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# Reactivity of Diiron Nonacarbonyl in Tetrahydrofuran. III.[1]
# A New Iron Carbonyl Complex of Acenaphthylene, $(C_{12}H_8)Fe(CO)_4$

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Acenaphthylene and diiron nonacarbonyl react at room temperature in THF to yield (34% after chromatography and recrystallization from hexane) the new compound $(C_{12}H_8)Fe(CO)_4$. The substance is air sensitive, decomposes with melting at around 60°, and has CO stretching bands at 2084 (s), 2021 (vs), 2009 (vs), and 1984 (vs) $cm^{-1}$. X-Ray crystallography shows that the $C_{12}H_8$ molecule is bound through its 1,2 double bond to an equatorial position of a substituted trigonal-bipyramidal molecule. Though no crystallographic symmetry is imposed, the molecule has an approximate plane of symmetry which includes the axial CO groups and the iron atom and bisects the $C_{12}H_8$ moiety. The mean Fe–C(ax) and Fe–C(eq) distances are 1.813 and 1.793 Å, in satisfactory agreement with those for $(C_2H_4)Fe(CO)_4$ but in total disagreement with those (1.99, 1.76 Å) for $(CH_2CHCN)Fe(CO)_4$. The naphthalene portion of the $C_{12}H_8$ ligand has alternating C–C distances in excellent accord with the accepted values for naphthalene itself. Crystal data: space group $P2_1/c$; $a = 6.731$ (1) Å, $b = 21.311$ (2) Å, $c = 9.919$ (1) Å; $\beta = 99.716$ (9)°; $Z = 4$. With 1869 reflections for which $F_o^2 > 3\sigma(F_o^2)$, the structure has been refined anisotropically to $R_1 = 0.034$ and $R_2 = 0.049$. Hydrogen atoms were refined isotropically in the final cycles.

## Introduction

One iron carbonyl complex of acenaphthylene, $C_{12}H_8$-$Fe_2(CO)_5$, has already been reported[2] and its molecular structure is known.[3] This was obtained by reaction of $Fe_3(CO)_{12}$ with $C_{12}H_8$ for 10 hr in refluxing benzene. In an effort to prepare a sample of this compound for spectroscopic study we employed the reagent consisting of $Fe_2(CO)_9$ in tetrahydrofuran (THF), which has proven to be reactive at room temperature over short periods of time.[1] However, the reaction mixture became yellow-orange rather than violet, and it was apparent that the reaction product was quite different, probably mononuclear, in this case. When the infrared spectrum suggested that it was probably $(C_{12}H_8)Fe(CO)_4$, we decided to investigate the structure in detail, since, surprisingly, there had never been an accurate structure determination of a compound of the type (olefin)Fe(CO)₄.

## Experimental Section

**Preparation.** Diiron nonacarbonyl, dried *in vacuo* (1.70 g, 4.7 mmol), an excess of acenaphthylene (0.94 g, 6.3 mmol), and 50 ml of freshly distilled THF were stirred for 3 hr at room temperature under 1 atm pressure of carbon monoxide. The resulting orange solution was evaporated under vacuum to dryness. Some excess of acenaphthylene was removed by sublimation at room temperature. The resulting yellow-orange crystalline product was extracted with two 5-ml portions of degassed hexane and the extracts were transferred under nitrogen to a chromatography column (2.5 × 40 cm) packed with 100–200 mesh Florisil. The column was eluted under N₂ with hexane. The yellow-orange band was collected, evaporated to 10 ml, and cooled to –78°. The resulting yellow-orange crystals were recrystallized from hexane, yielding 0.51 g (34% based on Fe₂(CO)₉) of (acenaphthylene)tetracarbonyliron.

The compound is air sensitive, especially in solution. Its infrared spectrum in hexane has carbonyl bands at 2084 (s), 2021 (vs), 2009 (vs), and 1984 (vs) $cm^{-1}$ (±2 $cm^{-1}$). It has no sharp melting point but melts with decomposition at around 60°.

**Collection of X-Ray Data.** A single yellow-orange crystal of the compound grown from a solution in hexane at –5° was mounted in a glass capillary. The dimensions of the crystal were 0.2 × 0.1 × 0.1 mm.

