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Structure of Tricarbonyl(η^4-1,4-dibenzoyloxy-1,3-butadiene)iron(0)*

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Abstract. [Fe(CO)$_3$(C$_{18}$H$_{14}$O$_4$)], $M_r = 434\cdot2$, monoclinic, $P2_1/c$, $a = 6\cdot152$ (2), $b = 32\cdot318$ (10), $c = 10\cdot210$ (4) Å, $\beta = 104\cdot26$ (3)°, $V = 1967$ (1) Å^3, $Z = 4$, $D_x = 1\cdot47$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0\cdot802$ mm^{-1}, $F(000) = 888$, $T = 293$ K, $R = 0\cdot048$ for 2681 observed reflections. The X-ray study confirms that the solid-state structure of tricarbonyl(η^4-1,4-dibenzoyloxy-1,3-butadiene)iron(0) is as inferred from spectroscopic evidence. The molecule contains a diphenylester–vinyl unit bonded to the iron atom, to which are also bonded three carbonyl groups in an approximately trigonal arrangement. Both φ-COO– ester groups are planar and synclinal to each other about the central C(5)–C(6) bond. There is only one C–H···O intermolecular approach <3·3 Å. The crystal structure is stabilized by van der Waals forces.

Introduction. As part of our investigations concerning complexes between Fe(CO)$_3$ and vinyl ligands with various substituents, including phenyls, esters and acyl groups, the title compound (2) was synthesized. It was obtained from the reaction of tricarbonyl(η^4-syn-1,4-diacetoxy-1,3-butadiene)iron(0) (1) (170 mg, 1 mmol) and MeLi (6·2 ml, 0·8 M) with 15 ml of anhydrous tetrahydrofuran (THF) at 195 K in an argon atmosphere, to give a red solution. After 10 min of stirring, benzoic anhydride (1·13 g, 5 mmol) in 5 ml of

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THF was added, the temperature was raised to 298 K and stirring continued for 2 h. The brown product was purified by chromatographic methods and recrystallized from n-hexane to give pale yellow crystals, m.p. 455–456 K. Compound (2) was characterized by NMR, IR and mass spectrometry. The X-ray structure determination was undertaken to elucidate the stereochemistry of (2).

(1)   (2)
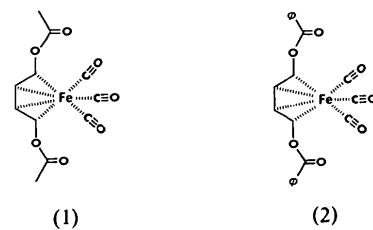
Experimental. Pale yellow crystal, 0·28 × 0·12 × 0·40 mm. Nicolet *R*3 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 machine-centred reflections with $5\cdot0 < 2\theta < 20\cdot2°$, 3482 reflections with $3 < 2\theta < 50°$ for two octants, 2681 independent with $I > 2\cdot5\sigma(I)$, index range h −7→7, k 0→38, l 0→12, ω-scan mode, variable scan speed, scan width 1·0° (θ), two standard reflections (041, 052) monitored every 50 measurements, Lp corrections and absorption ignored. Structure solved by combination of direct methods and partial structure expansion by iterative *E*–Fourier

