

sampled in our survey, we feel that the dominant geometrical features may have significance beyond the solid state. We would expect, for example, that the geometries of the bidentate and α modes would be relatively insensitive to environmental factors. The possibility remains that the observed distribution of the unidentate calcium-carboxylate geometries might be a consequence of crystallographic factors. Examination of nearest-neighbor interactions involving the carboxylate groups has not revealed any obvious crystallographic effects that might explain the restricted unidentate geometries, but a number of environmental factors that may be of significance have not been analyzed. Nevertheless, it appears likely that the unidentate distribution is also indicative of the calcium-carboxylate geometries that might be expected in other, noncrystalline environments.

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* See also Table 1.

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The Structure of Tricarbonyl(η^5 -cyclopentadienyl)rhenium(I)

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Abstract

[Re(C₅H₅)(CO)₃], CpRe(CO)₃ (Cp = η^5 -C₅H₅) crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.872$ (3), $b = 7.215$ (1), $c = 11.053$ (1) Å, $\beta = 116.46$ (2)°, $Z = 4$, $d_c = 2.626$ Mg m⁻³. The intensity data were obtained by the conventional θ - 2θ scan technique and the structure has been refined to $R_F = 0.0206$ and $R_w(F) = 0.0190$ for 1284 observed reflections [$I \geq 2\sigma(I)$]. The Re(CO)₃ moiety has C_{3v} symmetry; the average Re–C(O) distance is

1.894 (4) Å (*i.e.* very close to the predicted double-bond value of 1.94 Å) and the Re–C–O angle is 177.7 (4)°. The cyclopentadienyl ring is almost perfectly planar (largest deviation, 0.003 Å). The variation of C–C bond lengths within the ring indicates some tendency for localized bonding, which is quite unexpected for molecules of this type which possess effective cylindrical symmetry. This observation, however, may account for the anomalous vibrational spectroscopic results reported for this molecule, as well as for the deviation from D_{5h} symmetry of the Cp ring itself as

indicated by ^1H NMR spectra of the complex in nematic liquid-crystalline solvents.

Introduction

For the past few years, we have been interested in the comparative physicochemical properties of transition-metal carbonyls, thiocarbonyls and selenocarbonyls (Butler, 1977). One of our approaches has been a detailed comparison of their vibrational spectra including normal coordinate calculations. For example, some of the complexes that have been investigated are: $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5(\text{CX})$ (Jones, McDowell & Goldblatt, 1969; Butler, Garcia-Rodriguez, Plowman & Shaw, 1976; English, Plowman & Butler, 1981*a*), $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CX})$ (English, Plowman & Butler, 1981*b*), as well as $\text{CpMn}(\text{CO})_3$ and $\text{CpMn}(\text{CO})_2(\text{CX})$ (Sedman & Butler, 1981), where $X = \text{S}, \text{Se}$ and $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$. In order to extend this work to other metals, we decided to study the vibrational spectra of the Re^I complexes $\text{CpRe}(\text{CO})_3$ and $\text{CpRe}(\text{CO})_2(\text{CX})$. However, reasonably accurate bond distances and angles are needed for the normal coordinate calculations but there are no X-ray data available for the thio- and selenocarbonyl complexes, while only cell parameters from powder diffraction results appear to have been published for the tricarbonyl complex (Struchkov, Anisimov, Osipova, Kolobova & Nesmeyanov, 1967). Therefore, we felt that it was necessary to obtain accurate structural parameters for at least $\text{CpRe}(\text{CO})_3$ before proceeding with the proposed normal coordinate analyses.