Preliminary X-ray examination of the crystal and data collection were performed on a Syntex PĪ computer-controlled diffractometer equipped with a graphite-crystal monochromator. The operation of the diffractometer and other details of data collection have been described elsewhere[4] and only deviations from this description are included here.

The crystal was found to be monoclinic. It was of good quality with an ω-scan peak width at half-height of 0.20° for several strong reflections. Fifteen reflections were carefully centered and their setting angles refined by least squares to obtain unit cell dimensions and an

**Table I.** Crystal Data for $C_{12}H_8Fe(CO)_4$

| | |
|---|---|
| FW 320.04 | Monoclinic |
| $a = 6.731$ (1) Å | Space group $P2_1/c$ |
| $b = 21.311$ (2) Å | $F(000) = 648$ |
| $c = 9.919$ (1) Å | Mo Kα radiation |
| $\beta = 99.716$ (9)° | $\mu = 11.2$ $cm^{-1}$ |
| $V = 1402.5$ (3) Å³ | $d_{calcd} = 1.52$ g $cm^{-3}$ $(Z = 4)$ |

**Table II.** Atomic Positional Parameters[a]

| Atom | x | y | z |
|---|---|---|---|
| Fe | 0.0587 (1) | 0.1184 (1) | 0.2191 (1) |
| O(1) | 0.3203 (5) | 0.0124 (1) | 0.3196 (4) |
| O(2) | −0.3138 (4) | 0.1269 (2) | 0.3331 (3) |
| O(3) | −0.1827 (4) | 0.0408 (1) | 0.0064 (2) |
| O(4) | 0.2848 (4) | 0.1955 (1) | 0.4393 (3) |
| C(1) | 0.2257 (5) | 0.1625 (2) | 0.0777 (4) |
| C(2) | 0.0506 (5) | 0.1984 (1) | 0.0868 (3) |
| C(3) | −0.2755 (5) | 0.2152 (2) | −0.0981 (4) |
| C(4) | −0.3619 (6) | 0.1980 (2) | −0.2322 (4) |
| C(5) | −0.2678 (6) | 0.1597 (2) | −0.3113 (4) |
| C(6) | 0.0464 (7) | 0.0955 (2) | −0.3273 (4) |
| C(7) | 0.2313 (7) | 0.0764 (2) | −0.2630 (5) |
| C(8) | 0.3111 (6) | 0.0949 (2) | −0.1278 (5) |
| C(9) | 0.2004 (5) | 0.1343 (1) | −0.0598 (3) |
| C(10) | −0.0881 (5) | 0.1928 (1) | −0.0461 (3) |
| C(11) | 0.0122 (5) | 0.1542 (1) | −0.1293 (3) |
| C(12) | −0.0739 (5) | 0.1356 (2) | −0.2618 (3) |
| C(13) | 0.2188 (5) | 0.0528 (2) | 0.2794 (4) |
| C(14) | −0.1662 (5) | 0.1244 (1) | 0.2909 (3) |
| C(15) | −0.0847 (5) | 0.0708 (1) | 0.0854 (3) |
| C(16) | 0.1971 (5) | 0.1663 (2) | 0.3544 (4) |
| H(1) | 0.351 (5) | 0.171 (1) | 0.121 (3) |
| H(2) | 0.039 (5) | 0.235 (3) | 0.149 (3) |
| H(3) | −0.351 (5) | 0.242 (2) | −0.045 (4) |
| H(4) | −0.496 (6) | 0.214 (2) | −0.263 (4) |
| H(5) | −0.340 (5) | 0.149 (2) | −0.401 (4) |
| H(6) | 0.002 (5) | 0.084 (2) | −0.419 (4) |
| H(7) | 0.304 (6) | 0.053 (2) | −0.316 (5) |
| H(8) | 0.425 (6) | 0.080 (2) | −0.090 (4) |

[a] Figures in parentheses are estimated standard deviations occurring in the least significant digit.

orientation matrix for data collection. Unit cell dimensions and other crystal data are given in Table I. Data were collected at 22° using the θ–2θ scan technique and a variable-scan rate ranging from 4.0 to 24.0°/min depending on the intensity of the reflection. Standard reflections, collected every 100 reflections, showed no evidence for crystal movement and no significant crystal decomposition. Unique data were collected up to 2θ(Mo Kα) of 55° using a scan range from 2θ(Mo Kα₁) −0.7° to 2θ(Mo Kα₂) +0.7°. No absorption correction was made in view of the small variation of transmission factors of 84.9 ± 4.9%.

