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(*S*)-Tricarbonyl[(1,2,3,4-η)-(5*R*,6*S*)-1-chloro-5,6-dimethoxycyclohexa-1,3-diene]iron(0)

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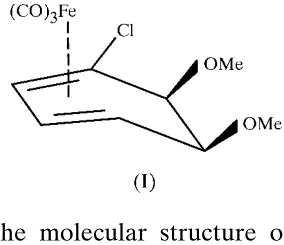
The title compound, [Fe($C_8H_{11}ClO_2$)(CO)$_3$], has been synthesized, isolated and characterized by single-crystal X-ray diffraction. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$. The metal–ligand arrangement is typical of (1,3-diene)tricarbonyliron complexes.

Comment

The title compound, (I), is a transition metal tricarbonyl and diene π-complex. This kind of compound is used extensively in organic synthesis. Those in which the diene has chiral centres are particularly useful because they offer an efficient approach to enantioselective synthesis. It has been reported that the stereocontrol is produced by the metal centre, which effectively hinders access to one side of the molecule (Johnson *et al.*, 1977; Howard *et al.*, 1989). The chiral dienic system in the present structure was prepared by microbial dioxygenation of chlorobenzene (Gibson *et al.*, 1970; Brovetto *et al.*, 1999) to give a homochiral *cis*-diol, followed by further treatment with methyl iodide to obtain the *cis*-dimethyl ether.



(I)

Fig. 1 shows the molecular structure of (I). The metal–ligand arrangement is similar to that observed in other (cyclohexa-1,3-diene)tricarbonyliron derivatives (Dunand & Robertson, 1982). All bond distances and angles (Table 1) are within the range of expected values (Guy *et al.*, 1976; Anderson & Robertson, 1984).

The determination of the absolute configuration of the molecule agrees with that of the parent dienic *cis*-diol (Gibson *et al.*, 1970). The chiral centres C5 and C6 (arising from the original enzymatic synthesis) are *R* and *S*, respectively. The descriptor for the entire complex is *S* because the fiduciary C1 atom (bonded to Fe and Cl) is in the *S* configuration. For all assignments of configuration, the occurrence of bonding to Fe was taken into account.

The diene moiety, C1/C2/C3/C4, is planar. The maximum absolute deviation from the mean plane is 0.014 (3) Å for C3. On the other hand, the planarity of the set C1/C6/C5/C4 is lower, with a maximum absolute deviation 0.06 (2) Å for C5 and C6. The dihedral angle of 41.9 (3)° between the two planes agrees well with the values observed for tricarbonyl[2–5-η-(dimethyl 2,4-cyclohexadiene-1α,2-dicarboxylate)]iron(0) (42.1°; Dunand & Robertson, 1982), tricarbonyl[2–5-η-(methyl 1α-phenyl-2,4-cyclohexadiene-1β-carboxylate)]iron(0) (42.2°; Anderson & Robertson, 1984) and tricarbonyl{(4–7-η)-3-acetyl-3a,7a-dihydro-6-methoxy-2-methylbenzo[*b*]furan]iron(0) (41.7°; Anderson & Robertson, 1983). Such a high value is characteristic of systems containing both electron-donating and electron-withdrawing ring substituents, as previously reported by Anderson & Robertson (1983).

The Fe(CO)$_3$ group and all the substituents are located on the same side of the six-membered ring. The carbonyl (C9/C10/C11) and the diene (C1/C2/C3/C4) planes are not parallel; the dihedral angle between these planes is 13.8 (3)°, with the carbonyl ligand C10═O4 closer to the diene plane. Atom O2 of the methoxy group bonded to C6 is in relatively close contact with the carbonyl group C11═O5, with separations O2$\cdots$C11 = 2.903 (5) and O2$\cdots$O5 = 3.130 (4) Å.

The presence of the Cl atom (an electron-withdrawing substituent) bonded to C1 removes the C1—C2/C3—C4 bond-length similarity (Dunand & Robertson, 1982), with the C1—C2 bond distance of 1.442 (5) Å significantly longer than the C3—C4 bond distance of 1.416 (6) Å.

The absence of hydrogen bonds and π-contacts suggests that the crystal packing is directed by van der Waals forces.

