CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

The Crystal and Molecular Structure of *trans*-1,4-Bis-(π-cyclopentadienyldicarbonyliron)buta-1,3-diene

BY MELVYN R. CHURCHILL AND JOHN WORMALD

Received January 9, 1969

The compound *trans*-1,4-bis-(π-cyclopentadienyldicarbonyliron)buta-1,3-diene, $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5) with $a = 6.794 \pm 0.005$ Å, $b = 11.471 \pm 0.010$ Å, $c = 11.787 \pm 0.007$ Å, $\beta = 113.14 \pm 0.02°$, and $Z = 2$. Observed and calculated densities are 1.60 ± 0.01 and 1.596 g cm^{-3}, respectively. A single-crystal X-ray diffraction study based on data out to $\sin \theta = 0.38$ (Mo Kα radiation) has led to the unambiguous location of all atoms, including the hydrogen atoms. The final discrepancy index for the 989 independent nonzero reflections is $R_F = 5.48\%$. The crystal consists of discrete molecular units of $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$, which have crystallographically imposed C_i symmetry. The FeCH=CHCH=CHFe system has an all-*trans* configuration and is closely planar, as are the π-cyclopentadienyl ligands. The iron–butadiene σ bonds are 1.987 ± 0.005 Å in length—*i.e.*, some 0.12 Å shorter than the Fe–C(sp^3) bond length of 2.11 ± 0.02 Å found in $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$ and 0.07 Å shorter than the Fe–C(sp^3) bond length of 2.06 ± 0.02 Å reported for $\pi\text{-}C_5H_5Fe(CO)_2(CH_2CO_2H)$. Carbon–carbon distances within the butadiene system are 1.340 ± 0.007, 1.450 ± 0.011, and 1.340 ± 0.007 Å.

Introduction

The reaction of $\pi\text{-}C_5H_5Fe(CO)_2Na$ with *cis*-3,4-dichlorocyclobutene proceeds exothermally, producing[1] the complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$. The room-temperature proton magnetic resonance (pmr) spectrum of this complex (at 60 Mc) shows two sharp singlets at τ 3.76 and 5.05 (relative integrated intensities 2:5). This unexpectedly simple spectrum at first suggested that the complex might contain a new type of metal–cyclobutadiene interaction and prompted the present X-ray diffraction study. Both the present authors[1a] and Davis[1b] have published preliminary accounts of this structure.

Unit Cell and Space Group

Orange crystals of $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$ were supplied by the late Professor G. F. Emerson of the State University of New York at Stony Brook. The complex is air stable and is not X-ray sensitive. Optical examination and the observed reciprocal lattice symmetry (C_{2h}; 2/m) indicated that the crystals belonged to the monoclinic system. Unit cell dimensions at 24 ± 2° obtained by a least-squares analysis of calibrated ($a_{NaCl} = 5.640$ Å) high-angle precession data taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) are $a = 6.794 \pm 0.005$ Å, $b = 11.471 \pm 0.010$ Å, $c = 11.787 \pm 0.007$ Å, and $\beta = 113.14 \pm 0.02.°$ The volume of the unit cell is 844.7 Å^3.

A survey of photographs for the zones $0kl$, $1kl$, $h0l$, $h1l$, $hk0$, and $hk1$ revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, compatible only with space group $P2_1/c$ (C_{2h}^5).[2] The observed density (1.60 ± 0.01 g cm^{-3}, by flotation in aqueous zinc iodide solution) indicates two molecules per unit cell. (The calculated density is 1.596 g cm^{-3} for $M = 405.70$, $Z = 2$.) Thus, provided the crystal is not disordered, the molecule is required to possess a crystallographically imposed center of symmetry.

Collection and Reduction of the X-Ray Diffraction Data

The crystals are well-formed parallelepipeds with large and distinct (100), (011), and (01$\bar{1}$) faces. Two crystals were used in the course of collecting intensity data: crystal I (0.20 × 0.20 × 0.26 mm) was mounted along its c axis, and crystal II (0.16 × 0.36 × 0.34 mm) was mounted along its b axis. [Dimensions refer sequentially to the [100], [011], and [01$\bar{1}$] directions in the crystal.]

Intensity data (Mo Kα radiation, $\bar{\lambda}$ 0.7107 Å) were collected on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer using the stationary-background, ω-scan, stationary-background method. Both the technique and the apparatus have been described in detail in a previous publication.[3]

Experimental details that are specific to the present structural investigation include the following. (i) The X-ray generator was stabilized at 48.6 kV/19.1 mA. (ii) The angle scanned (ω) is given by $\omega = 1.5 + (0.7/L)°$, where $1/L$ is the Lorentz factor. (iii) The speed of the ω scan was 2°/min. (iv) The initial and final backgrounds were each measured for one-fourth the time of the main scan. (v) Within each level a carefully preselected check reflection was remeasured after each batch of 20 reflections had been collected. No significant [*i.e.*, $\geqslant 3(\text{count})^{1/2}$] variations from the mean were detected. This confirms that the electronics were stable and that the crystal remained accurately aligned.[4] (vi) $I(hkl)$, the intensity of the reflection hkl, was calculated as: $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$, where $C(hkl)$ is the count associated with the ω scan, and $B_1(hkl)$ and $B_2(hkl)$ are the counts associated with the initial and the final backgrounds, respectively.

---

[1] (a) M. R. Churchill, J. Wormald, W. P. Giering, and G. F. Emerson, *Chem. Commun.*, 1217 (1968); (b) R. E. Davis, *ibid.*, 1218 (1968).

[2] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 99.

[3] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.* **7**, 1123 (1968).

[4] Each crystal was also checked photographically at the beginning and end of data collection. No problems of misalignment were encountered.

Using equiinclination Weissenberg geometry, data for the zones hkL (L = 0–10) were collected from crystal I, and data for the zones hKl (K = 0–12) were collected from crystal II. This represents, in each case, a single complete set of diffraction data to $\sin\theta = 0.38$, save for the few reflections in the range $0 \leqslant \theta \leqslant 4°$ which are shielded from the counter by the lead backstop. Long-exposure Weissenberg photographs had shown previously that there were few observable data beyond $\sin \theta = 0.38$.

Data were assigned standard deviations according to the following scheme (where $\delta(hkl) = 3[C(hkl) + B_1(hkl) + B_2(hkl)]^{1/2}$): $I(hkl) \geqslant 1225$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $1225 > I(hkl) \geqslant \delta(hkl)$, $\sigma\{I(hkl)\} = 3.5[I(hkl)]^{1/2}$; $I(hkl) < \delta(hkl)$, reflection rejected.

