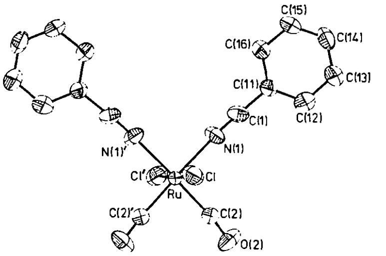

Fig. 1. Perspective view drawn with *ORTEP* (Johnson, 1965) of the molecular structure with the atom numbering. Ellipsoids represent the 50% probability level.

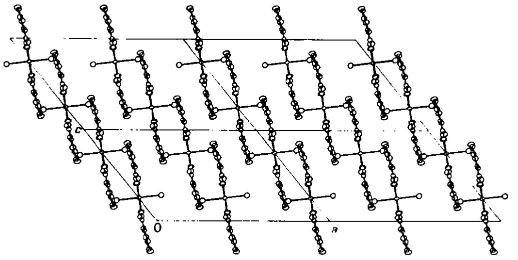

Fig. 2. View of four unit cells projected onto the *xz* plane.

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Tricarbonyl[2–5-η-(methyl 1α-phenyl-2,4-cyclohexadiene-1β-carboxylate)]iron(0), [$Fe(C_{14}H_{14}O_2)(CO)_3$]

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Abstract. $M_r = 354{\cdot}15$, monoclinic, $P2_1/c$, $a = 17{\cdot}499\,(3)$, $b = 7{\cdot}546\,(1)$, $c = 13{\cdot}243\,(2)$ Å, $\beta = 114{\cdot}87\,(2)^\circ$, $U = 1586{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}482$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}54051$ Å, $\mu = 7{\cdot}96$ mm^{-1}, $F(000) = 724$, $T = 293\,(2)$ K. Final $R = 0{\cdot}044$ for 1437 unique diffractometer data. The carboxylate group is characteristically slightly aplanar due to the presence of a proximal, short, intramolecular non-bonding interaction to a neighbouring carbonyl group.

Introduction. The use of $>Fe(CO)_3$ as a protective and/or directing group in regio- and stereospecific organic syntheses has been studied extensively by A. J. Birch and co-workers (*e.g.* Birch *et al.*, 1981). The organic precursors are commonly 1,4-cyclohexadienes (from Birch reduction of aromatics) and their reaction products with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ are commonly mixtures of isomeric 1,3-diene–$Fe(CO)_3$ complexes. Detailed characterization of both the reaction products and their isomeric distributions is an obvious prerequisite to the use of those products as synthetic intermediates. The present complex is the sole isomer obtained from the reaction of methyl 1-phenyl-2,5-cyclohexadiene-1-carboxylate with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ (Bandara, 1981). The stereochemistry could only be assigned with certainty by recourse to crystal-structure analysis.

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Experimental. Reflection intensities for one unique quadrant ($3 < 2\theta < 126°$) recorded on a Picker FACS-1 diffractometer, θ–2θ scan mode, scan velocity 2° min^{-1} (2θ), 2 × 10s backgrounds at extremes, Cu $K\bar{\alpha}$, graphite-crystal monochromator, 2886 reflections excluding standards; specimen-crystal dimensions 0·025 × 0·33 × 0·28 mm parallel to **a***, **b** and **c*** respectively, bounding faces {100}, {001}, (010), ($0\bar{1}3$) and ($0\bar{1}\bar{1}$); cell dimensions and standard errors from least-squares analysis of setting angles for 12 well dispersed reflections with $49 < 2\theta < 77°$ (Cu $K\alpha_1$ radiation). Intensities of three standard reflections (900, $\bar{4}08$ and $14\bar{2}$) decreased by 9·9, 4·3 and 3·3% respectively during data collection; reflection intensities corrected accordingly (Churchill & Kalra, 1974). Reflections with $I \geq 3\sigma(I)$ and background imbalance $\Delta < 3\sigma(\Delta)$ were reduced to $|F_o|$ and $\sigma(F_o)$ values with instrumental uncertainty constant $p^2 = 0{\cdot}002$ assumed (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967); data corrected for absorption (de Meulenaer & Tompa, 1965) but not for extinction (transmission factor range 0·49–0·91); sorting and averaging yielded 1437 unique data with $R_s = 0{\cdot}033$ (Robertson & Whimp, 1975). Structure solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) and refined by full-matrix least-squares analysis, minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma(F_o)]^{-2}$; all atoms refined; anisotropic thermal parameters for Fe, C and O, isotropic thermal parameters for H; scattering factors, with anomalous-dispersion corrections for Fe, C and O, from *International Tables for X-ray Crystallography* (1974); at convergence $R = 0{\cdot}044$, $R_w = 0{\cdot}042$, $S = 1{\cdot}52$; final Δ/σ all <0·05 and final $\Delta\rho$ excursions all $< |0{\cdot}32|$ e Å^{-3}; figures drawn with *ORTEP* (Johnson, 1976); calculations performed with *ANUCRYS* programs (McLaughlin, Taylor & Whimp, 1977) on the Australian National University Univac 1100/82 computer.

