measured. The final scan speed used was such that $\sigma(I)/I$ approaches 0.33 with a maximum counting time of 90 s; 3936 hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ reflections were prescanned ($2° < \theta < 60°$).

Three standard reflections measured every hour during the entire data collection period showed no significant trend in intensity.

The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations the Enraf-Nonius SDP/V16 package[19] was used.

Intensities were corrected for Lorentz, polarization, and absorption factors, the last being computed by numerical integration[20] (transmission factors between 0.04 and 0.25). The 3936 measurements were sorted and averaged, leading to a unique data set of 1807 reflections; 178 of these had $\sigma(I)/I > 0.4$ and were considered as unobserved. Finally, 1629 reflections were used for refining the structure.

The statistical distribution of E values in reciprocal space and the cumulative Nz test on $|F_{\text{obsd}}|$ excluded the noncentrosymmetric space group Cc. The structure was solved by a direct method using MULTAN.[21] All nonhydrogen atoms could be located in the Fourier map computed with the phases of the most probable set of MULTAN. Hydrogen atoms were introduced in structure factor calculation by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors (B_H = 6 Å^2) but not refined. The CH_3 hydrogen atoms were previously located in a difference map. The temperature factors of all converged to $R(F) = 0.038$ and $R_w(F) = 0.050$. The unit-weight observation was 1.24 with a fudge factor of 0.07. The final difference map showed no maxima greater than 0.2 e Å^{-3}. Table VI (supplementary material) gives h, k, l, F_o, and F_c times 10 for all observed structure factors.

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Registry No. **3**, 64367-53-9; **5**, R = Ph, 64367-52-8; **6**, 77611-22-4; **7**, 77611-23-5; **8**, 77611-24-6; **9**, 77611-25-7; **10**, 74363-92-1; **11**, 77611-26-8; **12**, 77629-03-9; (BDA)Fe(CO)$_3$, 38720-22-8.

Supplementary Material Available: Table VI, observed and computed structure factors for all observed reflections (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6,
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Reexamination of the Crystal and Molecular Structure of Tricarbonyl(η^5-cyclopentadienyl)manganese(I): Structural and Spectroscopic Evidence for a Distortion of the Cyclopentadienyl Ring Framework and Its Implications on Bonding in a Molecule Possessing Cylindrical Symmetry[1]

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The crystal and molecular structure of tricarbonyl(η^5-cyclopentadienyl)manganese(I), CpMn(CO)$_3$ (Cp = η^5-C_5H_5), has been reinvestigated by three-dimensional single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/a$ with unit cell parameters a = 12.077 (3) Å, b = 7.057 (2) Å, c = 10.913 (2) Å, β = 117.68 (2)°, V_{calcd} = 823.5 Å^3, mol wt 204.06, and d_{calcd} = 1.646 g cm^{-3}. Intensity data were collected with use of Mo Kα radiation with peak-profile analysis of the 2θ scan results. A total of 2415 symmetry-independent reflections were collected, of which 1619 had $I \geq 3\sigma(I)$ and were included in the structure refinement, which converged to conventional residuals of R_1 = 0.0286 and R_2 = 0.0205. Contrary to the earlier work of Berndt and Marsh, the C_5H_5 ring appears to deviate significantly from a regular pentagon so as to approach planar C_{2v} symmetry. This result is indicative of some localized C–C bonding throughout the ring, highly unexpected for a molecule that possesses effective cylindrical symmetry about the metal atom. These results are similar to those that have been reported earlier for the isostructural CpRe(CO)$_3$ compound. Thermal motion analyses for the various molecular fragments reveal that the apparent distortion is not due to the librational motion of the ring about the molecular axis, and the corrected individual C–C bond distances in the ring range between 1.400 (3) and 1.439 (3) Å. Vibrational studies of CpMn(CO)$_3$ in solution are also reported, which support a breakdown of the fivefold symmetry of the ring outside of the crystalline environment. The implications on the bonding within the cyclopentadienyl ring in these simple molecules and other related complexes are discussed in terms of possible solid-state and electronic effects.

Introduction

Recently, there has been renewed interest in the origin and magnitudes of inter- and intramolecular rotational barriers in substituted and unsubstituted arene- and cyclopentadienyl-metal complexes[3,4] and in the nature of the metal–Cp ring bonding in the latter class of compounds.[5] Tricarbonyl(η^5-cyclopentadienyl)manganese(I), CpMn(CO)$_3$ (Cp = η^5-C_5H_5), was one of the first half-sandwich complexes

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ever prepared.[6] This relatively simple molecule may be regarded as a prototype for the first-row transition-metal carbonyl complexes and their derivatives and is well suited for study due to its ready availability and reasonable stability. It has been fully characterized by numerous techniques including vibrational,[7] ^{13}C and ^{17}O NMR,[8,9] and microwave spectroscopy,[10] as well as by X-ray diffraction,[11] molecular orbital,[12] and photoelectron studies.[12] The applications of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ and CpMn(CO)$_3$ as gasoline additives have been extensively researched,[13] and these complexes have found some use as catalysts in a number of industrial processes.[14]

In their X-ray study of CpMn(CO)$_3$, Berndt and Marsh[11] concluded that the results were indicative of complete delocalization of electrons within the cyclopentadienyl ring. We have recently investigated the crystal structure of the analogous CpRe(CO)$_3$ compound and found it to be isostructural with the Mn complex.[15] However, there was some evidence to suggest partial localization of the π electrons within the Cp ring. In view of this, it seemed logical to consider whether similar effects might be observed in CpMn(CO)$_3$, especially since the individual C–C distances reported by Berndt and Marsh (ranging from 1.350 to 1.433 Å) and the level of accuracy achieved ($R = 0.08$) did not preclude the possibility of some form of incomplete delocalization or ring deformation. Several other factors in this earlier study contributed to our decision to reexamine the crystal structure of CpMn(CO)$_3$: (1) the questionable thermal parameters and atomic positions resulting from the absence of an absorption correction; (2) the fact that no refinement of hydrogen atom positional or thermal parameters was attempted and the value that was assumed for the isotropic temperature factor ($B = 2.0$ Å^2) was much too small; (3) the relatively low ratio of the number of observed reflections/refined parameter ($\simeq 6.5$) resulting from the pseudo body centering of the Mn atom and the visual estimation of intensities from films.

If the existence of such a distortion could indeed be established, this would be highly unexpected. There has been considerable controversy in the literature over the past two decades as to whether bond localization within a cyclopentadienyl ring can arise upon interaction with an ML$_x$ or $ML_xL'_y$ group. A recent X-ray structure determination of $(\eta^5\text{-}C_5(CH_3)_5)Co(CO)_2$ conclusively revealed the existence of a distortion from D_{5h} symmetry of the cyclopentadienyl ring,[5h] but this can be predicted on the basis of electronic and orbital overlap considerations arising from the noncylindrical symmetry of the Co(CO)$_2$ moiety. The degeneracy of the Cp e$_1''$ (ring → metal π donor) orbitals is removed on interaction with the metal since one of them donates into a *filled* d orbital on Co while the other component interacts with a *vacant* d orbital. A similar distortion was observed for the case of *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, which also lacks cylindrical symmetry about the metal atom.[5e] It is generally presumed, however, that on interacting with metal-containing fragments that possess cylindrical symmetry (ML$_x$, where $x > 2$), these e$_1''$ donor orbitals remain energetically degenerate.

Both CpMn(CO)$_3$ and CpRe(CO)$_3$ are cylindrically symmetrical, and yet there exists spectroscopic evidence in the literature that suggests the planar cyclopentadienyl ring does not exhibit the behavior expected on the basis of D_{5h} symmetry. An examination of the dipolar coupling constants in the ^{1}H NMR spectra of CpMn(CO)$_3$ oriented in nematic liquid crystalline solvents suggests that the cyclopentadienyl moiety is significantly distorted from a regular pentagon,[16–20] and similar evidence has recently been obtained for CpRe(CO)$_3$.[20] Attempts to attribute these results to puckering motions of the ring[18,21] have been disputed.[19] Deviations from the C_{5v} "local symmetry" approximation for the CpM (M = Mn, Re) fragment have also been observed in infrared and Raman spectra, both in the solid state and in solution.[7e–g] The M(CO)$_3$ group, however, does not appear to violate C_{3v} local symmetry. The observation of unexpected vibrational modes might result from a symmetry of the Cp ring that is actually lower than expected or from strong electronic interactions between the CpMn and Mn(CO)$_3$ fragments of the molecule such that the local symmetry approximation is no longer valid.[22] This latter possibility seems unlikely for CpMn(CO)$_3$, however, as molecular orbital calculations assuming D_{5h} symmetry for the ring indicate that this is not of major importance.[12e]

Clearly, as attempts are being undertaken to describe the bonding in derivatives of Cp–transition-metal complexes, it is essential to try to develop a more complete picture of the situation in the parent compounds. Thus it was hoped that a comparison of highly accurate structural data for CpRe(CO)$_3$ and CpMn(CO)$_3$ would yield an explanation for the conflicting spectroscopic observations outlined above and provide some insight into the extent and nature of possible ring distortions in these molecules. In this paper, we report the results of our new X-ray determination for CpMn(CO)$_3$ as well as of some vibrational studies and discuss their implications on the bonding in metal cyclopentadienyls. Complete details of the vibrational spectra and normal-coordinate cal-

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culations on $CpMn(CO)_3$ and $CpRe(CO)_3$ will be published elsewhere.[23]

Experimental Section

High-resolution infrared spectra (Table XII and Figure 3) were recorded on a Nicolet Instrument Co. Model 6000 Fourier transform infrared spectrometer and were calibrated against the vibrational–rotational lines of carbon monoxide.[24] The wavenumbers reported are considered accurate to ±0.5 cm^{-1}.