**Table III.** Thermal Parameters

A. Anisotropic Thermal Parameters[a] for Nonhydrogen Atoms

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Fe | 0.0216 (1) | 0.0022 (1) | 0.0109 (1) | 0.0000 (0) | −0.0006 (1) | −0.0001 (1) |
| O(1) | 0.0417 (10) | 0.0031 (1) | 0.0328 (6) | 0.0028 (2) | −0.0109 (6) | 0.0011 (2) |
| O(2) | 0.0306 (8) | 0.0060 (1) | 0.0177 (4) | −0.0011 (2) | 0.0065 (4) | −0.0026 (2) |
| O(3) | 0.0331 (7) | 0.0027 (1) | 0.0149 (3) | −0.0018 (2) | −0.0014 (4) | −0.0008 (1) |
| O(4) | 0.0335 (7) | 0.0041 (1) | 0.0171 (4) | −0.0009 (2) | −0.0030 (4) | −0.0028 (1) |
| C(1) | 0.0220 (8) | 0.0027 (1) | 0.0144 (4) | −0.0011 (2) | −0.0010 (5) | 0.0005 (1) |
| C(2) | 0.0304 (9) | 0.0021 (1) | 0.0123 (4) | −0.0004 (2) | 0.0001 (5) | 0.0003 (1) |
| C(3) | 0.0285 (9) | 0.0023 (1) | 0.0144 (4) | 0.0014 (2) | 0.0011 (5) | 0.0008 (1) |
| C(4) | 0.0297 (10) | 0.0031 (1) | 0.0151 (5) | 0.0018 (3) | −0.0002 (5) | 0.0016 (2) |
| C(5) | 0.0333 (10) | 0.0030 (1) | 0.0115 (4) | −0.0010 (2) | 0.0013 (5) | 0.0014 (2) |
| C(6) | 0.0392 (13) | 0.0034 (1) | 0.0124 (4) | −0.0003 (3) | 0.0066 (6) | 0.0002 (2) |
| C(7) | 0.0388 (13) | 0.0036 (1) | 0.0176 (6) | 0.0009 (3) | 0.0120 (7) | 0.0000 (2) |
| C(8) | 0.0250 (9) | 0.0036 (1) | 0.0190 (6) | 0.0012 (3) | 0.0068 (6) | 0.0013 (2) |
| C(9) | 0.0232 (8) | 0.0026 (1) | 0.0136 (4) | −0.0004 (2) | 0.0039 (4) | 0.0011 (1) |
| C(10) | 0.0282 (8) | 0.0019 (1) | 0.0125 (4) | 0.0003 (2) | 0.0014 (4) | 0.0008 (1) |
| C(11) | 0.0255 (8) | 0.0021 (1) | 0.0118 (4) | −0.0005 (2) | 0.0031 (4) | 0.0008 (1) |
| C(12) | 0.0312 (9) | 0.0026 (1) | 0.0118 (4) | −0.0009 (2) | 0.0045 (5) | 0.0011 (1) |
| C(13) | 0.0274 (9) | 0.0029 (1) | 0.0159 (5) | 0.0004 (2) | −0.0029 (5) | −0.0001 (2) |
| C(14) | 0.0274 (9) | 0.0034 (1) | 0.0106 (4) | −0.0004 (2) | 0.0002 (4) | −0.0008 (1) |
| C(15) | 0.0245 (8) | 0.0020 (1) | 0.0122 (4) | −0.0003 (2) | 0.0013 (4) | 0.0004 (1) |
| C(16) | 0.0245 (8) | 0.0029 (1) | 0.0132 (4) | 0.0007 (2) | 0.0000 (5) | −0.0005 (2) |