It was also hoped that a comparison of metal–Cp and metal–C(X) bond distances would give additional insight into the comparative σ -donor/ π -acceptor capacities of the isoelectronic CO, CS and CSe ligands in these complexes. However, both the Mn and Re thio- and selenocarbonyl complexes are considerably unstable and would most likely require data collection by conventional scan methods at or near 77 K. We have also been experimenting with applications of the stationary-crystal-stationary-counter method utilizing the nearly monochromatic $K\beta_1$ wavelengths of both Mo and Ag, which eliminates the 2θ dependence of intensities resulting from $K\alpha_1/K\alpha_2$ variable overlap, to the study of transition-metal complexes. The increased speed of intensity measurement provided by this technique might provide the only possibility for collecting data at ambient temperature on such organometallic derivatives which decay rapidly on prolonged exposure to X-rays. We report here the results of our investigation of the parent complex $\text{CpRe}(\text{CO})_3$ by the usual θ – 2θ scan technique. In a subsequent publication, the results obtained by both the θ – 2θ scan and stationary-crystal-stationary-counter techniques for this and several other compounds will be

compared. In addition, some general observations concerning the applicability of the latter method to various structural problems will be presented.

Experimental

A sample of $\text{CpRe}(\text{CO})_3$ was prepared by a modification of the procedure reported by Green & Wilkinson (1958). Dirhenium decacarbonyl, $\text{Re}_2(\text{CO})_{10}$ (3.0 g, 4.6 mmol), was refluxed in 25 ml dicyclopentadiene for *ca* 10 h. The reaction was monitored by TLC on silica gel plates using hexanes as eluent. Petroleum ether (303–333 K, 50 ml) was added and the solution was cooled to 195 K. The grey solid obtained was introduced onto a sintered glass filter packed with alumina, and washed repeatedly with petroleum ether to remove unreacted $\text{C}_{10}\text{H}_{12}$. The pure complex was then eluted from the alumina with diethyl ether. White crystals of $\text{CpRe}(\text{CO})_3$ (m.p. 383–384 K) were obtained by sublimation (0.1 Pa, 343 K).

Single crystals suitable for the X-ray study were grown by slow sublimation (0.1 Pa, 303 K) onto a glass finger while maintaining a small temperature gradient. A transparent, roughly equidimensional, single crystal was selected for data collection and ground into a sphere of diameter 0.275 mm in a Bond sphere grinder lined with an anti-static cloth. In view of the 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.

Crystal data and intensity-data collection

$\text{C}_8\text{H}_5\text{O}_3\text{Re}$, $M_r = 335.2$, monoclinic, $a = 11.872$ (3), $b = 7.215$ (1), $c = 11.053$ (1) Å, $\beta = 116.46$ (2)°, $V = 847.6$ Å³, $d_c = 2.626$ Mg m⁻³, $Z = 4$, $F(000) = 608$, space group $P2_1/n$ (C_{2h}^5 , alternative setting of $P2_1/a$, No. 14); systematic absences: $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$; general equivalent positions $\pm [x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z]$; Mo $K\beta_1$ radiation, $\lambda = 0.632288$ Å, $\mu = 11.166$ mm⁻¹.

The unit-cell parameters reported by Struchkov *et al.* (1967) ($a = 12.31$, $b = 7.13$, $c = 11.32$ Å, $\beta = 120$ °; space group $P2_1/a$, $Z = 4$) were not confirmed, nor were they sufficient to index the observed X-ray powder diffraction pattern.*

* Lists of structure factor amplitudes, anisotropic thermal parameters for non-hydrogen atoms, principal lines in the observed and calculated powder diffraction pattern of $\text{CpRe}(\text{CO})_3$, r.m.s. amplitudes of vibration, equations of selected least-squares planes and non-hydrogen intermolecular contacts less than 3.5 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35876 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal was transferred to a Picker FACS-I four-circle automated diffractometer equipped with a scintillation counter and a pulse-height analyzer. 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 $2\theta-$ using Cu $K\beta_1$ radiation ($\lambda = 1.392218 \text{ \AA}$, $58 < 2\theta < 71^\circ$). The mosaic spread of the crystal was determined to be acceptable by performing narrow-source open-counter ω scans through several intense low-angle reflections (Furnas, 1957); they exhibited peak widths at half-maximum of $< 0.2^\circ$.