$CpMn(CO)_3$ was a generous gift from Ethyl Corp. Dirhenium decacarbonyl was purchased from Strem Chemical Co. and used without further purification. Dicyclopentadiene (technical) was purchased from Eastman Organic Chemicals.

Preparation of Tricarbonyl(η^5-cyclopentadienyl)rhenium(I). A sample of $CpRe(CO)_3$ was prepared by a modification of the procedure reported by Green and Wilkinson.[25] Dirhenium decacarbonyl (3.0 g, 4.6 mmol) was refluxed in 25 mL of dicyclopentadiene for ca. 10 h. The reaction was monitored by TLC on silica gel plates using hexanes as eluant. Petroleum ether (bp 30–60 °C, 50 mL) was added, and the solution was cooled to −78 °C. The gray solid obtained was introduced onto a sintered-glass filter packed with alumina and washed repeatedly with petroleum ether to remove unreacted $C_{10}H_{12}$. The pure complex was then eluted from the alumina with diethyl ether. White crystals of $CpRe(CO)_3$ (mp 110–111 °C) were obtained by sublimation (10^{-3} mmHg, 70 °C) to give 1.63 g (53% yield).

Crystal Data for $CpMn(CO)_3$: $C_8H_5O_3Mn$, mol wt 204.06; monoclinic with $a = 12.077\ (3)$, $b = 7.057\ (2)$, $c = 10.913\ (2)$ Å; $\beta = 117.68\ (2)°$; $V_{calcd} = 823.5$ Å^3; $d_{calcd} = 1.646$ g cm^{-3}; $Z = 4$; $F(000) = 408$; space group $P2_1/a$ (C_{2h}^5, No. 14); systematic absences are $h0l$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$ (general equivalent positions in $P2_1/a$: $x, y, z; \bar{x}, \bar{y}, z; {}^1/_2 + x, {}^1/_2 - y, z; {}^1/_2 - x, {}^1/_2 + y, \bar{z}$); reduced cell $P2_1/n$ (C_{2h}^5) with $a = 11.937\ (3)$ Å and $\beta = 116.37\ (2)°$; absences in $P2_1/n$ are $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$ (general equivalent positions: $x, y, z; \bar{x}, \bar{y}, \bar{z}; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$); Mo K$\alpha$ radiation, $\lambda = 0.709\,32$ Å; $\mu_{Mo\,K\alpha} = 16.36$ cm^{-1}.

X-Ray Data Collection. Powdered $CpMn(CO)_3$ was purified by sublimation immediately prior to use. Single crystals suitable for the X-ray work were grown by slow sublimation (10^{-3} mmHg, 25 °C) onto a glass finger while a small temperature gradient was maintained. Yellow crystals ranging in largest dimension from ca. 0.5 to 3 mm were deposited. A transparent, roughly equidimensional, single crystal was selected for data collection and ground into a sphere of diameter 0.36 mm in a Bond sphere grinder lined with an antistatic cloth. In view of the high volatility of the compound, the crystal was sealed inside a thin-walled (0.01-mm) glass capillary of the quality typically employed for obtaining X-ray powder patterns.

The crystal was mounted on a modified Picker FACS-1 four-circle diffractometer equipped with a scintillation counter and a pulse-height analyzer, which was operated by a PDP-8/E computer employing the National Research Council of Canada (NRCC) Fortran diffractometer program.[26] The monoclinic space group $P2_1/a$ observed by Berndt and Marsh[11] was confirmed by measuring a preliminary set of reflections. However, the proper reduced cell is the unconventional setting $P2_1/n$ because of the shorter a direct axis. In view of the earlier work on this compound, the refinement was carried out in the $P2_1/a$ setting. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 12 high-angle reflections, which were automatically centered at $2\theta_+$ and $2\theta_-$ by using Cu Kβ_1 radiation ($\lambda = 1.392\,218$ Å, $55 \leq 2\theta \leq 69°$). The mosaic spread of the crystal was determined to be acceptable from an examination of Laue photographs and by performing narrow-source, open-counter 2θ scans through several intense, low-angle reflections; they exhibited peak widths at half-maximum of ≤0.2°.

Intensity data were collected at 25 °C with use of graphite-monochromatized Mo Kα radiation. The profile counts were read every 0.3 s (corresponding to 0.01° 2θ) while the 2θ angle was scanned at 2° min^{-1} from 0.9° before the calculated Kα_1 position to 0.9° after the expected Kα_2 peak. Backgrounds were measured at each end of the scan for 10% of the scan time. Attenuators were inserted whenever the counting rate exceeded 10 000 counts s^{-1}. The accumulated profile was then analyzed for abnormalities and remeasured, if necessary. It was then processed in the manner described by Grant and Gabe.[27] Three standards (80$\bar{5}$, 333, and 4$\bar{4}$1), chosen from widely different regions of reciprocal space, were measured every 50 reflections in order to monitor the direct-beam intensity and extent of crystal damage. Their measurements exhibited maximum fluctuations of less than 1.5% from the mean within each of the two sets of data collected.

A total of 5391 reflections comprising two symmetry-related quadrants of data were collected in the range $3° \leq 2\theta \leq 60°$. After being averaged, the data were reduced to 2415 unique intensities of which 1619 had $I \geq 3\sigma(I)$ and were classified as observed. Intensities were corrected for the measured direct-beam polarization ($K = 0.970$ for Mo Kα radiation)[28] and for the usual Lorentz factor by means of the expression

$$1/Lp = (1 + K)(\sin (2\theta))/(K + \cos^2 (2\theta))$$

A spherical absorption correction for $\mu r = 0.30$ would result in less than a 1% correction to the observed intensities,[29] and consequently none was applied.

Refinement of the Structure. All calculations unless otherwise indicated were performed on a PDP-8/E computer employing the NRCC crystal structure package.[30] The atomic scattering curves for Mn, C, and O were taken from Cromer and Mann,[31] and for hydrogen those of Stewart et al.[32] were used. The anomalous dispersion of Mn, C, and O was taken from the data tabulated by Cromer and Lieberman[33] and included in all structure factor calculations.

The positional parameters for the 12 nonhydrogen atoms were introduced directly from Berndt and Marsh's work,[11] together with an estimate of their isotropic temperature factors. Three cycles of full-matrix least-squares refinement employing isotropic thermal parameters were followed by five cycles of block-diagonal anisotropic refinement weighted from counting statistics. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$. The values of $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.0414 and 0.0476, respectively, with three reflections having $w\Delta^2 > 10\,000$. A difference Fourier synthesis revealed the five hydrogen atoms, approximately in the positions assumed by Berndt and Marsh,[11] and they were introduced with arbitrary $U = 0.10$ Å^2 thermal parameters. The residuals immediately dropped, the cyclopentadienyl carbon atoms shifted significantly, and the largest $w\Delta^2$ became less than 2000, indicating the importance of including H atoms in refinements. During the final stages the hydrogen thermal parameters were allowed to vary, and the block-diagonal refinement converged for both positional and thermal parameters with no shift larger than 0.20σ on the last cycle. The final residuals were $R_1 = 0.0286$ and $R_2 = 0.0205$, while $R_1 = 0.0525$ and $R_2 = 0.0206$, including the unobserved reflections. No systematic trends of F_c/F_o as a function of $\sin \theta$ or F_o were observed, and the final difference Fourier map exhibited no peak larger than 0.22 e Å^{-3}.

The final positional and thermal parameters are presented in Table I. A compilation of root-mean-square amplitudes of vibration for all nonhydrogen atoms (Table II) and a listing of the final observed and calculated structure factor amplitudes (Table XIII) are available as supplementary material.

