carbon atoms), the "effective contraction" of the Fe–CO bond length, relative to the Fe–CF_2 distance, is ~0.15 A.[23]

Since such species as $(C_nH_{2n+1})_2Fe(CO)_4$ are not known, no comparison of analogous alkyl and fluoroalkyl complexes is possible. There are, however, a number of polynuclear iron–carbonyl species which, formally at least, contain simple iron–carbon σ bonds, but a wide variety of bond lengths have been observed. For example, the ferracyclopentadiene species $(CH_3C_2OH)_2Fe_2(CO)_6$,[24] $C_6H_5C_2C_6H_5Fe_2(CO)_6$,[25] and black $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[26] have iron–carbon σ bonds ranging from 1.948 to 2.063 A in length. The acetylene complex violet $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[26] has eight iron–carbon σ bonds varying from 1.954 to 2.057 A. The heterocyclic $(C_6H_5C_2H)_3CoFe_2(CO)_5$[27] has iron–carbon σ bonds of 2.006, 2.088, and 2.097 A, and the σ-vinyl complex, $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$, has an iron–carbon distance of 1.99 A.[28] In each of the above molecules there is a considerable likelihood that the iron–carbon linkage is part of a large delocalized system, rather than being an isolated σ bond.

However, the complex $\overline{(OC)_2FeC_5H_4\text{–}CH_2Fe(CO)_4}$ *does* have a distinct Fe–CH_2 bond of length 2.123 A,[29] but, since the iron atom is in a formal +1 oxidation state and the over-all configuration may well involve some strain in the Fe–CH_2 linkage, a direct comparison of this bond length with the Fe–CF_2 distance in *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$ is not strictly valid. The crystal structure of π-$C_5H_5Fe(CO)_2(\sigma$-$C_5H_5)$ has recently been determined;[30] the Fe^{II}–CH< distance is found to be 2.11 ± 0.02 A, but the structure is of limited accuracy. Thus, although further substantiation would be welcome, it seems that the contraction in iron–carbon bond length caused by fluorinating the α-carbon atom is probably about 0.05 A in Fe(II) complexes.

The Crystal Structure

All intermolecular contacts less than 3.5 A are collected in Table VII. The shortest F···F contact is 2.91 A between F_5 and F_5 ($^1/_2 - x$, $1 - y$, $^1/_2 - z$). There are several F···O contacts below 3.0 A, and it is possible that these participate in distorting the iron atom coordination sphere from strict C_{2v} symmetry.

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[23] The "effective contraction" defined here is one of the few possible measures of the relative amounts of π bonding in metal–carbon linkages. A comparison with values for other molecules may be made by consulting Table V of ref 4.

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

The Crystal and Molecular Structure of Azulene Diiron Pentacarbonyl

BY MELVYN R. CHURCHILL

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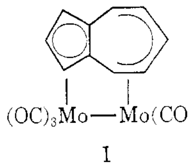
Azulene diiron pentacarbonyl, $C_{10}H_8Fe_2(CO)_5$, crystallizes in the triclinic space group $C\bar{1}$ (no. 2) with $a = 7.32 \pm 0.01$ A, $b = 14.48 \pm 0.02$ A, $c = 14.76 \pm 0.02$ A, $\alpha = 116.2 \pm 0.2°$, $\beta = 92.3 \pm 0.2°$, $\gamma = 93.0 \pm 0.2°$, $Z = 4$. A three-dimensional single-crystal X-ray analysis, based on 2579 independent nonzero reflections collected with an automated diffractometer, has been completed ($R_F = 10.75\%$). The carbon atoms from the five-membered ring of the azulene form a π-cyclopentadienyl system which is bonded to an $Fe(CO)_2$ group, while three atoms of the seven-membered ring participate in a π-allyl linkage to an $Fe(CO)_3$ group. Unequal Fe–C(allyl) bond lengths, a distortion of the azulene ligand from planarity, and a rather long iron–iron bond of 2.782 A indicate that the molecule may be rather strained.

Introduction

The preparation of molybdenum- and iron–azulene complexes such as $C_{10}H_8Mo_2(CO)_6$[1] and $C_{10}H_8Fe_2(CO)_5$[2] was reported in 1958. An investigation of their proton magnetic resonance spectra led to the suggestion of a number of structures, each involving metal–diene or metal–triene bonding, but no unique formulation was possible.[3] King and Bisnette[4] have pointed out that recent developments make it likely that $C_{10}H_8Mo_2(CO)_6$ is represented as in I, with a π-cyclopentadienyl–metal



I

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linkage. A comparison of $[C_{10}H_8Mn(CO)_3]_2$[3] and $[C_{10}H_8V(CO)_4]_2$[5] with related mononuclear complexes has indicated that in these systems, as well as in $C_{10}H_8Mo_2(CO)_6$, the five-membered ring of the azulene may function as a π-cyclopentadienyl ligand.[4] Although mass spectral studies have confirmed[6] the stoichiometry of $C_{10}H_8Fe_2(CO)_5$, no unambiguous suggestion of its structure has been made. (However, a number of other possible structures have been considered.[7])

In an attempt to clarify this situation, a single-crystal X-ray structural analysis of $C_{10}H_8Fe_2(CO)_5$ was undertaken. A preliminary account of this work has been published.[8]

Collection and Reduction of X-Ray Data

The compound was prepared from the reaction of azulene with diiron enneacarbonyl, $Fe_2(CO)_9$, in refluxing pentane[9] and shown to be identical with the product obtained by using iron pentacarbonyl.[3]

The crystal used in the analysis was needlelike, with dimensions 0.30 × 0.13 × 0.12 mm. It was mounted along its needle axis, *a*, and inserted in a 0.2-mm diameter thin-walled capillary tube. The absorption coefficient, μ, is 21.5 cm^{-1}. If the specimen is regarded as approximating to a cylinder of radius 0.063 mm, then μR = 0.135 cm^{-1} and the variation of absorption with θ is negligible.[10] Data were collected using a 0.01°-incrementing Buerger automated diffractometer (which uses Weissenberg geometry), in conjunction with a Phillips transistorized scintillation counter and a Phillips electronics panel. The scintillation counter was adjusted to receive Mo Kα radiation, the Mo Kβ component being eliminated by a zirconium filter, 0.003 mm in thickness. The diffractometer was programmed to collect all data in a given Weissenberg zone, using a stationary-background, ω-scan, stationary-background counting sequence.[11] The angle scanned, ω, is given by $\omega = (2.0 + 1.0/L)$ degrees where $1/L$ is the Lorentz factor. (This allows for divergence of the X-ray beam usually associated with distorted low-order reflections on upper level data.[12])

