

THE CRYSTAL STRUCTURE DETERMINATION OF π -C₅H₅Fe(CO)₂Mn(CO)₅

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INTRODUCTION

In 1960, Abel, Singh and Wilkinson¹ reported "the first carbonyl complex with a metal-metal bond between different transition metals". Numerous compounds of this type have since been reported; however, we believe this to be the first reported crystal structure determination of such a compound. The structure of π -C₅H₅Fe(CO)₂Mn(CO)₅ first became of interest owing to its relationship to two closely related compounds [π -C₅H₅Fe(CO)₂]₂ and [Mn(CO)₅]₂. The structure of the former, reported by Mills², contains two bridging carbonyls and an Fe-Fe bond which appears to be a normal covalent bond of length 2.49 Å. On the other hand, the structure of the latter, reported by Dahl and Rundle³, contains no bridging carbonyls and a rather long Mn-Mn bond length of 2.92 Å. Thus the primary purpose of this investigation was to establish the skeletal geometry of the molecule and to determine the Fe-Mn bond length.

EXPERIMENTAL

The compound used in this X-ray investigation was prepared by King, Treichel and Stone⁴ from the reaction of NaMn(CO)₅ with π -C₅H₅Fe(CO)₂I. Single crystals were grown in this laboratory by vacuum sublimation at about 40°. Mounting of the crystals in thin-walled, Lindemann glass capillaries was necessary owing to the instability of the compound in air.

The red, platelike crystals were found, from systematic extinctions, to have space group symmetry $P 2_1/b$. The unit cell parameters obtained from precision measurements using a General Electric single crystal orienter are as follows:

$$\begin{array}{ll} a = 7.220 \pm 0.006 \text{ \AA} & b = 30.387 \pm 0.008 \text{ \AA} \\ c = 12.498 \pm 0.002 \text{ \AA} & \gamma = 90.21 \pm 0.10^\circ \end{array}$$

the calculated density of 1.80 g/cc, based on eight molecules per unit cell, compares favorably with the observed density of 1.78 g/cc, found by the flotation method using a ZnCl₂ solution.

Within a 2θ sphere of approximately 145° , complete three-dimensional X-ray diffraction intensity data were taken with V-filtered Cr-radiation, utilizing a General Electric XRD-5 X-ray unit equipped with a goniostat and scintillation counter. The measurements were made using a one hundred second, $3\frac{1}{3}$ degree -2θ scan with a

θ - 2θ coupling. Although about 1700 independent intensities were recorded, one hundred reflections, suspect of significant error due to non characteristic radiation, together with about four hundred "unobserved" reflections were not included in the subsequent computations. The intensities were corrected for Lorentz and polarization factors, crystal and capillary absorption, and crystal decomposition. The crystal from which the intensity data were obtained had a linear absorption coefficient of 83.9 cm^{-1} and the general dimensions of $0.23 \times 0.10 \times 0.16 \text{ mm}$. An absorption correction program for polyhedral crystals, adapted from one originally written by Busing and Levy, was used to make this correction.

STRUCTURE DETERMINATION

The presence of eight molecules in a unit cell with space group symmetry of order four requires two crystallographically independent molecules. With each molecule containing one manganese, one iron, twelve carbon and seven oxygen atoms, the structure contains 126 independent positional parameters (neglecting hydrogen atoms) plus temperature factors.

The positions of two of the heavy atoms were obtained from an analysis of the Harker sections of a sharpened Patterson map. Using these two atoms to determine the signs, an electron-density map was computed which revealed the positions of the two remaining heavy atoms in the asymmetric unit. The positions of the twelve Harker and twenty-four non-Harker peaks corresponding to these four heavy atoms were subsequently verified in the sharpened Patterson map. The positions of the carbon and oxygen atoms were then obtained by employing conventional "heavy atom" techniques.

A full matrix least-squares refinement was initiated with the four heavy atoms being refined anisotropically and the thirty-eight lighter atoms being refined isotropically. The computations were performed on an IBM 7074 computer. Following several cycles of least-squares refinement a difference electron-density map was computed which revealed some maxima in positions consistent with the cyclopentadienyl ring hydrogens. The positions of the hydrogens were then calculated, assuming a C-H distance of 1.0 \AA and included, although not varied, in the ensuing refinement. Also included at this point was an anomalous dispersion correction (real part only) of the iron and manganese scattering factors.