Intensity data were collected at 293 K using graphite-monochromatized Mo $K\beta_1$ radiation at a take-off angle of 6° by the usual θ - 2θ scan technique, except that the β radiation of Mo was employed and no correction for wavelength dispersion was considered. Stationary background counts were measured 1.5° on either side of the calculated peak position. Three standards, chosen from widely different regions of reciprocal space and monitored every 30 reflections, decreased by approximately 7% during the period required to complete the data collection.

A total of 1568 unique intensities were measured in the range $3^\circ \leq 2\theta (\text{Mo } K\beta_1) \leq 45^\circ$, and an additional 139 are systematically absent in space group $P2_1/n$. The value of $\sum \Delta\sqrt{I}/\sum \sqrt{I}$ was equal to 0.0306 for the 697 symmetry-related reflections measured during the experiment, and the criterion $I \geq 2\sigma(I)$ resulted in 1284 reflections being classified as observed. A spherical absorption correction for $\mu R = 1.54$ was applied to all the measured intensities (Bond, 1959).

Solution and refinement of the structure

All calculations, unless otherwise indicated, were performed on an IBM 370/158 computer employing the programs of XRAY 76 (Stewart, 1976). The atomic scattering curves for Re, C and O were taken from Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965) were used. Intensities were corrected for the usual Lorentz and polarization effects. The anomalous dispersion of Re was included in all structure factor calculations, and the values of $f' = -0.86$ and $f'' = 6.20$ for Mo $K\beta_1$ radiation were taken from the values tabulated by Hazell (1967).

The structure was solved by a combination of Patterson and Fourier techniques. The Re atom position was determined from an analysis of the three-dimensional Patterson function. A peak of height comparable to that of the origin near $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ indicated a pseudo- I lattice which had not been noticed at the time of data collection. Most high-angle reflections with $h + k + l = 2n + 1$ are unobserved; however, some are observed with an intensity too large to be entirely due

Table 1. Analysis of refinement results for reflections expected to be systematically weak as a consequence of the pseudo- I lattice in $\text{CpRe}(\text{CO})_3$

	θ - 2θ scan method (Mo $K\beta$ radiation)		
	$h + k + l = 2n$	$h + k + l = 2n + 1$	Total hkl
Number of reflections	860	708	1568
Observed [$I \geq 2\sigma(I)$]	817 (95.0%)	467 (66.0%)	1284 (81.9%)
$\sum \Delta\sqrt{I}/\sum \sqrt{I}$	—	—	0.0306
Unobserved	43 (5.0%)	241 (34.0%)	284 (18.1%)
R_f	0.016	0.048	0.0206
$R_w(F)$	0.018	0.033	0.0190

to the organic ligands in the molecule ($\bar{6}43$, for example). Thus the y coordinate of the Re atom is not exactly zero, and this was confirmed from an examination of the peak shape near $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ which revealed that it extended slightly more along v than along u or w . Since changing the sign of the y coordinate of the Re atom is equivalent to selecting an alternative origin at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, y was chosen positive. A Fourier synthesis phased on the heavy-atom contribution revealed the remaining 12 non-hydrogen atoms. Several cycles of full matrix least-squares refinement on $\sum w(|F_o| - |F_c|)^2$ were followed by a difference Fourier synthesis which revealed the positions of the cyclopentadienyl H atoms. They were introduced in idealized positions with arbitrary temperature factors of $U = 0.10 \text{ \AA}^2$ assuming a planar ring with C-H distances of 0.95 \AA (Churchill, 1973). These H atom coordinates and thermal parameters were subsequently refined.

A breakdown of the final residuals obtained for the structural refinement of $\text{CpRe}(\text{CO})_3$ is presented in Table 1. The pseudo body-centering of the Re atom (see above) is also reflected by the systematic trends in the number of observed reflections and in the residuals achieved for reflections classed as $h + k + l = 2n$ versus $2n + 1$.