In collecting data for the reflection ***hkl***, having vertical and horizontal Weissenberg components $\Upsilon(hkl)$ and $\Phi(hkl)$,[13] the counter was first positioned to $\Upsilon(hkl)$ where it remained stationary. The crystal was then rotated to an angle $\phi_1 = \Phi(hkl) - \omega(hkl)/2$ where the first background (B_1) was counted for *t* seconds. Then the angle ϕ was increased by $\omega(hkl)$ degrees to $\phi_2 = \Phi(hkl) + \omega(hkl)/2$ in 2*t* seconds at a constant rate of 2°/min, the integrated count being *C*. The second background, B_2, was then counted for *t* seconds. Data for which the corrected intensity, $I = C - (B_1 + B_2)$, was less than, or equal to, zero were discarded. The reflections were weighted as follows: $\sigma = 50$ for $I \leqslant 500$; $\sigma = 0.1I$ for $I \geqslant 500$.

Using the equiinclination method, data were collected for the zones 0*kl* through 8*kl*, representing complete data to sin θ = 0.45. Data for the zones *h*0*l* and *h*1*l*, taken with a cleaved portion of the previous crystal (0.17 × 0.13 × 0.12 mm), were used to place the nine

TABLE I

FINAL ATOMIC COORDINATES[a] FOR $C_{10}H_8Fe_2(CO)_5$

Atom	*x/a*	*y/b*	*z/c*
Fe_1	0.18189 (12)	0.81231 (7)	0.29587 (7)
Fe_2	0.36439 (12)	0.65087 (7)	0.15788 (7)
C_1	0.5315 (10)	0.7566 (6)	0.1307 (6)
C_2	0.6112 (10)	0.6609 (6)	0.0939 (6)
C_3	0.6454 (10)	0.6379 (6)	0.1767 (6)
C_4	0.5797 (9)	0.7181 (6)	0.3636 (5)
C_5	0.4713 (11)	0.7736 (7)	0.4342 (6)
C_6	0.3508 (10)	0.8501 (6)	0.4362 (5)
C_7	0.3782 (11)	0.9207 (6)	0.3933 (6)
C_8	0.4383 (10)	0.8912 (6)	0.2968 (6)
C_9	0.5127 (8)	0.7942 (5)	0.2364 (5)
C_{10}	0.5847 (9)	0.7190 (6)	0.2657 (6)
C_{11}	0.0831 (9)	0.6950 (6)	0.2917 (6)
C_{12}	0.0956 (10)	0.8105 (6)	0.1808 (6)
C_{13}	0.0037 (9)	0.8895 (6)	0.3601 (6)
C_{14}	0.2196 (11)	0.6081 (6)	0.0483 (6)
C_{15}	0.2996 (10)	0.5447 (6)	0.1807 (6)
O_1	0.0052 (7)	0.6310 (5)	0.3012 (5)
O_2	0.0415 (10)	0.8129 (6)	0.1090 (5)
O_3	−0.1140 (9)	0.9349 (5)	0.3987 (5)
O_4	0.1310 (9)	0.5763 (5)	−0.0257 (5)
O_5	0.2647 (9)	0.4714 (5)	0.1910 (6)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit of the preceding number.

TABLE II

FINAL ANISOTROPIC THERMAL PARAMETERS (×10^4) FOR $C_{10}H_8Fe_2(CO)_5$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	*B*,[a] A^2
Fe_1	165.9	46.5	40.4	8.8	13.8	14.5	3.158
Fe_2	162.0	43.3	46.3	9.9	11.0	17.5	3.197
C_1	184	68	60	−17	18	26	4.22
C_2	198	67	66	10	23	27	4.45
C_3	187	67	67	17	20	21	4.39
C_4	172	95	47	8	0	28	4.44
C_5	223	85	54	−13	1	31	4.76
C_6	219	82	36	−2	11	7	4.22
C_7	211	72	58	−8	4	19	4.47
C_8	184	61	61	1	8	29	4.09
C_9	154	55	49	−11	15	19	3.47
C_{10}	144	66	58	15	8	27	3.85
C_{11}	159	56	58	5	3	29	3.72
C_{12}	192	72	51	29	19	28	4.17
C_{13}	160	76	57	33	24	10	4.16
C_{14}	225	54	56	4	−5	16	4.12
C_{15}	215	51	57	6	13	24	3.98
O_1	204	77	92	3	30	45	5.33
O_2	372	140	67	94	21	54	7.33
O_3	289	106	76	70	22	1	6.20
O_4	357	90	76	4	−36	27	6.31
O_5	331	80	128	22	56	57	7.13

[a] *B* is the "equivalent isotropic temperature factor," obtained by averaging $4b_{11}/a^2$, $4b_{22}/b^{*2}$, and $4b_{33}/c^{*2}$.

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TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{10}H_8Fe_2(CO)_5$ (k, l, F_o, AND F_c IN BLOCKS OF CONSTANT h)