Of the 1196 reflections obtained from crystal I, 253 were rejected; of the 1192 reflections obtained from crystal II, 148 were rejected. Intensities were corrected for Lorentz and polarization effects $[(Lp)^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)]$[5] and an absorption correction was applied[6] (μ = 17.86 cm^{-1} for Mo Kα radiation); calculated transmission coefficients ranged from 0.688 to 0.745 for data from crystal I (volume 0.0093 mm^3) and from 0.577 to 0.756 for data from crystal II (volume 0.0197 mm^3). Duplicate "check reflections" were removed, the median value being retained in each case. The two sets of data were then merged to a common scale by a least-squares analysis of common reflections.[7] The resulting 989 independent, nonzero reflections were used in a Wilson plot,[8] which put the data on an approximately absolute scale and yielded the over-all isotropic thermal parameter, $\bar{B}$ = 2.45 Å^2.

Elucidation and Refinement of the Structure

A three-dimensional Patterson synthesis,[9] which had been sharpened such that the average intensity was invariant with θ, revealed a set of vectors consistent with an iron atom at $x = 0.1315$, $y = 0.1621$, $z = -0.2359$. A three-dimensional "difference-Fourier" synthesis phased only by the iron atom ($R_F = 35.4\%$)[10] quickly and unambiguously revealed the locations of all nonhydrogen atoms in the molecule. Five cycles of full-matrix least-squares refinement of all positional and isotropic thermal parameters led to convergence at $R_F = 11.56\%$ and $R_{wF^2} = 8.35\%$. A second "difference-Fourier" map at this stage showed considerable residual electron density in the plane of the π-cyclopentadienyl ring and showed asymmetric features about all atoms other than C_6 and C_7. The hydrogen atoms of the π-cyclopentadienyl system could not be identified unambiguously, but those of the butadiene system (*i.e.*, H_6 and H_7) stood out clearly with peak heights of 0.5 and 0.7 e$^-$/Å^3.

All seven hydrogen atoms were now included in the structure factor calculation (using calculated[11] positions and having isotropic thermal parameters set at B = 6.0 Å^2) but were not allowed to refine. Seven cycles of full-matrix least-squares refinement of positional and anisotropic thermal parameter refinement for the 12 nonhydrogen atoms resulted in convergence at $R_F = 5.48\%$ and $R_{wF^2} = 2.12\%$. The maximum suggested shift in any coordinate was less than 2.5% of the appropriate standard deviation.

An "observed" electron density synthesis showed the following peak heights: 4.3–4.9 e$^-$/Å^3 for carbon atoms of the π-cyclopentadienyl system, 5.3–7.3 e$^-$/Å^3 for other carbon atoms, and 7.2–7.8 e$^-$/Å^3 for oxygen atoms. A "difference-Fourier" map showed no significant residual electron density, except in the vicinity of the iron atom.

A test was now made to see whether or not the inclusion of all seven hydrogen atoms constituted a legitimate procedure. The structure was allowed to refine to convergence omitting all hydrogen atoms from the structure factor calculations. The discrepancy indices thus obtained ($R_F = 6.22\%$, $R_{wF^2} = 3.05\%$) confirm that inclusion of the hydrogen atoms leads to an improvement that is significant[12] with a level of confidence greater than 99.5%. A final set of electron density maps, through the plane of the π-cyclopentadienyl system, led to the unambiguous location of the five hydrogen atoms of this system, with individual peak heights ranging from 0.41 to 0.55 e$^-$/Å^3 (see Figure 1).

Throughout the analysis, the scattering factors for neutral oxygen, carbon and hydrogen were used.[13a] The Thomas–Fermi–Dirac values for neutral iron[13b] were corrected for dispersion ($\Delta f'$ = 0.4 e$^-$; $\Delta f''$ = 1.0 e$^-$).[13c] The residual minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma\{F^2(hkl)\}]^{-2}$.

Observed and calculated structure factors are collected in Table I. Final positional parameters are shown in Table II. Anisotropic thermal parameters are listed in Table III; their appropriate thermal vibration ellipsoids are defined in Table IV and are illustrated in Figure 2.

The Molecular Structure

The results of the crystallographic analysis show that the molecule is the all-*trans* form of 1,4-bis(π-cyclopentadienyldicarbonyliron)buta-1,3-diene. The molecule possesses a crystallographically imposed center of symmetry (in the center of the C(7)–C(7′) bond at $x = 0, y = {}^1/_2, z = {}^1/_2$). As may conveniently be seen in Figure 3, atoms of the basic asymmetric unit are unprimed; those in the "other half" of the molecule (which is related to the basic asymmetric unit by the transformation: $x' = -x, y' = 1 - y, z' = 1 - z$) are each labeled with a prime.

---

(5) $\bar{\mu}$ is the equiinclination angle, Υ is the vertical Weissenberg coordinate, and θ is the Bragg angle.

(6) Using a local modification of the IBM 7094 program GNABS—a general absorption correction program by C. W. Burnham.

(7) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(8) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(9) All computations were performed under the CRYM system. CRYM is an integrated sequence of crystallographic routines for the IBM 7094, written under the direction of Professor R. E. Marsh at the California Institute of Technology.

(10) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

(11) Hydrogen atom positions were calculated with d(C–H) = 1.080 Å and with the H–C* vector bisecting the appropriate C–C*–C or Fe–C*–C angle.

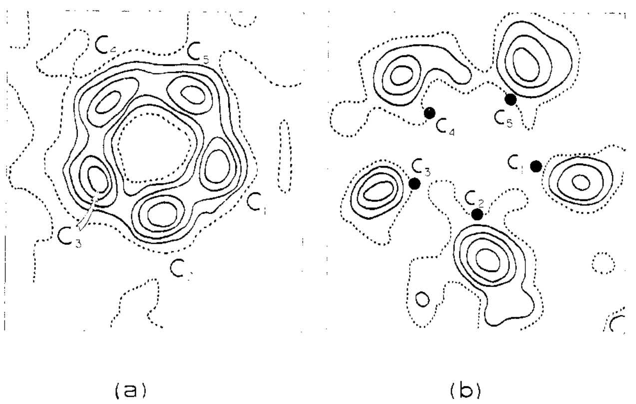
(12) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(13) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$ (IN ELECTRONS × 10.00)