Following several additional cycles of full matrix least-squares refinement, a final agreement factor, $R = \sum [|F_o| - |F_c|] / \sum |F_o|$, of 0.064 was obtained.

DISCUSSION

The molecular structure of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ is shown in Fig. 1. The crystal structure consists of discrete molecules which may be envisioned as the adducts of the monomeric forms of dimanganese deca carbonyl, $[\text{Mn}(\text{CO})_5]_2$, and di- π -cyclopentadienyl-diiron tetracarbonyl, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, with the two moieties held together solely by an Fe-Mn bond of length 2.843 \AA .

The structure unambiguously contains no bridging carbonyls, a finding which is entirely consistent with the absence of any carbonyl bands in the bridging C-O region of the infrared spectrum obtained by King, Treichel and Stone¹ (using a C_2Cl_4

solution) or by the authors (using a CCl₄ solution). Any assumption that one or more of the carbonyls is a bridging carbonyl, would necessitate a metal-carbon bond length of at least 2.99 Å (the shortest metal to carbonyl carbon "nonbonded" distance) compared to the usual value of about 1.85 Å. Regarding the metal-metal linkage, the structure is therefore quite similar to the Mn₂(CO)₁₀ structure and quite unlike the [π -C₅H₅Fe(CO)₂]₂ structure.

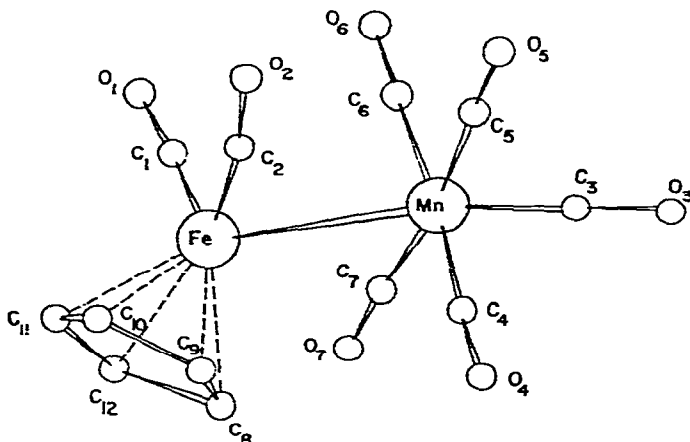


Fig. 1. The molecular configuration of π -C₅H₅Fe(CO)₂Mn(CO)₅.

As would seem reasonable, the equatorial carbonyls in Mn₂(CO)₁₀ assume a highly symmetrical staggered conformation; however, as can be seen (Fig. 2), the equatorial carbonyls in π -C₅H₅Fe(CO)₂Mn(CO)₅ assume a conformation which is

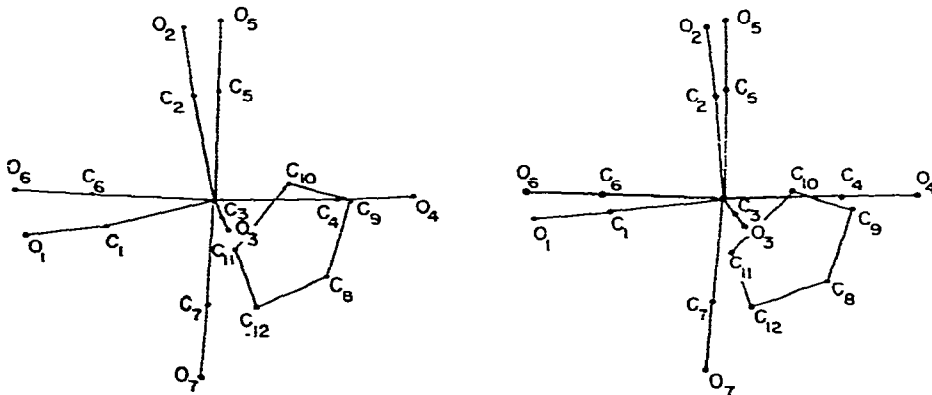


Fig. 2. The conformations of the two crystallographically independent molecules of π -C₅H₅Fe(CO)₂Mn(CO)₅.