Results and Discussion

Selected intramolecular bond distances and angles are presented in Table III, and the bond lengths have been corrected for the shortening effects of thermal libration (vide infra). Table IV contains relevant least-squares planes and

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Table I. Final Positional and Thermal Parameters ($U_{ij} \times 10^2$ Å^2)[a] for $CpMn(CO)_3$ with Their Estimated Standard Deviations[b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0.287 67 (2)	0.007 45 (4)	0.262 42 (2)	0.05312 (13)	0.04666 (14)	0.04392 (12)	0.00184 (17)	0.02545 (10)	−0.00058 (16)
C(1)	0.408 27 (19)	−0.202 67 (31)	0.248 89 (19)	0.0800 (15)	0.0759 (16)	0.0760 (14)	0.0255 (13)	0.0319 (12)	−0.0149 (13)
C(2)	0.356 48 (19)	−0.093 98 (29)	0.127 57 (20)	0.1046 (16)	0.0616 (14)	0.0886 (14)	−0.0159 (13)	0.0738 (13)	−0.0172 (12)
C(3)	0.229 57 (19)	−0.114 89 (31)	0.063 67 (18)	0.0973 (16)	0.0731 (15)	0.0506 (11)	−0.0016 (14)	0.0330 (11)	−0.0114 (11)
C(4)	0.197 58 (20)	−0.235 04 (32)	0.142 94 (21)	0.0928 (16)	0.0744 (16)	0.0976 (16)	−0.0350 (14)	0.0587 (14)	−0.0320 (14)
C(5)	0.307 08 (22)	−0.290 53 (28)	0.256 12 (19)	0.1522 (22)	0.0459 (12)	0.0735 (13)	0.0143 (14)	0.0758 (14)	0.0063 (11)
C(11)	0.403 17 (16)	0.188 27 (27)	0.334 26 (17)	0.0594 (12)	0.0500 (12)	0.0654 (12)	0.0080 (10)	0.0247 (10)	−0.0039 (10)
C(12)	0.165 87 (16)	0.177 42 (29)	0.193 74 (17)	0.0606 (12)	0.0697 (14)	0.0521 (10)	0.0042 (11)	0.0266 (9)	0.0010 (10)
C(13)	0.273 74 (17)	−0.014 42 (28)	0.417 70 (17)	0.0824 (13)	0.0610 (13)	0.0591 (10)	0.0166 (12)	0.0411 (10)	0.0045 (11)
O(11)	0.477 70 (13)	0.305 47 (21)	0.379 43 (15)	0.0769 (10)	0.0669 (11)	0.1159 (12)	−0.0129 (8)	0.0300 (8)	−0.0191 (9)
O(12)	0.086 49 (12)	0.288 22 (23)	0.146 83 (13)	0.0752 (10)	0.1086 (13)	0.0861 (10)	0.0370 (10)	0.0335 (8)	0.0204 (10)
O(13)	0.263 98 (16)	−0.032 26 (23)	0.516 31 (14)	0.1556 (14)	0.1117 (14)	0.0751 (9)	0.0392 (12)	0.0823 (10)	0.0195 (10)
atom	**x**	**y**	**z**	**U, Å^2**	**atom**	**x**	**y**	**z**	**U, Å^2**
H(1)	0.4900 (16)	−0.2234 (26)	0.3143 (16)	0.104 (7)	H(4)	0.1183 (16)	−0.2723 (26)	0.1222 (16)	0.096 (6)
H(2)	0.4011 (17)	−0.0178 (24)	0.0996 (17)	0.101 (6)	H(5)	0.3220 (16)	−0.3673 (27)	0.3276 (17)	0.112 (7)
H(3)	0.1681 (16)	−0.0447 (25)	−0.0208 (18)	0.109 (7)					

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. [b] The block-diagonal refinement performed tends to underestimate the errors associated with the individual atomic coordinates and temperature factors. Thus, the true standard deviations for these parameters are expected to be somewhat larger.

Table III. Bond Distances (Å) and Angles (Deg) in $CpMn(CO)_3$[a]

Bond Distances

	uncor	cor[b]		uncor	cor
Mn–C(1)	2.131 (2)[c]	2.155	C(1)–C(2)	1.401 (3)	1.434
Mn–C(2)	2.122 (2)	2.144	C(2)–C(3)	1.365 (3)	1.400
Mn–C(3)	2.128 (2)	2.153	C(3)–C(4)	1.388 (3)	1.421
Mn–C(4)	2.120 (2)	2.148	C(4)–C(5)	1.382 (3)	1.416
Mn–C(5)	2.121 (2)	2.145	C(5)–C(1)	1.405 (3)	1.439
Mn–C(11)	1.781 (2)	1.798	C(1)–H(1)	0.922 (16)	
Mn–C(12)	1.772 (2)	1.785	C(2)–H(2)	0.909 (18)	
Mn–C(13)	1.786 (2)	1.800	C(3)–H(3)	1.005 (17)	
C(11)–O(11)	1.151 (2)	1.162	C(4)–H(4)	0.914 (17)	
C(12)–O(12)	1.156 (2)	1.164	C(5)–H(5)	0.897 (18)	
C(13)–O(13)	1.143 (2)	1.152			

Bond Angles

C(1)–Mn–C(2)	38.46 (8)	C(11)–Mn–C(12)	91.59 (9)
C(2)–Mn–C(3)	37.47 (8)	C(11)–Mn–C(13)	92.52 (9)
C(3)–Mn–C(4)	38.15 (8)	C(12)–Mn–C(13)	91.96 (8)
C(4)–Mn–C(5)	38.04 (9)	C(5)–C(1)–H(1)	122.2 (11)
C(5)–Mn–C(1)	38.59 (9)	C(2)–C(1)–H(1)	131.7 (11)
C(5)–C(1)–C(2)	106.05 (17)	C(1)–C(2)–H(2)	124.6 (11)
C(1)–C(2)–C(3)	109.02 (18)	C(3)–C(2)–H(2)	126.3 (11)
C(2)–C(3)–C(4)	108.61 (18)	C(2)–C(3)–H(3)	126.2 (10)
C(3)–C(4)–C(5)	107.59 (18)	C(4)–C(3)–H(3)	124.8 (10)
C(4)–C(5)–C(1)	108.72 (17)	C(3)–C(4)–H(4)	125.7 (10)
Mn–C(11)–O(11)	179.33 (16)	C(5)–C(4)–H(4)	126.7 (10)
Mn–C(12)–O(12)	178.83 (15)	C(4)–C(5)–H(5)	132.1 (11)
Mn–C(13)–O(13)	178.56 (19)	C(1)–C(5)–H(5)	119.2 (11)

[a] The numbers in parentheses are estimated standard deviations in the least significant digits. [b] Distances involving the CpMn moiety have been corrected in the rigid-body approximation ($R_{wU} = 0.013$). All remaining distances have been corrected by treating the $Mn(CO)_3$ fragment as a rigid group ($R_{wU} = 0.031$). See text. [c] Block-diagonal refinement tends to underestimate the errors in the atomic coordinates and thermal parameters. Thus, the true standard deviations in the bond distances and angles are expected to be somewhat larger than those reported in the table.

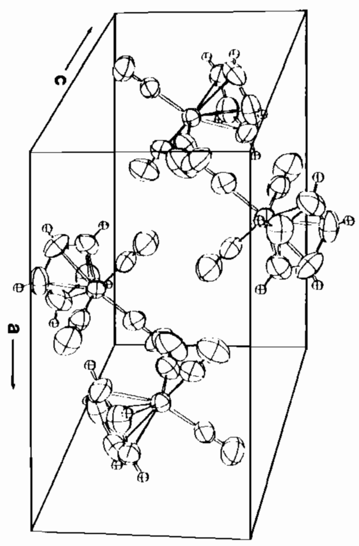

Figure 1. View of the crystallographic unit cell of $CpMn(CO)_3$ plotted by ORTEP. Thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms have been introduced as spheres with arbitrary $B = 1.0$ Å^2 temperature factors.

axes, and intermolecular approaches less than 3.5 Å are listed in Table V. A view of the crystallographic unit cell is shown in Figure 1, and a projection of an isolated molecule down the molecular axis is illustrated in Figure 2. While many of the qualitative features of the structure are essentially the same as those reported earlier by Berndt and Marsh,[11] a number of aspects deserve comment in light of the much higher accuracy achieved in the present study and the rigorous thermal motion analysis which was performed.

