

1.675 (7) Å, typical of exocyclic thiones (Form, Raper & Downie, 1976). The endocyclic S—C(*sp*²) and S—C(*sp*³) distances range from 1.724 (7) to 1.744 (7) Å and from 1.791 (10) to 1.823 (10) Å, respectively. They agree well with the corresponding data found for similar systems (Stanković, Ribár, Kálmár & Argay, 1980).

The C—N and C—C distances and bond angles for both coordinated and uncoordinated molecules are similar to each other and to those found in 3-(*p*-bromobenzyl)-1,3-thiazolidine-2-thione (Bryan, Hartley, Peckler, Fujita, Nagao & Seno, 1980). The bond lengths suggest the thione form for all the ttz molecules in our structure. However, the very short N(1)—C(1), N(2)—C(4) and N(3)—C(7) bonds, and the near equality of the exocyclic and endocyclic S—C(*sp*²) bonds point to some contribution also from the thiol form.

Though the three independent ttz rings in the unit cell are very similar in their geometry, significant differences occur in their conformation.

The two coordinated ligands have the twist form with C(2), C(3) and C(5), C(6) deviating significantly from the plane defined by the remaining atoms of their respective rings (Table 4). The thiazolidine ring of the solvating molecule is, however, strictly planar. These differences in conformation are presumably due to packing effects and to the coordination of ligand to metal ion. The crystal packing is illustrated in Fig. 1.

The Cl⁻ ion is hydrogen bonded to the N atom of each of the three independent ttz molecules. The N—H...Cl angles (154–168°) and N...Cl distances (3.16–3.25 Å) are in good agreement with published

data for such hydrogen bonds (Hamilton & Ibers, 1968).

The Cl⁻ anions which are relatively close to the Pd atom [3.504 (2) Å] complete the pseudooctahedral coordination sphere around the metal.

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Acta Cryst. (1982). **B38**, 2034–2037

Tricarbonyl[2-5-η-(methyl 3,5-dimethoxy-1α-methyl-2,4-cyclohexadiene-1β-carboxylate)]iron(0)

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Abstract. C₁₄H₁₆FeO₇, *M_r* = 352.13, triclinic, *P* $\bar{1}$, *a* = 7.590 (1), *b* = 8.445 (1), *c* = 12.175 (1) Å, α = 81.49 (1), β = 85.30 (1), γ = 82.85 (1)° (293 K), *U* = 764.2 Å³, *Z* = 2, *D_c* = 1.531 Mg m⁻³, *F*(000) = 364,

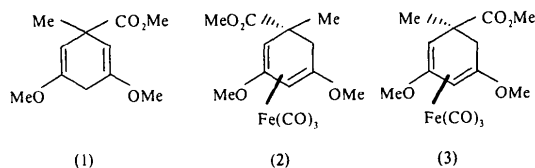
μ (Mo *K*α) = 1.049 mm⁻¹. Refinement converged with *R* = 0.028, *R_w* = 0.045 for 2582 diffractometer data [*I* ≥ 3σ(*I*)]. The metal–ligand bonding follows the expected pattern for 1,3-dienetricarbonyliron(0) complexes.

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Introduction. Substituent directive effects in the reactions of substituted cyclohexadienes with iron carbonyls have been studied extensively in these

laboratories, by A. J. Birch and co-workers, with a view to exploiting the complexes so formed in organic synthesis (Birch *et al.*, 1981; Kelly, 1981). The title complex results from reaction of the 2,5-diene (1) with Fe(CO)₃ to yield both the α and β isomers (2 and 3) in equal amounts (Kelly, 1981). The isomers were separable by chromatography but the stereochemistry could only be assigned with certainty by crystal-structure analysis.



