the odd ligand, the O-donor, N-ethyl-N′-oxo-1,4-diazabicyclo[2.2.2]octonium cation, has a field strength much lower than triphenylphosphine but still appreciably greater than the bromide ligands. Finally, the $[Co(L_N{}^+)(NCS)_3]$ complex is expected to have a very small value for D_T (that is, no appreciable trigonal distortion), because the ligand field strength of the odd ligand, the N-donor, N-ethyl-1,4-diazabicyclo[2.2.2]-octonium cation, does not differ substantially from that of the three isothiocyanato ligands, NCS.

Structural Characterization of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, a Bimolecular Condensation Product of *o*-Bis(phenylethinyl)benzene: Steric Equivalence of Fe(CO)(cyclobutadiene) and $Fe(CO)_3$ Groups

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Abstract: An X-ray crystallographic investigation of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ was undertaken in order to determine the nature of one of the products, $Fe_2(CO)_4C_{44}H_{28}$, of a reaction between *o*-bis(phenylethinyl)benzene and iron pentacarbonyl. The product forms crystals with four formula units in a monoclinic cell of symmetry $P2_1/n$ and of lattice parameters $a = 13.56 \pm 0.02$ Å, $b = 24.00 \pm 0.04$ Å, $c = 11.32 \pm 0.02$ Å, $\beta = 93° 55' \pm 10'$. Refinement of the determined structure by anisotropic–isotropic least squares yielded unweighted R_1 and weighted R_2 values of 9.9% for the 1880 independent nonzero diffraction maxima collected photographically. The organoiron carbonyl complex was found to contain a Fe(CO)(cyclobutadiene) fragment which is coordinated to a ferracyclopentadiene ring system. This unusual molecular system originates from the *intermolecular* condensation of two molecules of *o*-bis(phenylethinyl)benzene with a $Fe(CO)_3$ and a Fe(CO) fragment. One pair of acetylenes forms a cyclobutadiene ring, while the other pair of acetylenes produces the five-membered ferracyclopentadiene ring by the incorporation of the $Fe(CO)_3$ fragment. Molecular stabilization is achieved through the interaction of the cyclobutadiene ring with the Fe(CO) fragment, which is also coordinated to the ferracyclopentadiene ring *via* both a (*cis*-butadiene)–iron interaction and an iron–iron electron pair bond; the resulting iron–iron single bond distance is 2.494 (5) Å. The striking stereochemical principle which emerges from a detailed comparison of the molecular parameters of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ with those of $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ is that the cyclobutadiene ligand may sterically behave as only a bidentate ligand by the effective occupation of *two* metal coordination sites in place of two terminal carbonyl groups.

The reactions of alkynes with $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$ have yielded a large number of organoiron complexes with a remarkable variety of configurations.[2, 3] One such complex was isolated by Whitlock and Sandvick[4,5] in low yields from the reaction of *o*-bis(phenylethinyl)benzene with either iron pentacarbonyl or triiron dodecacarbonyl under vigorous conditions. Elemental analysis and molecular weight determination by vapor pressure osmometry[6] indicated that the compound has the molecular formula $Fe_2(CO)_4C_{44}H_{28}$. The presence of only terminal carbonyl groups was indicated from its infrared absorption spectrum in solution.[7] Attempts to characterize the structure further by chemical and physical methods were not successful.

Since *o*-bis(phenylethinyl)benzene *per se* exhibits intramolecular interaction between the triple bonds on reaction with electrophilic, nucleophilic, or radical reagents,[4,5] it was of interest to determine whether this behavior is also exhibited on reaction with iron pentacarbonyl and triiron dodecacarbonyl. In order to resolve this question and ascertain the molecular geometry of the compound, a three-dimensional X-ray analysis of *o*-bis(phenylethinyl)benzene diirontetracarbonyl, $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, was carried out. The determination of the molecular structure of this organodiiron complex instead revealed an *inter*molecular polymerization of two molecules of *o*-bis(phenylethinyl)benzene with two iron carbonyl fragments to give an unusual kind of transition metal complex.

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(1) This manuscript is based in part on a dissertation submitted by Earl F. Epstein to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1969.

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(3) *Cf.* F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968), and references therein.

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(6) The empirical formula $C_{48}H_{28}O_4Fe_2$ was based on the following: *Anal.* Calcd: C, 73.87; H, 3.62; Fe, 14.31. Found: C, 74.14; H, 3.45; Fe, 14.04; mol wt: 750, 772, 790, 810 (vapor pressure osmometer).[5]

(7) The infrared spectrum in CCl_4 shows strong absorption bands at 2070, 1996, and 1894 cm^{-1}.[5]

Experimental Section

Data Collection. Crystals of $Fe_2(CO)_4C_{44}H_{28}$ were generously supplied to us by Professor Howard Whitlock and Dr. Paul Sandvick of the University of Wisconsin. Several crystals were mounted and used initially for the characterization of the symmetry of the crystal system. One of these crystals was selected for the collection of Weissenberg and precession intensity data with Zr-filtered Mo $K\bar{\alpha}$ radiation (λ 0.7107 Å). From Weissenberg data with a *c* axis rotation setting, eleven zones of nonintegrated, equiinclination data (*hkn*, n = 0–10) were obtained by the multiple film technique with packets of eight films and successive exposure times of 72, 12, and 2 hr (the latter only until the intensities of the reflections on higher reciprocal layers became too weak to be judged). Timed-exposure precession photographs were taken of the *h0l*, *0kl*, *1kl*, and *2kl* reciprocal zones. The same crystal was used throughout the data collection with no apparent decay. All intensities were estimated visually by comparison with a calibrated set of spots obtained from the same crystal. The intensities were averaged,[8] and corrections for Lorentz polarization effects and nonzero spot extension[9] were applied.

The averaging procedure[8] excluded reflections which were so weak that they were observed on only one film of a given packet. Those individual judgings of intensity for a given reflection which did not statistically agree with the other judgings for this reflection were removed by the consideration of the "variance" for each estimated intensity. For a particular judging from the jth film, the "variance" is defined as $|I_j^*(hkl)-I(hkl)|$, where $I_j^*(hkl)$ is the scaled intensity of the reflection from the jth film and $I(hkl)$ is the average of all the scaled intensities for this reflection. If the "variance" for the individual intensity estimation of a given reflection was greater than 20% of the average intensity for that reflection, then the individual intensity value was discarded, and the average intensity was redetermined from the remaining judgings.