K	L	FO	FC
H = -7			
0	2	107	105
0	4	108	106
1	2	135	136
1	3	90	79
1	4	188	188
1	5	139	143
1	6	189	188
1	7	160	165
2	3	132	127
2	4	68	66
2	5	160	153
2	6	69	70
2	7	56	84
3	4	42	29
3	5	227	211
3	6	107	107
H = -6			
0	0	84	39
0	6	137	112
0	8	280	270
0	10	209	219
1	0	248	256
1	1	204	205
1	2	252	246
1	3	68	60
1	4	208	195
1	5	106	103
1	6	234	243
1	7	142	136
1	8	194	188
1	9	80	74
1	10	113	113
2	0	67	60
2	1	53	53
2	2	65	75
2	3	103	106
2	5	79	81
2	6	73	56
2	7	136	135
2	8	93	89
2	9	137	144
2	10	98	103
3	1	249	246
3	3	281	267
3	5	167	146
3	6	81	51
3	7	175	163
3	9	257	255
4	3	59	51
4	4	72	76
4	5	130	125
4	6	49	46
4	7	61	50
4	9	104	102
5	0	138	137
5	1	65	77
5	2	206	199
5	3	35	34
5	4	283	262
5	5	51	52
5	6	159	154
5	7	104	101
5	8	234	231
6	2	52	55
6	6	67	66
6	7	66	51
H = -5			
0	0	232	216
0	2	172	183
0	4	133	122
0	6	323	316
0	8	491	485
0	10	335	315
1	0	225	233
1	1	162	168
1	2	312	321
1	3	75	78
1	4	364	363
1	5	164	172
1	6	211	219
1	8	40	27
1	9	98	101
1	10	51	55
2	0	100	110
2	1	156	158
2	2	83	91
2	3	163	156
2	4	213	214
2	5	185	178
2	6	241	237
2	7	328	320
2	8	138	142
2	9	281	280
2	10	149	156
2	11	206	210
3	0	41	30
3	1	246	259
3	2	102	102
3	3	313	319
3	4	105	107
3	5	91	92
3	6	66	48
4	0	147	158
4	1	189	189
4	2	72	80
4	3	244	238
4	4	55	40
4	5	341	339
4	6	104	87
4	7	195	190
4	8	143	145
4	9	181	183
4	10	168	190
5	0	135	130
5	2	121	124
5	3	44	37
5	4	123	114
5	6	95	41
5	7	66	44
5	8	164	156
5	9	47	51
5	10	42	26
6	0	164	180
6	2	210	212
6	4	226	219
6	5	100	96
6	6	218	210
6	8	234	219
6	9	65	59
7	0	90	95
7	1	109	109
7	3	149	147
7	4	40	40
7	5	108	112
7	6	149	136
7	7	104	110
8	0	49	57
8	1	109	119
8	2	59	70
8	3	226	226
8	5	238	234
8	7	258	248
H = -4			
0	0	449	482
0	2	878	892
0	4	558	545
0	6	405	412
0	8	410	407
0	10	180	187
0	12	148	159
1	0	67	86
1	1	80	85
1	2	84	87
1	3	98	113
1	4	206	192
1	5	41	47
1	6	158	161
1	7	161	168
1	8	169	163
1	9	148	153
1	10	164	165
1	11	47	42
1	12	174	196
2	0	223	241
2	1	402	423
2	2	284	290
2	3	579	582
2	4	391	389
2	5	458	453
2	6	145	141
2	7	403	405
2	8	52	33
2	9	177	189
2	10	174	176
2	11	87	96
2	12	78	81
3	1	172	184
3	2	107	107
3	3	79	75
3	4	103	92
3	5	131	143
3	7	199	200
3	8	99	94
3	9	195	203
3	10	60	66
3	11	224	234
4	0	286	306
4	1	255	270
4	2	223	226
4	3	365	372
4	4	286	262
4	5	447	440
4	6	199	187
4	7	98	96
4	8	112	110
4	9	139	124
4	10	120	124
4	11	107	114
5	0	80	79
5	1	47	57
5	2	44	47
5	4	158	175
5	6	212	210
5	8	81	78
5	9	130	133
5	10	154	157
5	11	126	128
6	0	303	330
6	1	114	114
6	2	323	326
6	3	64	63
6	4	279	279
6	5	167	158
6	6	165	178
6	7	48	22
6	8	129	131
6	9	112	112
6	10	135	129
7	0	105	112
7	2	165	167
7	3	35	22
7	4	116	119
7	5	111	111
7	6	67	53
7	7	104	113
7	8	151	155
7	9	89	99
8	0	97	68
8	1	198	210
8	2	76	81
8	3	268	260
8	5	241	234
8	7	273	267
9	2	50	43
9	3	44	38
9	4	49	33
9	5	48	40
9	6	65	17
9	7	134	133
10	1	92	99
10	2	146	141
10	3	131	129
10	4	116	111
H = -3			
0	0	354	373
0	4	133	115
0	6	432	409
0	8	238	230
0	10	113	122
0	12	81	73
1	0	310	330
1	1	350	371
1	2	569	573
1	3	375	373
1	4	637	637
1	5	336	337
1	6	501	496
1	7	268	276
1	8	387	339
1	9	203	216
1	10	255	277
1	11	74	88
1	12	189	212
2	0	97	101
2	1	256	269
2	2	48	44
2	3	51	65
2	4	252	223
2	5	235	228
2	7	409	396
2	9	58	52
2	10	41	44
2	11	60	55
2	12	90	105
3	0	186	197
3	1	480	523
3	2	73	72
3	3	583	584
3	4	246	231
3	5	434	415
3	6	140	140
3	7	393	380
3	8	71	61
3	9	308	313
3	10	49	56
3	11	266	280
4	0	332	357
4	1	220	231
4	2	317	331
4	3	280	281
4	4	178	180
4	5	323	297
4	9	71	72
4	10	52	67
4	11	57	60
5	0	113	126
5	1	101	101
5	2	536	534
5	3	45	49
5	4	523	506
5	5	35	32
5	6	441	424
5	7	65	72
5	8	228	230
5	9	113	103
5	10	215	229
5	11	63	63
6	0	403	443
6	1	55	49
6	2	415	425
6	3	40	42
6	4	276	265
6	7	92	88
6	8	106	104
6	9	116	116
6	10	60	64
7	0	183	192
7	1	187	202
7	2	172	186
7	3	165	159
7	4	320	291
7	5	153	158
7	6	239	227
7	7	195	188
7	8	220	215
7	9	214	209
7	10	96	103
8	0	67	75
8	1	171	189
8	2	105	103
8	3	147	150
8	5	123	108
8	6	42	27
8	7	107	96
8	8	95	94
8	9	53	48
9	0	113	108
9	1	139	146
9	3	128	130
9	4	62	51
9	5	151	150
9	7	219	227
9	8	97	92
10	0	101	115
10	1	37	39
10	2	153	153
10	3	42	50
10	4	104	87
10	5	64	52
10	6	118	107
11	2	106	103
H = -2			
0	0	167	142
0	2	196	199
0	4	90	95
0	6	53	55
0	8	407	401
0	10	346	354
0	12	143	152
1	0	92	81
1	1	78	72
1	2	240	220
1	3	377	367
1	4	605	556
1	5	388	384
1	6	594	572
1	7	245	236
1	8	351	346
1	9	202	195
1	10	102	102
1	12	52	49
2	0	37	29
2	1	400	396
2	2	386	369
2	3	553	531
2	4	71	68
2	5	280	262
2	6	307	293
2	7	170	177
2	8	111	110
2	9	291	290
2	11	179	195
2	12	105	115
3	0	122	132
3	1	829	895
3	2	77	77
3	3	579	633
3	4	326	302
3	5	500	572
3	7	449	443
3	8	88	77
3	9	209	210
3	11	161	162
4	0	36	19
4	1	49	55
4	3	243	223
4	4	121	92
4	5	411	382
4	6	181	167
4	7	311	314
4	8	156	157
4	9	50	54
4	10	147	158
4	11	121	135
5	0	447	489
5	1	414	415
5	2	771	765
5	3	259	252
5	4	516	501
5	5	161	147
5	6	539	529
5	7	121	101
5	8	235	228
5	9	78	83
5	10	160	163
6	0	153	162
6	1	64	64
6	2	111	102
6	3	122	117
6	4	78	73
6	5	40	29
6	6	266	267
6	7	44	45
6	8	244	257
6	9	48	23
6	10	170	185
7	0	347	372
7	1	310	340
7	2	286	286
7	3	232	225
7	4	434	403
7	5	180	185
7	6	253	239
7	7	180	183
7	8	153	198
7	9	134	133
8	0	81	88
8	1	29	24
8	2	31	31
8	3	41	44
8	5	95	76
8	6	51	62
8	7	116	109
8	8	80	87
8	9	172	179
9	0	152	169
9	1	269	286
9	2	73	74
9	3	269	255
9	4	70	55
9	5	179	155
9	6	56	65
9	7	132	129
9	8	109	97
10	0	56	55
10	1	24	21
10	3	88	90
10	4	69	20
10	5	57	97
10	6	39	17
10	7	72	67
11	0	181	202
11	1	26	36
11	2	215	204
11	4	216	197
12	1	33	32
H = -1			
0	4	245	186
0	6	338	334
0	8	415	418
0	10	296	287
0	12	133	140
1	3	721	671
1	4	177	175
1	5	41	42
1	6	93	75
1	7	44	24
1	10	41	17
1	11	99	108
1	12	43	27
2	0	72	62
2	1	554	598
2	2	127	119
2	3	648	592
2	4	519	479
2	5	653	613
2	6	217	211
2	7	459	459
2	8	53	59
2	9	349	357
2	10	54	53
2	11	189	201
2	12	100	95
3	0	174	183
3	1	961	961
3	2	222	215
3	3	487	440
3	4	459	401
3	7	94	93
3	8	50	48