A crystal with dimensions 0.25 × 0.30 × 0.33 mm parallel to [151], [001] and [10 $\bar{1}$], respectively, was used for data collection. Reflection intensities were measured on a Picker FACS-1 diffractometer in the θ -2 θ continuous scan mode [scan velocity 2° min⁻¹ (2 θ), 2 × 10s background counts at extremes, 3° < 2 θ < 52.5°, Mo K α radiation, graphite-crystal monochromator, forms recorded: $\pm h, +k, \pm l$, 3105 reflections including standards (3 every 97 data)]. Data were corrected for Lorentz, polarization, crystal degradation [linear decay rate 0.101 (17) × 10⁻⁵ per reflection measured; Churchill & Kalra, 1974] and absorption effects (de Meulenaer & Tompa, 1965). The 2582 unique data with $I > 3\sigma(I)$ were accorded Σ_2 weights (with $p^2 = 0.002$ assumed; Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967) for use in subsequent refinement. R_s for this data set (Robertson & Whimp, 1975) was 0.011. Cell dimensions and standard errors derive from least-squares analysis of the setting angles for 12 well separated reflections in the range 37° < 2 θ < 41° [Mo K α_1 radiation, $\lambda = 0.70926$ Å, $T \approx 293$ K].

The structure was solved by standard heavy-atom Patterson/Fourier synthesis techniques. H atoms were located from a difference synthesis. Full-matrix least-squares refinement with anisotropic thermal parameters for Fe, O and C, and isotropic thermal parameters for H atoms converged with $R = 0.028$, $R_w =$

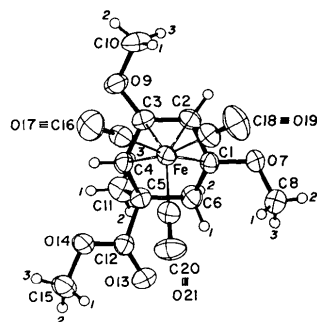


Fig. 1. The labelling scheme of [Fe(CO)₃(C₁₁H₁₆O₄)].

0.045 and $[\sum w\Delta^2/(n-s)]^{1/2} = 1.56$. An extinction correction (Zachariasen, 1963) applied to F_c refined to $6.2(4) \times 10^{-6}$. A final difference synthesis revealed no features higher than 0.3 e Å⁻³. Scattering factors, with dispersion corrections for Fe, C and O, were taken from *International Tables for X-ray Crystallography* (1974). Calculations were performed using ANUCRYS programs (McLaughlin, Taylor & Whimp, 1977) and the Australian National University Univac 1100/82 computer. The figures were drawn with ORTEP (Johnson, 1976). Atom nomenclature is defined in Fig. 1 and the corresponding coordinates are listed in Table 1.* Bond distances and angles are given in Tables 2 and

* Lists of structure amplitudes, anisotropic thermal parameters and deviations from planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36763 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates (× 10⁵ for Fe, × 10⁴ for C and O, × 10³ for H) and isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} [*] (Å ²)
Fe	21517 (3)	31622 (3)	22231 (2)	2.73
C(1)	1236 (2)	1911 (2)	1043 (1)	2.95
C(2)	-175 (2)	2919 (2)	1519 (1)	3.11
C(3)	-428 (2)	2566 (2)	2677 (1)	3.11
C(4)	836 (2)	1357 (2)	3186 (1)	3.00
C(5)	1222 (2)	-225 (2)	2712 (1)	2.96
C(6)	1441 (3)	121 (2)	1436 (1)	3.60
O(7)	1558 (2)	2381 (2)	-86 (1)	3.71
C(8)	3239 (3)	1787 (4)	-557 (2)	4.83
O(9)	-1668 (2)	3331 (2)	3338 (1)	3.96
C(10)	-2570 (3)	4815 (3)	2845 (2)	4.81
C(11)	-300 (3)	-1274 (3)	3092 (2)	4.33
C(12)	2899 (2)	-1212 (2)	3161 (1)	3.11
O(13)	3886 (2)	-2115 (2)	2663 (1)	4.87
O(14)	3100 (2)	-1022 (2)	4205 (1)	4.02
C(15)	4588 (3)	-1990 (3)	4725 (2)	4.61
C(16)	2177 (2)	4196 (2)	3406 (2)	3.77
O(17)	2191 (3)	4783 (2)	4194 (2)	5.99
C(18)	2652 (3)	4863 (3)	1223 (2)	3.89
O(19)	2967 (3)	5914 (2)	581 (1)	6.13
C(20)	4305 (2)	2071 (2)	2206 (2)	3.48
O(21)	5685 (2)	1371 (2)	2196 (2)	5.42
H(C2)	-77 (3)	376 (3)	107 (2)	4.1 (5)
H(C4)	83 (3)	130 (3)	392 (2)	4.2 (5)
H1(C6)	255 (3)	-38 (3)	116 (2)	4.8 (5)
H2(C6)	62 (3)	-30 (3)	119 (2)	4.2 (5)
H1(C8)	421 (5)	202 (5)	-15 (3)	8.6 (9)
H2(C8)	341 (4)	219 (4)	-121 (3)	6.8 (8)
H3(C8)	338 (3)	74 (4)	-57 (2)	5.3 (6)
H1(C10)	-170 (3)	553 (4)	251 (2)	5.1 (5)
H2(C10)	-325 (4)	519 (4)	338 (3)	7.0 (7)
H3(C10)	-333 (4)	463 (4)	221 (3)	5.9 (6)
H1(C11)	-39 (4)	-149 (4)	386 (3)	5.7 (6)
H2(C11)	-8 (3)	-229 (4)	283 (2)	5.7 (6)
H3(C11)	-151 (4)	-72 (4)	285 (2)	5.2 (6)
H1(C15)	558 (4)	-180 (4)	426 (2)	6.0 (7)
H2(C15)	462 (5)	-319 (5)	474 (3)	8.7 (9)
H3(C15)	443 (4)	-174 (4)	542 (3)	6.9 (7)