K	L	FO	FC	K	L	FO	FC
				14	1	-18	-13
•••••••••••••••				14	-1	28	28
				14	2	-12	-1
H = 0				14	-2	15	14
				14	3	-10	-12
0	0		728	14	-3	-32	-31
0	4	-67	-69	14	4	-9	-13
0	6	63	60	14	-4	-14	-9
0	7	125	124	14	-5	14	11
0	8	-65	-54	14	-7	14	9
0	9	-83	-75	14	-8	32	32
0	13	31	26	14	-10	-40	-42
0	14	19	14	14	-11	-12	-6
0	15	-41	-40	14	-12	22	17
0	16	-17	-8	14	-13	15	10
2	1	16	17	14	-14	17	15
2	2	-72	-65	14	-15	16	10
2	-3	-12	-12	14	-16	-21	-19
2	4	59	55	14	-17	-25	-21
2	-4	-53	-49	16	-1	-7	-4
2	5	153	159	16	-2	-9	-4
2	-5	40	40	16	-3	25	25
2	-6	14	13	16	-4	18	12
2	7	-90	-90	16	-5	-37	-36
2	-7	-28	-32	16	-6	-19	-20
2	-8	28	29	16	-7	18	13
2	9	-26	-25	16	-8	12	1
2	-9	47	47	16	-10	25	25
2	10	16	18	16	-11	-10	-9
2	-10	-31	-34	16	-12	-29	-31
2	11	43	45	16	-13	-9	-6
2	-11	-70	-71	16	-14	16	12
2	12	26	23	16	-15	9	4
2	13	-37	-30	18	-6	12	3
2	-13	11	8	18	-7	-23	-23