B. Isotropic Thermal Parameters for Hydrogen Atoms

| Atom | $B$, Å$^2$ | Atom | $B$, Å$^2$ | Atom | $B$, Å$^2$ |
|---|---|---|---|---|---|
| H(1) | 4.2 (7) | H(4) | 5.5 (8) | H(7) | 9.1 (11) |
| H(2) | 5.3 (7) | H(5) | 6.6 (8) | H(8) | 5.9 (9) |
| H(3) | 5.4 (8) | H(6) | 6.8 (9) | | |

[a] Defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Lorentz and polarization corrections were made;[5] no evidence for secondary extinction was observed. A total of 2773 reflections were collected, but only those 1869 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used for the refinement of the structure.

**Solution and Refinement of the Structure.** The iron atom was located using a three-dimensional Patterson function. The position of the iron atom was refined by least squares to give the agreement factors

$$R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.444$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.497$$

$|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and $w$ is the weighting factor given by $4|F_o|^2/\sigma^2$ where $\sigma$ is the esd of $|F_o|^2$. Scattering factors[6] and corrections for anomalous dispersion effects[7] due to the iron atom were taken from the usual sources. A difference Fourier map based on the iron atom position revealed the coordinates of all remaining nonhydrogen atoms except C(1).

The positions of these atoms were refined isotropically by two cycles of full-matrix least squares to give the residuals of $R_1 = 0.141$ and $R_2 = 0.150$. A new difference Fourier map revealed the coordinates of the C(1) atom. Three full-matrix least-squares cycles refining nonhydrogen atoms gave residuals of $R_1 = 0.050$ and $R_2 = 0.073$.

Hydrogen atoms were then found in a difference map. Refinement was continued treating the hydrogen atoms isotropically and the others anisotropically. Two cycles led to convergence with $R_1 = 0.034$ and $R_2 = 0.049$ and the esd for an observation of unit weight equal to 1.12. All parameter shifts in the final cycle were smaller than their esd's. In the final difference electron density map the highest peak was 0.40 e Å$^{-3}$ whereas the hydrogen atoms had been located on an earlier map as peaks of density 0.5–0.6 e Å$^{-3}$. A list of observed and final calculated structure factor amplitudes is available.[8]

**Results**

The atomic coordinates are presented in Table II, the thermal parameters are listed in Table III, and root-mean-square amplitudes of thermal vibration are listed in Table IV. A view of the molecular structure is given in Figure 1, where the numbering scheme is indicated. For the $C_{12}H_8$ moiety, the numbering scheme is identical with that used for nomenclatural purposes. The bond lengths are listed in Table

**Table IV.** Root-Mean-Square Amplitudes of Thermal Vibration (Å)

| Atom | Min | Intermed | Max |
|---|---|---|---|
| Fe | 0.203 (1) | 0.224 (1) | 0.251 (1) |
| O(1) | 0.220 (4) | 0.303 (4) | 0.451 (4) |
| O(2) | 0.250 (3) | 0.277 (3) | 0.388 (4) |
| O(3) | 0.215 (3) | 0.273 (3) | 0.307 (3) |
| O(4) | 0.216 (3) | 0.297 (3) | 0.353 (3) |
| C(1) | 0.208 (4) | 0.243 (4) | 0.288 (4) |
| C(2) | 0.218 (4) | 0.233 (4) | 0.278 (4) |
| C(3) | 0.211 (4) | 0.263 (4) | 0.277 (4) |
| C(4) | 0.210 (4) | 0.283 (4) | 0.299 (5) |
| C(5) | 0.212 (4) | 0.254 (4) | 0.309 (5) |
| C(6) | 0.235 (4) | 0.279 (4) | 0.299 (5) |
| C(7) | 0.235 (5) | 0.288 (5) | 0.329 (5) |
| C(8) | 0.225 (5) | 0.271 (4) | 0.323 (5) |
| C(9) | 0.215 (4) | 0.237 (4) | 0.273 (4) |
| C(10) | 0.199 (4) | 0.244 (4) | 0.264 (4) |
| C(11) | 0.206 (4) | 0.240 (4) | 0.251 (4) |
| C(12) | 0.206 (4) | 0.262 (4) | 0.271 (4) |
| C(13) | 0.222 (4) | 0.256 (4) | 0.310 (4) |
| C(14) | 0.213 (4) | 0.261 (4) | 0.284 (4) |
| C(15) | 0.213 (4) | 0.228 (4) | 0.255 (4) |
| C(16) | 0.222 (4) | 0.247 (4) | 0.280 (4) |