As expected, the $Mn(CO)_3$ fragment possesses effective C_{3v} symmetry, and a common molecular axis passes through the midpoint of the Cp ring, the three carbonyl groups, and the manganese atom. The approximate nature of the overall molecular symmetry adopted in the crystal, however, is clearly apparent from an examination of Figure 2. The plane that

Table IV. Selected Least-Squares Planes for $CpMn(CO)_3$ and the Distances of the Atoms (Å) from the Planes[a]

Plane 1: Cyclopentadienyl Ring C Atoms

$-0.3529X + 0.7819Y + 0.5139Z + 1.1782 = 0$

C(1)	0.001	H(1)	−0.020
C(2)	0.002	H(2)	0.043
C(3)	−0.004	H(3)	0.075
C(4)	0.005	H(4)	−0.003
C(5)	−0.004	H(5)	−0.008
Mn	1.766		

Plane 2: Mn, C(11), O(11), Ring Centroid

$0.0857X - 0.5251Y + 0.8467Z - 2.3051 = 0$

C(12)	−1.290	O(12)	−2.146
C(13)	1.268	O(13)	2.088

Plane 3: Mn, C(4), Ring Centroid, Midpoint of C(1)–C(2) Bond

$-0.0133X - 0.5571Y + 0.8304Z - 2.0523 = 0$

C(1)	0.700	C(3)	−1.117
C(2)	−0.700	C(5)	1.118

Plane 4: Mn, C(13), O(13), Ring Centroid

$0.8406X + 0.0218Y + 0.5412Z - 3.1772 = 0$

C(11)	1.268	O(11)	2.087
C(12)	−1.278	O(12)	−2.113

Plane 5: Mn, C(5), Ring Centroid, Midpoint of C(2)–C(3) Bond

$0.8860X + 0.0999Y + 0.4527Z - 3.0527 = 0$

C(1)	1.144	C(3)	−0.685
C(2)	0.681	C(4)	−1.121

Plane 6: Mn, C(1), Ring Centroid, Midpoint of C(3)–C(4) Bond

$-0.5566X - 0.6209Y + 0.5520Z - 0.1740 = 0$

C(2)	−1.118	C(4)	0.694
C(3)	−0.694	C(5)	1.124

Angles between Normals to Planes (Deg)

planes	2-3	5.93	planes	4-5	7.25

[a] Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to the orthogonal coordinates X, Y, and Z, which were obtained from the fractional coordinates by applying the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c(\cos\beta) \\ 0 & b\sin\gamma & c(\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma \\ 0 & 0 & c(\sin\alpha\sin\beta) \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Table V. Nonhydrogen Intermolecular Distances Less Than 3.5 Å in $CpMn(CO)_3$

	generated atom	symmetry operation	dist, Å
O(11)	C(5)	$x, y + 1, z$	3.407 (2)
O(11)	C(13)	$1 - x, \bar{y}, 1 - z$	3.458 (2)
O(11)	O(12)	$x + {}^1/_2, {}^1/_2 - y, z$	3.421 (3)
O(11)	O(13)	$x + {}^1/_2, {}^1/_2 - y, z$	3.457 (2)
O(11)	O(13)	$1 - x, \bar{y}, 1 - z$	3.383 (2)
O(12)	C(2)	$x - {}^1/_2, {}^1/_2 - y, z$	3.446 (3)
O(12)	C(2)	${}^1/_2 - x, {}^1/_2 + y, \bar{z}$	3.471 (3)
O(12)	C(4)	$\bar{x}, \bar{y}, \bar{z}$	3.440 (2)
O(12)	O(13)	${}^1/_2 - x, {}^1/_2 + y, 1 - z$	3.495 (2)
O(13)	C(5)	${}^1/_2 - x, {}^1/_2 + y, 1 - z$	3.434 (3)

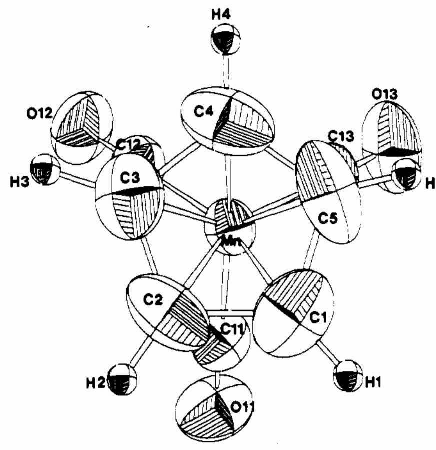

Figure 2. ORTEP projection of $CpMn(CO)_3$ down the molecular axis, illustrating the atomic numbering system. Thermal ellipsoids are drawn at the 50% probability level. For the sake of clarity, spheres with isotropic temperature factors $B = 1.0$ Å^2 were used for the hydrogen atoms.

Table VI. Results of the Thermal Motion Analysis on $CpMn(CO)_3$ Assuming Various Models for Rigid-Body Motion

rigid group	no. of indep atoms	librating group	R_{wU}	rms ΔU^{ij}, Å^2	mean σ^{ij}, Å^2
CpMn	6	none	0.013	0.0005	0.0013
$Mn(CO)_3$	7	none	0.031	0.0012	0.0010
$CpMn(CO)_3$	12	none	0.072	0.0034	0.0012
	12	CpMn	0.043	0.0017	0.0012

contains the atoms Mn, C(11), and O(11) is twisted 5.93° clockwise from that comprising atoms C(4), Mn, and the midpoints of the ring and the C(1)–C(2) bond. Alternatively, the Mn–C(13)–O(13) group is 7.25° in the opposite sense from being eclipsed with respect to C(5). In addition, small but significant deviations between presumed equivalent C–C distances within the cyclopentadienyl ring are observed (vide infra). Thus the true molecular symmetry is C_1.

Thermal Motion Analysis. As a consequence of the generally large root-mean-square amplitudes of vibration under ambient conditions (Table II) and the extreme anisotropy of thermal libration of the cyclopentadienyl ring, a rigorous thermal motion analysis using the program THMI-2[34,35] (performed on an IBM 370/158 computer) was undertaken to evaluate the influence of this librational motion on the observed bond distances. Calculations were performed with the assumption of a rigid-body motion of the entire molecule, as well as of the CpMn and $Mn(CO)_3$ fragments alone (with the exception of the hydrogen atoms in all cases). The results are summarized in Table VI, where

$$R_{wU} = \left[\frac{\sum(\sigma_{U_{\text{obsd}}}{}^{ij})^{-2}(U_{\text{obsd}}{}^{ij} - U_{\text{calcd}}{}^{ij})^2}{\sum(\sigma_{U_{\text{obsd}}}{}^{ij})^{-2}(U_{\text{obsd}}{}^{ij})^2} \right]^{1/2}$$

as defined in ref 35. Agreement between the observed structural parameters and the assumed rigid-body model was judged on the basis of R_{wU} and a comparison of the mean $U_{\text{obsd}}{}^{ij} - U_{\text{calcd}}{}^{ij}$ with the mean $\sigma_U{}^{ij}$.[36]

It is obvious from these results that $CpMn(CO)_3$ does not strictly behave as a rigid body ($R_{wU} = 0.072$), but this is not unexpected.[37] However, excellent agreement is obtained if the rigid-body approximation is confined to the C_5Mn moiety ($R_{wU} = 0.013$) and the distances in Table III have been corrected accordingly. The hydrogen atoms are expected to undergo additional riding motion, but the C–H distances have been left uncorrected. The overall effect has been an average 0.034-Å increase in the C–C distances within the cyclopentadienyl ring, while the Mn–C(ring) distances have increased by an average 0.025 Å.

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(34) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **B24**, 63 (1968).

(35) K. N. Trueblood, *Acta Crystallogr., Sect. A*, **A34**, 950 (1978).

(36) For the reader who is unfamiliar with the treatment of rigid-body behavior, Trueblood[35] examines numerous examples from the literature where a rigid-body description, with allowance for intramolecular torsion, seems appropriate. The limitations of this type of analysis are discussed, and some feeling for the "semiquantitative" judgment required to determine the applicability of the rigid-body model to a given situation can be gained.

(37) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **B29**, 2516 (1973).

If rigid-body motion of the entire molecule is assumed with allowance for librational motion of the cyclopentadienyl ring around the molecular axis, R_{wU} is reduced to 0.043. The amplitude of libration is 9.94 (55)°, which is considerably smaller than the value of 12° estimated by Berndt and Marsh[11] and later derived by Bennett et al.[38] from a hindered-rotor refinement of the observed structure factors. This difference is undoubtedly related to the absence of a large absorption correction for Cu Kα radiation in the earlier work.

Bond distances involving the $Mn(CO)_3$ moiety were also corrected in the rigid-body approximation. Although this is not strictly valid (vide infra), it is considered to provide an adequate description of the shortening effects to be expected from the large thermal motion of the terminal atoms. The average increases in Mn–C(O) and C–O distances after correction were 0.015 and 0.009 Å, respectively.

An analysis of the mean-square vibrational amplitudes (MSVA) provides some explanation as to why $CpMn(CO)_3$ does not behave as a rigid body. For each pair of atoms (both bonded and nonbonded) in a *truly* rigid group, their MSVA along the vector between them should be equal,[39] i.e., $\Delta MSVA = U_{obsd,1\to 2} - U_{obsd,2\to 1} = 0$. Any violation of this condition for a given pair of atoms can be expected to yield information about the nature and magnitude of the internal motions within the molecule. As expected, the very low-energy vibrational modes involving the (O)C–Mn–C(O) and ring–Mn–C(O) bends (135–77 cm^{-1})[7g] have an appreciable thermal population under ambient conditions. Consequently, there are large relative motions between the carbonyl groups and the atoms of the Cp ring, the average intergroup ΔMSVA between the 30 nonbonded atom pairs being 84×10^{-4} Å^2. This seemingly uncorrelated motion is one of the major reasons for the observed nonrigidity of the entire molecule.