TABLE III (*Continued*)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
7	-6	-11	-13	-9	9	-5	-2	-13	5	21	22	7	-4	86	89	2	9	7	5	-6	-11	-14	-9	-8	1	42	41	10	-9	-21	-21	1	-4	-16	-15	3	-8	-13	-5	-7	3	-33	-33	11	-7	7	9
-7	6	36	35	9	-10	17	18	13	-6	-22	-18	-7	4	73	73	-2	-9	-13	-12	6	-11	25	28	-8	-2	13	11	-10	9	11	3	-1	4	-33	-37	-3	8	26	11	-7	-4	-22	-24	-11	7	-19	-18
7	7	-22	-24	-9	10	-21	-21	-13	6	9	3	7	5	-26	-24	2	-9	24	21	-6	11	-3	-3	8	-2	47	40	10	-10	8	0	1	5	-14	-10	-3	-9	14	15	7	-4	-18	-14	11	-8	-3	-5
-7	-7	13	12	9	-11	32	35	-13	7	-28	-31	-7	-5	-11	-14	-2	9	-10	-8	6	-12	19	17	-8	2	-11	-11	-10	10	14	15	-1	-5	34	32	3	-9	40	39	-7	4	12	0	-11	8	-14	-11
7	-7	-30	-29	-9	11	8	5	13	-8	28	30	7	-5	40	41	2	10	8	9	-6	12	-16	-19	8	3	-2	-3	10	-11	25	27	1	-5	-36	-35	-3	9	15	9	-7	-5	26	22	-11	9	17	9
-7	7	-25	-22	-9	12	16	13	-13	8	-16	-16	-7	5	-35	-38	-2	-10	-28	-27	6	-13	-13	-16	-8	-3	-23	-20	-10	11	-14	-9	-1	5	14	14	-3	-10	18	17	7	-5	-18	-18				
7	8	17	8	9	-13	-18	-19	13	-9	13	14	-7	-6	-25	-23	2	-10	17	16	-6	13	-17	-12	8	-3	5	7	10	-12	11	2	1	6	14	17	3	-10	3	4	-7	5	25	24	****************			
-7	-8	20	23	-9	13	4	5	-13	9	10	16	7	-6	-55	-57	-2	10	-30	-32	6	0	51	44	-8	3	-40	-41	-10	12	-27	-28	-1	-6	14	16	-3	10	9	5	-7	-6	28	26				
7	-8	53	55	9	-14	-7	-5	13	-10	-20	-21	-7	6	-69	-69	-2	-11	18	13	-6	0	-7	-7	8	4	11	11	10	-13	-6	-8	1	-6	-16	-13	3	-11	-19	-19	7	-6	15	16	H = 8			
-7	8	-47	-47	-9	14	13	2	-13	10	6	9	-7	-7	-17	-16	2	-11	-11	-2	6	1	16	14	-8	-4	-28	-30	-10	13	10	1	-1	6	18	18	-3	11	5	4	-7	6	-10	-0				
-7	-9	-8	-6	9	-15	-8	-7	13	-11	-13	-15	7	-7	-19	-14	-2	11	-2	-4	-6	-1	33	37	8	-4	-19	-20	-12	0	-12	-13	1	7	-8	-2	5	0	-15	-11	-7	-7	-12	-6	0	4	7	6
7	-9	53	55	-9	15	11	2	-13	11	-11	-0	-7	7	15	15	-2	-12	25	24	6	-1	-10	-7	-8	4	-16	-17	-12	-1	15	18	-1	-7	-18	-16	-5	0	-15	-16	7	-7	23	20	0	-4	6	8
-7	9	-11	-1	11	0	32	34	-13	12	12	12	7	8	13	2	2	-12	-9	-9	-6	1	-61	-63	8	5	13	14	12	-1	-6	-4	1	-7	34	35	5	1	5	6	-7	7	-10	-0	0	7	-11	-7
-7	-10	-10	-5	-11	0	7	10	13	-13	-8	-6	0	6	24	25	-2	12	7	6	6	2	-38	-37	-8	-5	23	22	-12	1	-25	-25	-1	7	4	2	-5	-1	36	34	-7	8	15	12	-2	0	-2	-6
7	-10	-25	-25	11	1	8	13	-13	13	-7	-4	0	-6	-6	-5	2	-13	11	1	6	-2	-17	-15	8	-5	-10	-10	-12	-2	21	10	1	8	-24	-27	5	-1	-8	-7	7	-9	-12	-8	2	-1	10	10
-7	10	-8	-4	-11	-1	-28	-25	-15	2	-16	-15	0	7	14	13	2	-14	-18	-16	-6	2	-6	-7	-8	5	25	24	12	-2	-13	-2	-1	-8	12	6	-5	1	-35	-34	-7	9	-20	-20	-2	1	9	7
7	-11	-10	-17	11	-1	-8	-11	-15	3	-13	-19	0	-7	35	35	4	0	-14	-14	6	3	-9	-4	-8	-6	21	20	-12	2	12	9	1	-8	14	16	5	2	30	32	7	-10	-12	-5	2	-4	1	0
-7	11	-5	-2	-11	1	-6	-6	-15	4	16	9	0	8	-35	-38	-4	0	-23	-25	-6	-3	-23	-22	8	-6	-4	-5	12	-3	10	3	-1	8	10	15	-5	-2	14	15	-7	10	-23	-25	2	5	-5	-3
-7	12	21	21	11	2	-19	-20	-15	5	18	9	0	-8	19	19	4	1	-9	-6	6	-3	15	15	-8	6	16	15	-12	3	11	10	-1	-9	-13	-11	5	-2	-24	-23	-7	11	15	11	-2	5	-16	-12
7	-13	-13	-11	-11	-2	-26	-27	-15	6	-16	-3	0	9	-14	-12	-4	-1	-49	-48	-6	3	39	38	-8	-7	10	0	12	-4	-22	-22	1	-9	-17	-15	-5	2	-5	-4	7	-12	-7	-5	-2	-5	7	3
7	-14	-5	-7	11	3	-13	-4	-15	7	19	12	0	-11	-5	-8	4	-1	23	22	6	4	14	17	8	-7	-19	-16	12	-5	-8	-8	-1	9	-8	-3	5	-3	-27	-25	9	0	-13	-15	-2	-7	-15	-10
-7	14	-21	-16	-11	-3	25	28	-15	8	19	4	0	-12	-22	-24	-4	1	42	43	-6	-4	20	20	-8	7	9	4	-12	5	21	20	-1	-10	-27	-26	-5	3	17	15	-9	-1	-21	-19	-2	-8	-25	-21
7	-15	20	23	11	-3	10	6	-15	9	-25	-20	0	-13	10	8	4	2	50	47	6	-4	-25	-24	8	-8	6	3	12	-6	23	27	1	-10	11	5	5	4	-25	-27	9	-1	-14	-6	2	-8	9	20
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9	0	-15	-13	-11	-4	22	18					-2	0	-14	-16	4	-2	-16	-15	6	5	-7	-2	8	-9	36	37	-12	7	-24	-26	-1	-11	7	4	5	-4	29	29	-9	-2	-16	-14	-4	-1	25	24
9	1	-7	-8	11	-4	-28	-26	****************				2	1	13	13	-4	2	-11	-10	-6	-5	-13	-12	-8	9	-14	-13	-12	8	-20	-19	1	-12	-18	-18	-5	4	8	7	9	-2	28	26	-4	1	-24	-24
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9	-1	-12	-6	-11	-5	-13	-10	H = 6				-2	1	34	35	-4	-3	37	37	-6	5	7	11	8	-11	-13	-11	-12	9	8	9	-3	0	-10	-11	-5	-5	-29	-29	-9	-3	16	15	-4	2	-15	-14
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9	2	30	32	-11	5	-35	-34	0	0	36	34	-2	-2	-31	-32	-4	3	14	15	-6	-6	-43	-42	-8	12	19	17	-12	11	-10	-2	-3	-1	-36	-40	-5	5	-7	-1	-9	3	22	19	-4	-6	-23	-21
-9	-2	9	6	11	-6	30	30	0	1	-62	-43	2	-2	27	29	4	4	-40	-41	6	-6	27	25	8	-13	-11	-16	-12	12	19	5	3	-1	-31	-31	5	6	7	11	-9	-4	15	16	-4	6	11	5
9	-2	-33	-31	-11	6	-23	-21	0	-1	34	36	-2	2	42	43	-4	-4	18	16	-6	6	46	43	8	-14	-6	-8	-14	2	-16	-13	3	2	-9	-8	-5	-6	-26	-28	9	-4	-12	-12	-4	-7	13	12
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9	3	22	17	11	-8	-23	-22	0	-2	-12	-12	-2	-3	-23	-23	-4	4	34	35	-6	-7	22	21	-10	0	10	10	-14	4	7	11	-3	2	5	6	5	-7	23	27	9	-5	6	3	4	-8	-12	-16
-9	-3	-35	-34	-11	8	16	16	0	3	-10	-5	2	-3	48	46	4	5	-5	-0	6	-7	69	69	-10	-1	-23	-26	-14	5	18	14	3	3	-8	-6	-5	7	-9	-11	-9	5	-15	-13	-4	8	-21	-15
9	-3	14	10	11	-9	-11	-15	0	-3	14	13	-2	3	-38	-37	-4	-5	-37	-37	-6	7	-20	-17	10	-1	7	2	-14	6	11	2	-3	-3	36	34	-5	-8	27	27	-9	6	-16	-8	4	-9	6	26
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9	-4	39	38	11	-12	-5	-3	7	0	-10	-13	-2	4	-38	-39	4	-6	-22	-23	-6	-9	-13	-4	-10	2	11	9					-3	-4	14	13	-5	9	14	13	9	-9	15	16	-6	-5	17	16
-9	4	-30	-32	-11	12	-25	-26	-7	0	-35	-35	2	5	6	7	-4	6	-69	-68	6	-9	-21	-23	-10	-3	23	25	H = 7				3	-4	-3	-8	-5	10	19	21	-9	9	6	7	-6	5	16	11
9	5	-19	-15	11	-13	31	35	7	1	-27	-23	-2	-5	49	48	-4	-7	-18	-16	-6	9	10	10	10	-3	-16	-12					-3	4	26	25	5	-11	30	31	9	-10	5	0	6	-6	7	0
-9	-5	18	22	-11	13	10	6	-7	-1	-99	-102	2	-5	-4	-5	4	-7	-22	-23	6	-10	7	2	-10	3	25	26	1	0	24	24	3	5	-6	-2	-5	11	-8	-3	-9	10	10	7	-6	7	-7	-1
9	-5	18	17	-11	14	27	22	7	-1	-5	-7	-2	5	-11	-11	-4	7	9	5	-6	10	15	13	-10	-4	14	13	-1	0	-8	-8	-3	-5	-10	-10	5	-12	13	9	9	-11	-16	-11	6	-9	-7	-10
-9	5	13	11	13	0	-21	-16	-7	1	-72	-19	2	6	-37	-37	4	8	8	9	6	-11	-28	-27	10	-4	35	33	1	1	-33	-32	3	-5	-5	-3	7	0	34	33	-9	11	-21	-13	-8	1	12	9
9	6	17	6	-13	0	-21	-23	7	2	59	55	-2	-6	27	30	-4	-8	-27	-28	-6	11	6	4	-10	4	-9	-0	-1	-1	14	15	-3	5	-17	-16	-7	0	12	7	-11	0	-12	-11	-8	2	-7	-7
-9	-6	23	19	-13	-1	25	20	-7	-2	32	29	2	-6	-5	-2	4	-8	4	0	6	-12	-3	-5	-10	-5	-17	-1	-1	1	29	26	3	6	-29	-33	-7	-1	-7	-2	-11	-1	11	13	8	-4	-26	-21
9	-6	-25	-24	13	-1	14	13	7	-2	-60	-62	-2	6	13	12	-4	8	21	20	-6	12	12	8	10	-5	15	16	1	2	-29	-31	-3	-6	-6	-2	7	-1	19	22	-11	1	-27	-26	-8	5	-26	-21
-9	-7	-12	-6	-13	1	-22	-23	-7	2	-32	-31	2	7	-16	-16	4	9	12	12	6	-13	25	27	-10	5	-35	-34	-1	-2	-21	-19	3	-6	9	7	-7	1	11	20	-11	2	11	9	8	-6	16	11
9	-7	-17	-17	-13	-2	12	15	7	3	42	42	-2	-7	-23	-26	-4	-9	30	26	-6	13	11	10	10	-6	-12	-12	1	-2	8	6	-3	6	-34	-35	7	2	-19	-19	-11	3	13	16	8	-7	19	16
-9	7	11	6	13	-2	21	23	-7	-3	83	86	2	-7	-27	-26	4	-9	-24	-24	6	-14	11	11	-10	6	-29	-30	-1	2	31	33	-3	-7	-18	-15	-7	-2	15	10	11	-4	21	21	-8	7	7	4
-9	-8	-6	-1	-13	2	12	10	7	-3	-66	-64	-2	7	5	6	-4	9	12	9	8	0	-21	-18	10	-7	-6	-6	-1	-3	-43	-47	3	-7	-29	-28	7	-2	-16	-11	-11	4	-12	-2	-10	6	-5	-1
9	-8	-9	-1	13	-4	-6	-5	-7	3	30	33	2	8	10	12	-4	-10	24	25	-8	0	8	11	-10	7	18	18	1	-3	14	14	-3	7	10	9	-7	2	-12	-13	11	-5	2	7				
-9	8	20	22	-13	4	3	6	7	4	-28	-30	2	-8	8	7	4	-10	-10	-8	8	1	-14	-13	10	-8	6	3	-1	3	-22	-24	3	8	13	12	-7	-3	-22	-22	-11	5	13	10	****************			
9	-9	-16	-17	13	-9	12	0	-7	-4	10	10	-2	8	10	10	-4	10	16	14	-8	-1	-17	-15	-10	8	19	19	1	4	11	10	-3	-8	-25	-24	7	-3	-16	-13	-11	6	6	3				