3	9	69	74
3	10	104	109
4	0	144	157
4	1	42	36
4	2	227	219
4	3	812	747
4	4	368	359
4	5	756	741
4	6	278	287
4	7	446	432
4	8	248	240
4	9	203	202
4	10	192	205
4	11	167	177
5	0	383	420
5	1	164	159
5	2	336	314
5	3	94	78
5	4	207	212
5	5	107	112
5	6	285	270
5	11	37	39
6	0	334	370
6	1	110	96
6	2	363	355
6	3	164	150
6	4	402	403
6	5	32	39
6	6	434	447
6	8	328	372
6	9	46	45
6	10	224	237
7	0	133	153
7	1	289	285
7	3	157	157
7	4	88	92
7	5	140	139
7	6	95	84
7	7	65	64
7	8	144	136
7	10	53	51
8	0	146	152
8	1	351	374
8	2	34	37
8	3	330	318
8	5	335	314
8	6	68	32
8	7	250	240
8	8	112	126
8	9	176	183
9	0	81	64
9	1	165	161
9	3	147	160
9	4	29	42
9	5	41	44
10	0	219	245
10	1	125	123
10	2	221	215
10	3	194	174
10	4	197	193
10	5	157	140
10	6	165	170
10	7	55	57
11	0	105	113
11	1	102	93
11	2	56	61
11	3	31	21
11	4	69	56
11	5	32	13
12	0	98	109
12	1	55	55
12	2	168	156
H = 0			
0	4	314	317
0	6	319	329
0	8	256	246
0	10	233	227
1	3	104	111
1	4	405	382
1	5	150	125
1	6	255	260
1	7	53	74
1	8	160	194
1	9	176	177
1	10	157	156
1	11	135	143
2	2	558	556
2	3	370	361
2	4	354	333
2	5	473	463
2	6	44	18
2	7	294	308
2	8	94	88
2	9	231	240
2	10	61	55
2	11	96	104
3	1	125	116
3	2	237	215
3	4	167	162
3	5	178	161
3	6	57	20
3	7	372	354
3	8	61	31
3	9	268	262
3	10	66	64
3	11	151	155
4	0	262	268
4	1	29	24
4	2	511	482
4	3	640	609
4	4	367	357
4	5	276	270
4	6	187	189
4	7	275	270
4	8	181	185
4	9	124	124
4	10	125	118
5	1	49	45
5	2	133	127
5	4	212	167
5	5	119	76
5	6	150	174
5	7	123	136
5	8	224	224
5	9	158	145
5	10	107	104
6	0	357	391
6	1	194	177
6	2	484	450
6	3	441	407
6	4	396	386
6	5	59	51
6	6	320	313
6	7	58	50
6	8	220	201
6	9	39	33
6	10	105	94
7	1	99	61
7	2	156	152
7	3	169	155
7	4	150	147
7	5	127	102
7	6	129	136
7	7	114	73
7	8	109	111
7	9	71	63
8	0	204	218
8	1	398	384
8	3	256	279
8	5	372	354
8	6	63	68
8	7	229	223
8	8	73	28
9	1	131	71
9	2	105	97
9	3	102	80
9	5	138	132
9	7	118	129
10	0	245	255
10	1	176	159
10	2	130	123
10	3	201	167
10	4	162	151
10	5	150	133
10	6	159	153
11	1	65	60
11	2	66	76
11	3	39	23
11	4	123	103
11	5	43	25
12	0	126	139
12	1	62	50
12	2	207	197
H = 1			
0	4	557	510
0	6	172	160
0	8	61	62
0	10	52	49
1	1	565	579
1	2	777	791
1	3	298	302
1	4	648	643
1	5	139	148
1	6	546	539
1	7	248	240
1	8	357	376
1	9	211	213
1	10	198	212
2	0	76	62
2	1	85	94
2	2	811	786
2	3	45	46
2	4	224	197
2	5	274	259
2	7	54	32
2	8	71	70
2	9	46	16
2	10	96	103
3	0	172	163
3	1	511	524
3	2	94	97
3	3	310	278
3	4	68	61
3	5	437	430
3	7	365	369
3	8	39	40
3	9	225	230
3	10	44	38
4	0	144	157
4	1	310	313
4	2	255	253
4	3	408	386
4	4	38	32
4	5	38	43
4	6	40	34
4	8	67	70
4	9	118	115
5	0	386	419
5	1	235	250
5	2	284	281
5	3	108	115
5	4	475	456
5	6	346	349
5	8	204	206
5	9	66	57
6	0	340	376
6	1	74	85
6	2	411	384
6	3	121	127
6	4	176	169
6	5	50	51
6	7	87	79
6	8	52	47
7	0	142	153
7	1	238	229
7	2	401	368
7	3	284	265
7	4	245	231
7	5	262	258
7	6	146	134
7	7	192	195
7	8	114	105
8	0	141	152
8	1	131	168
8	3	105	105
8	5	153	142
8	6	49	52
9	0	66	64
9	1	322	329
9	2	113	99
9	3	265	265
9	5	205	196
9	6	41	45
9	7	173	166
10	0	221	245
10	1	86	85
10	2	75	65
10	3	49	51
10	4	116	102
11	0	116	113
11	2	163	162
11	3	46	47
11	4	186	174
12	0	96	109
12	1	51	49
H = 2			
0	0	166	142
0	2	244	254
0	4	215	211
0	6	344	327
0	8	210	217
1	0	88	81
1	1	640	664
1	2	569	566
1	3	223	224
1	4	525	511
1	5	140	132
1	6	374	364
1	7	207	207
1	8	140	133
1	9	59	52
2	0	41	29
2	1	123	141
2	2	228	219
2	3	352	350
2	4	138	137
2	5	255	257
2	6	119	122
2	7	188	184
2	8	123	116
2	9	89	103
3	0	125	132
3	1	590	623
3	2	102	106
3	3	670	667
3	4	188	173
3	5	425	418
3	6	73	70
3	7	120	123
3	8	51	54
3	9	91	85
4	0	36	19
4	1	61	64
4	2	73	56
4	3	162	155
4	4	206	209
4	5	195	195
4	6	120	118
4	7	92	93
4	8	75	73
4	9	135	126
5	0	452	489
5	1	451	462
5	2	307	302
5	3	240	235
5	4	465	447
5	6	151	145
5	8	105	95
6	0	156	162
6	1	129	127
6	2	109	110
6	4	113	106
6	5	101	100
6	6	126	122
6	7	63	46
6	8	144	135
7	0	357	372
7	1	204	216
7	2	342	341
7	3	247	249
7	4	59	58
7	5	166	163
7	6	87	97
7	7	94	85
8	0	90	88
8	1	84	91
8	2	133	136
8	3	105	109
8	5	93	80
9	0	153	169
9	1	377	398
9	2	180	178
9	3	181	187
9	4	72	60
9	5	121	115
10	0	57	56
10	1	33	38
10	3	89	85
11	0	184	202
11	1	55	50
11	2	184	192
H = 3			
0	0	356	373
0	2	537	520
0	4	349	340
0	6	183	174
0	8	153	147
1	0	315	330
1	1	382	409
1	3	93	95
1	5	68	64
1	6	77	80
1	7	68	71
2	0	95	101
2	1	436	463
2	2	124	126
2	3	503	508
2	5	276	268
2	6	121	123
2	7	159	162
2	8	89	78
3	0	186	197
3	1	188	197
3	2	59	57
3	3	267	250
3	4	63	41
3	5	73	53
3	6	87	80
3	8	50	31
4	0	339	357
4	1	336	357
4	2	287	291
4	3	304	297
4	4	180	209
4	5	313	303
4	6	137	126
4	7	198	197
5	0	105	126
5	1	94	111
5	2	118	119
5	4	165	164
5	6	55	41
6	0	404	443
6	1	36	44
6	2	298	290
6	4	235	243
6	6	237	235
7	0	182	192
7	1	128	125
7	3	126	110
7	4	57	58
7	6	56	50
8	0	54	75
8	1	186	159
8	2	100	91
8	3	195	191
8	4	48	52
8	5	156	151
9	0	108	108
9	1	183	192
9	2	75	71
10	0	94	115
10	1	62	55
10	2	130	143
H = 4			
0	0	456	482
0	2	401	391
0	4	166	174
0	6	114	112
1	0	87	86
1	1	66	64
1	2	128	117
1	3	119	114
1	4	68	68
1	6	66	57
2	0	227	241
2	1	305	317
2	3	315	306
2	4	67	65
2	5	168	153
2	6	108	106
3	1	112	116
3	3	55	28
3	5	181	168
3	6	69	33
4	0	286	306
4	1	144	147
4	2	257	246
4	3	104	105
4	4	220	195
4	5	242	234
4	6	114	110
5	0	77	79
5	3	123	121
5	4	117	106
5	5	102	106
6	0	302	330
6	1	90	99
6	2	239	244
6	4	223	207
6	5	83	91
7	0	109	112
7	1	34	28
7	2	102	98
7	4	166	159
8	0	91	68
8	1	173	174
8	2	122	123
8	3	166	165
9	0	36	26
H = 5			
0	0	211	216
0	2	272	268
1	0	221	233
1	1	157	152
1	2	192	189
1	3	131	134
1	4	163	180
2	0	103	110
2	1	186	193
2	3	79	87
2	4	72	79
3	1	216	202
3	2	50	41
3	3	202	189
4	0	148	158
4	1	51	58
4	2	79	82
4	3	40	13
4	4	51	49
5	0	135	130
5	1	59	65
5	2	190	185
5	3	76	81
6	0	161	180
6	2	94	84
7	0	91	95
7	1	132	133
8	0	48	57
H = 6			
0	0	72	39
0	2	108	104
0	4	198	173
1	0	251	254
1	1	97	107
1	2	176	166
2	0	58	60
2	1	52	48
2	2	67	62
3	1	226	219
4	1	71	62
5	0	143	137
5	0	143	137