Since the $Mn(CO)_3$ group possesses effective C_{3v} symmetry, the differences in the mean-square vibrational amplitudes between equivalent C–C and O–O atom pairs are expected to be close to zero, as is observed. However, the ΔMSVA between nonbonded C–O pairs is $\sim 54 \times 10^{-4}$ Å^2. This relatively large difference can be attributed to the fact that the terminal O atoms undergo much larger displacements than the C atoms in the low-frequency bending modes.[40]

Surprisingly, it is the bonded atoms that are significantly nonrigid—the average ΔMSVA between Mn and the three C atoms is 104×10^{-4} Å^2 and between bonded C–O atom pairs is 68×10^{-4} Å^2. On the basis of atomic mass considerations, the C atom is expected to undergo a larger displacement than the Mn atom in the normal coordinate for the Mn–C(O) stretch. Since the Mn–C–O linkage is approximately linear, the MSVA for the C atom will also include components from vibrations that contain appreciable contributions of C–O stretching. Thus there is no reason to expect the MSVA of Mn and C along the bond direction to be identical, and the observed values reflect these trends: Mn, 0.0469 Å^2; C, 0.0574 Å^2; O, 0.0506 Å^2. This illustrates one of the limitations in generalizing Hirschfeld's rigid-bond postulate[39] (which holds well for atoms of comparable mass) to the study of organometallic systems. There is no simple explanation for the observed nonrigidity of the C–O bond since the oxygen is expected to ride on the carbon atom during the Mn–C stretch; i.e., the change in the C–O bond distance is approximately 2.8% of that in the Mn–C.[41] A detailed summary of the observed mean-square vibrational amplitudes is available as supplementary material (Tables VII–IX).

Table X. Bonding in $CpM(CO)_3$ Complexes

direction of charge donation	$C_5H_5^-$ orbital (D_{5h})	principal metal orbitals of overlap	$(CO)_3$ orbital (C_{3v})	direction of charge donation
metal → ring (negligible)	e_2'', δ symmetry	d_{xy} $d_{x^2-y^2}$	e (2π)	metal → CO (large)
ring → metal (large)	e_1'', π symmetry	d_{xz}, d_{yz}	e (5σ)	CO → metal (large)
ring → metal (small)	a_2'', σ symmetry	d_{z^2}	a_1 (5σ)	CO → metal (small)
			a_1 (2π)	metal → CO (large)

Table XI. Comparison of the Observed Metal–Cp and Metal–C(O) Bond Distances in $CpMn(CO)_3$[a] and $CpRe(CO)_3$[b] with the Expected Sum of Covalent Radii

	obsd dist,[c] Å	sum of covalent radii,[d] Å	bond shortening, Å	charge donation
Mn–Cp	1.766	3.09	1.324	π donation, Cp → metal
Re-Cp	1.955	>3.21	>1.255	
Mn–C(O)	1.780	2.09	0.310	π back-bonding, metal → CO; σ donation, CO → metal
Re–C(O)	1.903	>2.21	>0.307	

[a] Present work. [b] P. J. Fitzpatrick, Y. Le Page, and I. S. Butler, *Acta Crystallogr., Sect B,* **B37**, 1052 (1981). [c] Thermally uncorrected distances. [d] Assumed covalent radii: Mn, 1.39 Å; Re, >1.51 Å; sp carbon, 0.70 Å; Cp ring, 1.70 Å (van der Waals radius in direction perpendicular to ring as no value for the covalent radius of a π-bonded ring appears to have been reported).

Metal–Cp and Metal–C(O) Bonding. Several molecular orbital calculations on $CpM(CO)_3$ systems have been reported in which the molecule is generally treated as an $M(CO)_3^+$ fragment interacting with the $C_5H_5^-$ ring.[12] Under its local D_{5h} symmetry, the p orbitals of the ring combine to give rise to filled a_2'' and e_1'' orbitals that possess σ and π symmetry, respectively, with respect to the metal–ring bond and vacant e_2'' orbitals of δ symmetry with respect to the metal–ring axis. These orbitals interact with the $M(CO)_3^+$ moiety in the manner shown in Table X.

The observed M–Cp and M–C(O) bond distances in $CpM(CO)_3$, where M = Mn and Re (from our earlier work[15]), are compared with the expected sum of the covalent radii in Table XI. Several conclusions can be drawn regarding these results. First, there is essentially no difference between $CpMn(CO)_3$ and $CpRe(CO)_3$ with respect to metal ⇄ CO σ-donor/π-acceptor capacities. This is in agreement with the very small difference observed in the primary CO stretching force constants [$CpMn(CO)_3$, 16.025 mdyn Å^{-1}; $CpRe(CO)_3$, 15.975 mdyn Å^{-1}].[42] The average Mn–C(O) distance of 1.780 (1) Å represents a considerable shortening from the single-bond value as the result of back-donation into the carbonyl 2π acceptor levels. The Mn–C–O angles do not differ significantly from 180°, although Kettle has demonstrated that linearity is not an imposed condition since the 2π orbital is substantially localized on the C atom.[43]

By contrast, the (O)C–M–C(O) angle in such systems is extremely sensitive to the extent of mixing between carbonyl molecular orbitals and to the nature of the other coordinating ligands.[44] In $CpMn(CO)_3$, this angle has expanded to 92.02

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(38) M. J. Bennett, W. L. Hutcheon, and B. M. Foxman, *Acta Crystallogr., Sect. A*, **A31**, 488 (1975).

(39) F. L. Hirshfeld, *Acta Crystallogr., Sect. A*, **A32**, 239 (1976).

(40) For example, see the normal-coordinate analyses of $M(CO)_6$ (M = Cr, Mo, W) by L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

(41) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, New York, 1975, p 26.

(42) J. Sedman, unpublished results from an energy-factored force field calculation using harmonic ν(CO) data.

(43) S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965); *J. Chem. Soc. A*, 420 (1966).

Chart I

	$(CH)_n^{n-6}$				
	C_6H_6	$C_5H_5^-$		$C_4H_4^{2-}$	
complex	$(C_6H_6)Cr(CO)_3$[a]	$CpRe(CO)_3$[b]	$CpMn(CO)_3$[c]	$(C_4H_4)Fe(CO)_3$[d]	$(C_4Ph_4)Fe(CO)_3$[e]
(O)C–M–C(O), deg	88.22 (8)	90.0 (2)	92.02 (5)	95.6	97.03 (3)

increasing π-donor capacity of the cyclic polyene
increasing energy of the $(CH)_n^{n-6}$ π orbital →
decreasing pyramidality of the $M(CO)_3$ fragment

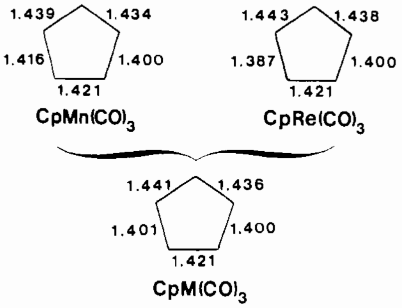
[a] B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, B29, 2516 (1973). [b] P. J. Fitzpatrick, Y. Le Page, and I. S. Butler *Acta Crystallogr., Sect. B*, B37, 1052 (1981). [c] Present work. [d] Value for $(C_4H_4)Fe(CO)_3$ was calculated by M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest, and D. R. Lloyd, *Mol. Phys.*, 30, 839 (1975), from the crystal structure of $(C_4H_6)Fe(CO)_3$ (O. S. Mills and G. Robinson, *Acta Crystallogr.*, 16, 758 (1963)) and from the electron diffraction study of $(C_4H_4)Fe(CO)_3$ (M. I. Davis and C. S. Speed *J. Organomet. Chem.*, 21, 401 (1970)). [e] R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, 18, 614 (1965).

(5)°, which is consistent with the strong donating capacity of the cyclopentadienyl ring compared with other $(CH)_n^{n-6}$ systems[44] (Chart I). The smaller (O)C–Re–C(O) angle [90.0 (2)°] and longer Re–Cp distance (longer by 0.069 Å after correction for the covalent radii) is consistent with the decreased ring-to-metal π donation as the metal acceptor orbitals are shifted to higher energy. Metal → Cp back-donation is expected to be small or negligible since the e_2'' orbitals of the ring, which are antibonding in character, lie much higher in energy than the metal donor orbitals. The Cp → metal charge donation in the Mn complex has been reported to be 0.610 e, whereas only 0.053 e is accepted by the ring from the metal.[12b] The extent of back-donation may be slightly more significant for $CpRe(CO)_3$ since the highest occupied metal d orbitals are less stable.