neither perfectly staggered nor eclipsed. If the iron moiety were rotated about the Fe-Mn bond, such that the iron and manganese carbonyls assume a perfectly staggered conformation, atom C₈ (the ring carbon atom which is in closest proximity to the manganese moiety and its associated hydrogen) would be eclipsed by one of the

manganese equatorial carbonyls. In like manner, a conformation in which atom C₆ is perfectly staggered, results in the eclipsing of the iron carbonyls. Surprisingly, the two crystallographically independent molecules do not assume identical conformations. The difference in the amount of the rotation about the metal-metal bond appears to be approximately seven degrees. Apparently the energy minimum is broad and the environmental differences are sufficient to produce significant differences in the intermolecular forces, thus leading to the conformational disparity.

The arrangement of the carbonyls about the manganese atom in this structure is virtually identical to that found in the Mn₂(CO)₁₀ structure. In both structures there are four equatorial carbonyls whose Mn-C distance is significantly longer than that of a lone axial (or apical) carbonyl. The values of the averages for these two distances in π -C₅H₅Fe(CO)₂Mn(CO)₅ are respectively 1.825 Å and 1.749 Å, while those reported for Mn₂(CO)₁₀ are 1.83 Å and 1.79 Å. Although the equatorial Mn-C distances compare very favorably, the axial Mn-C distances differ by approximately 0.04 Å. It is reasonable that these two distances would differ, since the species which are *trans* to the axial carbonyls, *i.e.* π -C₅H₅Fe(CO)₂- and Mn(CO)₅-, have not only a different chemical composition, but also occupy a slightly different position relative to the axial carbonyl. In this structure the Fe-Mn-C_{ax} angle has an average value of 168.9° whereas the corresponding Mn-Mn-C_{ax} angle in Mn₂(CO)₁₀ equals, within experimental error, 180°. Possibly this "bent" Fe-Mn bond (probably resulting from the repulsive forces between the two iron carbonyls and the two manganese carbonyls in closest proximity) produces a weaker Fe-Mn bond and consequently a stronger Mn-C bond.

It should also be noted that the average axial C-O bond in this structure is an extremely long 1.195 Å, while the average equatorial C-O bond is a normal 1.156 Å. Generally with metal carbonyls, one finds that as the metal-carbon bond order increases, the carbon-oxygen bond order decreases. This would lead one to expect a lengthened axial C-O distance to accompany the shortened axial Mn-C bond length. [Interestingly, Dahl and Rundle³ detected no such difference in Mn₂(CO)₁₀, but Bailey and Dahl⁵ recently reported an even greater disparity in the technetium analog Tc₂(CO)₁₀, in which the average equatorial C-O distance was 1.12 Å while the axial distance was 1.20₅ Å.] Since a carbonyl bond length of 1.195 Å approaches that expected for a bridging carbonyl group, one might expect that an infrared spectrum would show an absorption peak in or near the bridging carbonyl stretching frequency range of approximately 1750 to 1875 cm⁻¹. Examination of the previously mentioned infrared spectrum however, reveals the existence of no peaks with a frequency lower than 1944 cm⁻¹. But, it should be emphasized that such a bond length is not ruled out by this evidence, since the absorption frequency is certainly not a function of interatomic distance alone.

It is unlikely that the long C-O distance and the very short axial Mn-C distance are merely the result of random errors in the axial carbon positional parameters, since there are two crystallographically independent molecules in this structure, and the two values for each of these two distances differ by no more than 0.002 Å, as can be seen in Table 3. Admittedly a systematic error could be responsible for these atypical results. Dahl and Rundle³ noted that an anisotropic refinement resulted in a rather large shift of the axial carbon atom in Mn₂(CO)₁₀ from the position found by an isotropic refinement; however, most likely the anisotropy of the manganese atom rather than that of the carbon atom was responsible for this shift. And, although the light

TABLE 1

FINAL HEAVY ATOM ATOMIC PARAMETERS AND STANDARD DEVIATIONS
(A) POSITIONAL PARAMETERS AND STANDARD DEVIATIONS

Atom ^a	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	σ_x	σ_y	σ_z
Fe	0.4211	0.1361	0.3160	0.00041	0.00008	0.00021
Mn	0.3536	0.2253	0.3705	0.00043	0.00008	0.00022
Fe'	0.0749	0.0289	0.7534	0.00042	0.00008	0.00021
Mn'	0.1461	0.1162	0.8246	0.00042	0.00008	0.00021

