nonvanishing multipole moment, the quadrupole moment, should be independent of origin. As a test of the program, we computed θ with respect to both the Fe and F atoms. The results differed by 0.00002×10^{-24} esu cm^2. The octupole moment tensor of Table IV was calculated with respect to the Fe atom point charge nucleus.

The calculated potentials at the nuclei and diamagnetic shielding should be within a few per cent of experiment. The electric field E_z(Fe) is zero by symmetry and E_z(F) would be zero for an exact Hartree–Fock calculation at equilibrium geometry. Perhaps the least reliable of the predicted properties are the electric field gradient tensors. Experience has shown[4] that using comparable basis sets, calculated field gradients may differ by as much as 50% from experiment.

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Conformations of Fused Cycloalkanes in Organometallic Complexes. The Crystal and Molecular Structure of Tricyclo[6.3.0.0^{2,7}]undeca-3,5-dienetricarbonyliron, $(C_{11}H_{14})Fe(CO)_3$[1]

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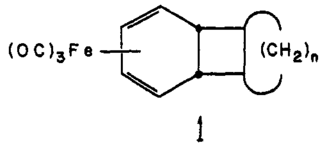
Abstract: The molecular structure of the tricarbonyliron adduct of tricyclo[6.3.0.0^{2,7}]undeca-3,5-diene has been determined by X-ray crystallography. Two independent data sets, one consisting of 1539 nonzero reflections collected at 24 ± 1° and the other of 3495 nonzero reflections collected at 3 ± 1° were used for full-matrix least-squares refinements in which all hydrogen atoms were refined isotropically. Only slight differences, of no chemical significance, were found between the results of the two refinements. The space group is $P\bar{1}$ with $Z = 2$, and dimensions at 3 ± 1° of $a = 8.390$ (3), $b = 10.700$ (4), $c = 7.981$ (2) Å; $\alpha = 107.13$ (2)°, $\beta = 97.26$ (2)°, $\gamma = 67.95$ (2)°. The unit cell edges a and b at 24 ± 1° were each about 0.10 to 0.20% larger, while c was 0.13% smaller than those at 3°. The $Fe(CO)_3$ group is symmetrically bonded to the butadiene moiety formed by C(3) to C(6) of the tricycloolefin. The central cyclobutane ring is essentially square and planar, with the average C–C distance equal to 1.559 (2) Å, while the cyclopentane ring has an envelope conformation with a dihedral angle of 38° between the two planes. Both ring fusions are cis, and the five- and six-membered ring have an anti relationship relative to the central four-membered ring. The dimensions of the 1,3-butadieneirontricarbonyl moiety, as found in this and 11 other structures are summarized and discussed critically. In this study the three C–C distances are of equal length, while the weighted average for all structures shows the central bond to be shorter by 0.021 (2) Å. This is in contrast to the pattern in a free 1,3-butadiene group, where, for the ground state, the central, nominally single, bond is 0.09 Å longer and for the first excited state the central bond is 0.06 Å shorter.

A series of bicyclic and tricyclic polyolefins derived from the cyclooctatriene–bicyclooctadiene system by fusing on an additional four-, five-, or six-membered ring have been prepared. Complexes of these with $Fe_2(CO)_6$, $Fe(CO)_3$, $Mo(CO)_3$, and $Mo(CO)_2$ have been isolated as crystalline derivatives.[4,5] Some of these substances are of particular interest because they afford opportunities to study accurately the details of ring fusion geometry and the conformations of small and medium size rings. This is particularly true for the series of compounds **1a–c**. The tricyclic olefins themselves, **2a–c**, vary markedly in their stability relative to their respective bicyclic tautomers, **3a–c**. The



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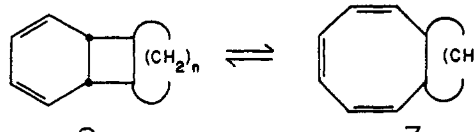

2 3

a: n = 2
b: n = 3
c: n = 4

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[4] F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, **38**, 147 (1972).

[5] F. A. Cotton and G. Deganello, *J. Amer. Chem. Soc.*, **94**, 2142 (1972); **95**, 396 (1973).

ratio of **2** to **3** at 25° is $\ll 1$ for **a**, ~ 30 for **b**, and ~ 1 for **c**. A preliminary discussion of possible reasons for this great variation has been presented earlier;[5] the conformational preferences of the appended four-, five-, and six-membered rings play a key role in this discussion. There was of course no way to determine with complete certainty from indirect (*i.e.*, spectroscopic) data alone the stereochemistry of the ring fusions. Therefore, X-ray crystallographic studies of the structures of **1a–c** have been carried out.

This paper reports the structural results for compound **1b**, which is unusually interesting, for the following reasons. The crystal structure confirms that the four-membered central ring is almost perfectly planar and that the five-membered ring has an envelope configuration. These results support the earlier, speculative discussion of the singular stability of **2b** *vs.* **3b**, when compared to the cases of **2a** *vs.* **3a** and **2c** *vs.* **3c**. Moreover, the compound affords a unique opportunity to examine in precise detail the ring conformation of a cyclopentane ring in an envelope configuration. While the fusion to the four-membered ring causes some perturbation to angles and distances compared to a discrete C_5H_{10} ring, any device for locking the five-membered ring into the envelope conformation will in some degree have such an undesired side effect. In this case such effects should not seriously diminish the significance of the results. This structure contains a (1,3-butadiene)-$Fe(CO)_3$ moiety, the structure of which has been determined here with accuracy significantly greater than in any previous structure save one. It is therefore appropriate, and opportune, to evaluate the implications of the structural data with respect to the metal–olefin bonding, with particular attention to the view that such bonding tends to distort the olefin structure toward that for the first electronic excited state.