While these MO results seem qualitatively reasonable, there has been considerable disagreement in the literature as to the extent of interaction between the Cp ring and the carbonyl groups, as well as to the relative charges on these ligands and on the metal atom itself. Lichtenberger and Fenske[12e] assumed on the basis of symmetry arguments that the Cp ring donates charge into metal orbitals that are incapable of overlap with the carbonyl 2π acceptor levels (Table X). This arises from the fact that the threefold symmetry of the $M(CO)_3$ fragment is not a subgroup of the *assumed* fivefold symmetry of the Cp ring. However, charges calculated for the $(CO)_3$ portion of the molecule range from 0.155–[10g] to 0.693–[12c] which must then come primarily from interaction with the metal d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals. The electronic configuration of the metal similarly has varied from $(Mn^{0.128+})$[12c] to $(Mn^{0.599+})$.[12g] The most recent calculations applying a CNDO/2 approach[12g] report an electronic configuration of $Cp^{0.412-}Mn^{0.599+}$-$(CO)_3{}^{0.188-}$. Clearly there is no real consensus.

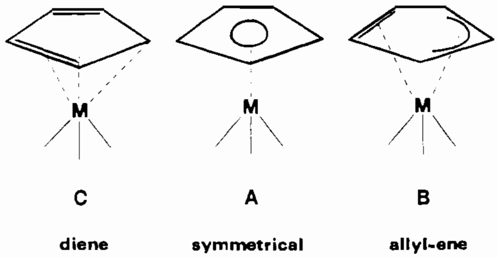
Evidence for Charge Localization within the Cp Ring. The results of the present study do not appear to support the conclusions of Berndt and Marsh[11] regarding the nature of the electronic distribution and mode of bonding in the cyclopentadienyl ring itself. There appears to be evidence for some degree of incomplete delocalization of electrons in the $C_5H_5^-$ ring upon complexation with the $Mn(CO)_3$ moiety. An examination of the dispersion of presumed equivalent C–C distances (Table III, uncorrected) reveals a range of 0.04 Å ($>13\sigma_{C-C}$). While the cyclopentadienyl carbon atoms remain coplanar, the C(2)–C(3) bond is significantly shorter (~10σ) than the mean of the other four bonds within the ring. The bond between C(4) and C(5) is also rather short, although the effect is not as significant. Even considering the fact that block-diagonal refinement tends to underestimate the errors involved (the errors reported are estimated to be ca. 20% smaller than the true errors in this case), the results still indicate that the Cp ring departs measurably from D_{5h} symmetry.

A comparison of the structural data for $CpMn(CO)_3$ with those of $CpRe(CO)_3$[15] makes the situation more apparent, crystallographically equivalent bond distances having been averaged below.



The plane containing the metal, C(1), and the midpoints of the ring and the C(3)–C(4) bond is an approximate mirror plane for the cyclopentadienyl ring in both complexes (Table IV), the bonding pattern being one of long–short–intermediate–short–long C–C bonds. No increase in the overall symmetry of the Cp ring is observed following the thermal motion analysis; consequently, the distortion is unlikely to be an artifact of the librational motion of the ring around the molecular axis. Since the compounds are isostructural in the solid state, no independent check is available as to whether packing effects make a contribution to the observed distortion. However, the shortest nonhydrogen intermolecular contact involving the cyclopentadienyl ring in $CpMn(CO)_3$ is 3.407 Å, and in general the packing is very loose.

Distortions involving the planarity of and/or C–C bond distances within the cyclopentadienyl ring in various transition-metal complexes have been reported in the literature.[5a–g] Three possible bonding modes have been proposed for π metal–Cp systems[5a,c,d]—the symmetrically π-bonded (A), "allyl–ene" (B), and diene (C) ring systems. With only one exception known to us,[5g] however, bond localization has been observed solely in molecules that lack cylindrical symmetry, a consequence of either nonequivalent substitution of the ring or differences in the remaining ligands bonded to the metal. In the latter case, the usual explanation involves a lifting of



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[44] M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 15, 1148 (1976).

the metal orbital degeneracy, which results in an unequal population of the orbitals available for bonding with the Cp ring. This, in turn, may lead to preferential overlap with either the e_1^+ or e_1^- ring orbitals (cf. Table X). If the predominance of one orbital over the other in the metal–Cp bonding is sufficiently large, some loss of aromaticity is expected to occur, although the quality of the data and the highly anisotropic thermal motion of the ring atoms may preclude its observation (particularly under ambient conditions). An extreme example of this loss of aromaticity in noncylindrical systems is illustrated by $(\eta^5\text{-}C_5(CH_3)_5)Co(CO)_2$[5h] (as mentioned in the Introduction) where the e_1^- ring orbital donates into a filled d orbital on cobalt whereas the e_1^+ component donates into a vacant d orbital. Thus $e_1^+ \rightarrow 3d_{xz}$ donation is more favorable than $e_1^- \rightarrow 3d_{yz}$, and this nonequivalent interaction results in a greater population of the e_1^- orbital and hence the observed "allyl–ene" structure.

This does not seem to be a possible explanation for the distortions observed in $CpMn(CO)_3$ and $CpRe(CO)_3$, however, since both compounds possess cylindrical symmetry. The e_1'' donor orbitals of the ring are degenerate, and there is nothing inherent in the symmetry of the $M(CO)_3$ fragment that would lift this degeneracy and result in unequal bond lengths. The e_2'' acceptor orbitals are similarly degenerate, and any back-donation cannot lift their degeneracy. Thus, if the explanation is unrelated directly to the $M(CO)_3$ portion of the molecule, three possibilities are left to consider: (1) an *external* constraint such as the crystal lattice imposes the observed departure of the ring from fivefold symmetry, (2) the distortion arises as the result of some nonequivalent intramolecular interaction between the carbon and hydrogen atoms of the Cp ring with the carbonyl groups, which is not electronic in nature, or (3) the distortion is essentially a property of the Cp ring *alone*, which arises from the metal–Cp bonding interaction.

Site-Symmetry Effects. The intrinsic electronic barrier to rotation of the Cp ring about the molecular axis in $CpMn(CO)_3$ has been estimated to be only 0.002 kcal mol^{-1},[3] while a larger barrier is imposed by the crystal lattice. The total barrier must be fairly small, however, as the wide-line NMR spectrum of $CpMn(CO)_3$ suggests that the ring is freely rotating even at 77 K.[45] This barrier has been determined to be 1.73 kcal mol^{-1} from spin–lattice relaxation (T_1) measurements over the temperature range 296–90 K,[46] which is in excellent agreement with the value of 1.78 (14) kcal mol^{-1} derived by Bennett et al.[47] from a hindered-rotor refinement of the observed structure factors taken from the X-ray study by Berndt and Marsh.[11] Thus the equilibrium orientation of the ring with respect to the carbonyl groups (which is presumably the position of minimum potential energy in the lattice) is determined by intermolecular packing considerations and the minimization of interatomic interactions and might be expected to change with temperature.[48] A preliminary investigation on the nature and magnitude of the rotational barrier in $CpMn(CO)_3$ by performing potential energy calculations reveals that it is the nonbonded intermolecular C···H and O···H interactions that are predominantly responsible for the observed barrier.[46] The Mn–C and Mn–H contributions to the total potential energy are essentially independent of the rotation angle and consequently have no effect on the barrier.[49] The observation that $CpMn(CO)_3$ and $CpRe(CO)_3$ are isostructural in the solid state supports the concept that the M–C and M–H interactions are not involved in determining the conformation.

While the Cp ring is indeed rotating, on the basis of T_1 measurements it does so with a correlation time of 6.45×10^{-13} s.[46] An X-ray photon thus effectively sees the ring as a static system since the carbon atoms are not disordered. As the molecule occupies a C_1 site in the crystal lattice, the electronic and vibrational states of crystalline $CpMn(CO)_3$ cannot be rigorously classified according to any symmetry except C_1. In this case, the degeneracy of the e_1^+ and e_1^- ring orbitals might be lifted since the site symmetry is different from the local symmetry of the CpMn moiety. There is no way a priori of predicting which, if either, of these orbitals might be favored energetically. There might also be the possibility of conformational effects, induced by the crystal lattice, giving rise to nonequivalent interactions between the carbon and hydrogen atoms of the Cp ring with the carbonyl groups, which might also be capable of lifting the degeneracy of the ring orbitals. However, the magnitudes of these effects are uncertain.[50]

Vibrational Considerations for $CpM(CO)_3$ (M = Mn, Re) in Noncrystalline Environments. As outlined in the Introduction, spectroscopic studies of $CpMn(CO)_3$ in the vapor phase and in solution have indicated that the symmetry of the cyclopentadienyl ligand is lower than the fivefold symmetry expected.[7c,g] These results are consistent with the possibility that the observed distortion may originate in the electronic structure of the individual molecules rather than from simply solid-state effects.