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
Fe	−49 (1)	4309 (1)	2682 (1)	37 (1)
C(1)	−2585 (6)	4269 (1)	3213 (4)	55 (1)
O(1)	−4176 (5)	4246 (1)	3588 (4)	93 (2)
C(2)	1223 (6)	3824 (1)	3287 (4)	53 (1)
O(2)	1957 (7)	3511 (1)	3640 (4)	95 (2)
C(3)	1571 (6)	4591 (1)	4113 (4)	48 (1)
O(3)	2557 (5)	4774 (1)	5014 (3)	75 (1)
C(4)	−1329 (7)	4067 (1)	747 (4)	46 (1)
C(5)	790 (7)	4249 (1)	855 (4)	46 (1)
C(6)	996 (6)	4662 (1)	1277 (4)	45 (1)
C(7)	−950 (7)	4846 (1)	1533 (4)	45 (1)
O(5)	−564 (4)	5240 (1)	2135 (3)	49 (1)
C(8)	−2334 (7)	5494 (1)	2009 (4)	48 (1)
O(7)	−4236 (5)	5390 (1)	1493 (3)	66 (1)
C(9)	−1658 (7)	5913 (1)	2555 (4)	47 (1)
C(10)	−3281 (8)	6211 (1)	2463 (4)	59 (2)
C(11)	−2700 (10)	6613 (2)	2907 (4)	73 (2)
C(12)	−498 (10)	6711 (1)	3458 (5)	73 (2)
C(13)	1109 (9)	6412 (2)	3568 (5)	76 (2)
C(14)	570 (7)	6017 (1)	3120 (5)	63 (2)
O(4)	−1412 (4)	3638 (1)	448 (3)	51 (1)
C(15)	−3234 (7)	3429 (1)	573 (4)	52 (1)
O(6)	−4646 (5)	3575 (1)	1066 (3)	72 (1)
C(16)	−3318 (7)	3001 (1)	21 (4)	49 (1)
C(17)	−5059 (7)	2748 (1)	128 (4)	66 (2)
C(18)	−5282 (10)	2358 (2)	−446 (5)	78 (2)
C(19)	−3787 (10)	2224 (2)	−1151 (5)	81 (2)
C(20)	−2042 (9)	2476 (2)	−1258 (5)	76 (2)
C(21)	−1783 (8)	2864 (1)	−666 (4)	64 (2)

procedure using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms treated anisotropically; H atoms of the butadiene moiety were located from electron density difference maps and their positional parameters refined. All H atoms including those riding on bonded C of the phenyl rings had a fixed $U = 0.06 \text{ Å}^2$. $\sum w |\Delta F|^2$ minimized with $w = 1/[\sigma^2(F_o) + 0.001(F_o)^2]$, where σ is standard deviation of observed amplitudes, based on counting statistics; $S = 1.215$. An empirical correction for secondary extinction was used, $F_c^{corr} = F_c(1 - xF_c^2/\sin\theta)$ with $x = 0.00001$. In the last cycle $(\Delta/\sigma)_{max} = 0.527$; $\Delta\rho$ from −0.26 to 0.46 e Å^{-3}; final $R = 0.048$, $wR = 0.056$; scattering factors from *International Tables for X-ray Crystallography* (1974). All computations were performed on a Nova 4S computer and plots were drawn on a Tektronix plotter with the *SHELXTL* system of programs.

Discussion. Atomic coordinates are given in Table 1.* A perspective molecular drawing is shown in Fig. 1. The bond lengths and angles for non-H atoms are listed in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44300 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Fe—C(1)	1·779 (4)	Fe—C(2)	1·795 (4)
Fe—C(3)	1·800 (4)	Fe—C(4)	2·090 (3)
Fe—C(5)	2·063 (4)	Fe—C(6)	2·055 (4)
Fe—C(7)	2·091 (3)	C(1)—O(1)	1·138 (5)
C(2)—O(2)	1·129 (5)	C(3)—O(3)	1·136 (5)
C(4)—C(5)	1·409 (6)	C(4)—O(4)	1·417 (4)
C(5)—C(6)	1·401 (5)	C(6)—C(7)	1·417 (6)
C(7)—O(5)	1·408 (4)	O(5)—C(8)	1·345 (5)
C(8)—O(7)	1·208 (5)	C(8)—C(9)	1·484 (5)
C(9)—C(10)	1·374 (6)	C(9)—C(14)	1·391 (6)
C(10)—C(11)	1·394 (6)	C(11)—C(12)	1·370 (8)
C(12)—C(13)	1·368 (8)	C(13)—C(14)	1·368 (6)
O(4)—C(15)	1·342 (5)	C(15)—O(6)	1·202 (6)
C(15)—C(16)	1·490 (6)	C(16)—C(17)	1·372 (6)
C(16)—C(21)	1·381 (7)	C(17)—C(18)	1·382 (6)
C(18)—C(19)	1·371 (9)	C(19)—C(20)	1·373 (8)
C(20)—C(21)	1·385 (7)		