When several of the authors moved from the Massachusetts Institute of Technology (MIT) to Texas A&M University (TAMU) samples of the title compound became available at both institutions. Inadvertently, data collection was carried out independently in both Laboratories. The structure was solved and refined at TAMU before the simultaneous MIT data collection was discovered. At this point it was decided to proceed with the refinement at MIT using the parameters derived at TAMU. The parallel data sets provide an interesting comparison of different data collection procedures and different crystallographic computer programs. The two studies differ in the crystals used, the number of data collected, the mode of data collection, the temperature at which data were collected, and the set of computer programs used in structure refinement. Because comparisons such as these have been made in the past, the results are only summarized briefly here.[6]

Experimental Section

Crystals of tricyclo[6.3.0.0^{2,7}]undeca-3,5-dienetricarbonyliron suitable for the X-ray examination were prepared by Dr. G. Deganello.[5] Preliminary examination of the compound using Weissenberg and precession techniques indicated only $\bar{1}$ symmetry. An appropriate triclinic cell was chosen with $P\bar{1}$ as the probable space group; this assignment was fully confirmed during subsequent refinement of the structure. For data collection a crystal of overall dimensions 0.58 × 0.48 × 0.43 mm was cleaved from a larger irregular crystal, cemented to a glass fiber, and protected from the atmosphere with a coating of shellac; there was no evidence of deterioration of this crystal during the data collection process.

Least-squares refinement of 15 reflections, chosen to give a good sampling of reciprocal space and instrument settings ($2\theta > 30°$) and recorded at a temperature of 3°, gave the following lattice constants: $a = 8.390$ (3), $b = 10.700$ (4), $c = 7.981$ (2) Å; $\alpha = 107.13$ (2)°, $\beta = 97.26$ (2)°, and $\gamma = 67.95$ (2)°. With two molecules per cell the calculated and experimental densities are 1.50 and 1.49 g cm^{-3}, respectively.

The data were obtained at 3 ± 1° utilizing Zr-filtered Mo Kα radiation, a takeoff angle of 2°, and a θ–2θ scanning technique on a Syntex $P\bar{1}$ computer-controlled four-circle diffractometer. A fixed scan rate of 3°/min and a symmetric range of $2\theta_{\mathrm{Mo\ K}\alpha_1} -1.5°$ to $2\theta_{\mathrm{Mo\ K}\alpha_2} +1.5°$ were used. A total of 3851 independent reflections were measured in concentric shells of increasing 2θ, out to a maximum value of 60.5° (the equivalent of 1.3 limiting Cu spheres). Five intense reflections were monitored after every 200 reflections collected to check for possible loss of alignment and/or deterioration of the crystal; no evidence of either developed during data collection.

The linear absorption coefficient of the crystal for Mo Kα radiation is 12.0 cm^{-1} yielding a μR value of 0.36 for a spherical crystal of the same volume as the data crystal used. Since the maximum variation in intensity due to crystal absorption for the essentially cube-shaped specimen was only ±3%, no absorption corrections were made. The intensities were reduced to relative amplitudes, $|F_o|$, by means of standard Lorentz and polarization corrections. Of the 3851 unique reflections collected, 356 were rejected as unobserved by applying the criterion that $F_o^2 < 1.0\sigma(F_o^2)$. The remaining 3495 reflections were used in the solution and refinement of the structure.

Solution and Refinement.[7] A three-dimensional Patterson function revealed the positions of the Fe atom and several possible C atoms. The Fe coordinates were refined in a least-squares cycle, and this was followed by a difference Fourier synthesis that gave the positions of eight C atoms and three O atoms. The remaining three C atoms were found from a subsequent least-squares and difference Fourier procedure. Several cycles of isotropic refinement of the nonhydrogen atoms resulted in the unweighted agreement factor $R_1 = \Sigma(||F_o| - |F_c||/\Sigma|F_o| = 0.096$.

Unit weighting was used and the function minimized was $\Sigma w(||F_o| - k|F_c||)^2$. Atomic scattering factors employed were those of Cromer and Mann.[8] Several final cycles of full-matrix least-squares refinement of 229 parameters employing anomalous dispersion corrections[9] for the iron atom, anisotropic temperature factors for all atoms except the hydrogens, which were refined isotropically, application of a secondary extinction correction of the type $1/(1 + 2gI_c)^{1/2}$ (with refinement of g to the value 3.08×10^{-7}), and unit weighting gave $R_1 = 0.036$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.040$. Examination of a $|\Delta F|$ *vs.* $|F_o|$ plot showed that little or nothing was to be gained by departing from unit weighting.

In the last cycle of refinement, the average parameter shift for a nonhydrogen parameter was $0.04\sigma_p$, while for a hydrogen atom parameter it was $0.21\sigma_p$, where σ_p is the estimated standard deviation of the parameter.

The atomic coordinates and anisotropic thermal parameters for nonhydrogen atoms are given in Table I. Coordinates and isotropic thermal parameters for hydrogen atoms are given in Table II. A table of observed and calculated structure factor amplitudes is given in the microfilm edition.[6]

For the 18 nonhydrogen atoms the positional parameters obtained in the MIT and TAMU refinements agree to within 2.6 times the estimated standard deviation of the difference, *i.e.*, $(\sigma_{\mathrm{MIT}}^2 + \sigma_{\mathrm{TAMU}}^2)^{1/2}$. The esd's are an average of only about 30% greater

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[6] A more detailed experimental section for TAMU data and a list of derived parameters will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to code number JACS-73-4522. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

[7] The following computer programs were used at MIT on the IBM 370. A modified version of FORDAPII by A. Zalkin for Fourier calculations; ORFLS-E, a modified version of the Busing, Martin, and Levy's ORFLS, for least-squares refinements; and STAN1 by B. G. DeBoer for distance and angle calculations.