The infrared spectra of $CpMn(CO)_3$ and $CpRe(CO)_3$ in CS_2 solution, in the 1450–700-cm^{-1} region, are shown in Figure 3, and the assignments are presented in Table XII. This region contains all of the vibrations expected for the cyclopentadienyl group, with the exception of the C–H stretching vibrations and those vibrations associated with the metal–Cp interaction. All fundamental modes of the $M(CO)_3$ fragment are assigned to bands below 700 cm^{-1} or above 1900 cm^{-1}, and these assignments are consistent with C_{3v} local symmetry. Overtone and combination bands due to vibrations of the $M(CO)_3$ group also appear in this region, but these have been identified from our assignments of the fundamentals.[23]

For an M–Cp fragment, with C_{5v} local symmetry, 2 A_1 + 1 A_2 (inactive) + 3 E_1 + 4 E_2 modes are expected in this region of which the A_1 and E_1 modes are IR active and the A_1, E_1, and E_2 modes are Raman active. After assignment of the A_1 and E_1 modes in the IR spectra of both $CpMn(CO)_3$ and $CpRe(CO)_3$, there remain three bands that are coincident with Raman bands and, therefore, may be assigned as due to vibrations of E_2 symmetry, formally forbidden in the IR. In addition we have found one Raman band, assigned to an E_2 mode, to be polarized (rather than depolarized) whereas the

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(45) D. F. R. Gilson, G. Gomez, and P. J. Fitzpatrick, unpublished results.

(46) P. J. Fitzpatrick, D. F. R. Gilson, G. Gomez, and I. S. Butler, to be submitted for publication.

(47) See ref 38. The authors caution that the value reported here cannot be interpreted as a *genuine* activation energy but rather as information on the sharpness of the potential function near the potential minimum. This arises from the use of a fixed-form potential function with the barrier height as the only adjustable parameter. However, this value has been interpreted as the true rotational barrier when the results seem intuitively reasonable.

(48) For an example of this temperature dependence, see ref 5e. These authors report a 9.4° rotation of the Cp ring in $[CpFe(CO)_2]_2$ upon cooling from ambient temperature to 77 K. As the lattice contracts, the intermolecular distances are reduced while the intramolecular distances remain essentially unchanged. Obviously the constitution of the total intermolecular potential has been sufficiently altered to favor a different equilibrium conformation of the ring.

(49) Similar behavior was reported in calculations on ferrocene, ruthenocene, and $(\eta^6\text{-}C_6H_6)_2Cr$: A. J. Campbell, C. A. Fyfe, D. Harold-Smith, and K. R. Jeffrey, *Mol. Cryst. Liq. Cryst.*, **36**, 1 (1976). However, as pointed out by W. R. Busing, *J. Phys. Chem. Solids*, **39**, 691 (1978), the calculated rotational barriers for these molecules are in error. R. K. Boyd and C. A. Fyfe, *J. Phys. Chem. Solids*, **39**, 693 (1978), have commented on the implications of this error in the parameter sets chosen to describe nonbonded C···C, C···H, and H···H interactions.

(50) Lichtenberger and Fenske,[12c] in their MO calculations on an isolated molecule of $CpMn(CO)_3$, considered such ligand–ligand interactions to be very small. However, the possible effects of this type of interaction on the geometry of the cyclopentadienyl ligand in similar complexes are currently being investigated by M. B. Hall and J. Chinn.

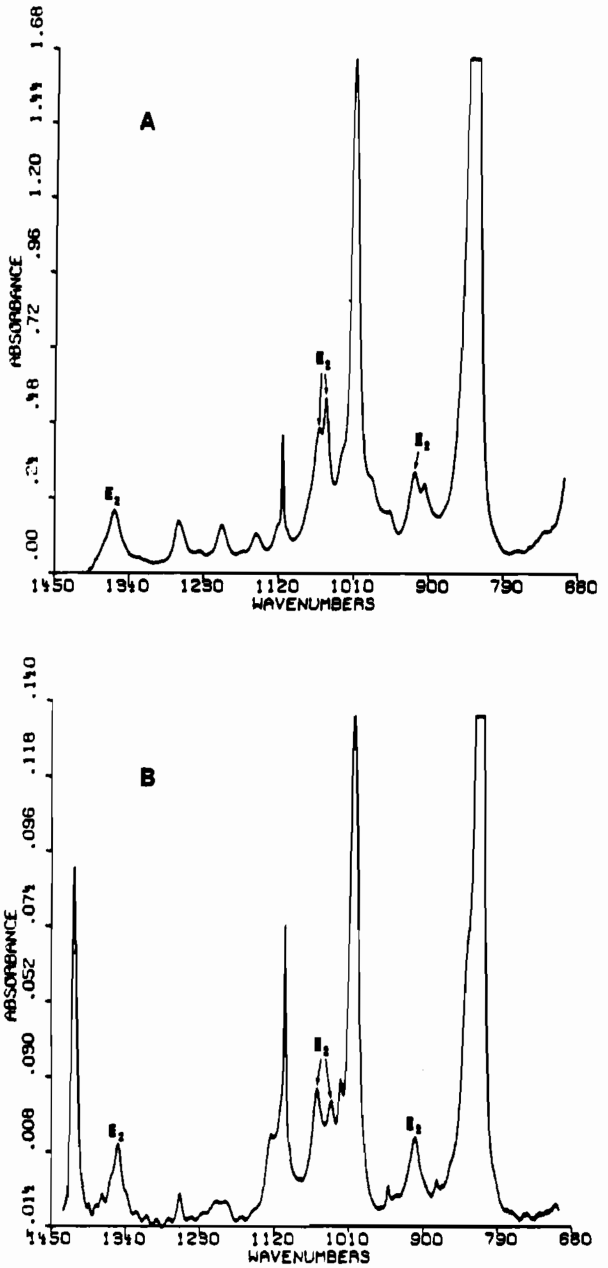

Figure 3. (A) Infrared spectrum of $CpMn(CO)_3$ in CS_2 solution (1.0-mm path length) in the 1450–700-cm^{-1} region. Sample absorptions above 1400 cm^{-1} were obscured by solvent absorption. (B) Infrared spectrum of $CpRe(CO)_3$ in CS_2 solution (0.2-mm path length) in the 1450–700 cm^{-1} region. Both spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer.

depolarization ratios of some of the weaker bands have not been established with certainty due to the photosensitivity of the complexes in the laser beam. Nevertheless, in line with observations of previous workers,[7e,g,51] there is considerable evidence for the breakdown of C_{5v} selection rules in the *solution* vibrational spectra of both $CpMn(CO)_3$ and $CpRe(CO)_3$.

The ^{1}H NMR spectra of these molecules partially oriented in nematic liquid crystalline solvents[16–21] also provide fairly convincing evidence that the Cp ring does not exhibit its expected fivefold symmetry even outside of the crystalline environment. While the importance of perturbation on the molecule exerted by the crystal lattice cannot be underestimated, we feel that there may also be a plausible electronic

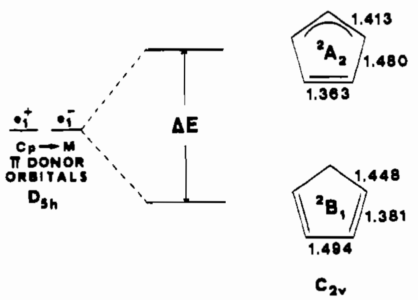

Figure 4. Possible explanation for the distortions observed in the cylindrically symmetrical molecules $CpMn(CO)_3$ and $CpRe(CO)_3$. Two nondegenerate structures for the C_5H_5 radical, each possessing C_{2v} symmetry, have been calculated by Bischof.[54] A suitable population-weighted average of these two orbital representations, if we assume the diene to be lower in energy, would fairly closely represent the distortion observed for the case of $CpM(CO)_3$ (M = Mn, Re).

explanation for the observed loss of aromaticity, which we will now consider.