No corrections for either absorption or anomalous dispersion were made. The crystal used for the data collection was close to a rhombohedron in shape, with approximately 0.025-cm sides and a 70° angle between edges. For Mo $K\bar{\alpha}$ radiation the linear absorption coefficient (μ) is 8.65 cm^{-1}, for which the maximum intensity variation on a given reciprocal layer due to absorption was estimated to be less than 11%. For Mo $K\bar{\alpha}$ radiation the value of the dispersion corrections to the atomic scattering factor for iron are $\Delta f' = 0.4$ and $\Delta f'' = 1.0$.[10] Since the crystal possesses centrosymmetric space group symmetry, these relatively small dispersion corrections are presumed not to affect significantly the atomic coordinates.[10]

A variance was assigned to the intensity of each reflection according to the following relation: if $I > \sqrt{10}\, I_{\min}$, then $\sigma(F) = 0.05F$; if $I \leq \sqrt{10}\, I_{\min}$, then $\sigma(F) = 0.05F[10I_{\min}/I]^2$, where $I_{\min}$ represents the minimum observed intensity for each reciprocal Weissenberg or precession layer. The intensity data were placed on a single relative scale by a consideration of the 344 reflections common to the 1753 Weissenberg and 411 precession data. The Sutton–Glick data correlation program[11] was used, and the resulting discrepancy factor for the merging of data was 3.5%.

Crystal Data. The dark red, approximately rhombohedral crystals of $Fe_2(CO)_4C_{44}H_{28}$ crystallize in the monoclinic system with dimensions $a = 13.56 \pm 0.02$, $b = 24.00 \pm 0.04$, $c = 11.32 \pm 0.02$ Å, $\beta = 93°\ 55' \pm 10'$. These cell parameters were obtained from NaCl-calibrated precession photographs of the *0k0* and *h0l* reciprocal zones taken at room temperature. Errors in the lattice parameters were estimated from the precision of the measurements and from experience with the precession camera used. All measurements were made with Zr-filtered Mo $K\bar{\alpha}$ radiation (λ 0.7107 Å). The cell volume is 3648 Å^3; $F(000)$, the total number of electrons in the unit cell, is 1600.

Weissenberg and precession photographs exhibited systematic absences for $\{h0l\}$ with $h + l$ odd, and for $\{0k0\}$ with k odd. These extinctions uniquely indicate the centrosymmetric space group $P2_1/n$ [nonstandard setting of $P2_1/c$ (C_{2h}^5, No. 14)][12] which was confirmed by the structural determination. The experimental density, obtained by the flotation technique from mixtures of 1-bromonaphthalene and diethyl malate, gave a value of 1.40 ± 0.02 g/cm^3; for *four* molecules in the unit cell, ρ_{calcd} = 1.42 g/cm^3. No molecular symmetry is imposed by the crystallographic symmetry. All independent nonhydrogen atoms were found from the structural analysis to occupy the following fourfold set of positions: $\pm(x,\ y,\ z;\ {}^1/_2 + x,\ {}^1/_2 - y,\ {}^1/_2 + z)$.

Solution of the Structure. The structural problem consisted of the location of the coordinates of 2 iron, 4 oxygen, 48 carbon, and 28 hydrogen atoms which correspond to one molecule. A calculated three-dimensional Patterson function[13] based on corrected intensities yielded the expected *eight* metal–metal double weighted peaks of approximately equal magnitude plus the *two* metal–metal peaks of single weight. An interpretation of these vector positions provided initial coordinates for the two independent iron atoms. A Fourier synthesis phased on these iron atoms was computed, and an interpretation of this map gave initial positions for 3 oxygen and 15 carbon atoms. Another Fourier synthesis phased on the positional parameters of these 20 atoms was calculated, and the remaining nonhydrogen atoms were located. Full matrix isotropic least-squares refinement[14] was begun with individual atomic thermal parameters for nonphenyl atoms. The scattering factors obtained by Hanson, *et al.*,[15] from Hartree-Fock-Slater wave functions were used for all atoms. The six phenyl groups were treated as rigid bodies in the refinement with an isotropic thermal parameter for each phenyl ring. After five cycles, all positional and thermal parameter shifts were less than ${}^2/_3$ their respective standard deviations. The discrepancy values were $R_1 = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o| = 0.103$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.104$. At this point an individual isotropic thermal parameter was assigned to each phenyl carbon atom and allowed to vary in subsequent least-squares cycles. All shifts in *positional* parameters in these latter cycles were less than one standard deviation. The final value of both R_1 and R_2 is 0.099 for the 1880 independent nonzero reflections. During the process of least-squares refinement,[11] reflections were removed from the list of observations because the observed and calculated values of these data disagreed considerably, and reexamination of the films indicated that the reflections which corresponded to these data were affected by white-radiation streaks from other reflections. The value of the standard deviation of an observation of unit magnitude (*i.e.*, the error of fit function $[\Sigma w||F_o| - |F_c||^2/(N_o - N_v)]^{1/2}$ where $(N_o - N_v)$ is the difference between the number of observed reflections and the number of variables in the least-squares process), which corresponds to the weighting scheme described here, was 1.68.

Examination of the final variance–covariance matrix revealed 19 covariances greater than 0.400. Two of these related the overall scale factor to the thermal parameters of the two heavy atoms. No attempt was made to reduce this correlation by means of anisotropic thermal parameters for the heavy atoms, because a three-dimensional difference Fourier synthesis based on the final parameters gave residual peaks in the vicinity of the iron atoms of less than 1.5 electrons/Å^3; no other remaining peaks were greater than +0.6 electron/Å^3. The remaining 17 covariances related one of the angles, which defined the orientation of a rigid body, to one of the origin parameters of the same rigid body.

In order to verify the overall correctness of the structure, unobserved but experimentally accessible data (*i.e.*, those reflections either too weak to be judged or actually observed) for which $\sin\theta \leq 0.40$ were assigned an intensity equal to the minimum observed intensity for the given reciprocal level. After correction of these intensities for Lorentz polarization effects and spot extension, a comparison of the derived structure factors $F_o(\min)$ with the corresponding calculated ones showed that no F_c exceeded $1.5F_o(\min)$.