[8] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

[9] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

Table I. Positional Parameters and Anisotropic Thermal Parameters for Nonhydrogen Atoms[a]

Atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.09843 (5)	0.21706 (5)	0.15219 (5)	0.0352 (1)	0.0409 (1)	0.0315 (1)	−0.0170 (1)	−0.0042 (1)	0.0085 (1)
O(1)	0.0809 (4)	0.5020 (3)	0.1842 (4)	0.075 (1)	0.051 (1)	0.062 (1)	−0.028 (1)	−0.011 (1)	0.023 (1)
O(2)	−0.2623 (3)	0.2398 (3)	0.1284 (4)	0.042 (1)	0.085 (1)	0.067 (1)	−0.027 (1)	−0.008 (1)	0.013 (1)
O(3)	0.1311 (4)	0.0835 (4)	−0.2265 (3)	0.089 (1)	0.100 (2)	0.038 (1)	−0.053 (1)	−0.008 (1)	0.003 (1)
C(1)	0.3766 (4)	0.2520 (3)	0.6413 (4)	0.042 (1)	0.046 (1)	0.038 (1)	−0.023 (1)	−0.009 (1)	0.016 (1)
C(2)	0.2496 (4)	0.3160 (3)	0.5019 (3)	0.032 (1)	0.038 (1)	0.032 (1)	−0.014 (1)	−0.001 (1)	0.008 (1)
C(3)	0.1140 (4)	0.2536 (3)	0.4302 (4)	0.032 (1)	0.053 (1)	0.035 (1)	−0.020 (1)	−0.001 (1)	0.013 (1)
C(4)	0.1612 (4)	0.1096 (4)	0.3403 (4)	0.049 (1)	0.049 (1)	0.047 (1)	−0.030 (1)	−0.015 (1)	0.020 (1)
C(5)	0.2977 (4)	0.0573 (3)	0.2224 (4)	0.048 (1)	0.035 (1)	0.044 (1)	−0.014 (1)	−0.010 (1)	0.005 (1)
C(6)	0.3684 (4)	0.1549 (3)	0.2102 (4)	0.035 (1)	0.046 (1)	0.034 (1)	−0.011 (1)	−0.001 (1)	0.003 (1)
C(7)	0.3987 (4)	0.2591 (3)	0.3724 (4)	0.032 (1)	0.039 (1)	0.037 (1)	−0.015 (1)	0.000 (1)	0.010 (1)
C(8)	0.5279 (4)	0.1967 (3)	0.5116 (4)	0.032 (1)	0.041 (1)	0.044 (1)	−0.011 (1)	−0.008 (1)	0.010 (1)
C(9)	0.6473 (5)	0.2758 (5)	0.5987 (5)	0.037 (1)	0.076 (2)	0.054 (1)	−0.029 (1)	−0.013 (1)	0.018 (1)
C(10)	0.5343 (5)	0.4082 (4)	0.7260 (5)	0.061 (1)	0.054 (1)	0.056 (1)	−0.035 (1)	−0.015 (1)	0.009 (1)
C(11)	0.4178 (5)	0.3581 (4)	0.7983 (4)	0.049 (1)	0.061 (1)	0.034 (1)	−0.023 (1)	−0.010 (1)	0.008 (1)
C(12)	0.0847 (4)	0.3910 (3)	0.1680 (4)	0.044 (1)	0.051 (1)	0.037 (1)	−0.019 (1)	−0.009 (1)	0.015 (1)
C(13)	−0.1217 (4)	0.2324 (4)	0.1374 (4)	0.041 (1)	0.052 (1)	0.039 (1)	−0.018 (1)	−0.005 (1)	0.009 (1)
C(14)	0.1207 (4)	0.1363 (4)	−0.0777 (4)	0.049 (1)	0.060 (1)	0.039 (1)	−0.029 (1)	−0.003 (1)	0.011 (1)

[a] The numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits. [b] The form of the temperature factor expression is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

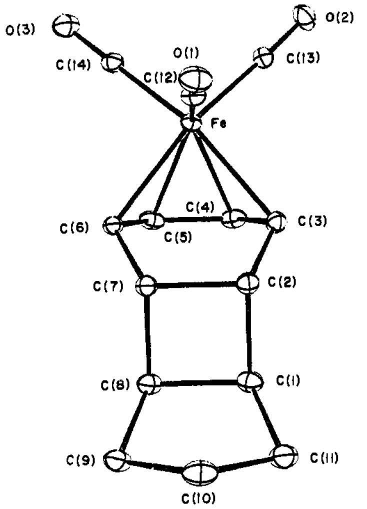

Figure 1. A view of $(C_{11}H_{14})Fe(CO)_3$ showing the approximate mirror symmetry. The 50% probability ellipsoids are shown; the hydrogen atoms have been omitted for clarity. The crystallographic numbering scheme defined here is consistent with the chemical numbering scheme.

Table II. Positional and Isotropic Thermal Parameters for Hydrogen Atoms[a]

Atom	x	y	z	B, Å^2
H(1)	0.349 (5)	0.187 (4)	0.678 (5)	1.5 (5)
H(2)	0.196 (5)	0.425 (4)	0.539 (5)	1.2 (5)
H(3)	0.011 (6)	0.283 (4)	0.482 (5)	2.5 (6)
H(4)	0.087 (5)	0.060 (4)	0.348 (5)	2.2 (6)
H(5)	0.332 (5)	−0.029 (4)	0.150 (5)	2.3 (6)
H(6)	0.446 (5)	0.120 (4)	0.114 (5)	2.3 (6)
H(7)	0.429 (5)	0.329 (4)	0.339 (5)	1.7 (5)
H(8)	0.587 (5)	0.098 (4)	0.471 (5)	1.4 (5)
H(9,1)	0.703 (6)	0.280 (5)	0.510 (6)	3.8 (8)
H(9,2)	0.730 (6)	0.226 (5)	0.652 (6)	2.4 (7)
H(10,1)	0.588 (7)	0.452 (5)	0.803 (7)	4.4 (9)
H(10,2)	0.457 (5)	0.480 (4)	0.663 (5)	1.5 (5)
H(11,1)	0.477 (5)	0.316 (4)	0.898 (5)	2.0 (6)
H(11,2)	0.310 (7)	0.430 (5)	0.844 (6)	3.4 (7)

[a] Hydrogen atoms are numbered according to the carbon atoms to which they are attached.

for TAMU data set, even though it is less than half the size (44%) of the MIT data set. Since the unit cell dimensions varied anisotropically from 3 to 24°, with a and b increasing ~0.1% while c decreased ~0.1%, no attempt at a more detailed discussion of the differences seems warranted. The thermal parameters from the TAMU refinement (24° data) are, as expected, uniformly greater, by about 25% than those from the MIT refinement (3° data).