* $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^*$; actual *B* values for H atoms.

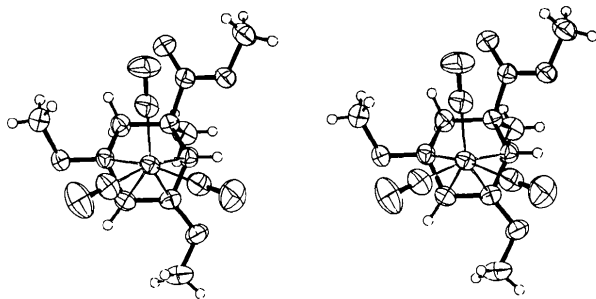


Fig. 2. Stereoscopic view of [Fe(CO)₃(C₁₄H₁₆O₄)] perpendicular to the diene plane. Vibration ellipsoids correspond to 50% probability surfaces and H atoms are depicted as 0.1 Å radius spheres.

Table 2. Bond lengths (Å)

Fe—C(1)	2.112 (2)	O(7)—C(1)	1.384 (2)
Fe—C(2)	2.070 (2)	O(7)—C(8)	1.419 (3)
Fe—C(3)	2.092 (2)	O(9)—C(3)	1.353 (2)
Fe—C(4)	2.087 (2)	O(9)—C(10)	1.426 (3)
Fe—C(16)	1.794 (2)	C(11)—C(5)	1.543 (3)
Fe—C(18)	1.798 (2)	C(12)—C(5)	1.527 (2)
Fe—C(20)	1.773 (2)	C(12)—O(13)	1.196 (2)
C(16)—O(17)	1.145 (3)	C(12)—O(14)	1.328 (2)
C(18)—O(19)	1.128 (3)	O(14)—O(15)	1.441 (2)
C(20)—O(21)	1.137 (2)	C(2)—H(C2)	0.93 (2)
C(1)—C(2)	1.423 (2)	C(4)—H(C4)	0.89 (2)
C(2)—C(3)	1.399 (3)	C(6)—H1(C6)	0.95 (2)
C(3)—C(4)	1.419 (3)	C(6)—H2(C6)	0.85 (3)
C(4)—C(5)	1.519 (2)	C(Me)—H	0.94 ± 0.12
C(5)—C(6)	1.536 (2)		
C(6)—C(1)	1.509 (3)		

Table 3. Valency angles (°)