**Table V.** Bond Lengths (Å)

| | | | |
|---|---|---|---|
| Fe–C(1) | 2.156 (4) | Fe–C(14) | 1.783 (4) |
| Fe–C(2) | 2.146 (3) | Fe–C(15) | 1.812 (3) |
| Fe–C(13) | 1.804 (4) | Fe–C(16) | 1.815 (3) |
| C(1)–C(2) | 1.421 (5) | C(6)–C(7) | 1.362 (6) |
| C(1)–C(9) | 1.473 (5) | C(6)–C(12) | 1.410 (5) |
| C(2)–C(10) | 1.486 (4) | C(7)–C(8) | 1.414 (6) |
| C(3)–C(4) | 1.407 (5) | C(8)–C(9) | 1.373 (5) |
| C(3)–C(10) | 1.366 (4) | C(9)–C(11) | 1.402 (4) |
| C(4)–C(5) | 1.361 (5) | C(10)–C(11) | 1.415 (5) |
| C(5)–C(12) | 1.411 (5) | C(11)–C(12) | 1.400 (4) |
| C(13)–O(1) | 1.129 (4) | C(15)–O(3) | 1.133 (3) |
| C(14)–O(2) | 1.143 (4) | C(16)–O(4) | 1.131 (4) |
| C(1)–H(1) | 0.89 (3) | C(5)–H(5) | 0.96 (4) |
| C(2)–H(2) | 1.01 (3) | C(6)–H(6) | 0.94 (4) |
| C(3)–H(3) | 0.97 (4) | C(7)–H(7) | 0.93 (5) |
| C(4)–H(4) | 0.96 (4) | C(8)–H(8) | 0.85 (4) |

**Table VI.** Bond Angles (deg)

| | | | |
|---|---|---|---|
| C(1)–Fe–C(2) | 38.6 (1) | C(1)–C(9)–C(11) | 106.6 (3) |
| C(1)–Fe–C(13) | 101.9 (2) | C(2)–C(10)–C(11) | 105.9 (3) |
| C(1)–Fe–C(15) | 92.3 (1) | C(9)–C(11)–C(10) | 111.6 (3) |
| C(1)–Fe–C(16) | 88.7 (1) | C(4)–C(3)–C(10) | 118.3 (3) |
| C(2)–Fe–C(14) | 104.5 (2) | C(3)–C(4)–C(5) | 122.8 (3) |
| C(2)–Fe–C(15) | 92.4 (1) | C(4)–C(5)–C(12) | 120.7 (3) |
| C(2)–Fe–C(16) | 87.8 (1) | C(7)–C(6)–C(12) | 121.1 (4) |
| C(13)–Fe–C(14) | 115.1 (2) | C(6)–C(7)–C(8) | 122.1 (4) |
| C(13)–Fe–C(15) | 91.4 (1) | C(7)–C(8)–C(9) | 119.1 (4) |
| C(13)–Fe–C(16) | 89.2 (1) | C(8)–C(9)–C(11) | 117.6 (3) |
| C(14)–Fe–C(15) | 87.1 (1) | C(3)–C(10)–C(11) | 118.9 (3) |
| C(14)–Fe–C(16) | 91.6 (1) | C(9)–C(11)–C(12) | 125.0 (3) |
| C(15)–Fe–C(16) | 178.7 (1) | C(10)–C(11)–C(12) | 123.3 (3) |
| O(1)–C(13)–Fe | 178.6 (3) | C(5)–C(12)–C(6) | 129.0 (3) |
| O(2)–C(14)–Fe | 177.4 (3) | C(5)–C(12)–C(11) | 115.9 (3) |
| O(3)–C(15)–Fe | 176.1 (3) | C(6)–C(12)–C(11) | 115.1 (3) |
| O(4)–C(16)–Fe | 179.2 (3) | H(1)–C(1)–Fe | 109 (2) |
| Fe–C(1)–C(9) | 115.6 (2) | H(1)–C(1)–C(2) | 126 (2) |
| Fe–C(2)–C(10) | 115.2 (2) | H(1)–C(1)–C(9) | 118 (2) |
| C(2)–C(1)–C(9) | 108.1 (3) | H(2)–C(2)–Fe | 104 (2) |
| C(1)–C(2)–C(10) | 107.7 (3) | H(2)–C(2)–C(1) | 127 (2) |
| | | H(2)–C(2)–C(10) | 120 (2) |