(a) (b)

Figure 1.—Electron density maps in the plane of the π-cyclopentadienyl ligand. (a) The "observed" electron density map, with contours at 1-electron intervals. The lowest (dashed) contour represents zero electron density. (b) The "difference" synthesis, showing the positions of the five π-cyclopentadienyl hydrogen atoms. Contours are at 0.1-electron intervals, the dashed line representing the 0.1 e⁻/Å³ contour.

Bond lengths are collected in Table V, while interatomic angles are shown in Table VI.

The complex may be regarded as a d^6 Fe(II) derivative; if, as is customary, the π-cyclopentadienyl ligand is regarded as tridentate, then the central iron atom has a pseudooctahedral coordination. Angles between the monodentate ligands—*viz.*, C(6)–Fe–C(8) = 90.6°, C(6)–Fe–C(9) = 86.0°, C(8)–Fe–C(9) = 94.1° (each with σ = 0.3°)—are each close to the ideal octahedral value of 90°. In keeping with the observed diamagnetism of the complex, each Fe(II) ion reaches the appropriate

TABLE II

FINAL POSITIONAL PARAMETERS FOR $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$[a–c]

Atom	x	y	z
Fe	0.13069 (12)	0.33888 (7)	0.26566 (7)
O(1)	−0.1348 (9)	0.1767 (4)	0.3299 (6)
O(2)	−0.2285 (9)	0.4553 (5)	0.0774 (5)
C(1)	0.3256 (12)	0.2119 (7)	0.2347 (9)
C(2)	0.3016 (12)	0.2994 (8)	0.1567 (7)
C(3)	0.3784 (12)	0.4004 (7)	0.2189 (9)
C(4)	0.4593 (11)	0.3760 (10)	0.3442 (10)
C(5)	0.4212 (12)	0.2540 (10)	0.3525 (8)
C(6)	0.0966 (8)	0.4570 (5)	0.3799 (5)
C(7)	0.0015 (8)	0.4521 (5)	0.4603 (5)
C(8)	−0.0302 (10)	0.2410 (5)	0.3043 (6)
C(9)	−0.0861 (11)	0.4081 (6)	0.1504 (6)
H(1)	0.2783	0.1224	0.2109
H(2)	0.2299	0.2913	0.0574
H(3)	0.3809	0.4857	0.1808
H(4)	0.5327	0.4367	0.4191
H(5)	0.4628	0.2049	0.4370
H(6)	0.1678	0.5405	0.3768
H(7)	−0.0775	0.3720	0.4661

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the last digit of the preceding number. [b] Hydrogen atoms are in calculated positions.[11] [c] Hydrogen atoms are numbered similarly to the carbon atoms to which they are attached.