|			
C(1)—Fe—C(2)	99·9 (2)	C(1)—Fe—C(3)	98·1 (2)
C(2)—Fe—C(3)	93·2 (2)	C(1)—Fe—C(4)	96·1 (2)
C(2)—Fe—C(4)	91·6 (2)	C(3)—Fe—C(4)	164·0 (2)
C(1)—Fe—C(5)	134·6 (2)	C(2)—Fe—C(5)	92·5 (2)
C(3)—Fe—C(5)	124·8 (2)	C(4)—Fe—C(5)	39·7 (2)
C(1)—Fe—C(6)	134·6 (2)	C(2)—Fe—C(6)	122·8 (2)
C(3)—Fe—C(6)	94·6 (2)	C(4)—Fe—C(6)	70·1 (1)
C(5)—Fe—C(6)	39·8 (1)	C(1)—Fe—C(7)	95·8 (2)
C(2)—Fe—C(7)	162·2 (2)	C(3)—Fe—C(7)	93·1 (2)
C(4)—Fe—C(7)	78·2 (1)	C(5)—Fe—C(7)	70·3 (2)
C(6)—Fe—C(7)	40·0 (2)	Fe—C(1)—O(1)	178·1 (4)
Fe—C(2)—O(2)	177·5 (3)	Fe—C(3)—O(3)	178·5 (4)
Fe—C(4)—C(5)	69·2 (2)	Fe—C(4)—O(4)	123·8 (2)
C(5)—C(4)—O(4)	114·1 (3)	C(4)—C(5)—C(6)	115·7 (4)
Fe—C(5)—C(6)	69·8 (2)	Fe—C(6)—C(7)	71·4 (2)
Fe—C(6)—C(5)	70·4 (2)	Fe—C(7)—C(6)	68·7 (2)
C(5)—C(6)—C(7)	116·1 (3)	C(6)—C(7)—O(5)	113·6 (3)
Fe—C(7)—O(5)	120·8 (2)	O(5)—C(8)—O(7)	123·1 (4)
C(7)—O(5)—C(8)	117·7 (3)	O(7)—C(8)—C(9)	124·8 (4)
O(5)—C(8)—C(9)	112·1 (3)	C(8)—C(9)—C(14)	122·1 (4)
C(8)—C(9)—C(10)	118·8 (3)	C(9)—C(10)—C(11)	120·5 (4)
C(10)—C(9)—C(14)	119·0 (4)	C(11)—C(12)—C(13)	119·5 (4)
C(10)—C(11)—C(12)	119·8 (5)	C(9)—C(14)—C(13)	119·7 (4)
C(12)—C(13)—C(14)	121·4 (5)	O(4)—C(15)—O(6)	123·3 (4)
C(4)—O(4)—C(15)	117·2 (3)	O(6)—C(15)—C(16)	124·1 (4)
O(4)—C(15)—C(16)	112·5 (4)	C(15)—C(16)—C(21)	121·7 (4)
C(15)—C(16)—C(17)	118·5 (4)	C(16)—C(17)—C(18)	120·4 (5)
C(17)—C(16)—C(21)	119·6 (5)	C(18)—C(19)—C(20)	119·5 (5)
C(17)—C(18)—C(19)	120·2 (5)	C(16)—C(21)—C(20)	119·5 (5)
C(19)—C(20)—C(21)	120·7 (5)		
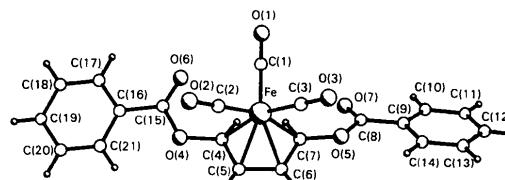
Fig. 1. A molecule of the title compound showing the atom labelling.
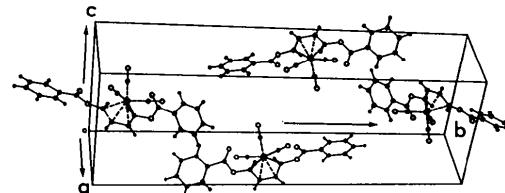
Fig. 2. A perspective drawing of the contents of one unit cell.