(B) ANISOTROPIC TEMPERATURE COEFFICIENTS^b AND STANDARD DEVIATIONS

Atom ^a	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0289	0.0013	0.0055	0.0005	-0.0017	-0.0002
σ	0.00092	0.00004	0.00023	0.00014	0.00037	0.00007
Mn	0.0260	0.0010	0.0080	-0.0007	-0.0009	0.0003
σ	0.00091	0.00004	0.00028	0.00014	0.00039	0.00008
Fe'	0.0309	0.0010	0.0057	-0.0008	0.0006	-0.0002
σ	0.00090	0.00004	0.00021	0.00013	0.00037	0.00007
Mn'	0.0246	0.0010	0.0057	-0.0005	-0.0008	0.0001
σ	0.00090	0.00004	0.00023	0.00013	0.00039	0.00008

^a Unprimed atoms refer to molecule 1 and primed to molecule 2. ^b Anisotropic temperature factors of the form: $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$.

atoms in the π -C₅H₅Fe(CO)₂Mn(CO)₅ structure received only an isotropic refinement, the heavy atoms were refined anisotropically.

As in the structure of Mn₂(CO)₁₀, it was also found that the manganese equatorial carbonyls in this structure are bent inward towards the other half of the molecule such that the manganese atoms lie respectively 0.116 Å and 0.102 Å out of the least-squares plane fitted to atoms C₄, C₅, C₆ and C₇ in each independent molecule. [Dahl and Rundle³ reported this distance to be 0.12 Å in Mn₂(CO)₁₀.] The average value of the eight C_{ax}Mn-C_{eq} angles is 93.4°. Since the equatorial carbonyls are all bent inward toward the iron moiety, one might expect all of the angles defined by two adjacent equatorial carbon atoms and a manganese atom (at the vertex), *i.e.* C_{eq}-Mn-C_{eq}, to be acute; however, one of these angles in each molecule, the C₇-Mn-C₄ angle, is obtuse. The two values of this angle are 92.3° and 93.7° *versus* an average 88.7° for the other six members of the set. This effect is apparently due to the close proximity of the cyclopentadienyl ring (see Figs. 1 and 2). It may be seen in Table 4 that angles Fe-Mn-C₄ and Fe-Mn-C₇ are significantly smaller than angles Fe-Mn-C₅ and Fe-Mn-C₆.

Although the Mn-C-O angles all appear to be within experimental error of 180°, the Fe-C-O angles range from 169.5° to 173.9°; apparently this non-linearity tends to maximize certain critical intramolecular and intermolecular distances.

Concerning the equivalency of the C-C bond lengths and of the Fe-C_{ring} distances, early in the analysis of the results of this crystal structure determination, the authors noted a marked ordering of the deviations of the individual C-C and Fe-C_{ring} distances from their respective mean values. As may be seen in Table 3, in both molecules, the C₈-C₉ distance is the longest, the C₉-C₁₀ and C₁₁-C₁₂ distances are respectively the second and third longest, while the C₁₀-C₁₁ and C₁₂-C₈ distances are

TABLE 2

(A) FINAL LIGHT ATOM ATOMIC PARAMETERS

Atom	x/a	y/b	z/c	B
<i>Molecule 1</i>				
C ₁	0.2891	0.1433	0.2072	7.02
O ₁	0.1758	0.1432	0.1351	8.85
C ₂	0.2344	0.1258	0.4023	4.80
O ₂	0.1213	0.1151	0.4591	6.63
C ₃	0.3538	0.2822	0.3910	8.01
O ₃	0.3503	0.3209	0.4078	10.23
C ₄	0.5489	0.2166	0.4628	6.06
O ₄	0.6664	0.2122	0.5234	7.22
C ₅	0.1999	0.2128	0.4808	6.03
O ₅	0.1012	0.2063	0.5511	8.13
C ₆	0.1526	0.2275	0.2824	6.77
O ₆	0.0252	0.2287	0.2271	9.05
C ₇	0.5073	0.2290	0.2546	7.75
O ₇	0.6032	0.2317	0.1785	9.02
C ₈	0.7150	0.1410	0.3259	6.05
C ₉	0.6489	0.1133	0.4094	6.09
C ₁₀	0.5556	0.0783	0.3580	6.85
C ₁₁	0.5694	0.0848	0.2487	7.15
C ₁₂	0.6661	0.1238	0.2281	7.00