Results and discussion

The final positional and thermal parameters from the θ - 2θ scan results are presented in Table 2. Selected intramolecular bond distances and angles are presented in Table 3 and the bond lengths have been corrected for the shortening effect of thermal libration (Trueblood, 1978). A view of the crystallographic unit cell is shown in Fig. 1, and a projection of an isolated molecule down the molecular axis is illustrated in Fig. 2.

In the solid state, $\text{CpRe}(\text{CO})_3$ exists as discrete molecules which are held together by van der Waals forces. The shortest non-hydrogen intermolecular contacts are 3.359 \AA for $\text{O} \cdots \text{O}$, 3.376 \AA for $\text{C} \cdots \text{O}$ and 3.631 \AA for $\text{C} \cdots \text{C}$ approaches; the corresponding distances in $\text{CpMn}(\text{CO})_3$ are 3.383 , 3.407 and

3.710 Å, respectively. CpRe(CO)₃ is indeed isostructural with its Mn analog (Berndt & Marsh, 1963; Fitzpatrick, Le Page, Sedman & Butler, 1981) upon transformation of the coordinates of the latter from the $P2_1/a$ cell to its proper reduced cell [$P2_1/n$ with $a = 11.937(3)$, $b = 7.057(2)$, $c = 10.913(2)$ Å and $\beta = 116.37(2)^\circ$]. Thus, as expected, the Re(CO)₃ fragment possesses effective C_{3v} symmetry and the molecular axis passing through the midpoint of the Cp ring is coincident with the C_3 axis of the Re(CO)₃ moiety. The overall molecular symmetry adopted in the crystal, however, is C_1 . As the intramolecular barrier to rotation of the Cp ring around the molecular axis has been estimated to be very small [*ca* 0.008 kJ mol⁻¹ for CpMn(CO)₃ (Albright, Hofmann & Hoffmann, 1977)], the equilibrium orientation of the Cp ring is determined

Table 2. Final positional and equivalent isotropic thermal parameters for CpRe(CO)₃ with their estimated standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)*
Re	0.20901 (2)	0.51047 (3)	0.47459 (2)	0.0380 (2)
C(1)	0.0888 (10)	0.2800 (12)	0.3334 (11)	0.068 (6)
C(2)	0.1409 (12)	0.3856 (11)	0.2642 (9)	0.065 (6)
C(3)	0.2687 (11)	0.3695 (13)	0.3275 (10)	0.070 (6)
C(4)	0.2998 (11)	0.2518 (13)	0.4371 (10)	0.068 (7)
C(5)	0.1925 (13)	0.1978 (10)	0.4413 (9)	0.080 (7)
C(11)	0.0874 (7)	0.7024 (9)	0.4285 (8)	0.056 (5)
C(12)	0.3374 (7)	0.6912 (9)	0.5343 (7)	0.053 (4)
C(13)	0.2183 (7)	0.4970 (9)	0.6499 (7)	0.059 (4)
O(11)	0.0122 (5)	0.8185 (7)	0.3982 (7)	0.079 (4)
O(12)	0.4184 (5)	0.7984 (7)	0.5671 (6)	0.075 (4)
O(13)	0.2265 (6)	0.4822 (8)	0.7582 (5)	0.091 (4)
H(1)	0.007 (6)	0.258 (9)	0.309 (7)	0.05 (2)
H(2)	0.100 (7)	0.440 (9)	0.199 (7)	0.06 (3)
H(3)	0.323 (7)	0.408 (10)	0.324 (8)	0.05 (3)
H(4)	0.372 (6)	0.228 (9)	0.478 (8)	0.06 (3)
H(5)	0.181 (8)	0.129 (11)	0.498 (8)	0.09 (3)