C(1)—Fe—C(2)	39.78 (7)	C(3)—C(4)—H(C4)	114.5 (15)
C(2)—Fe—C(3)	39.26 (7)	C(5)—C(4)—H(C4)	116.9 (17)
C(3)—Fe—C(4)	39.69 (7)	C(4)—C(5)—C(6)	109.4 (1)
C(16)—Fe—C(18)	94.56 (9)	C(4)—C(5)—C(11)	109.7 (1)
C(16)—Fe—C(20)	101.48 (8)	C(4)—C(5)—C(12)	111.4 (1)
C(18)—Fe—C(20)	97.77 (9)	C(6)—C(5)—C(11)	111.1 (2)
Fe—C(16)—O(17)	176.6 (2)	C(6)—C(5)—C(12)	109.7 (1)
Fe—C(18)—O(19)	178.8 (2)	C(11)—C(5)—C(12)	105.6 (1)
Fe—C(20)—O(21)	179.9 (2)	C(1)—C(6)—C(5)	110.9 (1)
C(2)—C(1)—C(6)	119.6 (2)	C—C(6)—H	109.6 ± 3.1
C(2)—C(1)—O(7)	112.5 (1)	H1(C6)—C(6)—H2(C6)	107.5 (22)
C(6)—C(1)—O(7)	116.5 (1)	C(1)—O(7)—C(8)	116.0 (1)
C(1)—C(2)—C(3)	113.9 (1)	C(3)—O(9)—C(10)	116.5 (2)
C(1)—C(2)—H(C2)	119.3 (13)	C(5)—C(12)—O(13)	124.8 (2)
C(3)—C(2)—H(C2)	126.7 (13)	C(5)—C(12)—O(14)	112.0 (1)
C(2)—C(3)—C(4)	115.2 (1)	O(13)—C(12)—O(14)	123.0 (2)
C(2)—C(3)—O(9)	126.3 (2)	C(12)—O(14)—C(15)	116.0 (2)
C(4)—C(3)—O(9)	118.4 (2)	C(O)—C(Me)—H	110.1 ± 8.5
C(3)—C(4)—C(5)	118.3 (1)	H—C(Me)—H	108.8 ± 15.2

3 respectively, and a stereoview of the molecule is shown in Fig. 2.

Discussion. The metal–ligand bonding arrangement conforms closely to that observed in other (1,3-cyclohexadiene)tricarbonyliron derivatives (Cotton & Troup, 1974, and references therein; Ireland, Brown, Stanford & McKenzie, 1974; Guy, Reichert & Shel-

drick, 1976; Johnson, Lewis, Parker, Raithby & Sheldrick, 1978). The dihedral angle between the sets C(1), C(2), C(3), C(4) and C(4), C(5), C(6), C(1) (42.5°) is larger than has been reported to date (36.3–40.6°)* but agrees well with values observed in these laboratories for 2–5- η -(dimethyl 2,4-cyclohexadiene-1 α ,2-dicarboxylate)Fe(CO)₃ and 2–5- η -(dimethyl 2,4-cyclohexadiene-1 β ,2-dicarboxylate)Fe(CO)₃ (42.1 and 43.4°, Dunand & Robertson, 1982) and for 2–5- η -(methyl 1 α -phenyl-2,4-cyclohexadiene-1 β -carboxylate)Fe(CO)₃ (42.2°, Anderson, Bandara, Birch & Robertson, 1982). The C(4), C(5), C(6), C(1) set is closely planar [$\Delta_{\max} = 0.006$ (2) Å] whereas the diene fragment [C(1), C(2), C(3), C(4) set] is slightly aplanar [$\Delta_{\max} = 0.022$ (2) Å] with a torsion angle [about C(2)—C(3)] of 4.6 (2)°. While O(9) is closely coplanar with the diene fragment, O(7) and the H atoms H(C2) and H(C4) are each displaced towards the Fe atom [by 0.155 (1), 0.12 (2) and 0.18 (2) Å respectively]. The methyl groups in both methoxy substituents are tilted further towards the metal from the diene plane; hence the torsion angles C(2)—C(1)—O(7)—C(8), 18.6 (2) and C(2)—C(3)—O(9)—C(10), –12.7 (3)°. Each methoxy O is in van der Waals contact with one carbonyl group of the Fe(CO)₃ moiety at distances O(7)···C(18), 3.043 (3), O(7)···O(19), 3.515 (2), O(9)···C(16), 3.106 (2) and O(9)···O(17), 3.598 (3) Å respectively. It is remarkable that the dihedral angles defined by the planes through C(1), O(7), C(8) and C(1), O(7), C(18) [about the C(1)—O(7) hinge], and through C(3), O(9), C(10) and C(3), O(9), C(16) [about the C(3)—O(9) hinge], take equivalent values of 92.3 and 91.6° respectively. That the methoxy-group orientation is imposed by methoxy–carbonyl group interactions is open to speculation.