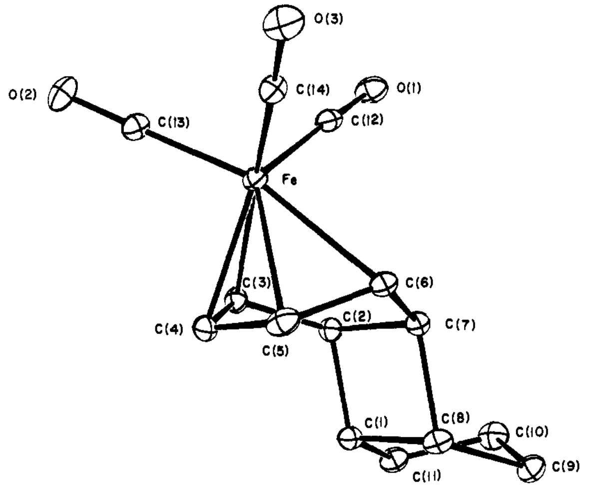

Figure 2. A view of $(C_{11}H_{14})Fe(CO)_3$ depicting the conformation of the fused ring system. In particular, the envelope-shape of the five-membered ring is clearly evident.

The positional parameters for the hydrogen atoms as obtained from the two data sets agree satisfactorily. All of the parameters differ by less than 2.2 times the esd of the difference, except for one pair where the difference is 3.3 times its esd. The isotropic thermal parameters differ in the expected way, those from the TAMU data set, being consistently larger than those based on the MIT data set.

Results

The numbering system used here for the $C_{11}H_{14}$ moiety is identical with that which would be used in the conventional chemical notation for the free molecule.

Although the TAMU and MIT data sets were collected and refined under different conditions, the resulting structures differ but little. The structure is composed of discrete monomeric $(C_{11}H_{14})Fe(CO)_3$ molecules, shown in Figures 1 and 2. All intermolecular contacts are equal to or greater than the sum of normal van der Waals radii, and the molecular structure appears to be free from any unusual deformation due to intermolecular forces. The $Fe(CO)_3$ moiety is within bonding distance of four carbon atoms in a six-membered ring. This ring is cis fused to a four-membered ring which, in turn, is cis fused to a five-membered ring. The tricyclic diene structure is qualitatively the same as that predicted from ir and pmr studies.[5] The suggested anti arrangement of the five- and six-membered rings relative to the central four-membered ring is now proved to be correct. A quantitative description and discussion of the structure now follows. Unless otherwise stated, all quantities are those derived from the MIT data; in all cases these quantities agree with the corresponding TAMU values to within three times their respective estimated standard deviations (esd's), and in most cases to within two esd's.

Discussion

Bond distances and angles are presented in Tables III and IV, respectively. Equations for important molecular planes, and dihedral angles between these planes, are given in Table V.

Table III. Intramolecular Bond Lengths (Å)

Fe–C(2)	2.982 (2)	Fe–C(12)	1.788 (3)
Fe–C(3)	2.132 (2)	Fe–C(13)	1.783 (2)
Fe–C(4)	2.053 (2)	Fe–C(14)	1.783 (2)
Fe–C(5)	2.053 (2)	C(12)–O(1)	1.144 (3)
Fe–C(6)	2.139 (2)	C(13)–O(2)	1.147 (3)
Fe–C(7)	2.984 (2)	C(14)–O(3)	1.154 (3)
C(1)–C(2)	1.563 (3)	C(1)–H(1)	0.94 (3)
C(1)–C(8)	1.562 (3)	C(2)–H(2)	1.04 (3)
C(1)–C(11)	1.525 (3)	C(3)–H(3)	0.91 (3)
C(2)–C(3)	1.500 (3)	C(4)–H(4)	0.97 (3)
C(2)–C(7)	1.545 (3)	C(5)–H(5)	0.89 (3)
C(3)–C(4)	1.417 (3)	C(6)–H(6)	0.96 (3)
C(4)–C(5)	1.411 (4)	C(7)–H(7)	0.99 (3)
C(5)–C(6)	1.412 (3)	C(8)–H(8)	0.96 (3)
C(6)–C(7)	1.504 (3)	C(9)–H(9,1)	0.92 (4)
C(7)–C(8)	1.564 (3)	C(9)–H(9,2)	0.85 (3)
C(8)–C(9)	1.522 (3)	C(10)–H(10,1)	0.85 (4)
C(9)–C(10)	1.525 (4)	C(10)–H(10,2)	1.02 (3)
C(10)–C(11)	1.515 (4)	C(11)–H(11,1)	1.01 (3)
		C(11)–H(11,2)	0.97 (3)

Table IV. Intramolecular Bond Angles (deg)

C(3)–Fe–C(4)	39.30 (9)	C(12)–Fe–C(13)	102.80 (11)
C(4)–Fe–C(5)	40.20 (10)	C(13)–Fe–C(14)	90.49 (11)
C(5)–Fe–C(6)	39.51 (9)	C(14)–Fe–C(12)	102.40 (11)
Fe–C(12)–O(1)	177.0 (4)		
Fe–C(13)–O(2)	178.7 (15)		
Fe–C(14)–O(3)	178.2 (5)		
Angles within Six-Membered Ring at Atom Specified			
C(2)	111.3 (2)	C(5)	115.9 (2)
C(3)	120.3 (2)	C(6)	120.5 (2)
C(4)	115.2 (2)	C(7)	110.0 (2)
Angles within Four-Membered Ring at Atom Specified			
C(1)	89.74 (15)	C(7)	90.33 (15)
C(2)	90.27 (15)	C(8)	89.64 (15)
Angles within Five-Membered Ring at Atom Specified			
C(1)	106.0 (2)	C(10)	103.5 (2)
C(8)	105.4 (2)	C(11)	104.4 (2)
C(9)	104.9 (2)		
C(1)–C(2)–C(3)	115.9 (2)	C(6)–C(7)–C(8)	116.1 (2)
C(2)–C(1)–C(11)	115.2 (2)	C(7)–C(8)–C(9)	115.1 (2)

