Mo | $\pi$-donor | 21.0 | S | DEYPEC | 37 |
| Cp*Mo(CO)$_3$H | Mo | $\sigma$-donor | 24.1 | S | | this work |
| Cp*Mo(CO)$_2$(CNBu$^t$)H[e] | Mo | $\sigma$-donor | 30.3 | S | SAPHUM | 3j |

[a] Smallest (absolute value of) torsion angle L–M–CEN–C(ring) (deg). [b] Eclipsed: torsion angle < 10°. Intermediate conformation: 10° ≤ torsion angle < 20°. Staggered: 20° ≤ torsion angle ≤ 36°. [c] Cambridge Structural Database REFCODE.[21] [d] Averaged over two crystallographically independent molecules. [e] As there was only one example of a Cp* complex, this closely related analogue has been included.

**Supplementary Material Available:** Complete data collection and structure refinement parameters, interatomic distances and angles, atomic positional parameters, and anisotropic displacement parameters for the X-ray diffraction study (Table S1) and interatomic distances and angles for the neutron diffraction study (Table S2) (7 pages). Ordering information is given on any current masthead page.