Our results are consistent with the mechanism described in a previous report (Howard *et al.*, 1989), where the methoxy groups were considered to play an important role in the

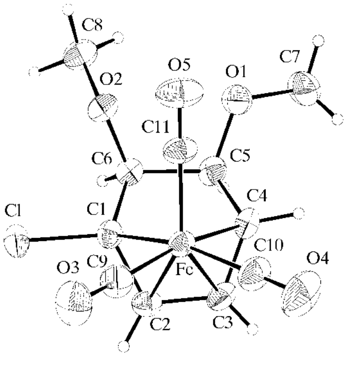


Figure 1
The molecular view of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radii.

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diastereoface selectivity of the complexation. According to that work, the complexation should first occur *via* the O atoms belonging to the methoxy groups and take place finally through the more favourable dienic system. Thus, the present work, which demonstrates that the binding of the tricarbonyliron moiety is located on the same side of the six-membered ring as the methoxy substituents, supports the importance of the methoxy groups for stereocontrol in these homochiral complexes with planar chirality, making them useful reagents in chiral synthesis.

Experimental

Compound (I) was synthesized following reported procedures for this type of compound (Howard *et al.*, 1989; Pearson *et al.*, 1992). The starting 1-chlorocyclohexa-1,3-diene-5,6-diol, obtained by microbial oxidation of chlorobenzene (Gibson *et al.*, 1970; Brovetto *et al.*, 1999), was treated with methyl iodide to give the dimethyl ether, and further reacted with $Fe_2(CO)_9$. Suitable crystals were grown as colourless plates from dichloromethane by slow cooling.

Crystal data

$[Fe(C_8H_{11}ClO_2)(CO)_3]$
$M_r = 314.50$
Orthorhombic, $P2_12_12_1$
$a = 7.139$ (2) Å
$b = 26.763$ (2) Å
$c = 6.815$ (2) Å
$V = 1302.0$ (6) Å^3
$Z = 4$
$D_x = 1.604$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 25.14$–$26.77°$
$\mu = 1.371$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
$0.30 \times 0.28 \times 0.10$ mm

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{min} = 0.684$, $T_{max} = 0.875$
1996 measured reflections
1715 independent reflections (plus 241 Friedel-related reflections)

1793 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -32 \rightarrow 34$
$l = -7 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

Fe—C10	1.785 (4)	C1—C2	1.442 (5)
Fe—C9	1.792 (5)	C1—C6	1.498 (5)
Fe—C11	1.798 (4)	C2—C3	1.402 (6)
Fe—C3	2.049 (4)	C3—C4	1.416 (6)
Fe—C2	2.061 (4)	C4—C5	1.514 (5)
Fe—C1	2.069 (3)	C5—C6	1.555 (5)
Fe—C4	2.108 (4)		
C3—Fe—C2	39.91 (17)	C3—C2—C1	113.4 (3)
C3—Fe—C1	70.52 (15)	C2—C3—C4	114.9 (3)
C2—Fe—C1	40.86 (14)	C3—C4—C5	117.9 (4)
C3—Fe—C4	39.81 (17)	C4—C5—C6	110.3 (3)
C1—Fe—C4	76.02 (15)	C1—C6—C5	108.7 (3)
C2—C1—C6	122.1 (3)		
C6—C1—C2—C3	46.6 (5)	C3—C4—C5—C6	52.4 (4)
C1—C2—C3—C4	−2.8 (5)	C2—C1—C6—C5	−36.9 (4)
C2—C3—C4—C5	−46.0 (5)	C4—C5—C6—C1	−10.6 (4)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.119$
$S = 1.062$
1956 reflections
197 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0877P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.25$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.046 (5)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (3)

All H atoms were found in difference Fourier maps and freely refined, except those belonging to C10, which were placed at geometrically suitable positions and refined with $U_{iso} = 1.2U_{eq}$ of the parent atom [C—H range 0.83 (8)–1.03 (5) Å].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON*98 (Spek, 1998) and CSD (Allen & Kennard, 1993; Cambridge Structural Database, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1099). Services for accessing these data are described at the back of the journal.

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