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$[a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	193.7 (3.2)	62.1 (0.9)	59.7 (1.1)	−3.7 (1.8)	105.5 (2.6)	−26.5 (1.1)
O(1)	446 (19)	90 (4)	218 (9)	−112 (14)	437 (25)	−60 (10)
O(2)	391 (18)	155 (6)	111 (5)	152 (17)	28 (18)	30 (11)
C(1)	275 (22)	108 (7)	176 (12)	38 (20)	245 (29)	−65 (15)
C(2)	306 (23)	169 (9)	110 (8)	48 (25)	221 (25)	−30 (16)
C(3)	314 (25)	104 (7)	188 (12)	−69 (20)	300 (31)	−37 (16)
C(4)	134 (18)	234 (12)	216 (13)	−72 (24)	132 (25)	−318 (19)
C(5)	284 (24)	261 (15)	118 (9)	283 (31)	205 (26)	122 (20)
C(6)	214 (16)	63 (5)	62 (5)	11 (14)	87 (16)	−3 (8)
C(7)	209 (16)	67 (5)	65 (5)	23 (14)	102 (16)	−7 (8)
C(8)	273 (19)	70 (5)	103 (7)	25 (17)	196 (20)	−43 (10)
C(9)	303 (22)	99 (6)	87 (7)	−35 (19)	152 (22)	−43 (11)

[a] The anisotropic thermal parameter, T, is defined as: $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}kh - \beta_{13}hl - \beta_{23}kl)$. [b] Estimated standard deviations are shown in parentheses.

TABLE IV

ATOMIC VIBRATION ELLIPSOIDS FOR $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$[a]

	$B_{\max}$, Å	B_{med}, Å^2	$B_{\min}$, Å^2
Fe	3.74	3.02	2.08
O(1)	11.38	4.70	3.50
O(2)	10.16	7.37	3.64
C(1)	9.10	5.55	2.79
C(2)	9.18	5.73	2.97
C(3)	9.19	5.37	3.39
C(4)	19.86	3.30	1.96
C(5)	15.60	4.58	2.77
C(6)	3.55	3.15	2.86
C(7)	3.81	3.22	2.66
C(8)	5.60	4.03	2.36
C(9)	5.92	4.48	3.12

[a] Axis dimensions for the vibration ellipsoids are presented in terms of the isotropic thermal parameter, B. The transformation to root-mean-square displacement is: $(\overline{U^2})^{1/2} = (B/8\pi^2)^{1/2}$.

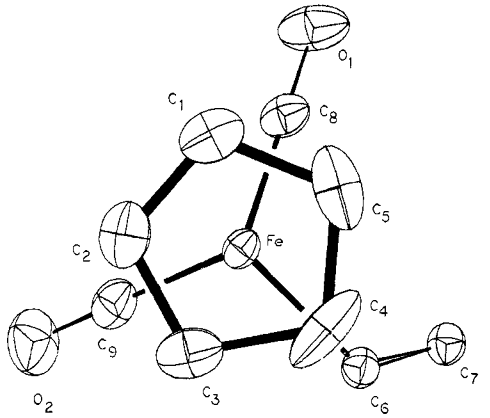


Figure 2.—The asymmetric unit of the molecule, projected in the plane of the π-cyclopentadienyl ring. The 68% probability contours of the atomic vibration ellipsoids are shown. (The diagram was constructed using OTLIPS, an IBM 1620 program written by Dr. P. H. Bird.)

noble gas configuration (*i.e.*, that of krypton) by the donation of six electrons from a π-cyclopentadienyl ligand, two electrons from each of the two carbonyl ligands, and two electrons from a butadiene-to-metal σ bond.[14]

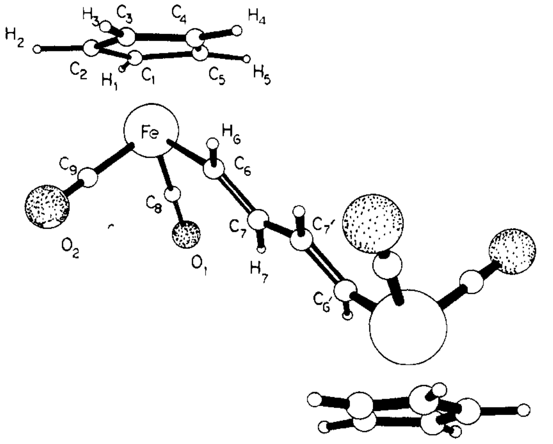


Figure 3.—Numbering of atoms in the $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$ molecule. Atoms related to the basic asymmetric unit by the transformation $(-x, 1-y, 1-z)$ are marked with a prime.

TABLE V

INTRAMOLECULAR DISTANCES WITHIN THE $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$ MOLECULE[a]

Atoms	Dist, Å	Atoms	Dist, Å
(a) Distances within the π-Cyclopentadienyl Ligand			
Fe–C(1)	2.094 (8)	C(1)–C(2)	1.327 (12)[b]
Fe–C(2)	2.091 (8)	C(2)–C(3)	1.360 (12)[b]
Fe–C(3)	2.088 (8)	C(3)–C(4)	1.387 (13)[b]
Fe–C(4)	2.097 (10)	C(4)–C(5)	1.433 (14)[b]
Fe–C(5)	2.074 (9)	C(5)–C(1)	1.369 (13)[b]
Fe–C (av)	2.089 (8)[c]	C–C (av)	1.375 (35)[c]
(b) Distances within the *trans*-Buta-1,3-diene Ligand			
Fe–C(6)	1.987 (5)	C(6)–C(7)	1.340 (7)
		C(7)–C(7′)	1.450 (11)
(c) Distances within the Carbonyl Ligands			
Fe–C(8)	1.747 (6)	C(8)–O(1)	1.143 (8)
Fe–C(9)	1.752 (7)	C(9)–O(2)	1.146 (9)
Fe–C (av)	1.750 (7)[c]	C–O (av)	1.145 (9)[c]

[a] Estimated standard deviations (esd's), shown in parentheses, are right-adjusted to the least significant digit in the preceding number. [b] Carbon–carbon distances within the π-cyclopentadienyl ring are almost certainly low, owing to a large amplitude of libration for this system. [c] Esd's for mean values are defined as the rms deviation or as σ_{mean} (whichever is the greater).

