properties; sodium formate is reported to decompose on gentle heating to sodium oxalate and hydrogen (Vogel, 1959), which indicates that the C–H bond is easily broken.

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Tetraphenylferrole-$Fe(CO)_3$: a Cycloheptatrieneiron Tricarbonyl–Diphenylacetylene Reaction Product

By Paul E. Riley and Raymond E. Davis

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, *U.S.A.*

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Abstract. $[(C_6H_5)_4C_4]Fe_2(CO)_6$, monoclinic, $P2_1$, $a=16·464$ (2), $b=7·822$ (2), $c=11·374$ (2) Å, $\beta=98·14$ (1)° at *ca.* −40 °C, D_c (−40 °C) = 1·463, D_m (22 °C) = 1·448 g cm^{-3}, $Z=2$. The molecule consists of two $Fe(CO)_3$ moieties joined by a normal Fe–Fe single bond [2·505 (1) Å], with one Fe σ-bonded to the terminal carbons of a tetraphenyl-substituted butadiene group – thereby forming a ferracyclopentadiene ring – and with the other Fe coordinated with the π electrons of the butadiene residue. Full-matrix least-squares refinement has converged with a weighted R index (on $|F|$) of 0·051 using the 2465 reflections with $I_o > 2·0\sigma(I_o)$.

Introduction. Single crystals of $[(C_6H_5)_4C_4]Fe_2(CO)_6$ formed as thin yellow-orange plates from an argon-degassed ether/methanol solution at *ca.* 5°C. Preliminary X-ray diffraction experiments conducted with a Syntex $P2_1$ automated four-circle diffractometer indicated the symmetry and systematic reflection absences consistent with monoclinic space groups $P2_1$ or $P2_1/m$. Intensity data collection details are given in Table 1. Standard deviations were assigned to the data and the usual corrections applied, including that for absorption (see Table 1), as described elsewhere (Riley & Davis, 1976). Only the 2465 reflections with $I > 2·0\sigma(I)$ were used in the ensuing solution and refinement of the structure.

Table 1. *Experimental summary for* $[(C_6H_5)_4C_4]Fe_2(CO)_6$

Syntex $P2_1$ autodiffractometer equipped with graphite monochromator and Syntex LT-1 low-temperature flow system
Radiation: Mo $K\alpha$, $\lambda = 0·71069$ Å
Mode: ω scan technique, recentered automatically after each batch of 750 reflections
Scan range: symmetrically over 1·0° about the $K\alpha_{1,2}$ maximum
Scan rate: variable, 1·5° to 4·0° min^{-1}
Background: offset 1·0° and −1·0° in ω from $K\alpha_{1,2}$ maximum
Check reflections: four remeasured after every 96 reflections; analysis* of 37 sets of check reflections indicated random fluctuation not exceeding 1·3% or 0·1 of an e.s.d. of the initial intensity set
3145 reflections measured in octants h,k,l and $\bar{h},k,l$; $4° \leq 2\theta \leq 52·5°$
Data crystal faces: six faces of {100}, {010}, {001}
Data crystal dimensions: 0·05 × 0·70 × 0·20 mm parallel to directions **a**, **b**, **c**
Data crystal volume = 0·00764 mm^3
Absorption coefficient: μ(Mo $K\alpha$) = 10·7 cm^{-1}
Transmission factor range: 0·81 to 0·95

* Henslee & Davis (1975).

Solution of the Patterson map suggested the non-centrosymmetric space group $P2_1$, and indicated the presence of two Fe atoms per asymmetric unit, separated by *ca.* 2·5 Å. Three successive difference maps, phased initially with the two Fe atoms, revealed the positions of all remaining non-hydrogen atoms of the structure. Full-matrix least-squares refinement, with the phenyl rings treated as rigid groups of D_{6h} symmetry (C–C = 1·392 Å, C–H = 1·00 Å, C–C–C = 120°), and non-group atoms ultimately as anisotropic thermal ellipsoids, converged with $R=\sum||F_o|-|F_c||/\sum|F_o|=0·062$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0·052$. The function minimized in refinement was $\sum w(|F_o|-|F_c|)^2$, where the weights w are $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation $|F_o|$. Neutral atom scattering factors for Fe, O, C (Cromer & Waber, 1965) and H (Stewart, Davidson & Simpson, 1965) were used. Corrections for the real ($\Delta f'$) and imaginary ($\Delta f''$) parts of anomalous scattering of Mo $K\alpha$ radiation were applied to the Fe scattering function (Cromer, 1965).

