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A μ -Oxo-bis[iron(III) porphyrin] Complex

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Abstract

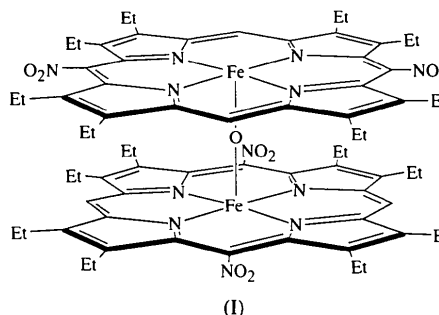
Partial nitration of iron(III) 2,3,7,8,12,13,17,18-octaethylporphyrin chloride $[\text{Fe}^{\text{III}}(\text{OEP})\text{Cl}]$ gives the μ -oxo-bis(5,15-dinitro) compound μ -oxo-bis[2,3,7,8,12,13,17,18-octaethyl-5,15-dinitroporphyrinato]iron(III)], $[\text{Fe}_2(\text{C}_{36}\text{H}_{42}\text{N}_6\text{O}_4)_2\text{O}]$, which is similar to other μ -oxo-iron(III) porphyrin complexes but with less ruffling of the porphyrin structure. The porphyrin planes are not parallel [the angle between plane normals is $169(2)^\circ$] and the Fe—O—Fe angle is $167.9(3)^\circ$. As expected, the Fe atoms are significantly displaced from the porphyrin planes towards the bridging O atom: 0.46 Å for Fe1 and 0.49 Å for Fe2. The two porphyrin residues are eclipsed with respect to their C atoms, but the nitro groups are staggered by 90° from one residue to the other.

Comment

The unsubstituted μ -oxo-bis[iron(III) octaethylporphyrin] complex is inactive as a catalyst for the oxidation of alkanes, but incorporation of highly electron-withdrawing groups in the *meso* position leads

to a soluble active catalyst for these reactions. Both dinitro and tetranitro porphyrins give active μ -oxo-dimer catalysts, with the tetranitro compound being roughly twice as active. Both species show similar selectivities in the production of alcohols from alkanes.

The dinitro compound described here, (I), is prepared by nitration of $\text{Fe}(\text{OEP})\text{Cl}$ by NO_2 under N_2 in CH_2Cl_2 (Ellis, Lyons & Shaikh, 1994).



An ORTEPII (Johnson, 1976) drawing of the title molecule, (I), is shown in Fig. 1, tilted about 12° from its least-squares plane and showing the numbering system. The two porphyrin skeletons are nearly superimposed. This is the same conformation as observed in μ -oxo-bis(iron 5,15-dimethyloctaethylporphyrin) (Lay, Buchler, Kenny & Scheidt, 1986) and in μ -oxo-bis[octaethylporphyrinatoiron(III)] (Cheng, Hobbs, Debrunner, Erlebacher, Shelmutt & Scheidt, 1995), but it is different from the staggered geometry found in the tetraphenyl derivative (Hoffman, Collins, Day, Fleischer, Srivastava & Hoard, 1972; Strauss, Pawlik, Skowrya, Kennedy, Anderson, Spartalian & Dye, 1987) and the tetrakis(pentafluorophenyl) compound (Gold, Jayaraj, Doppelt, Fischer & Weiss, 1988). In all these compounds, the Fe^{III} atom is significantly out of porphyrin mean plane [by 0.49 and 0.50 Å (Strauss *et al.*, 1987), and 0.67 Å (Gold *et al.*, 1988)]. The present dinitro compound shows the least displacement [0.46 and 0.49 Å]. Additionally, the porphyrin skeleton is less ruffled in the dinitro compound than in others with bulkier substituents in the β positions (see Henling, Schaefer, Hodge, Hughes, Gray, Lyons & Ellis, 1993, for two examples). The maximum displacements from the porphyrin plane are 0.24 Å in one porphyrin (by atom C15), and 0.18 Å in the other (C41). Again, these distances are comparable to those observed in the dimethyloctaethyl compound (Lay *et al.*, 1986) and the tetrakis(pentafluorophenyl) compound (Gold *et al.*, 1988), but slightly smaller than the maximum of 0.30 Å found in the tetraphenyl compound (Strauss *et al.*, 1987). The octaethyl compound (Cheng *et al.*, 1995) is the least ruffled of all, with maximum displacements of only 0.12 and 0.15 Å from the mean porphyrin plane. Highly ruffled porphyrins show pyrrole C atoms as much as 1.2 Å out of plane.