The positional parameters along with the isotropic temperature factors from the output of the last least-squares cycle appear in Table I.[16] Intramolecular distances and angles with estimated

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(10) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215; *Acta Cryst.*, 8, 842 (1955).

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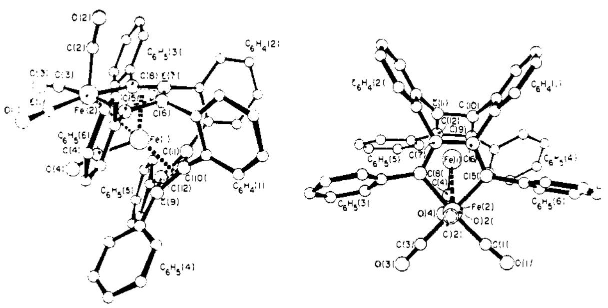

Figure 1. The molecular configuration of $Fe(CO)_3C_6H_5C_2$-$C_6H_4C_2C_6H_5)_2Fe(CO)$.

standard deviations (which include the effect of the estimated errors in lattice parameters) as calculated with the Busing–Martin–Levy function and error program[17] are given in Table II. Equations of least-squares planes determined by a weighted least-squares method[18] along with distances of atoms from these planes and angles between the normals of these planes are given in Table III. The orientations of the various phenyl groups are given in Table IV.

Discussion

Description of the Structure. The molecular structure of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ shown in Figure 1 consists of an Fe(CO)(cyclobutadiene) fragment coordinated to a ferracyclopentadiene ring system. This configuration is achieved by the *intermolecular* condensation of two molecules of *o*-bis(phenylethinyl)-benzene with an $Fe(CO)_3$ and an Fe(CO) fragment (from iron pentacarbonyl) such that one pair of acetylenes forms a cyclobutadiene ring while the other pair of acetylenes produces the heterocyclic ferracyclopentadiene ring system by the incorportation of the $Fe(CO)_3$ group. Stabilization of this polymerization product occurs through the interaction of the cyclobutadiene ring with the Fe(CO) fragment, which also is coordinated to the five-membered heterocyclic iron ring system *via* both a (*cis*-butadiene)–iron linkage and an iron–iron electron pair bond.

Both iron atoms in this diamagnetic compound conform to the 18-electron "noble gas" rule by a formal contribution to the nonring zerovalent iron atom of four electrons from the cyclobutadiene group, two electrons from the one terminal carbonyl group, and four electrons from the butadiene part of the ferracyclopentadiene ring; and by a formal donation to the ring iron atom of six electrons from its three terminal carbonyl groups, two electrons from the two σ-bonding diene carbon atoms of the ferracyclopentadiene ring, and the remaining two electrons from the nonring iron atom by a coordinate covalent iron–iron bond.

The crystal arrangement of the four molecules per monoclinic unit cell is illustrated in Figure 2. The closest intermolecular distances given in Table II indicate that the separations between molecules correspond to normal van der Waals contacts.

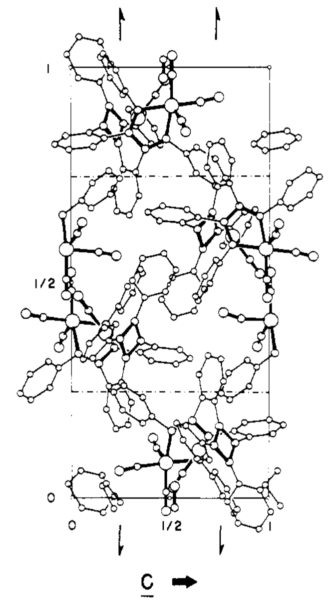

Figure 2. The arrangement of the four molecules of $Fe(CO)_3$-$(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ in the monoclinic unit cell (of symmetry $P2_1/n$) viewed down the [100] direction.

The angular placement of the Fe(CO)(cyclobutadiene) fragment in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe$-(CO) is not unlike that of the nonring iron tricarbonyl fragments relative to the ferracyclopentadiene rings in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$,[19] $Fe(CO)_3(C_6H_4CH$-$CC_6H_5)Fe(CO)_3$,[20] and $Fe_3(CO)_{10}(C_2H_2)_5$.[21] The one remaining carbonyl group in $Fe(CO)_3(C_6H_5C_2C_6H_4$-$C_2C_6H_5)_2Fe(CO)$ is oriented in an analogous manner as one of the three carbonyl groups of the nonring iron tricarbonyl fragment in these three stereochemically related compounds. The planar cyclobutadiene ring is symmetrically inclined with respect to the lone carbonyl group and the metal–metal direction, such that pseudo mirror plane symmetry is preserved for the geometry of the $Fe(CO)_3(C_2C_6H_4C_2)_2Fe(CO)$ fragment (*i.e.*, without the four terminal phenyl groups). The angle between the normals of the cyclobutadiene and ferracyclopentadiene planes is 47°.

The three carbonyl groups and the two terminal diene carbon atoms comprise a square-pyramidal-like polyhedron about the ring iron atom; besides a linkage with the other iron atom, there is an indication that the ring iron atom forms a weak positive interaction with the lone carbonyl carbon atom of the nonring iron atom (*vide infra*). For the nonring iron atom there is an ambiguity concerning the kind of coordination, depending upon whether the *cis*-butadiene portion is assumed to occupy two or three coordination sites. Based on the presumption that it occupies only the two double bond sites and that the cyclobutadiene ring in this molecule sterically takes up two coordination sites (due to its formal replacement of the two terminal carbonyl groups), the nonring iron atom may be formally considered to possess a trigonal prismatic-like environment with the one terminal carbonyl and the other iron atom occupying the other two coordination sites. If the *cis*-butadiene part is alternatively assumed to occupy three sites (*via* the other limiting bonding representation, consisting of two σ-alkyl bonds from the iron to the terminal diene carbon atoms and a μ bond to the

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(17) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

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Table I

A. Final Atomic Parameters with Their Standard Deviations from Rigid-Body Least-Squares Refinement for $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$