The 1,3-Butadienetricarbonyliron Moiety. The average Fe–C(carbonyl) distance of 1.785 (3) Å is comparable with the many previously reported values (1.75–1.80 Å) and requires no further comment. The "inner" carbon atoms, C(4) and C(5), of the diene portion of the six-membered ring are equidistant, at 2.053 (2) Å, from the Fe atom. Significantly longer distances of 2.132 (2) and 2.139 (2) Å are found for the "outer" carbon atoms, C(3) and C(6), of the diene. A similar trend has been observed for analogous structures as indicated by Table VI.[10] The reported differences, Δ_1's, range from 0.05 (2) to 0.3 (1) Å. The weighted average of the unbiased estimates of Δ_1 is 0.079 (17) Å, while the weighted average of the weighted estimates is 0.080 (11) Å. Both averages indicate a significant difference in these Fe–C distances. The difference of 0.083 Å observed here is in good agreement with this.

The second important feature of the (butadiene)-$Fe(CO)_3$ grouping on which we wish to comment is the difference, Δ_2, between the "inner" C–C distance and the average value of the "outer" C–C distances in Table VI. This difference is of importance in discussions of the diene-to-iron bonding, in a manner fully discussed elsewhere.[14] It may be seen in Table VI that Δ_2 is a small quantity; the weighted average value for all the molecules tabulated is 0.021 (2) Å. We note also that in the comparable ruthenium compound, $(C_8H_8)Ru(CO)_3$, Δ_2 is 0.05 (2) Å.[15]

Of the three or four structures in Table VI that are known with high precision the present compound shows a Δ_2 value that is essentially zero, *viz.*, 0.004 (5) Å, while the weighted average in the other three cases is 0.022 (5) Å. Thus, although the previously reported accurate structures show that Δ_2 *may* exceed zero to a statistically significant extent, the present study shows, with equal significance, that this is not so in every case. In any event, it matters little whether Δ_2 is *ca.* 0.00 or *ca.* 0.02 Å, since the meaningful reference point should not be 0.00 Å but rather the value in an unbound 1,3-diene group, for which Δ_2 is about -0.09 Å. The inner bond is nearly 0.1 Å longer than outer bonds, in the free 1,3-diene, and the important point is that complexation causes the inner bond to become significantly shorter and the outer bonds to become significantly longer. Whether Δ_2 has changed by ~0.09 or by ~0.11 Å is less important than the fact that it has changed quite a lot, namely by about 0.10 ± 0.01 Å.

The orientation of the $Fe(CO)_3$ group with respect to the butadiene moiety is such that one CO group lies over the "open" side of the cis C–C–C–C chain, while the other two CO groups lie over the outer C–C bonds. The orientation has been found in all (butadiene)$M(CO)_3$ (M = Fe, Ru) groups examined to date. There is essentially mirror symmetry, with the mirror plane passing through the metal atom, one CO group, and the midpoint of the inner C–C bond.

The arrangement of ligands about the metal atom can also be described, approximately, as tetragonal pyrami-

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(10) Table VI deals only with molecules in which the butadiene residue is part of a cyclic system and includes mainly the more recent and accurate structures. Compounds with substituents on the butadiene carbon atoms are also excluded. For a more general summary of earlier work, see ref 11–13.

(11) M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967).

(12) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **8**, 1941 (1969).

(13) S. M. Johnson and I. C. Paul, *J. Chem. Soc. B*, 1783 (1970).

(14) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience-Wiley, New York, N. Y., 1972, pp 731–733.

(15) F. A. Cotton and R. Eiss, *J. Amer. Chem. Soc.*, **91**, 6593 (1969).

Table V. Least-Squares Planes and Dihedral Angles[a]

Plane	Atoms defining the plane	Equation of mean plane[b]
I	C(3)–C(4)–C(5)–C(6)	$4.540x - 2.512y + 6.394z = 2.628$
II	C(2)–C(3)–C(6)–C(7)	$1.229x - 8.477y + 5.167z = 0.219$
III	C(1)–C(2)–C(7)–C(8)	$4.189x + 9.889y + 0.621z = 4.475$
IV	C(1)–C(8)–C(9)–C(11)	$1.549x - 8.226y + 5.190z = 1.841$
V	C(9)–C(10)–C(11)	$4.471x - 1.932y + 5.957z = 5.930$

Displacement of Atoms from Mean Plane (Å)

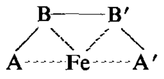
Plane I		Plane II		Plane III		Plane IV	
C(3)	0.001 (4)	C(2)	0.005 (4)	C(1)	−0.007 (4)	C(1)	−0.003 (4)
C(4)	−0.001 (4)	C(3)	−0.003 (4)	C(2)	0.006 (4)	C(8)	0.003 (4)
C(5)	0.001 (4)	C(6)	0.003 (4)	C(7)	−0.006 (4)	C(9)	−0.004 (6)
C(6)	−0.001 (4)	C(7)	−0.004 (4)	C(8)	0.007 (4)	C(11)	0.003 (5)

Dihedral Angles (deg)

Planes		Planes		Planes	
I–II	38.0	II–III	118.0	III–IV	116.0
I–III	80.0	II–IV	2.2	III–V	77.7
I–IV	36.1	II–V	40.3	IV–V	38.3
I–V	2.3				

[a] Calculations were made using TAMU positional parameters. [b] The equations of the planes are given in terms of the fractional triclinic coordinates.