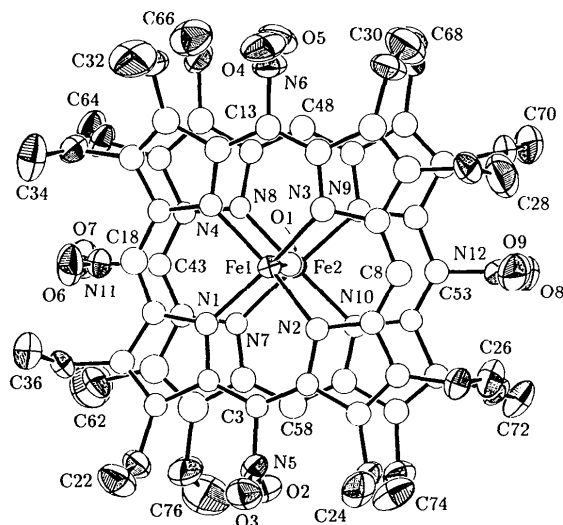


Fig. 1. An ORTEPII (Johnson, 1976) drawing of the molecule with 50% probability ellipsoids showing the atom-numbering system. H atoms are not shown. The numbering of porphyrin C atoms is regular around the ring; only a selection are numbered. Only methyl C atoms of the ethyl groups are numbered; the numbers of the adjacent CH₂ C atoms are 1 less. Atoms shown as open circles were refined with isotropic displacement parameters.

The geometry of the central cavity of this compound is virtually the same as those of the compounds mentioned above: the Fe—N distances average 2.090 (7) Å and the distance CT—N (CT is the average of the four N-atom coordinates) is 2.036 (5) Å. The Fe—O—Fe angle, 167.9 (3)°, is farther from 180° than in the other compounds, the smallest value of which is 174.5 (1)° (Hoffman *et al.*, 1972). There is no apparent steric or electronic reason for this. Table 2 gives selected distances and angles for the compound, while Table 3 gives average values for all distances.

A measure of the overlap of one porphyrin ring with the other in these compounds is the average torsion angle N—Fe—Fe'—N', which is 1.1 (20)° in the title

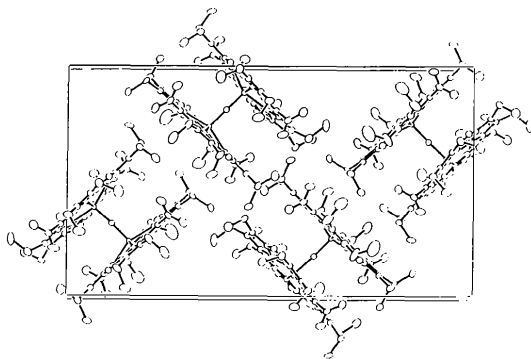


Fig. 2. An ORTEPII drawing of the contents of a unit cell, with a unit cell outlined. Atoms are shown as 25% probability ellipsoids; H atoms have been omitted for clarity.

compound, but 3.84° in the dimethyl compound (Lay *et al.*, 1986) and 16.8 and 17.0 in the two forms of the unsubstituted octaethyl porphyrin (Cheng *et al.*, 1995). We observe an interdigitation of ethyl groups in this compound similar to that in the unsubstituted one, with ethyl groups on both porphyrin residues pointing both 'out' (away from the bridging O atom) and 'in': for one residue, five point out and three point in, while for the other, six are out and two in (see Fig. 2). Because of the nearly eclipsed geometry, there are no instances of an ethyl group of one residue pointing between ethyl groups on the other, as Cheng *et al.* (1995) observed.

Experimental

A 12:1 molar mixture of NO₂ to Fe(OEP)Cl was stirred under N₂ in CH₂Cl₂ for 1 h at room temperature. The dinitro compound is a by-product and was obtained by chromatography on neutral alumina, eluting with a 1:3 CH₂Cl₂:hexane mixture. The material was recrystallized by slow addition of a 2-propanol:hexane mixture to a CH₂Cl₂ solution.