Discussion. Atom nomenclature is defined in Fig. 1 and the corresponding coordinates are listed in Table 1.† Bond distances and angles are in Table 2.

The metal–ligand bonding arrangement is similar to that observed in other tricarbonyl 1,3-cyclohexadiene iron derivatives (Dunand & Robertson, 1982*a*,*b*, and references therein; Anderson & Robertson, 1983). The carbonyl ligands are directed *trans* to C(1), C(4), and to the mid-point of the C(2)–C(3) diene bond. The symmetry of the hexadiene–Fe(CO)$_3$ moiety differs only marginally from exact C_s, the principal deviation being the inequivalence of the C(1)–C(2)–C(3) [113·7 (6)°] and C(2)–C(3)–C(4) [116·5 (6)°] bond angles. To within experimental error the four-atom diene set C(1), C(2), C(3), C(4) is accurately planar, the associated H atoms all being displaced out of the carbon plane towards the metal atom [$\Delta = 0{\cdot}03$ (5)–0·21 (4) Å]. In constrast, the C(4), C(5), C(6), C(1) set is slightly but significantly aplanar with a torsion angle [about C(5)–C(6)] of −3·7 (8)°. The dihedral angle between the two carbon sets [42·2 (7)°] is similar to values we have observed recently in other tricarbonyliron complexes of substituted 1,3-cyclohexadienes (41·7–43·4°; Anderson & Robertson, 1983; Dunand & Robertson, 1982*a*,*b*). These values are at the high end of the reported range and are substantially exceeded only by that in tricarbonyl(octafluoro-1,3-cyclohexadiene)iron (47·3°; Churchill & Mason, 1967). Electron localization at the C(1) and C(4) ring sites, in the complex, is apparently facilitated by both electron-donating (methyl, methoxy) and electron-withdrawing (fluoro, methoxycarbonyl) ring substituents.

The methoxycarbonyl set C(13), O(14), O(15), C(16) is also only marginally aplanar [$\Delta_{\max.} = 0{\cdot}027$ (9) Å; O(14)–C(13)–O(15)–C(16) torsion = 5·0 (8)°]. C(5) lies within 0·006 Å of the best plane through the set and the methyl H atoms are *trans*-staggered with respect to the C(13)–O(15) bond. C(13) of the methoxycarbonyl set is in relatively close contact with carbonyl group –C(19)≡O(20) [C(13)···C(19) = 3·105 (7), C(13)···O(20) = 3·242 (7) Å]. There is a consequent, small, pyramidal distortion of the C(5), C(13), O(14), O(15) set, with C(13) displaced by 0·029 (6) Å away from the C(5), O(14), O(15) plane *towards* the contacting carbonyl group. Both the deformation and the causative contacts are quantitatively similar to those observed in tricarbonyl[2–5-η-(methyl 3,5-dimethoxy-1-methyl-2,4-cyclohexadiene-1β-carboxylate)]iron(0) [$\Delta = 0{\cdot}023$ (2) Å; C···C

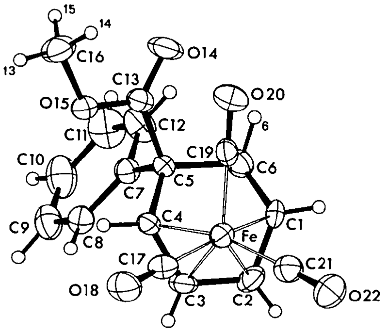

Fig. 1. Labelling scheme (Johnson, 1976). Except as indicated H atoms are numbered for attached C atoms [H(5) obscured by C(6)]. Vibration ellipsoids define 30% probability surfaces. H atoms are depicted as 0·11 Å radius spheres.

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† Lists of structure factors, anisotropic thermal parameters, deviations from the diene, phenyl and carboxylate planes, H-atom coordinates and a full list of bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38949 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$B_{\rm eq}$(Å^2)
Fe	0·8379 (1)	0·2657 (1)	0·4016 (1)	3·7
C(1)	0·7190 (4)	0·1928 (7)	0·2813 (5)	4·3
C(2)	0·7189 (4)	0·2144 (9)	0·3869 (5)	4·5
C(3)	0·7453 (4)	0·3800 (8)	0·4328 (5)	4·1
C(4)	0·7693 (3)	0·5000 (7)	0·3696 (4)	3·4
C(5)	0·7129 (3)	0·5227 (6)	0·2455 (3)	3·1
C(6)	0·6815 (4)	0·3372 (8)	0·1968 (5)	4·4
C(7)	0·6403 (3)	0·6519 (7)	0·2230 (4)	3·8
C(8)	0·6304 (4)	0·7486 (10)	0·3058 (5)	4·5
C(9)	0·5642 (5)	0·8644 (9)	0·2817 (7)	5·7
C(10)	0·5046 (5)	0·8865 (11)	0·1747 (8)	7·0
C(11)	0·5146 (5)	0·7920 (11)	0·0926 (7)	7·3
C(12)	0·5802 (4)	0·6761 (9)	0·1153 (6)	5·7
C(13)	0·7627 (3)	0·6056 (7)	0·1859 (4)	3·8
O(14)	0·7498 (3)	0·5770 (5)	0·0912 (3)	6·1
O(15)	0·8190 (2)	0·7230 (5)	0·2493 (2)	4·5
C(16)	0·8702 (6)	0·8066 (12)	0·2007 (7)	6·0
C(17)	0·9214 (4)	0·3634 (8)	0·5184 (5)	4·3
O(18)	0·9742 (3)	0·4290 (6)	0·5931 (3)	6·2
C(19)	0·8786 (3)	0·2863 (7)	0·3009 (4)	3·8
O(20)	0·9037 (3)	0·2994 (5)	0·2339 (3)	6·5
C(21)	0·8750 (4)	0·0493 (9)	0·4507 (5)	4·7
O(22)	0·9015 (3)	−0·0885 (6)	0·4853 (3)	6·7