**Figure 1.** An ORTEP projection of the molecule. The atom-numbering scheme is defined. Each atom is represented by an ellipsoid of thermal motion scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity.

V and bond angles are given in Table VI. The equations for several least-squares planes, the distances of atoms from these planes, and some dihedral angles are presented in Table VII.

The structure is essentially that of $Fe(CO)_5$, a trigonal bipyramid, with one equatorial CO ligand replaced by the 1,2 double bond of the acenaphthylene. The C–C axis of the double bond lies in the equatorial plane and the Fe–C(olefin) distances are essentially equal. The entire molecule possesses virtual mirror symmetry with the plane including Fe and axial CO groups and coinciding with the plane of symmetry possessed by the acenaphthylene molecule itself perpendicular to its skeletal plane. This plane is plane III, Table VII, and it can be seen there that the deviations from it are very slight. Of the atoms which should lie in it, only O(3) is out by more than 0.012 Å and pairs of distances from the plane to atoms which should be equivalent differ by 0.07 Å or less.

The plane of the acenaphthylene makes an angle of about 111° with the C(1)–C(2)–Fe plane.

## Discussion

The structure of the molecule is of particular interest since it is the first accurate structure of an (olefin)$Fe(CO)_4$ molecule to be reported. The only previous structural studies are the X-ray crystallographic studies of $(CH_2=CHCN)Fe(CO)_4$,[9] (–)-(fumaric acid)$Fe(CO)_4$,[10] and *rac*-(fumaric acid)Fe-

$(CO)_4$[11] and the gas-phase electron diffraction study of $(CH_2CH_2)Fe(CO)_4$,[12] all of which gave results with large esd's. Furthermore, the $(CH_2CHCN)Fe(CO)_4$ structure contains some distances which appear to be incorrect by 0.15–0.20 Å thus making the entire structure very suspect. The acrylonitrile complex is, in fact, a singularly unattractive subject for study because it is low melting (40°), volatile, and unstable toward both air and light; perhaps these properties somehow led to the gross error in two of the Fe–C bond lengths.
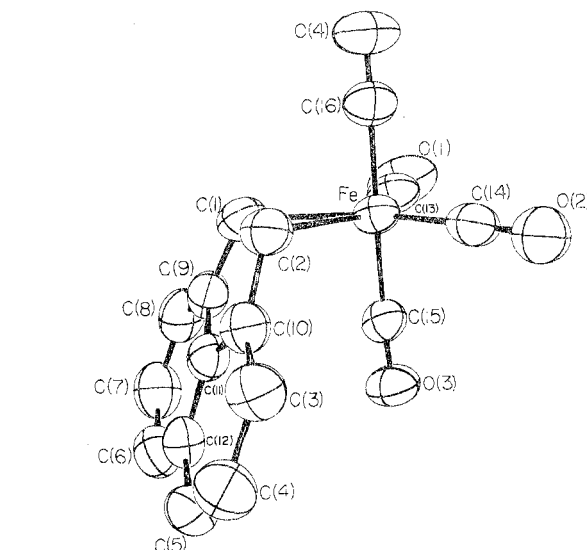
The present structure agrees qualitatively with the others in having the ethylenic ligand in an equatorial position with the ethylenic carbon atoms essentially in the equatorial plane of the trigonal bipyramid. Clearly, this is the preferred configuration; there is no indication of the barrier to rotation in (olefin)$Fe(CO)_4$ species although olefin complexes of Pd, Pt, and Ir have been studied extensively in this respect.[13]

The reported C–C distances in bound olefins in previous cases have ranged from 1.30[10] to 1.46.[12] Both of these extremes, certainly the former, are dubious. The remaining ones are about 1.42 Å, but in each case the esd is large, *viz.*, 0.02 Å or greater. We find a distance here of 1.421 (5) Å, which seems reasonable and agrees well with the probable mean of the previous values.