To determine whether the correct enantiomorph had been selected, additional cycles of least-squares refinement were carried out to convergence with the mirror image isomer. The error indices R and R_w decreased significantly to 0·061 and 0·051, respectively, and hence the atomic coordinates of this latter enantiomorph are presented in Table 2. The standard deviation of an observation of unit weight, $[\sum w(||F_o|-|F_c||)^2/(m-s)]^{1/2}$, is 1·95, where m (2465) is the number of observations ($|F_o|$), and s (186) the number of variables in least-squares refinement. For all 3145 reflections examined for this structure, R and R_w are calculated to be 0·084 and 0·052, respectively.* In the final cycle of least-squares refinement no non-group parameter shifted by more than 0·07 of its e.s.d., and no group parameter

Table 2. *Fractional coordinates and anisotropic thermal parameters for non-group atoms of* $[(C_6H_5)_4C_4]Fe_2(CO)_6$

See Fig. 1 for identity of the atoms and the rigid groups. Numbers in parentheses are the estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$, and are given $\times 10^4$ for the Fe atoms and $\times 10^3$ for the other atoms.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	−0·13041 (6)	−0·25000	−0·14277 (10)	226 (5)	366 (7)	449 (7)	−17 (6)	52 (5)	11 (7)
Fe(2)	−0·23187 (6)	−0·45670 (21)	−0·24798 (9)	297 (5)	282 (6)	367 (6)	−11 (6)	55 (5)	34 (7)
C(1)	−0·0330 (5)	−0·2248 (13)	−0·2004 (8)	36 (5)	50 (6)	60 (6)	−11 (5)	9 (5)	−13 (5)
O(1)	0·0280 (3)	−0·2075 (10)	−0·2325 (6)	37 (4)	94 (7)	110 (5)	−15 (4)	37 (4)	−35 (5)
C(2)	−0·0777 (5)	−0·3310 (12)	−0·0018 (9)	30 (5)	40 (5)	65 (6)	2 (4)	5 (5)	7 (5)
O(2)	−0·0433 (4)	−0·3794 (9)	0·0855 (6)	47 (4)	75 (5)	78 (5)	2 (4)	−21 (4)	20 (4)
C(3)	−0·1397 (5)	−0·0362 (15)	−0·0934 (9)	26 (5)	52 (7)	60 (6)	−1 (5)	13 (5)	4 (6)
O(3)	−0·1486 (4)	0·0988 (10)	−0·0607 (7)	67 (5)	46 (5)	89 (6)	5 (4)	24 (4)	−11 (4)
C(4)	−0·1289 (6)	−0·5330 (12)	−0·2178 (8)	53 (5)	33 (5)	44 (6)	3 (5)	14 (5)	6 (4)
O(4)	−0·0713 (4)	−0·6199 (9)	−0·2133 (6)	43 (4)	50 (4)	104 (6)	18 (3)	17 (4)	5 (4)
C(5)	−0·2815 (5)	−0·6362 (13)	−0·1918 (8)	36 (5)	46 (6)	47 (6)	0 (5)	6 (5)	3 (5)
O(5)	−0·3139 (4)	−0·7484 (11)	−0·1575 (6)	66 (4)	53 (4)	99 (5)	−22 (5)	21 (4)	22 (5)
C(6)	−0·2530 (6)	−0·5481 (11)	−0·3941 (8)	55 (5)	25 (5)	50 (6)	6 (5)	12 (5)	9 (4)
O(6)	−0·2673 (5)	−0·6115 (9)	−0·4837 (6)	117 (7)	39 (4)	51 (4)	−2 (4)	2 (4)	−10 (4)
C(7)	−0·1950 (4)	−0·2136 (10)	−0·2990 (7)	27 (4)	22 (5)	45 (4)	−5 (4)	10 (4)	−1 (4)
C(8)	−0·2821 (4)	−0·2143 (10)	−0·3043 (6)	30 (4)	26 (5)	30 (4)	1 (4)	5 (4)	6 (4)
C(9)	−0·3079 (4)	−0·2577 (11)	−0·1923 (6)	27 (4)	22 (4)	36 (4)	1 (5)	9 (3)	1 (4)
C(10)	−0·2415 (4)	−0·2982 (10)	−0·1031 (7)	21 (4)	32 (5)	40 (4)	0 (3)	7 (4)	3 (4)