	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
Fe(1)	0.2097 (2)	0.3875 (1)	0.1646 (2)	2.0 (1)
Fe(2)	0.3182 (2)	0.4165 (1)	0.0062 (2)	2.7 (1)
O(1)	0.2248 (10)	0.4354 (5)	−0.2325 (14)	6.2 (4)
O(2)	0.4967 (12)	0.3573 (6)	−0.0433 (13)	7.4 (4)
O(3)	0.3907 (9)	0.5315 (6)	0.0097 (11)	4.9 (3)
O(4)	0.1093 (11)	0.4747 (6)	0.0209 (13)	7.0 (4)
C(1)	0.2650 (14)	0.4249 (7)	−0.1425 (18)	4.7 (5)
C(2)	0.4253 (16)	0.3825 (8)	−0.0318 (17)	5.3 (5)
C(3)	0.3619 (14)	0.4877 (8)	0.0069 (16)	4.1 (4)
C(4)	0.1612 (14)	0.4410 (7)	0.0744 (17)	4.2 (5)
C(5)	0.2644 (11)	0.3406 (6)	0.0308 (14)	2.2 (4)
C(6)	0.2968 (12)	0.3171 (7)	0.1368 (14)	2.7 (4)
C(7)	0.3490 (11)	0.3534 (6)	0.2182 (14)	2.3 (4)
C(8)	0.3590 (11)	0.4076 (6)	0.1763 (14)	2.5 (4)
C(9)	0.0673 (12)	0.3753 (7)	0.2240 (15)	3.0 (4)
C(10)	0.1382 (10)	0.3303 (6)	0.2577 (13)	1.9 (4)
C(11)	0.1924 (12)	0.3699 (6)	0.3357 (14)	2.4 (4)
C(12)	0.1273 (13)	0.4142 (7)	0.3011 (15)	3.6 (4)
C_6H_4(1) Group[a]				
C(1–1)	0.250	0.264	0.183	3.1
C(1–2)	0.162	0.272	0.237	3.0
C(1–3)	0.111	0.226	0.279	3.2
C(1–4)	0.147	0.173	0.267	3.6
C(1–5)	0.235	0.164	0.212	4.0
C(1–6)	0.287	0.210	0.170	3.0
C_6H_4(2) Group[a]				
C(2–1)	0.364	0.342	0.348	2.5
C(2–2)	0.283	0.355	0.413	2.8
C(2–3)	0.289	0.349	0.535	4.2
C(2–4)	0.376	0.329	0.594	3.5
C(2–5)	0.457	0.316	0.529	3.6
C(2–6)	0.451	0.323	0.407	3.8
C_6H_5(3) Group[a]				
C(3–1)	0.418	0.450	0.243	3.0
C(3–2)	0.374	0.498	0.288	3.7
C(3–3)	0.432	0.537	0.352	4.6
C(3–4)	0.533	0.528	0.373	4.6
C(3–5)	0.577	0.481	0.329	5.0
C(3–6)	0.519	0.442	0.264	4.7
C_6H_5(4) Group[a]				
C(4–1)	−0.029	0.371	0.159	2.4
C(4–2)	−0.101	0.410	0.186	4.0
C(4–3)	−0.196	0.406	0.131	4.9
C(4–4)	−0.219	0.364	0.049	5.2
C(4–5)	−0.147	0.326	0.021	5.4
C(4–6)	−0.052	0.329	0.076	3.3
C_6H_5(5) Group[a]				
C(5–1)	0.113	0.470	0.346	2.8
C(5–2)	0.056	0.510	0.284	5.1
C(5–3)	0.043	0.563	0.333	5.4
C(5–4)	0.087	0.575	0.445	5.9
C(5–5)	0.144	0.535	0.508	6.1
C(5–6)	0.157	0.483	0.458	4.6
C_6H_5(6) Group[a]				
C(6–1)	0.218	0.307	−0.071	3.5
C(6–2)	0.271	0.262	−0.113	5.0
C(6–3)	0.233	0.232	−0.212	6.2
C(6–4)	0.142	0.248	−0.269	5.3
C(6–5)	0.090	0.293	−0.227	5.2
C(6–6)	0.128	0.322	−0.128	4.4

B. Final Rigid-Body Parameters from Least-Squares Refinement[b,c]

	ϕ, deg	θ, deg	ρ, deg	X_0	Y_0	Z_0
C_6H_4(1)	49.5 (4)	18.3 (4)	−159.0 (4)	0.2497 (8)	0.2637 (4)	0.1826 (9)
C_6H_4(2)	71.0 (4)	1.6 (4)	−96.6 (4)	0.3639 (8)	0.3425 (4)	0.3483 (7)
C_6H_5(3)	55.9 (4)	6.4 (4)	−31.8 (4)	0.4180 (8)	0.4502 (4)	0.2434 (10)
C_6H_5(4)	21.3 (5)	31.0 (4)	148.7 (5)	−0.0288 (6)	0.3713 (5)	0.1588 (9)
C_6H_5(5)	61.7 (8)	−54.5 (5)	−44.0 (8)	0.1134 (9)	0.4704 (4)	0.3460 (11)
C_6H_5(6)	−126.8 (4)	3.9 (4)	53.3 (4)	0.2182 (9)	0.3071 (5)	−0.0713 (9)

Table I (*Footnotes*)

[a] Idealized rigid-body crystallographic coordinates. [b] The three angles ϕ, θ, ρ, represent the series of Eulerian rotations which bring an orthonormal basis set of vectors (x, y, z) into coincidence with a second orthonormal set (x''', y''', z'''). The starting set (x, y, z) is defined according to: x along a of the crystallographic basis set, z along $a \times b$, and y along $z \times x$; this places b in the xy plane. The directions (x''', y''', z''') are defined for each phenyl (n) ring with respect to the crystallographic axes according to: x''' along the [C(n-1)–C(n-4)] vector, z''' along the [C(n-1)–C(n-4)] × [C(n-2)–C(n-5)] vector, and y''' along $z''' \times x'''$. The origin of the group is placed at the C(n-1) atom for each ring. The series of Eulerian rotations which take x, y, z into x''', y''', z''' are: ϕ about z to form (x', y', z'); θ about x' to form (x'', y'', z''); and ρ about y'' to form (x''', y''', z'''), all rotations counterclockwise. A carbon–carbon bond length of 1.392 Å and D_{6h} symmetry was assumed for each phenyl ring. [c] Estimated individual standard deviations of the last significant figure in parentheses.