**Table VII.** Weighted Least-Squares Planes

| Plane | Atoms defining plane | Equation of mean plane |
|---|---|---|
| I | Acenaphthylene | $-3.263X - 17.000Y + 4.268Z = -3.179$ |
| II | C(1)–C(2)–C(13)–C(14)–Fe | $2.441X + 11.699Y + 6.649Z = 2.993$ |
| III | Fe–C(11)–C(12)–C(15)–C(16) | $-5.678X + 11.385Y + 1.930Z = 1.4485$ |

Displacement of Atoms from Mean Plane, Å

| | | | | | | |
|---|---|---|---|---|---|---|
| Plane I | C(1) | 0.002 | C(5) | 0.010 | C(9) | -0.013 |
| | C(2) | 0.013 | C(6) | 0.007 | C(10) | -0.007 |
| | C(3) | 0.002 | C(7) | 0.004 | C(11) | -0.033 |
| | C(4) | 0.003 | C(8) | 0.005 | C(12) | -0.003 |
| Plane II | C(1) | -0.025 | C(14) | -0.009 | Fe | -0.009 |
| | C(2) | 0.028 | O(1) | 0.059 | C(15) | -1.819 |
| | C(13) | 0.016 | O(2) | -0.060 | C(16) | 1.85 |
| Plane III | Fe | -0.012 | O(1) | -2.510 | C(10) | 1.158 |
| | C(11) | -0.012 | O(2) | 2.422 | C(3) | 2.376 |
| | C(12) | 0.010 | C(13) | -1.551 | C(8) | -2.381 |
| | C(15) | 0.004 | C(14) | 1.474 | C(4) | 2.413 |
| | C(16) | 0.009 | C(1) | -0.730 | C(7) | -2.400 |
| | O(3) | 0.065 | C(2) | 0.690 | | |
| | O(4) | 0.009 | C(9) | -1.173 | | |

Dihedral Angle between Planes, Deg

| I–II | 110.8 | I–III | 89.9 | II–III | 88.5 |
|---|---|---|---|---|---|

The degree of deformation of a coordinated olefin from planarity is not well known and may not follow any consistent pattern.[14] In the present case it is impossible to be sure how much of the deviation of the $C_{12}H_8$ mean plane from perpendicularity to the equatorial plane of the trigonal bipyramid (110.8°) is due to steric repulsion and how much to electronic factors. The hydrogen atom positions are sufficiently inaccurate that the H–C–C angles, even though they carry nominal esd's of about 2°, are probably very untrustworthy. The C–C–C angles are constrained by the five-membered ring to have the observed values of *ca.* 108° and thus indicate nothing about the effect of metal–olefin bonding on hybridization at the bound olefin carbon atoms. In this respect, the present molecule is not a suitable representative of (olefin)$Fe(CO)_4$ molecules as a class.

The relative lengths of axial and equatorial Fe–CO bonds in $Fe(CO)_5$ and its derivatives have been a subject of considerable debate. The question is a tedious one because the difference is always small and probably subject to considerable variability depending on the identity of the substituent and its point of attachment (*i.e.*, axial or equatorial). For $Fe(CO)_5$ itself, the weight of evidence suggests[15] that the difference $\Delta$ = Fe–C(ax) – Fe–C(eq), is about 0.03 ± 0.01 Å. In axially substituted compounds $\Delta$ appears to vary with the substituent. With $Ph_2HP$, $\Delta \approx 0$,[16] whereas with substituents pyridine and pyrazine, $\Delta \approx 0.035$ Å.[17] For the equatorially substituted olefin compounds none of the previous results are accurate enough to reveal a small value of $\Delta$. None of the reported differences exceed the sum of the esd's of individual distances and the latter are all in the range 0.02–0.04 Å. The results for $(CH_2C-HCN)Fe(CO)_4$ show a large difference, but the axial Fe–C distances clearly suffer gross error. Our results give $\Delta \approx 0.020$ (7) Å. Thus, there does appear to be a slight difference, but since it is barely equal to $3\sigma$, it is just on the threshold of significance.