zones, $0kl$ through $8kl$, on a common scale. The absolute scale factor was determined from a Wilson plot, which also indicated an over-all thermal parameter, $\bar{B} = 2.96$ A^2.

Unit Cell and Space Group

The compound appeared to crystallize in a triclinic habit. Since a survey of the reciprocal lattice failed to indicate any diffraction symmetry other than that imposed by the Friedel condition, the crystals were assumed to be truly triclinic.

Zero-layer Weissenberg ($0kl$) and precession ($h0l$ and $hk0$) photographs, taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 A) and calibrated with sodium chloride ($a_{\mathrm{NaCl}} = 5.640$ A) gave rise to the unit-cell dimensions: $a = 7.32 \pm 0.01$ A, $b = 14.48 \pm 0.02$ A, $c = 14.76 \pm 0.02$ A, $\alpha = 116.2 \pm 0.2°$, $\beta = 92.3 \pm 0.2°$, and $\gamma = 93.0 \pm 0.2°$.

The systematic absence $h + k = 2n + 1$ indicated a C-face-centered cell; the space group is therefore C1 (no. 1) or C$\bar{1}$ (no. 2). The observed density, obtained by flotation in aqueous zinc iodide solution, $\rho_{\mathrm{obsd}} = 1.78 \pm 0.03$ g cm^{-3}, is in agreement with the value calculated for $M = 380$, $V = 1399$ A^3, and $Z = 4$ ($\rho_{\mathrm{calcd}} = 1.80$ g cm^{-3}). The asymmetric unit is therefore one molecule in C$\bar{1}$ or two molecules in C1. The analysis was begun assuming space group C$\bar{1}$ since it is statistically more probable. The accurate solution of the structure confirmed this assumption.

Solution and Refinement of the Structure

The positions of the two iron atoms ($X_1 = -0.183$, $Y_1 = 0.812$, $Z_1 = 0.298$; $X_2 = 0.367$, $Y_2 = 0.653$, $Z_2 = 0.158$) were found from a three-dimensional Patterson synthesis[14] which had been sharpened so that the average intensity was independent of $\sin \theta$ and which had the origin peak reduced to the height of a single iron–iron interaction. A three-dimensional electron density map, phased by the two iron atoms ($R_F = 0.47$) quickly and unambiguously revealed the positions of all light atoms other than hydrogens. Structure factor calculations,[15] phased by the two iron atoms, five oxygen atoms, and fifteen carbon atoms, had an initial discrepancy index, $R_F = 0.46$, which converged to a value of 0.13 in five cycles of positional and isotropic thermal parameter refinement. A difference Fourier at this stage showed evidence for anisotropic thermal motion, particularly for the oxygen atoms. Refinement was therefore continued using anisotropic thermal parameters (T) given by

$$T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$$

Owing to a restriction in the number of parameters that may be independently varied, the anisotropic refinement was carried out in two parts: first the iron atoms and the azulene carbon atoms were refined, and then the iron atoms and the carbonyl groups were refined. Finally all positional parameters were refined while the thermal parameters were held constant. The final discrepancy index is $R_F = 0.107$.

During the analysis the scattering factors for neutral iron, oxygen, and carbon were used;[16] contributions from the eight hydrogen atoms were not included in the calculation. Dispersion corrections are small and were ignored.[17] The residual minimized in the analysis was $\Sigma\omega||F_o|^2 - |F_c|^2|^2$.