Table II. Interatomic Distances and Angles[a]

A. Intramolecular Distances (Å) with Their Standard Deviations

Iron–iron distance

Fe(1)–Fe(2)	2.494 (5)

Iron–(carbonyl carbon) distances

Fe(2)–C(3)	1.800 (21)
Fe(2)–C(1)	1.799 (21)
	1.800 (av)
Fe(2)–C(2)	1.747 (22)
Fe(1)–C(4)	1.741 (20)
Fe(2)···C(4)	2.388 (20)

Ferracyclopentadiene distances

Fe(2)–C(5)	1.990 (15)
Fe(2)–C(8)	1.978 (16)
	1.984 (av)
C(5)–C(6)	1.370 (19)
C(7)–C(8)	1.393 (18)
	1.382 (av)
C(6)–C(7)	1.421 (19)
C(5)···C(8)	2.579 (21)

Iron(1)–(ferracyclopentadiene carbon) distances

Fe(1)–C(7)	2.109 (15)
Fe(1)–C(6)	2.098 (16)
	2.104 (av)
Fe(1)–C(5)	2.065 (16)
Fe(1)–C(8)	2.074 (16)
	2.070 (av)

Iron(1)–(cyclobutadiene carbon) distances

Fe(1)–C(11)	2.013 (16)
Fe(1)–C(10)	2.019 (15)
	2.016 (av)
Fe(1)–C(9)	2.108 (16)
Fe(1)–C(12)	2.069 (18)
	2.088 (av)

Cyclobutadiene distances

C(11)–C(12)	1.479 (18)
C(9)–C(10)	1.482 (21)
	1.480 (av)
C(9)–C(12)	1.419 (20)
C(10)–C(11)	1.462 (19)
	1.440 (av)

Carbonyl distances

C(3)–O(3)	1.128 (18)
C(1)–O(1)	1.148 (19)
C(2)–O(2)	1.156 (20)
C(4)–O(4)	1.207 (18)

Iron–(carbonyl oxygen) distances

Fe(2)···O(1)	2.940 (17)
Fe(2)···O(3)	2.928 (14)
	2.934 (av)
Fe(2)···O(2)	2.895 (17)
Fe(2)···O(4)	2.927 (16)
Fe(1)···O(4)	3.172 (16)

B. Intramolecular Angles (deg) with Their Standard Deviations

Angles centered on Fe(1)

C(5)–Fe(1)–C(8)	77.1 (6)	C(4)–Fe(1)–C(5)	96.5 (8)
C(7)–Fe(1)–C(8)	38.9 (5)	C(4)–Fe(1)–C(8)	101.2 (9)
C(5)–Fe(1)–C(6)	38.4 (5)		98.8 (av)
	38.6 (av)		
		C(4)–Fe(1)–C(9)	88.4 (8)
C(6)–Fe(1)–C(7)	39.5 (5)	C(4)–Fe(1)–C(12)	90.4 (8)
C(10)–Fe(1)–C(11)	42.5 (5)		89.4 (av)
C(11)–Fe(1)–C(12)	40.6 (6)		
C(9)–Fe(1)–C(10)	41.9 (5)	C(10)–Fe(1)–Fe(2)	153.2 (7)
	41.2 (av)	C(11)–Fe(1)–Fe(2)	149.8 (7)
			151.7 (av)
C(9)–Fe(1)–C(12)	41.5 (6)		
		C(12)–Fe(1)–Fe(2)	145.6 (6)
		C(9)–Fe(1)–Fe(2)	150.0 (7)
			147.8 (av)

Angles centered on Fe(2)

C(5)–Fe(2)–C(8)	81.1 (6)	C(1)–Fe(2)–C(4)	88.1 (7)
C(1)–Fe(2)–C(3)	90.2 (8)	C(3)–Fe(2)–C(4)	93.1 (7)
C(1)–Fe(2)–C(5)	96.1 (7)		90.6 (av)
C(3)–Fe(2)–C(8)	91.8 (7)		
	94.0 (av)	C(1)–Fe(2)–C(8)	172.5 (7)
		C(3)–Fe(2)–C(5)	170.9 (7)
C(2)–Fe(2)–C(4)	166.0 (8)		171.7 (av)

Table II (*Continued*)

C(1)-Fe(2)-C(2)	96.2 (9)	C(5)-Fe(2)-Fe(1)	53.4 (6)
C(3)-Fe(2)-C(2)	100.2 (9)	C(8)-Fe(2)-Fe(1)	53.7 (6)
	98.2 (av)		52.6 (av)
C(2)-Fe(2)-C(5)	85.7 (8)	C(1)-Fe(2)-Fe(1)	119.0 (7)
C(2)-Fe(2)-C(8)	90.4 (8)	C(3)-Fe(2)-Fe(1)	117.6 (6)
	88.0 (av)		118.3 (av)
C(4)-Fe(2)-C(5)	80.6 (6)		
C(4)-Fe(2)-C(8)	84.6 (6)		
	82.6 (av)		
Carbonyl angles		Cyclobutadiene angles	
Fe(2)-C(1)-O(1)	171.8 (17)	C(11)-C(10)-C(9)	88.3 (12)
Fe(2)-C(3)-O(3)	177.0 (19)	C(10)-C(11)-C(12)	92.5 (13)
	174.4 (av)		90.4 (av)
Fe(2)-C(2)-O(2)	171.7 (19)		
Fe(1)-C(4)-O(4)	166.4 (17)	C(10)-C(9)-C(12)	88.3 (12)
Fe(2)-C(4)-O(4)	120.3 (15)	C(11)-C(12)-C(9)	89.3 (13)
Fe(1)-C(4)-Fe(2)	72.4 (12)		89.0 (av)
Ferracyclopentadiene angles			
C(5)-C(6)-C(7)	115.5 (14)		
C(8)-C(7)-C(6)	114.1 (15)		
	114.8 (av)		
Fe(2)-C(5)-C(6)	113.6 (11)		
Fe(2)-C(8)-C(7)	113.8 (11)		
	113.7 (av)		
C. Intermolecular Distances Less than 3.5[b]			
O(2)···C(1-3)	3.30	O(4)···O(4′)	3.21
O(2)···C(1-4)	3.15	O(3)···O(3′)	3.35
O(3)···C(4-3)	3.35	O(3)···C(2)	3.24
O(3)···C(4-4)	3.46	O(3)···C(3)	3.43
O(3)···C(3-6)	3.47	C(3-3)···C(3-4)	3.48
O(2)···O(3)	3.09	C(3-4)···C(3-4′)	3.36

[a] Standard deviations of last significant figures are given in parentheses. [b] Pairs of atoms which are related by a symmetry operation are designated by C(*n*) and C(*n*′).

ligand π system, localized between the two central carbon atoms), then a seven-coordinated metal can be formulated involving a 4:3 distribution of ligands.