Table VI. A Comparison of (diene)Fe(CO)$_3$ Structures



Compound		Fe–A	Fe–B	Fe–B′	Fe–A′	Δ$_1$[a] Unbiased	Δ$_1$[a] Weighted	A–B	B–B′	A′–B′	Δ$_2$[a]	Ref
$C_6H_6COFe(CO)_3$		2.114 (9)	2.067 (10)	2.042 (10)	2.149 (10)	0.08 (2)	0.075 (10)	1.442 (13)	1.396 (13)	1.435 (14)	0.043 (16)	*b*
$C_8H_8Fe(CO)_3$		2.18 (1)	2.05 (1)	2.05 (1)	2.18 (1)	0.13 (1)	0.13 (1)	1.42 (1)	1.42 (2)	1.42 (1)	0.00 (2)	*c*
$C_8H_8[Fe(CO_3]_2$	Fe(1)	2.14 (2)	2.09 (3)	2.06 (3)	2.12 (3)	0.05 (2)	0.06 (3)	1.43 (3)	1.39 (4)	1.40 (4)	0.03 (5)	*c*
	Fe(2)	2.17 (3)	2.03 (3)	2.04 (2)	2.15 (3)	0.12 (1)	0.12 (3)	1.48 (4)	1.40 (4)	1.44 (3)	0.05 (5)	*c*
$C_8H_9NO_2Fe(CO)_3$		2.091 (10)	2.041 (10)	2.059 (9)	2.145 (8)	0.07 (3)	0.073 (9)	1.440 (12)	1.409 (13)	1.398 (14)	0.013 (16)	*d*
$C_{10}H_{12}Fe(CO)_3$		2.116 (6)	2.039 (6)	2.053 (7)	2.114 (5)	0.069 (7)	0.070 (6)	1.400 (8)	1.387 (8)	1.404 (7)	0.015 (10)	*e*
$C_{10}H_{12}[Fe(CO)_3]_2$		2.109 (10)	2.042 (10)	2.042 (11)	2.119 (12)	0.072 (5)	0.071 (11)	1.409 (14)	1.370 (15)	1.399 (16)	0.035 (20)	*f*
$C_{11}H_{14}Fe(CO)_3$		2.139 (2)	2.053 (2)	2.053 (2)	2.132 (2)	0.083 (4)	0.083 (2)	1.412 (3)	1.411 (4)	1.417 (3)	0.004 (5)	*g*
$C_{12}H_{12}O[Fe(CO)_3]_2$	Fe(1)	2.103 (3)	2.032 (3)	2.043 (3)	2.114 (2)	0.071 (8)	0.073 (3)	1.424 (4)	1.392 (4)	1.427 (4)	0.034 (5)	*h*
	Fe(2)	2.125 (2)	2.039 (2)	2.037 (2)	2.115 (2)	0.082 (5)	0.082 (2)	1.413 (4)	1.399 (4)	1.416 (3)	0.016 (5)	*h*
$C_{12}H_{12}O[Fe(CO)_3]_2$		2.105 (5)	2.047 (5)	2.055 (5)	2.108 (5)	0.056 (4)	0.056 (5)	1.413 (6)	1.401 (6)	1.422 (6)	0.017 (7)	*i*
$C_{12}H_{16}Fe(CO)_3$		2.157 (9)	2.071 (10)	2.025 (11)	2.155 (10)	0.11 (2)	0.106 (10)	1.420 (13)	1.393 (17)	1.440 (17)	0.03 (2)	*j*
$C_{16}H_{16}Fe(CO)_3$		2.12 (2)	2.07 (2)	2.10 (2)	2.14 (2)	0.05 (2)	0.05 (2)	1.46 (2)	1.41 (2)	1.42 (2)	0.03 (2)	*k*
$C_{16}H_{16}Fe(CO)_3$		2.122 (15)	2.027 (16)	2.038 (16)	2.128 (13)	0.093 (6)	0.093 (15)	1.40 (2)	1.38 (2)	1.41 (3)	0.04 (2)	*l*
$(C_{10}H_8)_2Fe_4(CO)_{10}$		2.138 (6)	2.045 (6)	2.055 (7)	2.134 (6)	0.086 (5)	0.087 (6)	1.444 (9)	1.371 (9)	1.434 (9)	0.068 (11)	*m*

[a] Δ$_1$ is the difference between the average of (Fe–A) and (Fe–A′) and the average of (Fe–B) and (Fe–B′). Δ$_2$ is the difference between (B–B′) and the average of (A–B) and (A′–B′). Formulas used here are derived from the following:

$$\text{unbiased estimate} = \bar{d} = (1/N)\sum_{i=1}^{N} d_i \qquad \text{weighted estimate} = \sum_{i=1}^{N}(d_i/\sigma_i^2)\Big/\sum_{i=1}^{N}(1/\sigma_i^2)$$

$$\text{esd for unbiased estimate} = \left[(1/N(N-1))\sum_{i=1}^{N}(d_i-\bar{d})^2\right]^{1/2} \qquad \text{esd for weighted estimate} = \left[1/\sum_{i=1}^{N}(1/\sigma_i^2)\right]^{1/2}$$

$$\text{esd on a difference} = [\sigma_1^2 + \sigma_2^2]^{1/2}$$

Here d_i is the *i*th distance with an esd σ_i and N is the number of distances to be averaged. For a discussion of formulas of this type see, for example, W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, especially p 43. [b] R. P. Dodge, *J. Amer. Chem. Soc.*, **86**, 5429 (1964). [c] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962). [d] See ref 13. [e] F. A. Cotton, B. A. Frenz, and J. M. Troup, *J. Amer. Chem. Soc.*, in press. [f] F. A. Cotton, B. A. Frenz, and J. M. Troup, *J. Organometal. Chem.*, in press. [g] This work. [h] G. I. Birnbaum, *J. Amer. Chem. Soc.*, **94**, 2455 (1972). [i] K. B. Birnbaum, *Acta Crystallogr., Sect. B*, **28**, 161 (1972). [j] F. A. Cotton, V. W. Day, and K. I. Hardcastle, manuscript in preparation. [k] A. Robson and M. R. Truter, *J. Chem. Soc. A*, 794 (1968). [l] K. I. G. Reid and I. C. Paul, *J. Chem. Soc. D*, 1106 (1970). [m] See ref 12.

dal with the unique CO group, C(12)–O(1) in this case, forming the quasifourfold axis. The basal positions are occupied by the other CO groups and the midpoints of the outer C–C bonds, C(3)–C(4) and C(5)–C(6), as shown schematically in Figure 3. The apex-to-base angles are 103° for the carbonyl groups and 110° for the C–C bond midpoints. The basal angles are 91, 62, and 95°, the small angle being that subtended by the two outer C–C bonds of the diene.