Molecule 2

C _{1'}	0.2279	0.0135	0.8526	6.05
O _{1'}	0.3335	-0.0003	0.9135	7.30
C _{2'}	0.2430	0.0384	0.6599	6.33
O _{2'}	0.3636	0.0411	0.5977	8.28
C _{3'}	0.1457	0.1699	0.8751	5.90
O _{3'}	0.1414	0.2066	0.9092	8.53
C _{4'}	-0.0407	0.1269	0.7310	6.25
O _{4'}	-0.1603	0.1345	0.6721	7.75
C _{5'}	0.3103	0.1296	0.7190	6.46
O _{5'}	0.4191	0.1388	0.6544	8.73
C _{6'}	0.3391	0.0996	0.9107	5.14
O _{6'}	0.4508	0.0910	0.9665	7.19
C _{7'}	-0.0097	0.0957	0.9293	5.69
O _{7'}	-0.1093	0.0832	0.9943	6.88
C _{8'}	-0.2191	0.0344	0.7601	6.77
O _{8'}	-0.1576	0.0264	0.6524	6.85
C _{10'}	-0.0563	-0.0146	0.6515	7.02
C _{11'}	-0.0679	-0.0306	0.7554	6.78
C _{12'}	-0.1594	-0.0007	0.8230	7.35

(B) AVERAGE STANDARD DEVIATIONS OF FINAL LIGHT ATOM ATOMIC PARAMETERS

Atom	x/a	y/b	z/c	B
C (carbonyl)	0.00279	0.00058	0.00152	0.90
O	0.00208	0.00043	0.00113	0.69
C (ring)	0.00278	0.00061	0.00156	0.92

TABLE 3

(A) INTERATOMIC DISTANCES (Å)

Atoms	Molecule 1	Molecule 2	Atoms	Molecule 1	Molecule 2
Mn-Fe	2.840	2.845	C ₁ -O ₁	1.217	1.158
Fe-C ₁	1.676	1.726	C ₂ -O ₂	1.129	1.170
Fe-C ₂	1.754	1.709	C ₃ -O ₃	1.194	1.195
Mn-C ₃	1.748	1.750	C ₄ -O ₄	1.146	1.159
Mn-C ₄	1.841	1.815	C ₅ -O ₅	1.148	1.160
Mn-C ₅	1.809	1.819	C ₆ -O ₆	1.152	1.153
Mn-C ₆	1.823	1.833	C ₇ -O ₇	1.180	1.150
Mn-C ₇	1.827	1.833	C ₈ -C ₉	1.421	1.439
Fe-C ₈	2.130	2.131	C ₉ -C ₁₀	1.413	1.410
Fe-C ₉	2.133	2.101	C ₁₀ -C ₁₁	1.384	1.388
Fe-C ₁₀	2.077	2.096	C ₁₁ -C ₁₂	1.398	1.407
Fe-C ₁₁	2.071	2.078	C ₁₂ -C ₈	1.374	1.396
Fe-C ₁₂	2.116	2.102			

(B) AVERAGE INDIVIDUAL STANDARD DEVIATIONS AND AVERAGE INTERATOMIC DISTANCES

Atoms	Average σ	Average dist.
Mn-Fe	0.004	2.843
Fe-C _{carbonyl}	0.025	1.716
Mn-C _{axial}	0.025	1.749
Mn-C _{equatorial}	0.026	1.825
Fe-C _{ring}	0.024	2.104
C-O _{Fe}	0.023	1.169
C-O _{Mn, ax}	0.025	1.195
C-O _{Mn, eq}	0.023	1.156
C-O _{alt}	0.023	1.165
C-C _{ring}	0.029	1.403