Final atomic coordinates are shown in Table I, with their standard deviations.[18] Anisotropic thermal pa-

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[14] Patterson and Fourier maps were calculated using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090 by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende.

[15] Structure factor calculations and full-matrix least-squares refinement of positional and thermal parameters were performed using OR-FLS, a Fortran least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

[16] "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England. Values for iron are taken from p 211; those for oxygen and carbon, from p 202.

[17] For iron ($Z = 26$), $\Delta f' = 0.4$ electron, $\Delta f'' = 1.0$ electron; see ref 16, p 215.

[18] The standard deviations $\sigma(j)$ are estimated by the least-squares program OR-FLS from the diagonal element (a_{jj}) of the matrix inverse to the normal equation matrix. $\sigma(j) = [a_{jj}(\Sigma\omega\Delta^2)/(m - n)]^{1/2}$ where m is the number of observations, n the number of variables in the refinement, and $\Sigma\omega\Delta^2$ the summed, weighted discrepancy between observed and calculated structure factors.

rameters are collected in Table II; observed and calculated structure factors are shown in Table III.

The Molecular Structure

Intramolecular distances are shown in Table IV and bond angles in Table V. The over-all geometry and the system of numbering atoms can clearly be seen in Figures 1 and 2. The molecule consists of an $Fe(CO)_2$ group and an $Fe(CO)_3$ group bonded to an azulene molecule. As predicted by dipole moment measurements,[3] the two iron atoms are on the same side of the azulene system (*i.e.*, the molecule has an over-all *cis* configuration). The $Fe(CO)_2$ group is associated symmetrically with all carbon atoms in the five-membered ring, which behaves as a substituted π-cyclopentadienyl ligand. Only three carbon atoms (C_6, C_7, C_8) of the seven-membered ring are associated with the $Fe(CO)_3$ group in forming a π-allyl–metal bond. The donation of six electrons from the π-cyclopentadienyl anion, four from the π-allyl anion, and two from each carbonyl ligand gives each of the d^7 Fe(I) ions a configuration one electron short of the closed shell; the observed Fe_1–Fe_2 distance of 2.782 A indicates a metal–metal bond, each iron atom thus obtaining a krypton configuration, in keeping with the observed diamagnetism[3] of the complex. The molecule may formally be written as in II.

Table IV

Intramolecular Distances[a,b] for $C_{10}H_8Fe_2(CO)_5$

Atoms	Distance, A	Atoms	Distance, A
Fe_1—Fe_2	2.782		
$Fe_1\cdots C_1$	3.482	Fe_2—C_1	2.094
$Fe_1\cdots C_2$	4.391	Fe_2—C_2	2.100
$Fe_1\cdots C_3$	4.294	Fe_2—C_3	2.094
$Fe_1\cdots C_4$	3.567	$Fe_2\ldots C_4$	3.082
$Fe_1\cdots C_5$	3.124	$Fe_2\ldots C_5$	3.689
Fe_1—C_6	2.200	$Fe_2\ldots C_6$	3.848
Fe_1—C_7	2.050	$Fe_2\ldots C_7$	3.911
Fe_1—C_8	2.142	$Fe_2\cdots C_8$	3.166
$Fe_1\cdots C_9$	2.596	Fe_2—C_9	2.090
$Fe_1\cdots C_{10}$	3.272	Fe_2—C_{10}	2.086
Fe_1—C_{11}	1.785	$Fe_2\cdots C_{11}$	2.811
$Fe_1\cdots C_{12}$	1.776	$Fe_2\cdots C_{12}$	3.028
Fe_1—C_{13}	1.779	$Fe_2\cdots C_{13}$	4.506
$Fe_1\cdots C_{14}$	3.578	Fe_2—C_{14}	1.741
$Fe_1\cdots C_{15}$	3.648	Fe_2—C_{15}	1.761
$Fe_1\cdots O_1$	2.900	$Fe_1\cdots O_4$	2.877
$Fe_1\cdots O_2$	2.908	$Fe_1\cdots O_5$	2.911
$Fe_1\cdots O_3$	2.904		
C_{11}—O_1	1.127	C_{14}—O_4	1.137
C_{12}—O_2	1.132	C_{15}—O_5	1.153
C_{13}—O_3	1.125		
C_1—C_2	1.415	C_{10}—C_4	1.453
C_2—C_3	1.418	C_4—C_5	1.325
C_3—C_{10}	1.430	C_5—C_6	1.443
C_{10}—C_9	1.452	C_6—C_7	1.432
C_9—C_1	1.422	C_7—C_8	1.391
		C_8—C_9	1.441
Av	1.427		

[a] Average estimated standard deviations are: σ(Fe–Fe) = 0.0013 A, σ(Fe–O) = 0.007 A, σ(Fe–C) = 0.008 A, σ(C–O) = 0.011 A, and σ(C–C) = 0.012 A; these values do not include any contribution in unit-cell errors, which are less than 1 part in 700. Allowing for unit-cell errors means that the probable error in the Fe–Fe distance is 0.004 A, but errors in other distances are not so drastically affected. [b] Distances have not been corrected for librational motion.

Table V

Bond Angles for $C_{10}H_5Fe_2(CO)_5$

Atoms	Angle, deg	Atoms	Angle, deg
Fe_1–C_{11}–O_1	169.0	C_9–C_1–C_2	109.3
Fe_1–C_{12}–O_2	177.7	C_1–C_2–C_3	107.8
Fe_1–C_{13}–O_3	177.2	C_2–C_3–C_{10}	108.7
		C_3–C_{10}–C_9	107.2
Fe_2–C_{14}–O_4	176.5	C_{10}–C_9–C_1	106.9
Fe_2–C_{15}–O_5	175.5		
		C_{10}–C_4–C_5	123.7
C_{14}–Fe_2–C_{15}	94.0	C_4–C_5–C_6	129.7
C_{14}–Fe_2–Fe_1	102.1	C_5–C_6–C_7	127.2
C_{15}–Fe_2–Fe_1	104.6	C_6–C_7–C_8	122.8
		C_7–C_8–C_9	125.0
Fe_2–Fe_1–C_{11}	72.2	C_8–C_9–C_{10}	130.1
Fe_2–Fe_1–C_{12}	79.9	C_9–C_{10}–C_4	127.6
Fe_2–Fe_1–C_{13}	161.7		
C_{11}–Fe_1–C_{12}	104.2	C_3–C_{10}–C_4	124.9
C_{11}–Fe_1–C_{13}	95.8	C_1–C_9–C_8	123.0
C_{12}–Fe_1–C_{13}	90.0		
		C_1–Fe_2–C_2	39.4
C_6–Fe_1–C_7	39.2	C_2–Fe_2–C_3	39.5
C_7–Fe_1–C_8	38.7	C_3–Fe_2–C_{10}	40.0
C_6–Fe_1–C_8	69.6	C_{10}–Fe–C_9	40.7
		C_9–Fe_2–C_1	39.7