Electronic Considerations. The distortion of C–C bond distances within the cyclopentadienyl ring observed in $CpM(CO)_3$ (M = Mn, Re) is consistent with a model in which the Cp → M π donation is fairly large. The following is proposed as one possible mechanism for lowering the expected D_{5h} symmetry of the Cp ring. As the extent of charge donation from the $C_5H_5^-$ anion to the metal increases, the ring can be considered to approach the electronic configuration of the $C_5H_5\cdot$ radical, i.e., the ring might be expected to adopt a greater $4n + 1$ radical character since the M → Cp back-bonding is expected to be small (vide supra).[12b,e] In fact, Bursten and Fenske[52] have described the primary bonding interaction in $CpMn(CO)_3$ as predominantly "ionic"[53] since the highest occupied Cp levels (e_1'') interact extensively with the lowest unoccupied metal levels, thus making Cp → M donation extremely favorable. Bischof[54] and also Borden and Davidson[55] have recently concluded from potential energy surface calculations that the C_5H_5 radical has an orbitally degenerate ground state and is subject to a Jahn–Teller distortion, which gives rise to two structures of lower symmetry (C_{2v}), one possessing "allylic" and the other "dienyl" character (Figure 4). However, Bischof[54] concluded that these two structures are not degenerate in energy as only the one of $^2B_1$ symmetry corresponds to a true minimum. Borden and Davidson[55] predicted a smaller energy difference between the two structures. The barrier to interconversion of these "isomers" has been estimated to be 0.14 kcal mol^{-1} by ESR measurements.[56]

From the bond lengths calculated for these structures,[54] it is apparent that only a small difference in energy between the two components of the e_1'' orbital would be sufficient to induce an observable distortion of the Cp ring. Furthermore, it seems reasonable to assume that if the $CpM(CO)_3$ molecules are susceptible to Jahn–Teller distortion, the degeneracy might be further lifted in the crystalline environment. An appropriate population-weighted average of such nondegenerate e_1^+ and e_1^- component orbitals of the Cp ring, possessing bonding distributions similar to those represented in Figure 4, would reproduce fairly well the distortions observed for these molecules. The observation in the solid-state structures of CpM-

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(51) B. V. Lokshin, Z. S. Klemenkova, and Yu. V. Makarov, *Spectrochim. Acta, Part A*, **28A**, 2209 (1972).

(52) B. E. Bursten and R. F. Fenske, *Inorg. Chem.*, **18**, 1760 (1979).

(53) The authors' use of the term "ionic" in this context is rather unconventional. It is presumed that they are referring to essentially one-way Cp → metal charge donation.

(54) P. Bischof, *J. Am. Chem. Soc.*, **99**, 8145 (1977).

(55) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **101**, 3771 (1979).

(56) G. R. Liebling and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965).

Table XII. Cyclopentadienyl Ligand Vibrations in the 1450–700 cm^{-1} Regions of the Infrared and Raman Spectra of CpM(CO)$_3$ (M = Mn, Re) in CS$_2$ Solution

M = Mn		M = Re		
IR[a]	Raman[b]	IR[a]	Raman[b]	assignt
1424.0 (m)	1424.5 (w, dp)	1416.5 (m)	1417.1 (w, dp)	ν(CC) E$_1$
1362.9 (w)	1363.8 (w, dp)	1351.9 (w)	1352.7 (w, dp)	ν(CC) E$_2$
	1212.7 (vw, p)		1216.6 (vw, p)	β(CH) E$_2$
1114.4 (w)	1113.2 (vs, p)	1104.8 (m)	1105.6 (vs, p)	ν(CC) A$_1$
1060.3 (w) 1051.1 (w)	1061.9 (s, dp)	1057.2 (w) 1035.8 (w)	1058.5 (s, dp)	γ(CH) E$_2$
1008.6 (m)	1009.8 (vw, dp)	1003.2 (m)	[1010.0 (w) 1000.3 (w)]	β(CH) E$_1$
921.8 (w)	[936.5 (w)]	913.2 (w)	[931.8 (w) 922.6 (w)]	α(CC) E$_2$
834 (sh)	[846.0 (m)]	834.4 (m, sh)	[841.4 (m)]	γ(CH) E$_1$
829.7 (s)	[835.7 (m)]	817.8 (s)	[824.4 (m)]	γ(CH) A$_1$

[a] Spectra recorded on a Nicolet Model 6000 FT-IR spectrometer; wavenumber accuracy ±0.5 cm^{-1}. [b] Spectra recorded on a Jarrell-Ash Model 25-300 Raman spectrometer with Kr$^+$ laser excitation (~30 mW); wavenumber accuracy ±2 cm^{-1}; wavenumbers in square brackets from spectra of solid samples.

(CO)$_3$ of the dienyl (C) bonding pattern, corresponding to the lower energy (and thus higher populated) component of the e$_1''$ orbital in the cyclopentadienyl radical, rather than the "allyl–ene" structure (B) is consistent with this model for what might be expected to occur in the limiting case of the donation of one full electron from the ring to the metal.[57] A Jahn–Teller distortion was invoked to explain the situation observed in low-spin Mn(η^5-C$_5$Me$_5$)$_2$.[5g] However, the bond localizations are less pronounced than those reported in the present study, although the use of the pentamethyl derivative undoubtedly increases the accuracy with which the C–C distances are known.

In addition, it is unclear what effect extensive π donation may have on the σ framework of the Cp ring, and it is possible that this might result in some form of a structural distortion through strong inductive effects etc. Such factors also do not appear to have been considered in any of the MO treatments on such systems.

Conclusions

In view of the low rotational barriers in these systems, there are obvious difficulties involved in attempting to determine highly accurate parameters for the Cp ring, and a thermal motion analysis should always be performed. Furthermore, as a result of the pseudo body centering of the heavy atom in the crystal lattices of CpMn(CO)$_3$ and CpRe(CO)$_3$, the intensities of half of the reflections are dominated by scattering from the metal atom. The remaining reflections, whose intensities are almost exclusively due to the organic moieties, are thus systematically weak. However, the low residuals achieved in both cases [R_1 = 0.0286, R_2 = 0.0205 for CpMn(CO)$_3$; R_1 = 0.020, R_2 = 0.019 for CpRe(CO)$_3$[15]] give us confidence in the parameters reported.

Obviously, additional chemical evidence and theoretical calculations are required to establish whether there is indeed an electronic basis for the apparent localized bonding in the Cp ring. However, recent MO calculations on (η^4-C$_4$H$_4$)Fe(CO)$_3$ have shown that an antiaromatic ligand such as cyclobutadiene gains aromaticity upon complexation, whereas a Hückel $4n + 2$ species such as C$_5$H$_5^-$ must be expected to lose some aromatic character upon interaction with a metal center.[52] On this basis, Bursten and Fenske predict that aromaticity decreases in the order (η^4-C$_4$H$_4$)Fe(CO)$_3$ > CpMn(CO)$_3$ > (η^6-C$_6$H$_6$)Cr(CO)$_3$. Localized bonding has been observed in (η^6-C$_6$H$_6$)Cr(CO)$_3$,[37] and the distortions reported here for CpM(CO)$_3$ (M = Mn, Re) support a similar loss of aromaticity. As suggested by Bursten and Fenske,[52] a Friedel–Crafts acylation competition reaction between (η^4-C$_4$H$_4$)Fe(CO)$_3$ and CpMn(CO)$_3$ should be performed in order to compare the aromaticities of these ring systems. A low-temperature X-ray or neutron diffraction study of CpMn(CO)$_3$ and CpRe(CO)$_3$ would also seem appropriate, as well as a reexamination of the crystal structures of other metal cyclopentadienyls to obtain more accurate structural parameters for these molecules. By the investigation of other simple M–Cp complexes that crystallize in different symmetries, the influence of the crystalline environment on the overall view of the structure in these systems would be minimized. In this manner, it should be possible to determine whether the observed distortions are a general phenomenon for cylindrically symmetrical M–Cp systems. The use of the C$_5$Me$_5$ ligand rather than C$_5$H$_5$ may also facilitate the acquisition of accurate structural data since the methyl group has a larger scattering power than a H atom and the barriers to ring rotation would be expected to be considerably higher. Clearly, it seems necessary to reexamine currently accepted assumptions regarding the bonding in simple M–Cp systems before applying them to more complicated molecules.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Quebec Department of Education. P.J.F. acknowledges a McGill University Graduate Research Fellowship. The authors are grateful to Dr. Eric Gabe for the use of X-ray facilities, as well as to Professor G. Donnay for assistance in preliminary work. We also wish to thank Professors Alan Shaver and D. F. R. Gilson for their interest in this work and advice in the preparation of the paper.

Registry No. CpMn(CO)$_3$, 12079-65-1; CpRe(CO)$_3$, 12079-73-1; dirhenium decacarbonyl, 14285-68-8.

Supplementary Material Available: Tables II, VII–IX, and XIII, giving root-mean-square amplitudes of vibration for all nonhydrogen atoms, mean-square vibrational amplitudes between pairs of atoms, a summary of the MSVA between bonded and nonbonded atoms within the CpMn and Mn(CO)$_3$ groups, and a listing of the observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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(57) Recent gas-phase photoelectron studies and MO calculations for [η^5-C$_5$H$_{5-n}$(CH$_3$)$_n$]M(CO)$_3$ (M = Mn, Re; n = 0, 1, 5) [D. C. Calabro, J. L. Hubbard, C. H. Blevins II, A. C. Campbell, and D. L. Lichtenberger, submitted for publication] indicate a lifting of the degeneracy of the Cp e$_1''$ orbitals and a difference in the C–C overlap populations within the ring. From their work, the authors predict a distortion from D_{5h} symmetry of the ring in these complexes arising from a variation of the C–C bond lengths (estimated to be ca. 0.01–0.02 Å). These results are in agreement with our conclusion that the distortions observed in the present study are at least partially of electronic origin, rather than arising from solid-state effects.