Group parameters†

Group	x_o	y_o	z_o	φ	θ	ϱ
PH(1)‡	−0·1540 (3)	−0·1574 (8)	−0·4036 (4)	4·090 (6)	−2·149 (3)	0·640 (6)
PH(2)‡	−0·3426 (3)	−0·1756 (7)	−0·4145 (4)	1·858 (4)	−2·319 (3)	0·206 (4)
PH(3)‡	−0·3967 (2)	−0·2525 (7)	−0·1719 (4)	1·639 (3)	2·829 (3)	−2·680 (3)
PH(4)§	−0·2543 (3)	−0·3280 (8)	0·0220 (4)	2·515 (7)	2·081 (3)	1·257 (7)

† A description of these group parameters is provided elsewhere (Eisenberg & Ibers, 1965). Angular coordinates are in radians.

‡ The internal coordinate system of a phenyl ring was as follows: the ring was defined to lie in the xy plane with atom C(1) – bound to a butadiene carbon – at the origin, vector C(1) to C(4) coincident with the positive y axis, and vector C(6) to C(2) parallel to the positive x axis.

§ To avoid singularity of the transformation matrix (Eisenberg & Ibers, 1965), the axes of this group were chosen so that vectors C(1) to C(5) and C(1) to C(2) were coincident with the positive y and x directions, respectively.

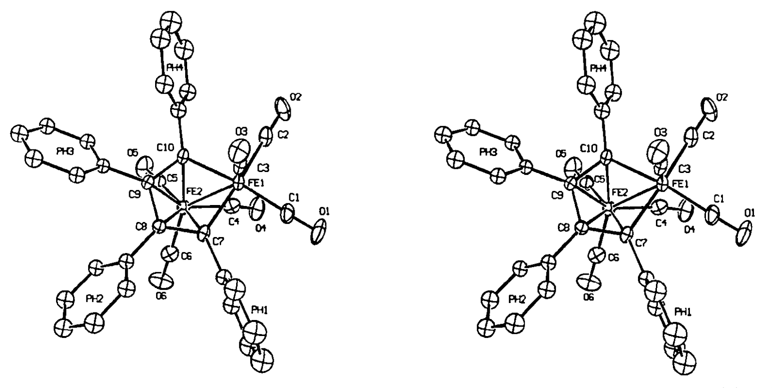

Fig. 1. A stereo view of $[(C_6H_5)_4C_4]Fe_2(CO)_6$, illustrating the atom numbering scheme. Ellipsoids of 30% probability are shown. Hydrogen atoms have been omitted for sake of clarity.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31293 (24 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Selected bond lengths* (Å) *of some ferracyclopentadiene complexes*

Numbers in parentheses are the estimated standard deviations in the last significant digit. The standard deviation of a mean bond length is defined as $[\sum(X_i-\bar{X})^2/(n-1)]^{1/2}$ where n is the number of observations.