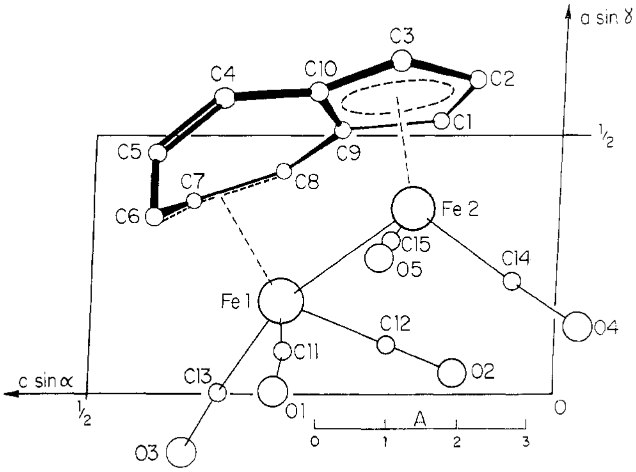
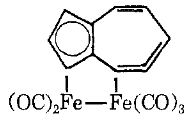


Figure 1.—The molecule $C_{10}H_8Fe_2(CO)_5$ viewed along *b*.



II

The Azulene Ligand

The bonding scheme within the azulene ligand is not grossly rearranged from that in the parent hydrocarbon. Within the limits of experimental error, the π-cyclopentadienyl ring defined by C_1, C_2, C_3, C_{10}, and C_9 has precise D_{5h} symmetry. The carbon–carbon bond lengths range from 1.414 to 1.452 A (esd 0.012 A), averaging 1.427 A. Bond angles are found to be from 106.9 to 109.3°, averaging 108.0°. The five carbon

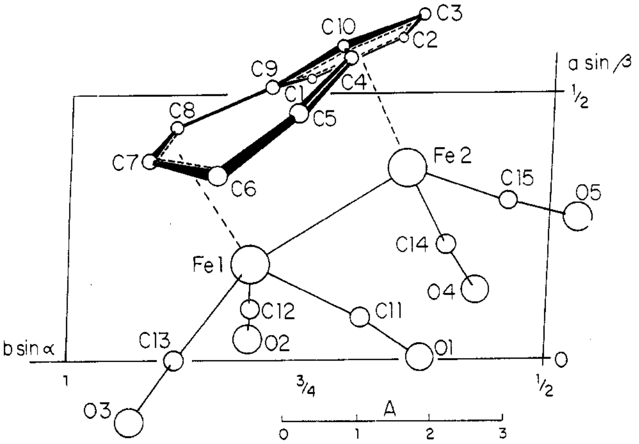


Figure 2.—The molecule $C_{10}H_8Fe_2(CO)_5$ viewed along *c*.

TABLE VI

DISTANCES OF ATOMS FROM PLANE OF π-CYCLOPENTADIENYL RING FOR $C_{10}H_8Fe_2(CO)_5$

Plane[a]: $0.8375X + 0.7555Y - 0.1249Z = 1$

Atom	Dev, A	Atom	Dev, A
C_1	+0.003	C_4	−0.133
C_2	−0.004	C_5	−0.576
C_3	+0.004	C_6	−0.908
C_9	−0.001	C_7	−0.282
C_{10}	−0.002	C_8	+0.026
Fe_2	−1.708	Fe_1	−2.077
C_{14}	−2.780	C_{11}	−3.386
C_{15}	−2.761	C_{12}	−2.531
O_4	−3.463	C_{13}	−2.836
O_5	−3.419	O_1	−4.267
		O_2	−2.796
		O_3	−3.365

[a] The equation for the plane is expressed in triclinic coordinates.

atoms have a root-mean-square deviation from planarity of only 0.003 A (see Table VI). The associated iron atom, Fe_2, is 1.708 A below this plane, the iron-carbon bond lengths ranging from 2.088 to 2.100 A (esd 0.008 A) and averaging 2.093 A.

In the seven-membered ring, two carbon atoms (C_9 and C_{10}) are already incorporated in the π-cyclopentadienyl–Fe(CO)$_2$ bonding, two (C_4 and C_5) are linked by a simple, uncoordinated ethylenic bond of length 1.325 ± 0.012 A, and the remaining three (C_6, C_7, and C_8) are within bonding distance of Fe_1. This group of three atoms makes a dihedral angle of 171.9° with the carbon atoms of the Fe(CO)$_3$ group and participates in a π-allyl–iron linkage. The value of 122.8° for the apical angle C_6–C_7–C_8 and the carbon–carbon bond lengths (1.432 ± 0.012, 1.391 ± 0.012 A) are in the range expected from crystallographic studies on π-allyl–palladium species.[19,20] The iron–carbon distances observed in the π-allyl–iron species $C_8H_8Fe_2(CO)_5$ are 2.136, 2.113, and 2.123 (±0.013) A.[21] The values obtained in the present azulene complex (2.200, 2.050, and 2.142 A, each ±0.008 A) as well as those determined in $Fe_2(CO)_6(C_6H_5C_2H)_3$ (1.975, 2.108, and 2.203 A, each ±0.011 A)[22] might be construed as indicative of some degree of σ–π bonding, as has been claimed for $[CH_2 \cdot C(CH_3) \cdot CH_2]Pd[(C_6H_5)_3P]Cl$.[23] However, the author believes that the variation of Fe–C(allyl) bond lengths in the present complex is best explained as part of a general pattern of strain in the molecule. The positioning of iron atoms vertically below the center of gravity of the π-cyclopentadienyl and π-allyl portions of a regular, planar azulene ligand would satisfy the bonding requirements of the unsaturated ligands but