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

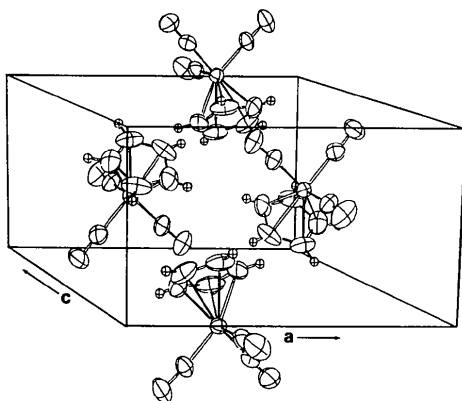


Fig. 1. View of the crystallographic unit cell of CpRe(CO)₃ plotted using ORTEP. Thermal ellipsoids are drawn at the 50% probability level, and the H atoms have been introduced as spheres with arbitrary temperature factors of $B = 1.0 \text{ \AA}^2$.

Table 3. Bond distances (Å) and angles (°) in CpRe(CO)₃

The numbers in parentheses are estimated standard deviations in the least significant digits.

	Uncorrected	Corrected*		
Re—C(1)	2.292 (9)	2.314		
Re—C(2)	2.280 (9)	2.300		
Re—C(3)	2.282 (13)	2.309		
Re—C(4)	2.284 (11)	2.314		
Re—C(5)	2.280 (7)	2.305		
Re—C(11)	1.899 (7)	1.914		
Re—C(12)	1.888 (7)	1.899		
Re—C(13)	1.894 (8)	1.907		
C(11)—O(11)	1.160 (9)	1.169		
C(12)—O(12)	1.159 (9)	1.166		
C(13)—O(13)	1.162 (10)	1.170		
C(1)—C(2)	1.404 (18)	1.438		
C(2)—C(3)	1.364 (17)	1.400		
C(3)—C(4)	1.388 (15)	1.421		
C(4)—C(5)	1.352 (20)	1.387		
C(5)—C(1)	1.408 (13)	1.443		
C(1)—H(1)	0.89 (7)			
C(2)—H(2)	0.78 (7)			
C(3)—H(3)	0.72 (9)			
C(4)—H(4)	0.79 (7)			
C(5)—H(5)	0.85 (10)			
C(1)—Re—C(2)	35.8 (4)	C(11)—Re—C(12)	89.4 (3)	
C(2)—Re—C(3)	34.8 (4)	C(11)—Re—C(13)	90.1 (4)	
C(3)—Re—C(4)	35.4 (4)	C(12)—Re—C(13)	90.5 (3)	
C(4)—Re—C(5)	34.5 (5)			
C(5)—Re—C(1)	35.9 (3)			
C(5)—C(1)—C(2)	105.0 (10)	Re—C(11)—O(11)	178.9 (8)	
C(1)—C(2)—C(3)	109.5 (8)	Re—C(12)—O(12)	176.8 (8)	
C(2)—C(3)—C(4)	107.6 (11)	Re—C(13)—O(13)	177.3 (7)	
C(3)—C(4)—C(5)	108.6 (9)			
C(4)—C(5)—C(1)	109.4 (10)			

* Distances involving the CpRe moiety have been corrected in the rigid-body approximation ($R_{wU} = 0.010$). All remaining distances have been corrected by treating the Re(CO)₃ fragment as a rigid group ($R_{wU} = 0.016$). The program employed was THMI-2 of Trueblood (1978).

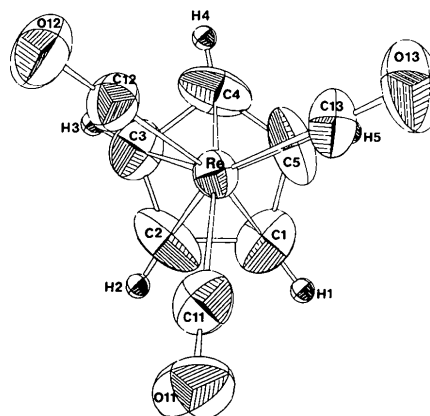


Fig. 2. ORTEP projection of CpRe(CO)₃ down the molecular axis, illustrating the atomic numbering system. Thermal ellipsoids are drawn at the 50% probability level. For the sake of clarity, a sphere with isotropic temperature factor $B = 1.0 \text{ \AA}^2$ was used for the H atoms.