Table 2. *Bond lengths* (Å) *and angles* (°)

Fe–C(1)	2·093 (5)	C(7)–C(8)	1·388 (10)
Fe–C(2)	2·046 (7)	C(7)–C(12)	1·382 (7)
Fe–C(3)	2·026 (7)	C(8)–C(9)	1·377 (10)
Fe–C(4)	2·078 (6)	C(9)–C(10)	1·372 (11)
Fe–C(17)	1·781 (5)	C(10)–C(11)	1·372 (15)
Fe–C(19)	1·763 (7)	C(11)–C(12)	1·372 (11)
Fe–C(21)	1·776 (7)	C(13)–O(14)	1·196 (7)
C(1)–C(2)	1·409 (10)	C(13)–O(15)	1·328 (6)
C(1)–C(6)	1·502 (8)	O(15)–C(16)	1·450 (12)
C(2)–C(3)	1·382 (9)	C(17)–O(18)	1·143 (6)
C(3)–C(4)	1·411 (9)	C(19)–O(20)	1·148 (8)
C(4)–C(5)	1·529 (6)	C(21)–O(22)	1·153 (8)
C(5)–C(6)	1·543 (8)		
C(5)–C(7)	1·527 (8)		
C(5)–C(13)	1·535 (9)		

C(1)–Fe–C(2)	39·8 (3)	C(5)–C(7)–C(8)	123·4 (4)
C(2)–Fe–C(3)	39·7 (3)	C(5)–C(7)–C(12)	119·7 (6)
C(3)–Fe–C(4)	40·2 (3)	C(8)–C(7)–C(12)	116·9 (6)
C(17)–Fe–C(19)	100·1 (3)	C(7)–C(8)–C(9)	121·5 (6)
C(17)–Fe–C(21)	91·3 (2)	C(8)–C(9)–C(10)	121·2 (9)
C(19)–Fe–C(21)	99·0 (3)	C(9)–C(10)–C(11)	117·4 (8)
C(2)–C(1)–C(6)	118·2 (6)	C(10)–C(11)–C(12)	122·0 (7)
C(1)–C(2)–C(3)	113·7 (6)	C(7)–C(12)–C(11)	121·0 (7)
C(2)–C(3)–C(4)	116·5 (6)	C(5)–C(13)–O(14)	124·6 (5)
C(3)–C(4)–C(5)	119·4 (4)	C(5)–C(13)–O(15)	112·1 (5)
C(4)–C(5)–C(6)	107·7 (4)	O(14)–C(13)–O(15)	123·1 (6)
C(4)–C(5)–C(7)	112·9 (5)	C(13)–O(15)–C(16)	116·2 (5)
C(4)–C(5)–C(13)	110·4 (4)	Fe–C(17)–O(18)	178·7 (5)
C(6)–C(5)–C(7)	112·1 (4)	Fe–C(19)–O(20)	178·8 (4)
C(6)–C(5)–C(13)	109·5 (5)	Fe–C(21)–O(22)	177·6 (5)
C(7)–C(5)–C(13)	104·2 (4)		
C(1)–C(6)–C(5)	112·3 (4)		

= 3·123 (3), C···O = 3·255 (3) Å (Dunand & Robertson, 1982*a*)]. Deformations of this type are commonly observed and have been attributed by Bürgi, Dunitz & Shefter (1974) to the proximity of the electrophilic carboxylate C atom to a nucleophile. The deformation is expected to increase as the contact distance decreases.

The phenyl substituent is closely planar [$\Delta_{\rm max.}$: C 0·007 (9), H 0·12 (6) Å] and eclipses the C(5)–C(4) bond [C(8)–C(7)–C(5)–C(4) torsion = 4·6 (8)°]. The methoxycarbonyl group has a perpendicular conformation about C(13)–C(5) with torsion angles O(14)–C(13)–C(5)–C(7) = −89·7 (6)° and O(15)–C(13)–C(5)–C(7) = 86·1 (5)°.

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