As Fig. 1 shows, this structure contains the diphenyl-ester–vinyl ligand complexed to the tricarbonyl unit as a four-electron ligand and can be represented by a resonance hybrid between the diene (A) and the 2σ–π structure (B). Thus, the whole molecular arrangement bears a very close similarity to the structures of butadieneiron tricarbonyl (Mills & Robinson, 1963), tricarbonyl(dimethyl 4-methyl-1-oxo-1,3-pentadiene-2,3-dicarboxylate)iron (Fischer & Ricard, 1982) and tricarbonyl(η^4-syn-1,4-diacetoxy-1,3-butadiene)iron(0) (Soriano-Garcia, Alvarez, Toscano & Cano, 1987).
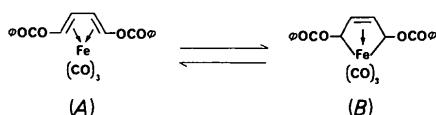
The molecule has approximate m symmetry: the mirror plane passes through the O(1)–C(1)–Fe atoms and bisects the C(5)–C(6) bond, while the other carbonyl groups [C(2)–O(2) and C(3)–O(3)] lie over the C(4)–C(5) and C(6)–C(7) bonds, respectively. A similar situation occurs in butadieneiron tricarbonyl and tricarbonyl(η^4-syn-1,4-diacetoxy-1,3-butadiene)-iron(0) structures.

The arrangement of ligands about Fe can be described as approximately square pyramidal, the base of the pyramid being formed by the carbonyl atoms C(2) and C(3) and by C(4) and C(7) of the butadiene system. The dihedral angle between planes formed by O(1)–C(1)–Fe and C(4)–C(5)–C(6)–C(7) is 47·8 (6)°, whereas in butadieneiron tricarbonyl and tricarbonyl(η^4-syn-1,4-diacetoxy-1,3-butadiene)iron(0) this angle is 61 and 75·4 (6)°, respectively.

The Fe–C bond distances vary over a small range [2·055 (4) to 2·091 (3) Å], reflecting the fact that the metal–ligand bonding is nearly the same for the four C atoms of the η^4-system in spite of the presence of the two phenyl rings.

The two φ-COO-ester groups are synclinal to each other about the C(5)–C(6) bond. Both φ-COO-ester

groups at C(4) and C(7) are planar within the limits of experimental error; maximum deviations are −0·105, 0·113 and −0·116 Å for C(7), O(4) and C(4) respectively. The dihedral angle between the two φ-COO-esters is 40·6 (6)°. Both phenyl rings show normal geometry and the C=O groups are syn to the C(4)–H, C(7)–H bonds, respectively (Mathieson, 1965; Chothia & Pauling, 1970).

The butadiene system is planar within ±0·002 (6) Å. The pairs of atoms [H(4), H(7)] and [H(5), H(6)] are displaced out of this plane away from and towards the Fe atom respectively, at distances of −0·521, −0·574 and 0·085, 0·065 Å from the plane. The dihedral angles between the butadiene system and the φ-COO-ester group at C(4) and C(7) are 18·6 (6) and 22·4 (6)°, respectively.

The molecular packing is shown in Fig. 2. There is only one intermolecular approach of non-hydrogen atoms $< 3·3$ Å, C(18)$\cdots$O(2) ($-1+x$, $0·5-y$, $-0·5+z$) $= 3·297$ (6) Å. The molecules are, therefore, held in the crystal by van der Waals forces.

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Ethyltriphenylphosphonium Dibromobis(succinimido)aurate(III)

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Abstract. $(C_6H_5)_3\overset{+}{P}C_2H_5.[AuBr_2(C_4H_4NO_2)_2]^-$, $M_r = 844·3$, monoclinic, $P2_1/n$, $a = 9·602$ (3), $b = 13·293$ (3), $c = 23·953$ (7) Å, $\beta = 104·87$ (2)°, $V = 2955$ (3) Å^3, $Z = 4$, $D_x = 1·90$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, μ(Mo $K\alpha$) $= 77·3$ cm^{-1}, $F(000) = 1624$. For 2313 observed reflections, $R =$