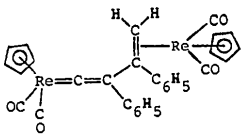
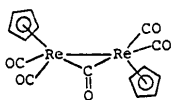
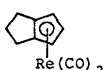
almost exclusively by intermolecular forces and consequently adopts no particular symmetry with respect to the carbonyl groups. The plane which contains the atoms Re, C(11) and O(11) is twisted 6.61° clockwise (Fig. 2) from that containing the atoms C(4), Re and the midpoint of the ring. Alternatively, the Re—C(13)—O(13) group is 4.92° in the opposite sense from being eclipsed with respect to C(5). The corresponding values in CpMn(CO)₃ are 5.93 and 7.25° , respectively.

The results in Table 4 illustrate the reasonable constancy of the basic structural parameters for (η^5 -cyclopentadienyl)rhenium complexes. With a value of 1.51 \AA for the covalent radius of Re (Doedens & Dahl, 1965; Alcock, 1967) and 0.70 \AA for C(sp) (Cotton & Wilkinson, 1972), the average Re—C(O) distance of $1.894(4) \text{ \AA}$ in CpRe(CO)₃ represents a considerable shortening from the expected bond length of a Re—C single bond as the result of back-donation of electrons from the metal *d* orbitals into the carbonyl 2π acceptor levels. In fact, the Re—C(O) linkage is very close to a double bond if a value of 1.24 \AA is used for the double-bond covalent radius of Re (Kolobova, Antonova, Khitrova, Antipin & Struchkov, 1977). The Re—C—O angle of $177.7(4)^\circ$ indicates a slight deviation of the Re—C—O group from linearity, although less seriously than in almost all of the other

Cp—Re carbonyl complexes studied to date (Table 4). This non-linearity may be the result of packing considerations, or because the 2π orbital is substantially localized on the C atom (Kettle, 1965, 1966), giving rise to an unsymmetrical charge distribution.

The (O)C—Re—C(O) angle in all of the Re tricarbonyl systems investigated is very close to 90° , which is slightly smaller than the value of $92.02(5)^\circ$ reported for CpMn(CO)₃ (Berndt & Marsh, 1963; Fitzpatrick, Le Page, Sedman & Butler, 1981). This difference may simply be a consequence of the reduction in non-bonded repulsions between carbonyl groups as the size of the central metal atom increases, coupled with the increase in *M*—C(O) bond length on going from Mn to Re. However, as Elian, Chen, Mingos & Hoffmann (1976) have pointed out, 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. This angle is expected to increase as the π -donating capacity of the aromatic ligand increases in the order $C_6H_6 < C_5H_5^- < C_4H_4^{2-}$. The smaller (O)C—*M*—C(O) angle and longer *M*—Cp distance (longer by 0.069 \AA after correction for the covalent radii) in CpRe(CO)₃ compared with CpMn(CO)₃ are consistent with decreased ring-to-metal π -donation in the Re complex as the *5d* metal

Table 4. Relevant structural parameters for various (η^5 -cyclopentadienyl)rhenium complexes