It is not possible to compare the dimensions of the $C_{12}H_8$ moiety with those of free acenaphthylene since the latter have never been reported. An interesting comparison can be made with the dimensions of napthalene; Cruickshank and Sparks[18] have discussed these and shown that the most accurate experimental values are in good agreement with theoretical prediction, using either simple LCAO–MO theory or the valence-bond superposition method. If we assume that interaction of the 1,2 double bond with the metal atom effectively divorces it from the rest of the $\pi$ system, what remains should be essentially the naphthalene $\pi$ system, perturbed to some slight extent by the deformation of the C(1)–C(9) and C(2)–C(10) $\sigma$ bonds away from their preferred directions. As Table VIII shows, the present distances are in excellent agreement with those in naphthalene. Only for C(11)–C(12) is the discrepancy (0.018 Å) larger than approximately 0.010 Å, and in the other cases it is statistically insignificant ($<3\sigma$). We believe that this attests to the accuracy of the present structure.

**Table VIII.** Comparison of C–C Bond Lengths with Those in Naphthalene

| | $C_{12}H_8Fe(CO)_4$ | $C_{10}H_8$ |
|---|---|---|
| C(11)–C(12) | 1.400 (4) | 1.418 |
| C(3)–C(4) | 1.407 (5) ⎫ 1.411 (4) | 1.415 |
| C(7)–C(8) | 1.414 (6) ⎭ | |
| C(10)–C(3) | 1.366 (4) ⎫ | |
| C(4)–C(5) | 1.361 (5) ⎪ 1.366 (4) | 1.364 |
| C(6)–C(7) | 1.362 (6) ⎬ | |
| C(8)–C(9) | 1.373 (5) ⎭ | |
| C(10)–C(11) | 1.415 (5) ⎫ | |
| C(5)–C(12) | 1.411 (5) ⎪ 1.410 (4) | 1.421 |
| C(6)–C(12) | 1.410 (5) ⎬ | |
| C(9)–C(11) | 1.402 (4) ⎭ | |

### References and Notes

(1) Parts I and II: F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 3438, 4422 (1974).
(2) (a) R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 4557 (1960); (b) R. B. King, *ibid.*, **88**, 2075 (1966).
(3) M. R. Churchill and J. Wormald, *Chem. Commun.*, 1597 (1968).
(4) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, **50**, 227 (1973).
(5) Computer programs used in data reduction and in the solution and refinement of the structure were as follows. DATARED by Frenz was used for data reduction. The Fourier program JIMDAP by Ibers is a version of Zalkin's FORDAP. NUCLS, a full-matrix least-squares program by Ibers and Doedens, closely resembles Busing and Levy's ORFLS program; the function minimized in the refinement is $\Sigma w(|F_o| - |F_c|)^2$. ORTEP by Johnson was used for drawing illustrations on a Gerber plotter. Atomic distances, angles, and errors were calculated using program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen.
(6) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, in preparation.
(7) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1971).
(8) See paragraph at end of paper regarding supplementary material.
(9) A. R. Luxmore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).
(10) C. Pedone and A. Sirigu, *Inorg. Chem.*, **7**, 2614 (1968).
(11) C. Pedone and A. Sirigu, *Acta Crystallogr.*, **23**, 759 (1967).
(12) M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, **21**, 401 (1970).
(13) J. Ashley-Smith, Z. Douek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 128 (1974), and references therein.
(14) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969).
(15) "Molecular Structure by Diffraction Methods," Vol. 1, The Chemical Society, London, 1973, p 147.
(16) B. T. Kilbourn, K. N. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969).
(17) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 3438 (1974).
(18) D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960).