Structural Comparison of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ with Related Complexes. (a) The Ferracyclopentadiene Ring. The structures of several organoiron complexes containing a ferracyclopentadiene ring coordinated to an iron tricarbonyl fragment have been previously determined by X-ray diffraction.[19-22] In three of the molecular compounds—*viz.*, $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$,[19] $Fe(CO)_3(C_6H_4CHCC_6H_5)Fe(CO)_3$,[20] and $Fe_3(CO)_{10}(C_2H_2)_5$[21]—the *cis*-butadiene part of the ferracyclopentadiene ring is coordinated to only one iron tricarbonyl fragment, whereas in the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$,[22] the *cis*-butadiene part of the ferracyclopentadiene ring is bonded to two symmetry-equivalent iron tricarbonyl fragments on opposite sides of the ring. A structural determination of a a dinuclear osmium analog, $Os(CO)_3(HC_2CH_3)_2Os(CO)_3$, containing an osmacyclopentadiene ring bonded to an $Os(CO)_3$ fragment has also been carried out.[23] The basic configuration of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ differs from the configurations of all of these related molecules in that two of the three carbonyls of the nonring metal tricarbonyl fragment have been formally replaced by an electronically equivalent cyclobutadiene ligand.

A detailed comparison of the molecular parameters of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ with those of $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$[19] is informative. Consistent with the idealized geometry of $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$, which possesses a mirror plane of symmetry, the configuration of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, except for the four C_6H_5 ligands, also approximately possesses bilateral symmetry. The maximum difference between the two perpendicular distances of a pair of related atoms from this pseudo mirror plane is only 0.04 Å, except for the two pairs C(1), C(3) and O(1), O(3), whose differences are 0.13 Å and 0.30 Å, respectively (see Table III, A(d)). The iron–iron distance in both compounds is 2.49 Å. In $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ the average distance of the nonring iron atom Fe(1) to the two terminal carbon atoms, C(5) and C(8), of the butadiene portion of the heterocyclic ring is 2.06 Å, as compared to a slightly greater average distance of 2.105 Å to the central diene carbon atoms, C(6) and C(7). The corresponding average distances in $Fe(HOC_2CH_3)_2Fe(CO)_3$ of 2.115 and 2.145 Å are 0.055 and 0.04 Å longer than those in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$. The ring iron to terminal diene carbon distances average 1.985 Å in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, compared to the somewhat smaller average dis-

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(22) R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965).

(23) R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 380 (1963).

Table III

A. Equations of Least-Squares Planes and Distances (Å) from These Planes[a]

(a) Plane containing C(5), C(6), C(7), and C(8)

$$0.8880X - 0.2524Y - 0.3844Z - 0.9647 = 0$$

C(5)	0.00	Fe(1)	−1.62	C(3–1)	0.12
C(6)	0.00	C(1)	0.37	C(6–1)	0.16
C(7)	0.00	C(2)	2.00	C(1–1)	−0.48
C(8)	0.00	C(3)	0.38	C(2–1)	−0.41
Fe(2)	0.31	C(4)	−2.07		

(b) Plane containing C(9), C(10), C(11), and C(12)

$$0.6112X + 0.2413Y - 0.7538Z - 0.7321 = 0$$

C(9)	−0.014	Fe(1)	1.77	C(1–2)	0.05
C(10)	0.011	Fe(2)	4.26	C(2–2)	0.04
C(11)	−0.013	C(4)	2.49	C(5–1)	−0.18
C(12)	0.017			C(4–1)	−0.25

(c) Plane containing C(1), C(3), C(5), and C(8)

$$0.8886X - 0.3530Y - 0.2929Z - 0.1711 = 0$$

C(1)	−0.009	Fe(2)	0.11	C(4)	−2.26
C(3)	0.009	Fe(1)	−1.59	C(6)	0.17
C(5)	0.006	C(2)	1.84	C(7)	0.17
C(8)	−0.006				

(d) Plane containing Fe(1), Fe(2), C(2), and O(2)

$$-0.4423X - 0.6307Y - 0.6376Z + 8.2527 = 0$$

Fe(1)	−0.000	O(1)	1.91	C(9)	0.63
Fe(2)	−0.003	O(3)	−2.20	C(12)	−0.85
C(2)	0.130	C(5)	1.30	C(10)	0.66
O(2)	0.098	C(8)	−1.28	C(11)	−0.80
C(1)	1.21	C(6)	0.73		
C(3)	−1.34	C(7)	−0.69		

(e) Plane containing C(1), C(2), and C(3)

$$0.6001X + 0.3420Y - 0.7231Z - 6.8751 = 0$$

Fe(2)	0.92	O(1)	0.53
O(2)	0.47	O(3)	0.58

B. Angles (deg) between Normals to Planes

a–b	40	*b–d*	87	*b–e*	6
a–c	8	*c–d*	89	*c–e*	51
a–d	89	*a–e*	44	*d–e*	91
b–c	47				

C. Angles (deg) between Interatomic Vectors and Normals to Planes

Vector	Plane	Angle
Fe(1)–Fe(2)	*a*	39
Fe(1)–Fe(2)	*b*	3
Fe(1)–Fe(2)	*c*	47
Fe(1)–Fe(2)	*d*	90
Fe(1)–Fe(2)	*e*	4
Fe(1)–C(9)	*b*	32
Fe(1)–C(10)	*b*	29
Fe(1)–C(11)	*b*	28
Fe(1)–C(12)	*b*	32
Fe(1)–C(5)	*a*	39
Fe(1)–C(6)	*a*	40
Fe(1)–C(7)	*a*	40
Fe(1)–C(8)	*a*	39
Fe(2)–C(2)	*a*	15

[a] The equations of the planes and distances were obtained from the Smith plane program.[18] The equation of the plane is expressed in orthogonal coordinates X, Y, Z, which are related to the crystallographic fractional coordinates x, y, z by the transformation: $X = ax + cz\cos\beta$; $Y = by$; $Z = cz\sin\beta$. Individual weights in the calculation of the planes were assigned according to the relation: $w_k = [abc\sigma(x_k)\sigma(y_k)\sigma(z_k)]^{-2/3}$, where $\sigma(x_k)$, $\sigma(y_k)$, and $\sigma(z_k)$ are the standard deviations of the atomic fractional coordinates x_k, y_k, and z_k, respectively.