	Mean \angle Re—C—O	Mean <i>d</i> [Re—C(O)]	Mean \angle (O)C— Re—C(O)	<i>d</i> [Re— C ₅ H ₄ X]	Mean <i>d</i> [Re— C(C ₅ H ₄ X)]	Reference
(η^5 -C ₅ H ₅)Re(CO) ₃	177.7 (4) ^o	1.894 (4) \AA	90.0 (2) ^o	1.957 \AA	2.284 (4) \AA	(e)
(η^5 -C ₅ H ₄ COCH ₃)Re(CO) ₃	177.8 (10)	1.91 (4)	91.0 (10)	n.r.	2.28 (4)	(f)
[η^5 -C ₅ H ₄ Si(CH ₃) ₃]Re(CO) ₃	175.5	1.855 (14)	91.1 (6)	1.949	2.300 (11)	(g)
	174.0 (14)	1.900 (12)	86.0 (7)	n.r.	2.308 (11), 2.332 (9) ^(a)	(h)
	n.r.	1.85 (2) [terminal] 2.06 (2) [bridging]	85.0 (10)	n.r.	2.24–2.34 (1)	(i)
(η^5 -C ₅ H ₅)Re(CH ₃) ₂ (η^4 -C ₆ H ₈)	—	—	—	1.89	Range from 2.160–2.341; ^(b) mean 2.245 (17)	(j)
	174.0 (30)	1.90 (4)	89.0 (15)	n.r.	2.28 (3)	(k)
[η^5 -(B ₉ C ₂ H ₁₁)Re(CO) ₃] ⁻ .Cs ⁺	176.3	1.893	89.7	—	2.31 ^(c)	(l)
(η^5 -C ₅ H ₅)Re(CO) ₂ (CH ₃)Br	172.0 (21)	1.890 (21)	102 ^(d)	n.r.	2.31	(m)
(η^5 -C ₅ H ₅)Re(CO) ₂ (H)Si(C ₆ H ₅) ₃	176.4 (6)	1.880 (7)	83.5 (5)	1.96 (1)	2.312 (5)	(n)

Notes and references: (a) Mean values for the two independent Re atoms in the molecule. (b) A range of values is given as the bonding within the Cp ring is reported to be unsymmetrical. (c) Mean Re—C(B₉C₂H₁₁) distance involving the two C atoms of the dicarbollide ligand. (d) Seven-coordinate Re^{III}, this is the angle between the 'trans' carbonyl groups. (e) Present work. (f) Khotsyanova, Kuznetsov, Bryukhova & Makarov (1975). (g) Harrison & Trotter (1972). (h) Kolobova *et al.* (1977). (i) Foust, Hoyano & Graham (1971). (j) Alcock (1967). (k) Joshi, Mais, Nyman, Owston & Wood (1968). (l) Zalkin, Hopkins & Templeton (1966). (m) Aleksandrov, Struchkov & Makarov (1973). (n) Smith & Bennett (1977).

n.r. = not reported.

acceptor orbitals are situated at higher energy than the corresponding $3d$ acceptor orbitals in the Mn compound.

The C atoms of the cyclopentadienyl ring are almost perfectly planar, the largest deviation being 0.003 (9) Å. The distances of the H atoms from this plane range from -0.06 (7) Å to 0.08 (7) Å, and are not significantly different from zero. However, the overall refinement of the H-atom positional and thermal parameters was not very satisfactory. The usual value for a C-H bond length derived from X-ray measurements is taken to be 0.95 Å (Churchill, 1973). One of the C-H bonds refined to a very short distance [0.72 (9) Å], while two of the others converged to values slightly less than 0.80 Å. The corresponding thermal parameters are also too small for atoms bonded to C atoms undergoing large, highly anisotropic thermal motion, but this is as expected since the calculated electron density has been drawn into the C-H bond. However, all of the C-H bond distances are within 2.5σ of chemically reasonable values.