TABLE 4

BOND ANGLES AND AVERAGE STANDARD DEVIATIONS

Atoms	Mol. 1	Mol. 2	Std. dev.	Atoms	Mol. 1	Mol. 2	Std. dev.
Fe-C ₁ -O ₁	169.5°	173.5°	2.0°	C ₃ -Mn-C ₄	93.0°	93.6°	1.0°
Fe-C ₂ -O ₂	173.1°	173.9°	1.9°	C ₅ -Mn-C ₅	95.4°	93.2°	1.0°
Mn-C ₃ -O ₃	177.9°	178.6°	2.2°	C ₅ -Mn-C ₆	92.9°	92.8°	1.0°
Mn-C ₄ -O ₄	177.1°	178.6°	1.9°	C ₅ -Mn-C ₇	93.3°	93.2°	1.0°
Mn-C ₅ -O ₅	177.8°	177.6°	2.1°	C ₄ -Mn-C ₅	87.8°	88.7°	1.0°
Mn-C ₆ -O ₆	179.6°	177.2°	2.0°	C ₅ -Mn-C ₆	88.9°	89.5°	1.0°
Mn-C ₇ -O ₇	178.5°	179.1°	2.1°	C ₆ -Mn-C ₇	90.1°	87.3°	1.0°
Mn-Fe-C ₁	88.2°	85.0°	0.7°	C ₇ -Mn-C ₄	92.3°	93.7°	1.0°
Mn-Fe-C ₂	83.5°	86.0°	0.7°	C ₄ -Mn-C ₆	173.5°	173.5°	0.9°
Fe-Mn-C ₃	168.6°	169.2°	0.8°	C ₅ -Mn-C ₇	171.2°	173.0°	1.0°
Fe-Mn-C ₄	83.0°	80.4°	0.7°	C ₈ -C ₉ -C ₁₀	105.6°	107.6°	1.9°
Fe-Mn-C ₅	95.1°	95.6°	0.7°	C ₉ -C ₁₀ -C ₁₁	107.8°	107.4°	2.0°
Fe-Mn-C ₆	91.7°	93.6°	0.7°	C ₁₀ -C ₁₁ -C ₁₂	109.8°	109.8°	2.1°
Fe-Mn-C ₇	76.2°	78.3°	0.7°	C ₁₁ -C ₁₂ -C ₈	106.5°	107.6°	2.1°
C ₁ -Fe-C ₂	94.9°	94.7°	1.1°	C ₁₂ -C ₈ -C ₉	110.2°	107.5°	2.0°

the shortest. A similar pattern also exists within the set of ten Fe-C_{ring} distances. (It should be noted that neither ring deviates significantly from perfect planarity. The maximum deviation of a carbon atom from the least-squares plane is 0.011 Å and the average deviation is only 0.006 Å.)

Since there have been reports of other structures of this type in which these distances were not equivalent, the existence of non-equivalent C-C and Fe-C_{ring} distances in this structure would certainly not be surprising. Theoretical explanations which might account for these bonds being chemically non-equivalent have been given by Dahl and Wei⁶, employing a simple valence bond approach and by Burnett *et al.*⁷, using a molecular orbital treatment.

Nevertheless, the authors feel that the magnitudes of the differences detected in this structure are not large enough for firm conclusions to be drawn. And it is conceivable that these results might merely be due to steric or packing effects or to some systematic error.

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SUMMARY

The crystal structure of π -C₅H₅Fe(CO)₂Mn(CO)₅, has been determined by single-crystal X-ray diffraction methods. Eight molecules crystallize in a monoclinic unit cell with dimensions $a = 7.220 \pm 0.006$, $b = 30.387 \pm 0.008$, $c = 12.498 \pm 0.002$ Å and $\gamma = 90.21 \pm 0.10^\circ$. The space group symmetry is $P2_1/b$. Full matrix least-squares refinement with Fe and Mn atoms anisotropic, resulted in a final R value of 6.4% for 1201 "observed" reflections. The π -C₅H₅Fe(CO)₂Mn(CO)₅ molecules contain a Mn-Fe bond of length 2.843 ± 0.004 Å and no bridging carbonyls. Both metal atoms may be envisioned as having distorted octahedral coordination. The six sites about the iron atoms are occupied by two carbonyl groups, the manganese atom, and the cyclopentadienyl ring (which essentially occupies three sites); about the manganese atoms there are five carbonyl groups and the iron atom.

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