Crystal data

[Fe₂(C₃₆H₄₂N₆O₄)₂O]

M_r = 1373.22

Monoclinic

*P*2₁/*c*

a = 15.163 (3) Å

b = 28.912 (8) Å

c = 16.286 (6) Å

β = 91.02 (2)°

V = 7138 (4) Å³

Z = 4

D_x = 1.28 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 4.5–10.5°

μ = 0.466 mm⁻¹

T = 296 K

Needle (diamond cross-section)

0.41 × 0.27 × 0.14 mm

Dark red–purple

Data collection

Enraf–Nonius CAD-4 diffractometer

ω scans

Absorption correction:

none

14033 measured reflections

6661 independent reflections

6661 observed reflections

(All reflections used, *F_o*² positive and negative)

R_{int} = 0.056

θ_{max} = 20°

h = -14 → 14

k = -27 → 27

l = 0 → 15

3 standard reflections

frequency: 150 min

intensity decay: <0.5%

Refinement

Refinement on *F*²

R(*F_o*² > 0) = 0.086

(5900 reflections)

R[*F_o*² > 3σ(*F_o*²)] = 0.052

(3872 reflections)

wR(*F*²) = 0.013

S = 1.40

6661 reflections

611 parameters

H-atom parameters not

refined, positions

calculated (C—H 0.95 Å)

w = 1/σ²(*F_o*²)