The C(2)-C(3) and C(4)-C(5) bond distances are considerably shorter than both C(1)-C(2) and C(1)-C(5); the C(3)-C(4) distance is intermediate between these two pairs. Thus the plane containing C(1), Re and the ring centroid is almost exactly a mirror plane for the cyclopentadienyl ring itself. Although the individual C-C distances are essentially equal within experimental error, these results do tend to suggest the possibility of some form of charge localization within the cyclopentadienyl ring. This result is highly unexpected since CpRe(CO)₃ is a cylindrically symmetrical molecule. It is generally presumed that the e_1'' Cp→metal donor orbitals and the e_2'' acceptor orbitals of the Cp ring, on interacting with metal-containing fragments which possess cylindrical symmetry (ML_x , where $x > 2$), remain energetically degenerate. As a result, complete delocalization of electrons within the ring is predicted. Byers & Dahl (1980), as well as Mitschler, Rees & Lehmann (1978), present detailed discussions of the type of bond localizations within the Cp ring which may occur in the case of non-cylindrical systems $\{[\eta^5\text{-C}_5(\text{CH}_3)_5\text{-Co}(\text{CO})_2 \text{ and } [\text{CpFe}(\text{CO})_2]_2, \text{ respectively}\}$.

However, vibrational spectra of both CpRe(CO)₃ and CpMn(CO)₃ exhibit features which indicate some breakdown of C_{5v} selection rules for the Cp-M fragments (Adams & Squire, 1973; Parker, 1974; Lokshin, Klemenkova & Makarov, 1972; Fitzpatrick, Sedman, Butler & Le Page, 1980), which is consistent with the possibility that there may be some inherent distortion of the Cp ring in the individual molecules. Further support for this concept comes from an analysis of the dipolar coupling constants obtained from ¹H NMR spectra of these molecules partially oriented in nematic liquid-crystalline solvents which indicate that the Cp ring deviates from a regular pentagon (Khetrapal, Kunwar & Kanekar, 1971;

Khetrapal, Kunwar & Saupe, 1976; Lindon & Dailey, 1971; Bailey, Buckingham, McIvor & Rest, 1973; Butler, Fitzpatrick, Gilson & Hamer, 1979). Thus there is reason to believe that the Cp ring in these molecules may not possess its expected fivefold symmetry even in solution. These results suggest that any distortion may be an inherent feature of the individual molecules rather than arising simply as the result of solid-state effects.

In view of this spectroscopic evidence, and in an effort to confirm the existence of any distortion in these systems, we feel that a re-determination of the crystal structure of CpMn(CO)₃ (originally reported by Berndt & Marsh, 1963) is warranted. The presence of the lighter Mn atom should permit more accurate location of the C and H atoms, and hopefully more statistically significant results for comparison of C-C bond distances within the Cp ring can be obtained. This study is being undertaken at both ambient and low temperature, and the results will be published shortly.

Finally, these results confirm that Mo $K\beta_1$ radiation can be successfully employed for intensity-data collection by the θ - 2θ scan technique.

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The Structure of the Monosodium Salt of Cytidine(5')diphosphoethanolamine

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Abstract

$C_{11}H_{19}N_4O_{11}P_2 \cdot Na^+ \cdot 7H_2O$, $M_r = 594.08$, is orthorhombic, space group $P2_12_12_1$, with $a = 6.946(2)$, $b = 12.503(4)$, $c = 28.264(8)$ Å, $U = 2454.6$ Å³, $D_x = 1.61$ Mg m⁻³, $Z = 4$, $\mu(Cu K\alpha) = 2.612$ mm⁻¹, $F(000) = 1244$. Final $R = 0.101$ for 1454 observed reflections. The cytosine base is in the *anti* conformation with respect to the sugar ($\chi_{CN} = 62.6^\circ$). The

ribose exhibits an uncommon C(1')*exo*–C(2')*endo* puckering. The pyrophosphate has a characteristic staggered geometry. The conformation about P(2)–O(7') is *trans* (-103.4°). This makes CDP-ethanolamine more extended compared to the folded geometry of CDP-choline, which has a *gauche* conformation (71.3°). The molecular interactions in the extended crystal structure, however, are similar to those found in CDP-choline, with the CMP-5' portions

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