TABLE VII

IRON–IRON DISTANCES IN SOME ORGANOMETALLIC MOLECULES

Molecule	Fe–Fe distance(s), A	Ref
Black $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$	2.428, 2.435 (±0.003)	25
Violet $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$	2.457, 2.469, 2.592 (±0.005)	25
$Fe_2(CO)_9$	2.46	26
$Fe_3(CO)_9(C_6H_5C_2C_6H_5)$	2.480, 2.501, 2.579 (±0.010)	*a*
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$	2.49 (±0.02)	27
$Fe_2(CO)_6(HOC \cdot CCH_3)_2$	2.493 (±0.002)	*b*
$Fe_2(CO)_6(C_6H_5C_2H)_3$	2.501 (±0.003)	22
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)$	2.51	*c*
$Fe_2(CO)_6(C_2H_2)_3$	2.527 (±0.006)	*d*
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNC_6H_5)$	2.53	*e*
$[C_2H_5SFe(CO)_3]_2$	2.537	*f*
$[SFe(CO)_3]_2 \cdot [S_2Fe_3(CO)_9]$	2.545, 2.582, 2.609 (±0.010)	*g*
$Fe_3(CO)_{12}$	2.55, 2.68, 2.69 (±0.01)	28
$[SFe(CO)_3]_2$	2.552 (±0.002)	*h*
$[(C_2H_5)_3NH][Fe_3(CO)_{11}H]$	2.577, 2.685, 2.696 (±0.003)	29
$Fe_5(CO)_{15}C$	2.587, 2.600, 2.636, 2.650, 2.652, 2.666, 2.667, 2.675 (±0.007)	*i*
ortho-$[\pi\text{-}C_5H_5FeS]_4$	2.618, 2.644 (±0.002)	*j*
$Se_2Fe_3(CO)_9$	2.64, 2.66 (±0.017)	*k*
mono-$[\pi\text{-}C_5H_5FeS]_4$	2.650 (±0.006)	*l*
$Fe_2(CO)_6(C_5H_4 \cdot CH_2)$	2.679 (±0.003)	*m*
$CsFe_4S_3(NO)_7 \cdot H_2O$	2.691, 2.702, 2.736 (±0.010)	*n*
$[C_2H_5SFe(NO)_2]_2$	2.720 (±0.003)	*o*
$C_8H_8Fe_2(CO)_5$	2.742 (±0.003)	21
$C_{10}H_8Fe_2(CO)_5$	2.782 (±0.004)	This work
$[Fe_2(CO)_8]^{2-}$	2.88	25b

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would leave an iron–iron distance of ~3.3 A (at which distance, of course, no appreciable metal–metal overlap would be possible). In order to accommodate simultaneous π-cyclopentadienyl–metal, π-allyl–metal, *and* metal–metal bonding, the molecule must distort. The observed stereochemistry has three anomalous features in keeping with this proposal.

(i) **The Azulene Ligand Is Nonplanar.**—This is easily shown by the dihedral angles (ϕ) between the five- and seven-membered rings: $\phi(C_2–C_1–C_9/C_9–C_8–C_7) = 16.1°$; $\phi(C_2–C_3–C_{10}/C_{10}–C_4–C_5) = 20.3°$. Although C_8 is approximately (+0.026 A) in the same plane as the π-cyclopentadienyl system, the remaining nonfused atoms of the seven-membered ring are all displaced in the direction of the metal atoms (see Table VI), the maximum displacement being that of C_6, which is 0.908 A below the plane of the π-cyclopentadienyl system. (Figures 1 and 2 illustrate the nonplanarity of the azulene ligand fairly clearly.)

(ii) **The Iron-π-Allyl Linkage Is Not Strictly Symmetrical.**—Since C_6 is the atom most displaced from the "plane of the undistorted azulene molecule," it is not surprising that the Fe–C_6 distance is still the longest of the three metal–carbon distances observed.

(iii) **The Iron–Iron Bond Is One of the Longest Yet Observed in Organometallic Complexes.**—Although the π-allyl group is pulled down from the π-cyclopentadienyl plane (the dihedral angle between the two planes being 25.5°) by a sufficient amount to allow simultaneous π-allyl–iron and iron–iron interaction, it is probable that the resulting metal–metal bond is still relatively weak.

The Carbonyl Ligands

Within the $Fe(CO)_2$ group the mean dimensions are: Fe–C = 1.751 A, C–O = 1.145 A, Fe–C–O = 176.0°; the $Fe(CO)_3$ group shows average distances of 1.780 A for Fe–C and 1.128 A for C–O. The Fe–C–O angles in the iron tricarbonyl residue are 169.0, 177.7, and 177.2°. Since this group is in a rather asymmetric environment, it is probable that the distortions of the Fe–C–O angles from linearity derive from an electronic origin[24] rather than from the van der Waals repulsive forces.

The Iron–Iron Bond

During recent years, crystallographic examination of organoiron complexes has revealed iron–iron bond lengths ranging from 2.43 A in *black* $Fe_3(CO)_8(C_6H_5C_2C_6H_5)$[25a] to 2.88 A in the $[Fe_2(CO)_8]^{2-}$ ion[25b] (see Table VII). In general, complexes with bridging sulfur atoms tend to have long Fe–Fe bonds; however, there is a distinct tendency for molecules with bridging carbonyl groups (*e.g.*, $Fe_2(CO)_9$[26] and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$[27]) to have Fe–Fe bonds rather shorter than those found in nonbridged complexes. For example, the structures of $Fe_3(CO)_{12}$[28] and $[(C_2H_5)_3NH][Fe_3(CO)_{11}H]$[29] show the *non*bridged Fe–Fe bonds to be more than 0.1 A longer than the bridged Fe–Fe bonds. An apparent exception to this rule is the complex $C_8H_8Fe_2(CO)_5$, a molecule with a bridging carbonyl group and an Fe–Fe distance of 2.74 A; however, this molecule is electron deficient.[21] The long internuclear distance of 2.78 A for the present complex is attributed partly to its nonbridged nature and partly to strain (*vide supra*).

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