(Δ/σ)_{max} = 0.01

Δρ_{max} = 0.56 e Å⁻³

Δρ_{min} = -0.46 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{iso}/U_{eq}
Fe1	0.2438 (1)	0.0661 (1)	0.3877 (1)	0.0308 (2)
N1	0.3805 (3)	0.0634 (2)	0.4012 (3)	0.034 (1)†
C1	0.5278 (4)	0.0815 (2)	0.4297 (4)	0.034 (2)†
C2	0.4365 (4)	0.0887 (2)	0.4523 (4)	0.031 (1)†
C21	0.6115 (5)	0.0980 (3)	0.4713 (5)	0.054 (2)
C22	0.6434 (5)	0.0658 (3)	0.5399 (5)	0.080 (3)
C3	0.4021 (4)	0.1160 (2)	0.5134 (4)	0.034 (2)†
C4	0.3158 (4)	0.1227 (2)	0.5382 (4)	0.032 (2)†
N5	0.4697 (4)	0.1452 (3)	0.5570 (4)	0.054 (2)
O2	0.4878 (4)	0.1828 (2)	0.5261 (4)	0.072 (2)
O3	0.5022 (4)	0.1299 (2)	0.6206 (4)	0.076 (2)
N2	0.2462 (3)	0.1009 (2)	0.5003 (3)	0.034 (2)†
C5	0.2829 (4)	0.1530 (2)	0.6028 (4)	0.037 (2)†
C6	0.1951 (4)	0.1501 (2)	0.6000 (4)	0.038 (2)†
C23	0.3332 (5)	0.1801 (2)	0.6687 (5)	0.051 (2)
C24	0.3498 (5)	0.1504 (3)	0.7440 (5)	0.073 (3)
C7	0.1721 (4)	0.1171 (2)	0.5366 (4)	0.036 (2)†
C25	0.1290 (5)	0.1766 (3)	0.6487 (5)	0.057 (2)
C26	0.0920 (6)	0.2176 (3)	0.6009 (6)	0.085 (3)
C8	0.0869 (5)	0.1029 (2)	0.5175 (4)	0.044 (2)†
C9	0.0592 (4)	0.0706 (2)	0.4606 (4)	0.040 (2)†
N3	0.1143 (3)	0.0452 (2)	0.4121 (3)	0.038 (2)†
C10	−0.0311 (5)	0.0571 (2)	0.4444 (4)	0.046 (2)†
C11	−0.0316 (5)	0.0240 (2)	0.3866 (4)	0.046 (2)†
C27	−0.1084 (5)	0.0791 (3)	0.4859 (5)	0.066 (3)
C28	−0.1341 (6)	0.1258 (4)	0.4508 (7)	0.113 (4)
C12	0.0606 (5)	0.0164 (2)	0.3652 (4)	0.043 (2)†
C29	−0.1136 (5)	0.0025 (3)	0.3487 (5)	0.069 (3)
C30	−0.1469 (6)	0.0305 (4)	0.2747 (6)	0.105 (4)
C13	0.0969 (5)	−0.0145 (2)	0.3103 (4)	0.041 (2)†
C14	0.1829 (5)	−0.0211 (2)	0.2858 (4)	0.042 (2)†
N6	0.0308 (5)	−0.0453 (3)	0.2675 (5)	0.063 (2)
O4	0.0119 (4)	−0.0817 (2)	0.3020 (4)	0.093 (2)
O5	0.0001 (4)	−0.0316 (2)	0.2020 (4)	0.090 (2)
N4	0.2505 (3)	0.0072 (2)	0.3140 (3)	0.032 (1)†
C15	0.2174 (5)	−0.0534 (2)	0.2254 (4)	0.046 (2)†
C16	0.3009 (5)	−0.0417 (2)	0.2136 (4)	0.040 (2)†
C31	0.1743 (5)	−0.0957 (3)	0.1885 (5)	0.070 (3)
C32	0.1819 (7)	−0.1371 (3)	0.2448 (7)	0.120 (5)
C17	0.3218 (4)	−0.0049 (2)	0.2710 (4)	0.035 (2)†
C33	0.3657 (5)	−0.0628 (3)	0.1545 (5)	0.056 (2)
C34	0.4185 (6)	−0.1022 (3)	0.1906 (6)	0.097 (3)
C18	0.4061 (5)	0.0129 (2)	0.2841 (4)	0.046 (2)†
C19	0.4351 (4)	0.0422 (2)	0.3458 (4)	0.037 (2)†
C20	0.5260 (4)	0.0531 (2)	0.3630 (4)	0.037 (2)†
C35	0.6032 (4)	0.0328 (3)	0.3185 (5)	0.056 (3)
C36	0.6239 (5)	−0.0165 (3)	0.3474 (6)	0.079 (3)
O1	0.2275 (3)	0.1111 (1)	0.3160 (3)	0.037 (1)†
Fe2	0.2343 (1)	0.1531 (1)	0.2390 (1)	0.030 (2)
N7	0.3699 (3)	0.1639 (2)	0.2278 (3)	0.031 (1)†
C41	0.5195 (5)	0.1558 (3)	0.2016 (5)	0.053 (2)†
C42	0.4296 (4)	0.1404 (2)	0.1803 (4)	0.035 (2)†
C61	0.6064 (5)	0.1446 (4)	0.1609 (7)	0.097 (5)
C62	0.6256 (7)	0.1763 (4)	0.0891 (8)	0.145 (5)
C43	0.4036 (4)	0.1082 (2)	0.1224 (4)	0.034 (2)†
C44	0.3196 (4)	0.0943 (2)	0.0979 (4)	0.030 (2)†
N11	0.4764 (4)	0.0842 (3)	0.0801 (5)	0.054 (2)
O6	0.5078 (4)	0.0495 (2)	0.1127 (4)	0.081 (2)
O7	0.4986 (4)	0.0999 (2)	0.0141 (4)	0.075 (2)
N8	0.2451 (3)	0.1138 (2)	0.1314 (3)	0.029 (1)†
C45	0.2939 (4)	0.0594 (2)	0.0370 (4)	0.037 (2)†
C46	0.2049 (5)	0.0590 (2)	0.0346 (4)	0.044 (2)†
C63	0.3476 (5)	0.0301 (3)	−0.0195 (5)	0.055 (2)
C64	0.3576 (5)	0.0524 (3)	−0.1042 (5)	0.071 (3)
C47	0.1744 (4)	0.0930 (2)	0.0932 (4)	0.036 (2)†
C48	0.0868 (4)	0.1036 (2)	0.1072 (4)	0.041 (2)†
C65	0.1427 (5)	0.0293 (3)	−0.0189 (5)	0.062 (3)
C66	0.1215 (7)	−0.0132 (3)	0.0266 (6)	0.099 (4)
C49	0.0523 (4)	0.1369 (2)	0.1579 (4)	0.036 (2)†
N9	0.1022 (3)	0.1646 (2)	0.2098 (3)	0.031 (1)†
C50	−0.0405 (4)	0.1469 (2)	0.1640 (4)	0.041 (2)†