The cyclopentadienyl ligand takes up the most symmetric possible rotational orientation such that the iron-to-butadiene linkage (Fe–C(6)) passes directly below

---

[14] An equally satisfactory way of enumerating electrons is to consider the molecule as an Fe(0) complex with five electrons donated from a neutral π-cyclopentadienyl ligand, two electrons from each carbonyl ligand, and one electron from the metal–carbon σ bond. The difference is one of formalism only.

Table VI

Interatomic Angles within the $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$ Molecule[a,b]

Atoms	Angle, deg	Atoms	Angle, deg
(a) Within the π-Cyclopentadienyl Ring			
C(1)–Fe–C(2)	37.0 (3)	C(1)–C(2)–C(3)	110.7 (8)
C(2)–Fe–C(3)	38.0 (3)	C(2)–C(3)–C(4)	108.1 (8)
C(3)–Fe–C(4)	38.7 (4)	C(3)–C(4)–C(5)	105.2 (9)
C(4)–Fe–C(5)	40.2 (4)	C(4)–C(5)–C(1)	107.5 (9)
C(5)–Fe–C(1)	38.4 (4)	C(5)–C(1)–C(2)	108.5 (8)
Av	38.5 (1.2)	Av	108.0 (1.8)
(b) Within the Buta-1,3-diene System			
Fe–C(6)–C(7)	131.8 (4)	C(6)–C(7)–C(7′)	123.8 (7)
(c) Within the Carbonyl Ligands			
Fe–C(8)–O(1)	179.7 (6)	Fe–C(9)–O(2)	178.2 (7)
(d) Between Ligands			
C(6)–Fe–c.o.g.	121.9 (3)	C(6)–Fe–C(8)	90.6 (3)
C(8)–Fe–c.o.g.	126.1 (4)	C(6)–Fe–C(9)	86.0 (3)
C(9)–Fe–c.o.g.	126.7 (4)	C(8)–Fe–C(9)	94.1 (3)

[a] See footnotes *a–c* to Table V. [b] The symbol "c.o.g." represents the centroid of the π-cyclopentadienyl system.

C(4) (with C(4)···C(6) = 2.815 ± 0.010 Å) while iron–carbonyl bonds pass beneath the C(1)–C(5) and C(2)–C(3) bonds such that C(1)···C(8) = 2.861 ± 0.010 Å, C(5)···C(8) = 2.895 ± 0.011 Å and C(2)···C(9) = 2.889 ± 0.011 Å, C(3)···C(9) = 2.935 ± 0.011 Å (see Figure 2).

The π-Cyclopentadienyl Ligand.—The root-mean-square deviation of the π-cyclopentadienyl carbon atoms from their least-squares plane $[-0.9797X + 0.2000Y + 0.0090Z + 0.5911 = 0]$ is only 0.005 Å (see Table VII). Individual bond angles around the five-membered ring range from 105.2 to 110.7°, averaging 108.0°—the ideal value for a regular planar pentagon. Carbon–carbon bond distances within the ring range from 1.327 to 1.433 Å and average 1.375 Å. This mean value is significantly lower than the carbon–carbon bond distance of 1.431 ± 0.005 Å found from an electron diffraction study of ferrocene[15] (and which is probably one of the most accurate estimates of a carbon–carbon bond length within a π-cyclopentadienyl system). Such discrepancies in other complexes have previously been ascribed to librational motion of the π-cyclopentadienyl ligand.[16] This must surely be true for the present case—it may be seen from Figure 2 that each of the π-cyclopentadienyl carbon atoms defines an ellipsoid of vibration in which the maximum amplitude of vibration is tangential to an imaginary circle drawn through the five carbon atoms. The observed carbon–carbon lengths (and their associated estimated standard deviations (esd's)) are thus underestimated by an uncertain amount. [It should be noted that the independent structural work of Davis[1b] on this complex also reveals large anisotropic motions for the atoms of the π-cyclopentadienyl system. Although no esd's are available, the average C–C distance is reported as 1.41 Å. The difference between this value and ours may, however, be derived from the hydrogen contributions being omitted in Davis's calculations.]

Table VII

Important Planes within the $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$ Molecule[a,b]

Atom	Dev, Å	Atom	Dev, Å
(a) π-Cyclopentadienyl Ring:			
$-0.9797X + 0.2000Y + 0.0090Z + 0.5911 = 0$			
C(1)	−0.001	C(4)	−0.007
C(2)	−0.003	C(5)	+0.005
C(3)	+0.006	Fe*	+1.731
(b) The Buta-1,3-diene System:			
$0.6232X - 0.3338Y + 0.7072Z - 0.4746 = 0$			
C(6)	0.000	Fe*	+0.051
C(7)	0.000		

[a] All planes are expressed in Cartesian coordinates (*X*, *Y*, *Z*). These are related to the natural crystal axes (*x*, *y*, *z*) by the transformations: $X = xa + zc\cos\beta$, $Y = yb$, $Z = zc\sin\beta$. [b] A plane is derived using unit weights for all atoms other than those marked with an asterisk.

Iron–carbon distances range from 2.074 ± 0.009 to 2.097 ± 0.010 Å, averaging 2.089 ± 0.008 Å (*cf.* 2.10 Å in the determination by Davis[1b]). The π-cyclopentadienyl system is thus linked symmetrically to the central metal ion.

The Carbonyl Ligands.—Each of the metal–carbonyl linkages is linear within the limits of experimental error, appropriate angles being ∠Fe–C(8)–O(1) = 179.7 ± 0.6° and ∠Fe–C(9)–O(2) = 178.2 ± 0.7°. The iron–carbonyl bond lengths are Fe–C(8) = 1.747 ± 0.006 Å and Fe–C(9) = 1.752 ± 0.007 Å (*cf.* 1.70 and 1.76 Å in Davis's study[1b]). The species most similar to the present compound for which crystallographic information is available are $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$[17] and $\pi\text{-}C_5H_5Fe(CO)_2(CH_2CO_2H)$.[18] The Fe–CO bond distances found in these molecules are 1.70 Å (average) and 1.72 Å (average), respectively.

The carbon–oxygen bond lengths of 1.143 ± 0.008 and 1.146 ± 0.009 Å in the present study (1.14 and 1.16 Å in Davis's independent study[1b]) are typical of carbonyl ligands bonded to a transition metal.

The Iron–Butadiene–Iron System.—The present crystallographic determination yields an Fe–C(sp^2) σ-bond distance of 1.987 ± 0.005 Å. (Davis's value for this bond length is 2.05 Å, with an unspecified esd.[1b]) We feel that our bond length has a sufficiently low esd for us to claim justifiably that this bond is significantly shorter than the iron–carbon bonds of unit bond order in $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$ [Fe–C(sp^3) = 2.11 ± 0.02 Å] and in $\pi\text{-}C_5H_5Fe(CO)_2(CH_2CO_2H)$ [Fe–C(sp^3) = 2.06 ± 0.02 Å]. After allowing for the difference of approximately 0.03 Å in the covalent radii of sp^2- and sp^3-hybridized carbon atoms, the present iron–carbon bond shows a contraction of *ca.* 0.04–0.09 Å from the regular Fe–C(sp^2) single-bond distance. This is,

---

(15) R. K. Bohn and A. Haaland, *J. Organometal. Chem.* (Amsterdam), **5**, 470 (1966).