Stereochemistry of the Tricycloolefin. The detailed stereochemistry of C_5–C_4–C_5 or C_6–C_4–C_5 ring fusions, achieved by various kinds of reactions, such as photoadditions of olefins has been of interest for some time.[16] While qualitative features of stereochemistry have been established by chemical and spectroscopic evidence, there have been only a few instances in which X-ray studies have been employed to define the structures with certainty. Even in these cases previous work has been of such low accuracy that structural details still remain imprecise. One of the purposes of the study reported here is to provide a precise characterization of the geometry of the system of fused rings present in the compound. In the future we shall report on related systems in which the five-membered ring is replaced by four- and six-membered rings.

The Cyclobutane Ring. The four-membered ring in this case is an almost perfect square. The angle at each carbon atom differs from 90° by only about two esd's, and deviations of the individual carbon atoms from their mean plane are not significant (see Table V). Three of the C–C distances are in the range 1.562–1.564 Å, while the fourth, along the fusion with the six-membered ring, is 1.545 (3) Å, which is about $4\sigma_{\mathrm{dif}}$ shorter than the average of the other three. It is well known[17] that in its equilibrium configuration an isolated cyclobutane ring is folded along one diagonal with a dihedral angle of about 35°, but that the barrier to flipping is quite low, *i.e.*, about 1.5 kcal/mol. Among the several substituted cyclobutanes previously studied crystallographically[18] some were reported to be planar and others not. The reasons for this variation are in general difficult to specify. From our studies of structures involving cyclobutane fused to (cyclohexadiene)-$Fe(CO)_3$ it appears that the four-membered ring tends to be planar because of the boat-shaped cyclohexadiene ring. However an additional ring fusion may force the cyclobutane ring to pucker. In the present case, the planarity of the cyclobutane ring appears to be due, at least in part, to the special compatibility of the planar conformation with the preferred conformation of the five-membered ring to which it is fused, as will be discussed further below.

It is noteworthy that the four-membered ring in bicyclo[2.1.0]pentane is planar.[19] Fusion with the three-membered ring doubtless promotes planarity in this case. For this molecule the average value of the C–C distances in the cyclobutane ring is 1.539 Å, but the individual values range from 1.528 (twice) through 1.536 to 1.565 Å. The authors proposed that the average value, 1.539 Å, ought to be optimum for all cyclobutane systems. Our results would suggest that this is not so, and we tend to agree with Margulis[20] that the typical C–C distance in a cyclobutane ring will be larger than the standard C–C single bond distance, with a typical value of about 1.56 Å.

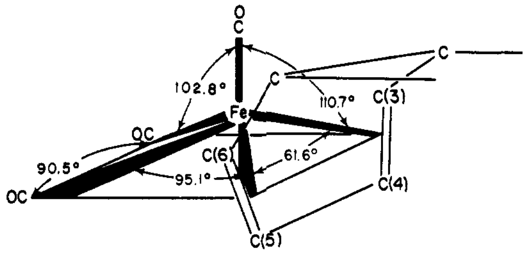


Figure 3. A schematic view of the iron coordination sphere. Here the diene portion of the ring system occupies two coordinating positions of a tetragonal pyramid with C(12)–O(1) at the apex.

The Cyclopentane Ring. The five-membered ring in this compound has an exemplary envelope conformation. The weighted least-squares mean plane derived from the four atoms C(1), C(8), C(9), and C(11) forms the body of the envelope; none of these atoms deviates significantly from this plane (Table V). The three atoms C(9), C(10), and C(11) define the flap of the envelope. These two planes make a dihedral angle of 38.3° and C(10) lies 0.58 Å from the mean plane of the other atoms in the ring.

It is generally recognized that the cyclopentane ring is less stable in a planar conformation, by ~5 kcal/mol, than in either of two puckered forms, *viz.*, the envelope form and the half-chair form. Both of the puckered forms have closely similar energies and each of those of one type provides a midway point in the interconversion of two of those of the other type. In this way a ripple runs continuously around the ring (psuedorotation).[21]

There has so far been very little straightforward structural information about cyclopentane ring conformations. A number of steroids, in which a cyclopentane ring (D) is fused to a cyclohexane ring (C) have been structurally characterized and discussed.[22] In all these cases the conformation is "intermediate" and is the resultant of several factors, such as the reciprocal effect of the fused rings upon each other and the effects of substituents on one or both of the rings. These systems do not provide good subjects for a clean-cut discussion of the structures of either the envelope or the half-chair conformations.

Because of the continual psuedorotation, cyclopentane itself is a very elusive subject for structural study. The best that has been done[21a] is to assume a pseudonormal coordinate for the pseudorotation. The data can then be analyzed to infer an amplitude of 0.427 ± 0.015 Å. From the conformational parameters (valence and torsion angles, ref 21a, Table II) one can calculate a displacement of 0.64 ± 0.04 Å for the unique

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(16) See, for example, R. M. Bowman, C. Calvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, **37**, 2084 (1972), and references cited therein.

(17) See, for example, the following recent articles, and earlier references therein: J. S. Wright and L. Salem, *J. Amer. Chem. Soc.*, **94**, 322 (1972); J. L. Nelson and A. A. Frost, *ibid.*, **94**, 3727 (1972).

(18) For references, see H. Booth, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 196 (1969).