Table IV. Orientation of the Phenyl Groups

Orientation of Phenyl Groups Attached to the Butadiene Fragment of the Ferracyclopentadiene Ring

	Twist[a]	Bend[b]
$C_6H_4(1)$ at C(6)	92	108
$C_6H_4(2)$ at C(7)	90	106
$C_6H_5(3)$ at C(8)	67	85
$C_6H_5(6)$ at C(5)	58	84

Orientation of the Phenyl Groups Attached to the Cyclobutadiene

	Twist[a]	Bend[b]
$C_6H_4(1)$ at C(10)	68	88
$C_6H_4(2)$ at C(11)	110	91
$C_6H_5(4)$ at C(9)	27	98
$C_6H_5(5)$ at C(12)	24	99

[a] The twist is defined as the angle between the normal to the reference plane and the normal to the phenyl ring. [b] The bend is defined as the angle between the normal to the reference plane and the C–C vector from the appropriate carbon atom of the reference plane to the bonded carbon atom of the phenyl ring.

tance of 1.945 Å in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$. The ring iron atom in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2$-Fe(CO) is displaced by 0.11 Å from the mean basal plane of the four coordinated carbon atoms, C(1), C(3), C(5), and C(8), in the direction of the apical carbon atom, C(2); in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ the similar perpendicular deviation of the iron atom from its mean basal plane toward the apical carbonyl group is 0.18 Å. In the *cis*-butadiene portion of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ the three carbon–carbon distances C(5)–C(6), C(6)–C(7), and C(7)–C(8) are 1.37 Å, 1.42 Å, and 1.39 Å, respectively, with the longest distance corresponding to the central diene carbon–carbon bond. Since each of the standard deviations in these bond lengths is 0.02 Å, the differences are not statistically significant. The corresponding bond lengths in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ are 1.42 Å, 1.43 Å, and 1.41 Å.

(b) Stereochemical Equivalence of the Fe(CO)(butadiene) and $Fe(CO)_3$ Fragments. The analogous orientations of the Fe(CO)(cyclobutadiene) and $Fe(CO)_3$ fragments in the $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe$-(CO) and $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ molecules, respectively, provides unequivocal evidence that a cyclobutadiene ring may be sterically equivalent to two carbonyl ligands in the formal occupation of two metal coordination sites. The similar stereochemical dispositions of these two fragments, relative to the common ferracyclopentadiene ring in their respective molecules, is exhibited from the angles involving the line from the centroid of the cyclobutadiene ring to the Fe(1) atom of the Fe(CO)(cyclobutadiene) fragment, being amazingly similar to the corresponding angles involving the line from a centroid of the two carbonyl carbon atoms to the iron atom of the $Fe(CO)_3$ fragment. These corresponding angles and their averages are given below with the first value listed for the $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)_3$ molecule and the second value for the $Fe(CO)_3(C_6H_5C_2C_6H_5)_2Fe(CO)_3$ molecule: centroid–Fe(1)–Fe(2) angle, 176° *vs.* 169°; centroid–Fe(1)–C(5) and centroid–Fe(1)–C(8) angles, 134° and 129° (av, 131°) *vs.* 136° and 138° (av, 137°); centroid–Fe(1)–C(6) and centroid–Fe(2)–C(7) angles, 108° and 106° (av, 107°) *vs.* 114° and 115° (av, 114°); centroid–Fe(1)–C(4) angle, 111° *vs.* 100°. The unexpected closeness of corresponding angles is somewhat remarkable, especially in view of the considerably different steric restrictions in the $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ molecule imposed by the simultaneous attachment of the cyclobutadiene and ferracyclopentadiene systems to the common phenyl rings.

(c) The Highly Asymmetrical Bridging Carbonyl Group. An examination of the molecular parameters of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ provides prime evidence for a weak but yet a distinct positive interaction of the one carbonyl carbon atom C(4), attached to Fe(1), with the ring iron atom, Fe(2). The tendency of this essentialy terminal carbonyl group C(4)–O(4) toward a highly unsymmetrical doubly bridging carbonyl configuration is manifested primarily by the Fe(2)–C(4) distance of only 2.39 Å, compared to the normal closest contact intramolecular nonbonding Fe···CO distances of 2.7 Å found in other iron carbonyl complexes. Futher support is given by the directional deformation of the Fe(1)–C(4)–O(4) angle of 166° from linearity, by 14°; the other three terminal Fe–C–O bond angles range from 172° to 177°. Similar small angular distortions of the corresponding carbonyl group toward a doubly bridging group have been observed in the related structures $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$,[19] $Fe(CO)_3(C_6H_4CHCC_6H_5)Fe(CO)_3$,[20] and $Fe_3(CO)_{10}(C_2H_2)_5$.[21] Although the distances from the second iron atom to the carbonyl atom are approximately 0.1 Å longer in these latter three molecules, there is no significant lengthening of the bonding Fe–CO distance of range 1.73–1.74 Å in all four molecules from the other terminal Fe–CO bond lengths. A more pronounced deformation toward a symmetrical doubly bridging carbonyl group was uncovered[22] in the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ which has two $Fe(CO)_3$ fragments bonded on opposite sides to a ferracyclopentadiene ring. Here, for the two asymmetrically doubly bridging carbonyl groups, the two pairs of Fe–CO distances are 1.77 and 1.99 Å and 1.84 and 1.99 Å, while the corresponding Fe–C–O angles are expectedly more acute at 148° and 144°. Other asymmetrical bridging carbonyl arrangements have also been found in the $Fe_4(CO)_{13}{}^{2-}$ anion,[24] in $Fe_3(CO)_{11}P(C_6H_5)_3$,[25] and in $Fe_3(CO)_{12}$.[26] These results all point to the existence of a spectrum of interactions of a metal carbonyl group with a second metal atom in which the carbonyl group may take on a number of geometries which are intermediate between the limiting terminal and symmetrically doubly bridging cases.