(16) P. J. Wheatley in "Perspectives in Structural Chemistry," Vol. 1, J. D. Dunitz and J. A. Ibers, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 9.

(17) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(18) M. L. H. Green, J. K. P. Ariyaratne, A. M. Bjerrum, M. Ishaq, and C. K. Prout, *Chem. Commun.*, 430 (1967).

of course, entirely consistent with previous studies showing metal–carbon bond contractions in other systems (such as acyls,[19] aryls,[20,21] or perfluoroaryls[20,22–24]) which are in conjugation with a metal atom.

Carbon–carbon bond lengths within the *trans*-buta-1,3-diene fragment are: C(6)–C(7) = 1.340 ± 0.007 Å, C(7)–C(7′) = 1.450 ± 0.011 Å, C(7′)–C(6′) = 1.340 ± 0.007 Å (1.36, 1.47, 1.36 Å from Davis's study[1b]). These distances are each in good agreement with the bond distances in *trans*-buta-1,3-diene itself—1.337 ± 0.005, 1.483 ± 0.010, 1.337 ± 0.005 Å, as determined from electron diffraction studies.[25]

Finally, it should be noted that possible reasons for the C_4H_4 moiety exhibiting a *single* proton magnetic resonance peak at τ 3.76 have been discussed in another publication.[1a]

The Crystal Structure

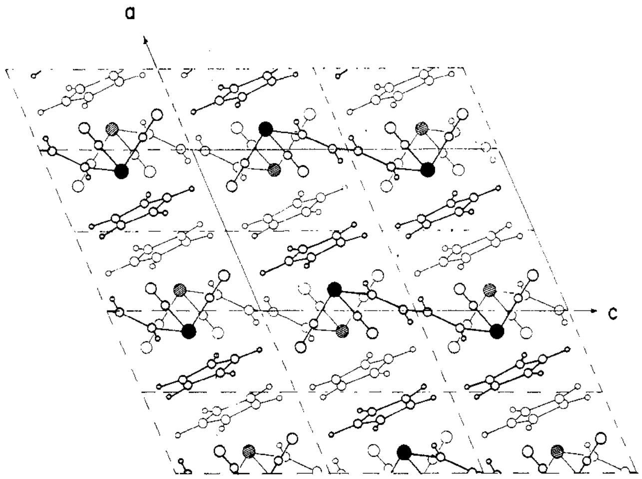


Figure 4.—Packing of molecules within the crystal, viewed down *b*.

Figure 4 shows the packing of molecules in the crystal as viewed down *b*. The closest intermolecular contacts (of each type) are: hydrogen···hydrogen, 2.48 Å; oxygen···hydrogen, 2.73 Å; carbon···hydrogen, 2.83 Å; oxygen···carbon, 3.25 Å; oxygen···oxygen, 3.41 Å; and carbon···carbon, 3.50 Å.

Acknowledgments.—We wish to thank the late Professor G. F. Emerson and Mr. W. P. Giering for suggesting this problem. This work has been generously supported by the National Science Foundation (Grant GP-8077) and the Advanced Research Projects Agency (Contract SD-88). J. W. acknowledges, with gratitude, the receipt of a Graduate National Fellowship from Harvard University for 1967–1969.

(19) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).
(20) M. R. Churchill, T. A. O'Brien, M. D. Rausch, and Y. F. Chang, *Chem. Commun.*, 992 (1967).
(21) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc., A*, 266 (1969).
(22) M. D. Rausch, A. K. Ignatowicz, M. R. Churchill, and T. A. O'Brien, *J. Am. Chem. Soc.*, **90**, 3242 (1968).
(23) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc., A*, 2970 (1968).
(24) M. R. Churchill and T. A. O'Brien, *ibid.*, *A*, 1110 (1969).
(25) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

The Molecular Structure of Diazulenetetrairon Decacarbonyl in Crystalline $(C_{10}H_8)_2Fe_4(CO)_{10}\cdot C_2H_4Cl_2$

BY MELVYN R. CHURCHILL[1] AND PETER H. BIRD

Received January 30, 1969

The reaction of azulene with an iron carbonyl is known to give rise to azulenediiron pentacarbonyl and a compound of high molecular weight, previously formulated as $(C_{10}H_8)_2Fe_5(CO)_{13}$. It is now shown that this latter complex is actually $(C_{10}H_8)_2Fe_4(CO)_{10}$ and that it crystallizes from a 1,2-dichloroethane–hexane mixture as $(C_{10}H_8)_2Fe_4(CO)_{10}\cdot C_2H_4Cl_2$. Unit cell data are: $a = 17.296 \pm 0.012$ Å, $b = 15.541 \pm 0.011$ Å, $c = 12.915 \pm 0.009$ Å, $\beta = 114.53 \pm 0.02°$, $Z = 4$, space group C2/c (C_{2h}^6; no. 15). Observed and calculated densities are 1.818 ± 0.015 and 1.805 g cm^{-3}, respectively. A single-crystal X-ray diffraction study has been completed using data to $\sin\theta = 0.40$ (Mo Kα radiation) measured with a scintillation counter. All nonhydrogen atoms have been located, the final discrepancy index being $R_F = 6.22\%$ for the 2040 independent, nonzero reflections. The crystal is composed of discrete molecular units of $(C_{10}H_8)_2Fe_4(CO)_{10}$ along with 1,2-dichloroethane of crystallization (which is disordered). The polynuclear azuleneiron–carbonyl complex has crystallographically imposed C_2 symmetry and is composed of a 4-*endo*,4′-*endo*-diazulene ligand whose five-membered rings are bridged by an $Fe_2(CO)_4$ moiety, while $Fe(CO)_3$ groups are linked to the 1,3-diene systems remaining in each of the seven-membered rings.

Introduction

The present paper is the sixth in our series on transition metal complexes of azulene and follows detailed reports on the crystal structures of $C_{10}H_8Fe_2(CO)_5$,[2] $[C_{10}H_8Mo(CO)_3CH_3]_2$,[3] $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$,[4] $C_{10}H_8Mn_2(CO)_6$,[5] and $(C_{10}H_8)_2Fe$.[6]

The reaction of azulene with an iron carbonyl (*i.e.*,

(1) Research Fellow of the Alfred P. Sloan Foundation, 1968–1970.
(2) M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).
(3) P. H. Bird and M. R. Churchill, *ibid.*, **7**, 349 (1968).
(4) M. R. Churchill and P. H. Bird, *ibid.*, **7**, 1545 (1968).
(5) M. R. Churchill and P. H. Bird, *ibid.*, **7**, 1793 (1968).
(6) M. R. Churchill and J. Wormald, *ibid.*, **8**, 716 (1969).