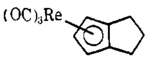
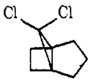
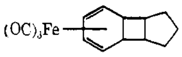
(19) R. D. Seunram and M. D. Harmony, *J. Chem. Phys.*, **56**, 3837 (1972).

(20) T. N. Margulis and M. S. Fischer, *J. Amer. Chem. Soc.*, **89**, 223 (1967).

(21) Leading references to the extensive earlier literature will be found in these articles: (a) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970); (b) L. A. Carreira, G. J. Jiang, W. B. Person, and J. N. Willis, Jr., *J. Chem. Phys.*, **56**, 1440 (1972).

(22) C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, **24**, 13 (1968).

Table VII. Ring Puckering Parameters in Envelope-Shaped Five-Membered Rings

Compound	Technique	Ring puckering displacement,[a] Å	Dihedral angle, deg	Displacement (Å) of fifth atom from plane of four	Ref
	Electron diffraction	$\langle q \rangle = 0.427$			*b*
		$q_e \approx 0.438$	40.9	0.64	
	Model force field	$q_e = 0.427$			*c*
	Model force field	$q_e = 0.49$			*d*
	Infrared	$q_o = 0.479$			*e*
	Raman	$q_e = 0.47 \pm 0.025$			*f*
	Thermodynamic	$q_{eff} = 0.48$			*g*
	Far infrared		23.3 ± 1.0		*h*
	Microwave		22.3 ± 2.0	0.35	*i*
	X-Ray diffraction		21.8	0.35	*j*
	X-Ray diffraction		9.7	0.15	*k*
	X-Ray diffraction		38.3	0.58	*l*

[a] The various displacement parameters *q* are defined in ref 21a. [b] Reference 21a. [c] S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968). [d] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); **85**, 4059 (1963). [e] J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **49**, 2118 (1968). [f] Reference 21b. [g] K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959). [h] J. Laane and R. C. Lord, *J. Chem. Phys.*, **47**, 4941 (1967). [i] G. W. Rathjens, Jr., *J. Chem. Phys.*, **36**, 2401 (1962); S. S. Butcher and C. C. Costain, *J. Mol. Spectrosc.*, **15**, 40 (1965). [j] K. K. Joshi, R. H. B. Mais, F. Nyman, P. G. Owston, and A. M. Wood, *J. Chem. Soc. A*, 318 (1968). [k] K. B. Wiberg, G. J. Burgmaier, K. Shen, S. J. La Placa, W. C. Hamilton, and M. D. Newton, *J. Amer. Chem. Soc.*, **94**, 7402 (1972). [l] This work.

carbon atom in the envelope conformer. This value and the one we find in the five-membered ring of our molecule (0.58 Å) are in quite good agreement. We believe that this agreement is real rather than fortuitous because the ring we have characterized comes very close to the ideal of being a cyclopentane ring subject to no perturbations other than the constraining of three consecutive C–C bonds to a common plane.

There are other structurally characterized molecules in which this particular perturbation or constraint is introduced *but not without significant additional perturbation*. In none of these other cases, summarized in Table VII, does the degree of bending of the envelope agree very well with that in cyclopentane itself or in the molecule described here. We believe that in each case this can be traced directly to the presence of an additional perturbing influence. In both cyclopentene and $(C_8H_9)Re(CO)_3$, this additional factor is the imposition of two adjacent C–C–C angles which are considerably larger than the angle appropriate to an unperturbed cyclopentane ring. The latter should be in the range 102–106°, as determined in the electron diffraction study,[24a] whereas in cyclopentene there are C–C–C angles of 117° at each of the olefin carbon atoms and in $(C_8H_9)Re(CO)_3$, the angles at the bridgehead carbon atoms are 114 ± 3°. In the compound we have studied, all angles, including those at the bridgehead carbon atoms, are within the range 103.5–106.0°, which matches very closely the range, mentioned above, for cyclopentane itself.

In the very recently reported case of 8,8-dichlorotricyclo[3.2.1.$0^{1,5}$]octane one bond in the cyclopentane ring is also part of a cyclopropane ring and a cyclobutane ring, which leads to highly unusual angles about the bridgehead carbon atoms (although those in the five-membered ring are nearly normal at 108.2°). In addition there are major steric problems, due for example to the chlorine atoms on C(8), which are not germane to the question of the dimensions of the unperturbed envelope conformation of cyclopentane.

One final point which requires attention is the role of intermolecular forces upon the conformation of the five-membered ring, and, for that matter, on all other conformational features of the molecule. There is no entirely rigorous way to resolve such questions, and we can only resort to the usual procedure of examining the crystal packing to see if there are any abnormally short contacts that might be indicative of intermolecular forces leading to deformation. All nonbonded distances <3.0 Å are listed in Table VIII. None of these are abnormally short.

Table VIII. Intermolecular Contacts Less Than 3 Å[a]

Atoms	Distance, Å	Atoms	Distance, Å
O(1)···H(2)	2.95 (3)	H(1)···H(8)	2.83 (6)
O(1)···H(3)	2.72 (4)	H(3)···H(9,1)	2.66 (6)
O(1)···H(10,1)	2.92 (5)	H(4)···H(9,1)	2.76 (6)
O(2)···H(7)	2.80 (3)	H(5)···H(6)	2.53 (5)
O(2)···H(9,1)	2.96 (5)	H(5)···H(11,1)	2.78 (6)
O(2)···H(10,2)	2.83 (4)	H(6)···H(6)	2.64 (8)
O(2)···H(11,1)	2.96 (5)	H(7)···H(10,2)	2.55 (5)
O(3)···H(1)	2.68 (4)	H(10,1)···H(11,1)	2.84 (7)
O(3)···H(8)	2.81 (4)	H(10,2)···H(10,2)	2.81 (8)
		H(10,2)···H(10,2)	2.81 (8)

[a] Distances and their standard deviations are derived from the TAMU data set.

In summary, we believe that the observed conformation of the cyclopentane ring in this molecule can be considered as a reasonably close model of the instantaneous, unperturbed envelope conformation of cyclopentane itself.