C51	−0.0477 (5)	0.1812 (2)	0.2202 (4)	0.043 (2)†
C67	−0.1120 (5)	0.1249 (3)	0.1123 (5)	0.064 (3)
C68	−0.1183 (6)	0.1445 (4)	0.0268 (6)	0.097 (4)
C52	0.0411 (4)	0.1923 (2)	0.2484 (4)	0.037 (2)†
C69	−0.1365 (5)	0.2035 (3)	0.2414 (6)	0.076 (3)
C70	−0.1624 (6)	0.2413 (3)	0.1833 (7)	0.111 (4)
C53	0.0704 (5)	0.2246 (2)	0.3073 (4)	0.038 (2)†
C54	0.1536 (4)	0.2367 (2)	0.3327 (4)	0.032 (2)†
N12	−0.0043 (4)	0.2490 (3)	0.3480 (5)	0.055 (2)
O8	−0.0302 (4)	0.2851 (2)	0.3167 (4)	0.080 (2)
O9	−0.0321 (4)	0.2320 (2)	0.4112 (4)	0.086 (2)
N10	0.2270 (3)	0.2151 (2)	0.3045 (3)	0.032 (1)†
C55	0.1794 (4)	0.2731 (2)	0.3930 (4)	0.039 (2)†
C56	0.2661 (4)	0.2708 (2)	0.4001 (4)	0.040 (2)†
C71	0.1238 (5)	0.3086 (3)	0.4361 (4)	0.051 (2)
C72	0.1136 (6)	0.3532 (3)	0.3863 (5)	0.072 (3)
C57	0.2977 (4)	0.2348 (2)	0.3453 (4)	0.039 (2)†
C73	0.3276 (5)	0.3002 (3)	0.4543 (5)	0.060 (3)
C74	0.3447 (6)	0.2753 (3)	0.5354 (5)	0.081 (3)
C58	0.3841 (5)	0.2232 (2)	0.3339 (4)	0.047 (2)†
C59	0.4195 (5)	0.1918 (2)	0.2794 (4)	0.042 (2)†
C60	0.5107 (5)	0.1865 (3)	0.2636 (5)	0.059 (2)†
C75	0.5851 (6)	0.2115 (4)	0.3118 (8)	0.115 (4)
C76	0.5933 (7)	0.2581 (5)	0.2856 (10)	0.180 (6)

† U_{iso} .

Table 2. Selected bond distances (Å) and angles (°)

Fe1—O1	1.763 (4)	Fe2—N10	2.090 (5)
Fe2—O1	1.751 (4)	N5—O2	1.233 (9)
Fe1—N1	2.083 (5)	N5—O3	1.221 (9)
Fe1—N2	2.092 (5)	N6—O4	1.229 (10)
Fe1—N3	2.099 (5)	N6—O5	1.221 (10)
Fe1—N4	2.086 (5)	N11—O6	1.228 (9)
Fe2—N7	2.091 (5)	N11—O7	1.219 (9)
Fe2—N8	2.097 (5)	N12—O8	1.225 (9)
Fe2—N9	2.078 (5)	N12—O9	1.222 (10)
Fe1—O1—Fe2	167.9 (3)	N7—Fe2—N10	88.8 (2)
N1—Fe1—N2	85.6 (2)	N7—Fe2—O1	103.7 (2)
N1—Fe1—N3	154.4 (2)	N8—Fe2—N9	89.1 (2)
N1—Fe1—N4	88.4 (2)	N8—Fe2—N10	153.7 (2)
N1—Fe1—O1	103.0 (2)	N8—Fe2—O1	103.2 (2)
N2—Fe1—N3	88.5 (2)	N9—Fe2—N10	85.4 (2)
N2—Fe1—N4	153.8 (2)	N9—Fe2—O1	101.9 (2)
N2—Fe1—O1	103.0 (2)	N10—Fe2—O1	103.1 (2)
N3—Fe1—N4	86.0 (2)	O2—N5—O3	125.2 (7)
N3—Fe1—O1	102.6 (2)	O4—N6—O5	126.0 (7)
N4—Fe1—O1	103.2 (2)	O6—N11—O7	125.1 (7)
N7—Fe2—N8	85.2 (2)	O8—N12—O9	125.5 (7)
N7—Fe2—N9	154.4 (2)		