(d) The Cyclobutadiene Ring. The geometry of the cyclobutadiene ring is of special interest. Detailed X-ray results have been previously reported for two molecular structures in which cyclobutadiene is bonded to a transition metal.[27,28] The $Fe(CO)_3[C_4(C_6H_5)_4]$ molecule contains a tetraphenylcyclobutadiene group symmetrically linked to an iron tricarbonyl fragment; the cyclobutadiene ring has a square-planar configuration to within the accuracy of the experiment with the average C–C bond length being 1.46 Å.[27] In $[Ni\{C_4(CH_3)_4\}Cl_2]_2 \cdot C_6H_6$ each nickel atom is symmetrically coordinated to a tetramethylcyclobutadiene ring, which has an average C–C bond length of 1.43 Å.[28] In $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ the determined dimensions of the cyclobutadiene ring are 1.48 Å for the pair of carbon–carbon bonds, C(9)–C(10) and C(11)–C(12), related by the pseudo mirror plane, and 1.42 Å and 1.46 Å for the C(9)–C(12) and C(10)–C(11) bonds, respectively.

In $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ the nonring iron Fe(1) is somewhat asymmetrically disposed with respect to the four carbon atoms of the cyclobutadiene ring. The two Fe(1)–C distances which involve the carbon atoms, C(10) and C(11), attached to the C_6H_4 rings (1) and (2) average 2.015 Å, whereas the two other Fe–C distances average 2.09 Å. A less pronounced asymmetric disposition of the iron atom Fe(1) with respect to the carbon atoms of the *cis*-butadiene portion of the ferracyclopentadiene ring occurs with the *longer* Fe(1)–C distances involving the carbon atoms which are attached to the C_6H_4 rings (1) and (2) (*vide supra*). These observed asymmetric orientations of the iron atom Fe(1) with respect to the carbon atoms of the four- and five-membered rings presumably result from constraints imposed by the common attachment of these rings to the C_6H_4 groups (1) and (2).

(e) Disposition of the Ring Substituents. Further evidence that the stereochemistry of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ is markedly influenced by the simultaneous attachment in an *ortho* configuration of the four- and five-membered rings to the two C_6H_4 rings is found from a stereochemical analysis of the ring substituents. The two planes, each of which contains one of these phenyl rings, are approximately perpendicular to the mean plane of the *cis*-butadiene portion of the ferracyclopentadiene ring. The two carbon atoms of these C_6H_4 rings which are directly attached to central diene carbon atoms, C(6) and C(7), of the *cis*-butadiene fragment are perpendicularly displaced from the mean *cis*-butadiene plane by 0.47 and 0.41 Å, respectively, *toward* Fe(1), whereas the two carbon atoms of the C_6H_5 rings (3) and (6), which are directly connected to the terminal carbon atoms, C(8) and C(5), of the *cis*-butadiene moiety are perpendicularly displaced out of the mean *cis*-butadiene plane by only 0.12 Å and 0.16 Å, respectively, away from Fe(1). This considerable nonplanar deformation of the C_6H_4 ring substituent carbon atoms out of the mean *cis*-butadiene plane of the ferracyclopentadiene ring *toward* the nonring iron atom is contrary to the nonplanar deformations of all the *cis*-butadiene substituents in the other related ferracyclopentadiene iron tricarbonyl complexes. In $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ both the hydroxy oxygen and methyl carbon substituents are vertically displaced from the mean *cis*-butadiene plane by average values of only 0.08 Å and 0.01 Å, respectively, *away* from the nonring iron atom. The more nearly planar configurations of the substituent atoms attached to the ferracyclopentadiene rings in these other previously mentioned iron complexes indicate the extent of angular deformation in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, due to the steric restrictions imposed by the interconnection of the ferracyclopentadiene and cyclobutadiene rings with the two C_6H_4 rings.

The normals of the two planes which contain C_6H_4 rings make an average dihedral angle of 21° with the normal of the idealized plane of the four cyclobutadiene ring carbon atoms. The carbon atoms of these C_6H_4 groups, which are directly attached to the atoms C(10) and C(11) of the cyclobutadiene ring, are perpendicularly displaced by 0.05 and 0.04 Å from the mean cy-

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clopentadiene plane *away* from the butadiene-coordinated nonring atom, Fe(1). Moreover, the two carbon atoms of the C_6H_5 rings (4) and (5), which are directly attached to carbon atoms C(9) and C(12) of the cyclobutadiene ring, are similarly displaced from the mean cyclobutadiene plane by 0.25 Å and 0.18 Å, respectively, *away* from Fe(1). These latter deformations from the mean cyclobutadiene plane away from the metal atom are in close agreement with the deformations uncovered for the cyclobutadiene ring substituents in the previously reported metal–cyclobutadiene systems, $Fe(CO)_3[C_4(C_6H_5)_4]$[27] and $[Ni\{C_4(CH_3)_4\}Cl_2]_2 \cdot C_6H_6$.[28]

The C_6H_5 rings (3) and (6), which are attached to the ferracyclopentadiene ring, are twisted in the same sense about the carbon–carbon bond which connects them with the terminal carbon atoms of the *cis*-butadiene fragment such that the normals of these planes form dihedral angles of 23° and 32°, respectively, with the normal of the mean *cis*-butadiene plane. The resulting asymmetrical orientation serves to destroy the approximate molecular mirror plane. The average angular twist for the four C_6H_5 rings attached to the *cis*-butadiene in the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$[22] is 35°.

The C_6H_5 rings (4) and (5) are twisted about the carbon–carbon bonds, which connect these rings with the cyclobutadiene ring, such that dihedral angles of 27° and 24°, respectively, are formed with the cyclobutadiene ring. For $Fe(CO)_3[C_4(C_6H_5)_4]$ the corresponding average angle of twist for the phenyl group substituents is 32°.[27] As in the case for $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$, the shortest *intermolecular* contacts in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ (given in Table II) of 3.1 Å and 3.2 Å are between oxygen atoms, with a few carbonyl–phenyl carbon contacts close enough to play some role in the balance of forces which determine molecular packing. The orientations of the C_6H_5 rings among the related compounds (Table IV) no doubt are a consequence of intermolecular as well as intramolecular forces.

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