	Bond types/bond averages						
Compound	Fe–Fe	Fe–CO	Fe–C(σ)	Fe–C(π) (terminal)	Fe–(Cπ) (central)	Fe(1)–C(4)	Ref.
$[(C_6H_5)_4C_4]Fe_2(CO)_6$	2·505 (1)	1·80 (2)	1·97 (1)	2·10 (1)	2·14 (1)	2·374 (9)	*a*
$[C_8H_6]Fe_2(CO)_6$ (symmetric)	2·508 (2)	1·79 (3)	1·96 (2)	2·051 (3)	2·19 (2)	2·48	*b*
$[C_8H_6]Fe_2(CO)_6$ (unsymmetric)	2·498 (2)	1·79 (2)	1·97 (1)	2·11 (1)	2·16 (1)	2·43	*b*
$[C_6H_8O_2]Fe_2(CO)_6$	2·493 (2)	1·78 (1)	1·95 (1)	2·12 (1)	2·15 (1)	2·48 (1)	*c*
$[\{(CH_3)_3SiOC\}_4]Fe_2(CO)_6$	2·500 (3)	1·78 (2)	1·92 (2)	2·13 (2)	2·19 (2)	–	*d*
$[C_{12}H_{16}]Fe_2(CO)_6$	2·462 (3)	1·74 (2)	1·96 (2)	2·07 (2)	2·18 (2)	2·32 (2)	*e*

(*a*) This work. (*b*) Barnett (1970). (*c*) Hock & Mills (1961). (*d*) Bennett, Graham, Smith & Stewart (1973). (*e*) Chin & Bau (1973).

by more than 0·15 of its e.s.d. The largest peak on a final difference Fourier map was 1·0 e Å^{-3} located near one of the phenyl rings. On a previous difference map, the density of a typical C atom was 3·7 e Å^{-3}.

Final atomic positional and thermal parameters, with estimated standard deviations as obtained from the inverse matrix, are presented in Table 2.

Discussion. Reaction of equimolar quantities of cycloheptatrieneiron tricarbonyl and diphenylacetylene in tetrahydrofuran under a N_2 atmosphere yielded two major products, the metal-free adduct 7,8-diphenylbicyclo[4,2,1]nona-2,4,7-triene and an unknown crystalline yellow-orange solid (Devon, 1974). The n.m.r. spectrum of the second product showed solely absorptions characteristic of aromatic protons, while the infrared spectrum was unambiguously interpretable only in the C≡O stretching region. Since elemental analysis seemed to be confusing, a single-crystal X-ray diffraction study was undertaken to elucidate the structure of this unknown material.

The molecular structure, as shown in Fig. 1, is another example of a rather common product of reactions between iron carbonyls and organic molecules. Two $Fe(CO)_3$ moieties are linked by a normal Fe–Fe bond (see Table 3). Fe(1) forms two σ bonds with the terminal carbon atoms of a butadiene group, thereby creating a ferracyclopentadiene ring, while Fe(2) completes its coordination by π bonding with the delocalized electron density of the butadiene residue of the ferracyclopentadiene ring.

As illustrated in Table 3, the molecular geometry of $[(C_6H_5)_4C_4]Fe_2(CO)_6$ agrees well with the corresponding features of other ferracyclopentadienyl-containing compounds; and as noted in previous structures, carbonyl atom C(4) may be considered to bridge Fe(1) and Fe(2) asymmetrically [Fe(2)–C(4) = 1·784 (9), Fe(1)–C(4) = 2·374 (9) Å in $[(C_6H_5)_4C_4]Fe_2(CO)_6$], and thus to occupy (remotely) a sixth coordination site about Fe(1). Hence '*trans* ligand atoms' C(3) and C(4) describe an angle of 175·3 (4)° at Fe(1). The Fe(1)··· C(4) 'non-bonded' distance here is not significantly different from the short distance [2·32 (2) Å] found in $[C_{12}H_{16}]Fe_2(CO)_6$ (Chin & Bau, 1973), and accordingly the Fe(2)–C(4)–O(4) angles in these complexes are distorted appreciably from near-linearity, 162·1 (8)° and 162 (3)° in $[(C_6H_5)_4C_4]Fe_2(CO)_6$ and $[C_{12}H_{16}]Fe_2(CO)_6$, respectively. Complete tabulations of bond lengths and bond angles, as well as selected least-squares planes, for $[(C_6H_5)_4C_4]Fe_2(CO)_6$ have been deposited.*

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* See previous footnote.