Table 3. Average bond distances (Å)

N	—	C ^a	1.375 (11)
C ^a	—	C(meso)	1.383 (9)
C ^a	—	C ^b	1.454 (15)
C ^b	—	C ^b	1.343 (15)
C ^b	—	C(ethyl)	1.516 (14)
C(ethyl)	—	C(ethyl)	1.51 (3)
C(meso)	—	N(O ₂)	1.496 (8)

Notes: (a) α -C atom in pyrrole ring; (b) β -C atom in pyrrole ring.

The locations of the Fe atoms were found from a sharpened Patterson map and the remaining non-H atoms were located by successive structure factor–Fourier calculations. The structure was refined in one full matrix with anisotropic displacement parameters for the Fe and ethyl C atoms. H atoms were assigned isotropic B values of $1.2B_{eq}$ of the bonded C atom and were repositioned several times during the refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *CRYM*.

Program(s) used to refine structure: *CRYM*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CRYM*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,4-Bis(*tert*-butoxy)-2,4-cyclopentadien-1-one and its *fac*-Tricarbonyliron(0) Complex

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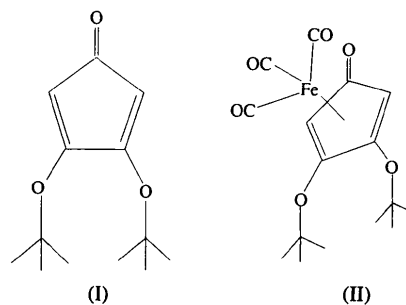
Abstract

The crystal structures of 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one, $C_{13}H_{20}O_3$, and *fac*- $[\eta^5$ -3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one]tricarbonyl-

iron(0), $[Fe(C_{13}H_{20}O_3)(CO)_3]$, have been determined. The organic compound is planar with the positions of the double bonds well defined. The inclusion of an $Fe(CO)_3$ moiety induces a loss of planarity, producing an envelope form and delocalization of the double bonds.

Comment

The ring of the 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one molecule, (II), is planar; the largest deviation of an atom from the mean plane is 0.001 (5) Å. The double bonds are well defined with $C(2)=C(3)$ and $C(4)=C(5)$ of average length 1.321 (6) Å, and $C(3)-C(4)$ of length 1.530 (5) Å.



The Fe atom of the iron complex, (I), is octahedrally coordinated to three carbonyl ligands in *fac* positions and the 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one moiety on the opposite face of the octahedron. The Fe—CO bond lengths [average value 1.807 (9) Å] are similar to those observed in other iron complexes with C_{sp^2} atoms *trans* to the carbonyl ligands (average value 1.790 Å) (Ros, Viñas, Mathieu, Solans & Font-Bardia, 1988; Yañez, Ros, Mathieu, Solans & Font-Bardia, 1990; Yañez, Ros, Solans, Font-Bardia & Mathieu, 1990; Yañez, Ros, Salans, Font-Altaba & Mathieu, 1990). The distance between the centroid of the five-membered ring and the Fe atom is 1.777 (4) Å, similar to that observed in ferrocenyl (1.64 Å) (Bosque, Font-Bardia, López, Sales, Silver & Solans, 1994; López, Solans & Tramuns, 1994).

The greatest π -donor character of C(1) in the five-membered ring produces a $C(8)-Fe-Cp-C(1)$ torsion angle of $-6.3(2)^\circ$ (Cp is the centroid of the cyclopentadienyl ring), thus avoiding a carbonyl group in the *trans* position. It also results in a lengthening of the Fe—C(1) bond [2.368 (4) Å] in comparison to the average of 2.106 (26) Å for the remaining Fe—C(ring) bond lengths, as well as the loss of planarity of the five-membered ring [envelope form, with C(1) $-0.298(4)$ Å out of the mean plane defined by the remaining four atoms]. This is associated with an electronic delocalization of the $C(3)-C(4)$ bond, which has a length of 1.444 (5) Å, similar to the average value of $C(2)-C(3)$ and $C(4)-C(5)$ [1.436 (5) Å]. Thus, the