The methoxycarbonyl set C(15), O(14), C(12), O(13) is planar within experimental error and adopts a perpendicular conformation about the C(5)—C(12) bond [torsion angles C(11)—C(5)—C(12)—O(13), 91.8 (2) and C(11)—C(5)—C(12)—O(14), –84.8 (2)°]. C(12) is in van der Waals contact with the third carbonyl group [–C(20)≡O(21)] of the Fe(CO)₃ [C(12)···C(20), 3.123 (3) and C(12)···O(21), 3.255 (3) Å]. *X*, the C(20)≡O(21) carbonyl bond mid-point, is near equidistant from the set C(5), O(13), O(14) and directly above C(12) [C(5)—C(12)···*X*, 88.1, O(13)—C(12)···*X*, 92.3 and O(14)—C(12)···*X*, 92.5°]. In turn, C(12) is displaced 0.023 (2) Å from the plane of the set C(5), O(13), O(14) towards *X* [C(12)···*X*, 3.139 Å]. The displacement of C(12) towards *X*, and the accompanying distortions of the methoxycarbonyl group, are consistent with the observation by Bürgi, Dunitz & Shefter (1973, 1974) that,

* Except for (octafluoro-1,3-cyclohexadiene)Fe(CO)₃ (Churchill & Mason, 1967).

for structures exhibiting short N...C=O or O...C=O contacts, the C atoms are generally displaced towards the N or O atoms respectively. The displacement exemplifies the effects of the interaction between a nucleophile and the electrophilic C atom of the carbonyl group.

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Acta Cryst. (1982). **B38**, 2037–2040

Tricarbonyl[2-5-η-(dimethyl 2,4-cyclohexadiene-1α,2-dicarboxylate)]iron(0) and Tricarbonyl[2-5-η-(dimethyl 2,4-cyclohexadiene-1β,2-dicarboxylate)]iron(0)

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Abstract. C₁₃H₁₂FeO₇, *M_r* = 336.09. Structures of both the 1α,2- (*A*) and 1β,2-bis(methoxycarbonyl) (*B*) isomers were determined. (*A*): monoclinic, *Pc*, *a* = 7.469 (2), *b* = 13.403 (5), *c* = 6.978 (2) Å, β = 93.85 (2)° (293 K), *U* = 697.0 Å³, *Z* = 2, *D_c* = 1.602 Mg m⁻³, *F*(000) = 344, μ(Mo *Kα*) = 1.143 mm⁻¹;

refinement converged with *R* = 0.019, *R_w* = 0.027 for 1665 diffractometer data [*I* ≥ 3σ(*I*)]. (*B*): triclinic, *P* $\bar{1}$, *a* = 6.883 (1), *b* = 8.949 (1), *c* = 11.438 (2) Å, α = 91.50 (1), β = 101.78 (1), γ = 96.48 (1)° (293 K), *U* = 684.4 Å³, *Z* = 2, *D_c* = 1.631 Mg m⁻³, μ(Mo *Kα*) = 1.164 mm⁻¹; refinement converged with *R* = 0.026, *R_w* = 0.039 for 3309 diffractometer data. An unusually short O...C=O contact in (*B*) [2.652 (2) Å, O(2-methoxycarbonyl)...C=O(1β-methoxycarbonyl)] generates an appreciable pyramidal distortion [0.043 (1) Å] of the four-atom C-(1β-carboxylate) set.

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