chains. The average non-bonded distance between C atoms of neighbouring chains is 4·3 Å. However, a number of C···C contacts within the range 3·71 (2)–4·15 (2) Å [mean value 3·98 (2) Å] contribute to stabilize the apolar region. The closest intermolecular contacts are that between C(5) and C(9) at $-x-3$, $y+\frac{1}{2}$, $z+\frac{1}{2}$ of 3·71 (2) Å, and that between C(3) and C(11) at $x-3$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$ of 3·80 (2) Å.

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Structures of Diene–Tricarbonyl Iron Complexed *erythro* and *threo* Carbonates, Key Intermediates for the Preparation of 5,6-Dihetes and Lipoxin A4

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Abstract. (1) *erythro*-Tricarbonyl(η^4-methyl 4-{5-[5-(*tert*-butyldiphenylsiloxy)-1,3-pentadienyl]-2-oxo-1,3-dioxolan-4-yl}butanoate)iron(*erythro*-carbonate), $C_{32}H_{36}FeO_9Si$, $M_r = 648{\cdot}6$, monoclinic, $C2/c$, $a = 37{\cdot}14\,(1)$, $b = 8{\cdot}51\,(1)$, $c = 20{\cdot}732\,(6)$ Å, $\beta = 91{\cdot}84\,(7)°$, $V = 6549\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}32$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 5{\cdot}43$ cm^{-1}, $F(000) = 2720$, $T = 293$ K, $R = 0{\cdot}049$ for 3491 reflections. (2) Major *threo*-carbonate, $C_{32}H_{36}FeO_9Si$, $M_r = 648{\cdot}6$, monoclinic, $C2/c$, $a = 37{\cdot}88\,(1)$, $b = 8{\cdot}175\,(5)$, $c = 20{\cdot}969\,(8)$ Å, $\beta = 91{\cdot}19\,(3)°$, $V = 6492\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 5{\cdot}48$ cm^{-1}, $F(000) = 2720$, T 293 K, $R = 0{\cdot}051$ for 2133 reflections. (3) Minor *threo*-carbonate, $C_{32}H_{36}FeO_9Si$, $M_r = 648{\cdot}6$, monoclinic, $P2_1/c$, $a = 24{\cdot}96\,(2)$, $b = 10{\cdot}646\,(6)$, $c = 12{\cdot}232\,(3)$ Å, $\beta =$

0108-2701/91/061173-05$03.00

Table 1. *Crystal and refinement data for compounds* (1), (2) *and* (3)

	(1)	(2)	(3)
Crystal size (mm)	0·10 × 0·25 × 0·30	0·05 × 0·12 × 0·15	0·05 × 0·05 × 0·10
2θ range (°)	2–50	2–50	2–50
h,k,l range	0–40, 0–10, ± 21	0–45, 0–9, ± 24	0–29, 0–12, ± 14
Standard reflections	$115, \bar{1}05, 0\bar{3}\bar{4}$	$12,0,\bar{4}, 10,0,\bar{2}, 10,0,2$	$\bar{2}04, 20\bar{4}, 203$
Decay of standards (%)	−0·4	−0·6	−0·9
Total reflections	6252	6241	4445
Unique reflections; $I > \sigma I$	3491	2123	894
$R_{\rm int}$	0·019	0·027	0·025
Parameters	407	407	174
R	0·056	0·054	0·056
wR*	0·049	0·051	0·052
S	1·52	1·66	2·6
N(obs)/N(var)	3491/407	2123/407	894/174
Max. $\Delta\rho$ (e Å^{-3})	0·40	0·32	0·45
Max. Δ/σ	0·006	0·007	0·010

* $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0{\cdot}04F_o^2)^2]^{-1/2}$.

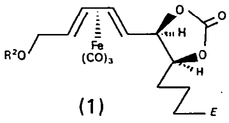
Table 2. *Atomic positional parameters and* $B_{\rm eq}$ *values for compound* (1)

	x	y	z	$B_{\rm eq}$ (Å^2)
Fe1	−0·16937 (2)	1·0450 (1)	0·09162 (5)	4·17 (2)
Si1	−0·06805 (5)	0·6389 (2)	0·11652 (9)	4·01 (4)
O1	−0·2085 (2)	1·2477 (8)	−0·0007 (3)	11·8 (2)
O2	−0·1058 (1)	1·0594 (6)	0·0130 (2)	6·9 (1)
O3	−0·1917 (1)	0·7256 (5)	0·0553 (3)	8·7 (2)
O4	−0·3301 (1)	0·3567 (6)	0·1325 (3)	10·3 (3)
O5	−0·3620 (2)	0·5649 (7)	0·1286 (4)	14·3 (3)
O6	−0·2966 (1)	1·0379 (6)	0·1931 (3)	7·7 (1)
O7	−0·2993 (2)	1·1806 (7)	0·2830 (3)	9·9 (2)
O8	−0·2561 (1)	1·2118 (5)	0·2133 (3)	7·4 (1)
O9	−0·1009 (1)	0·7699 (4)	0·1204 (2)	4·4 (1)
C1	−0·1935 (2)	1·167 (1)	0·0360 (4)	7·3 (2)
C2	−0·1310 (2)	1·0542 (7)	0·0450 (3)	5·5 (2)
C3	−0·1830 (2)	0·8453 (8)	0·0693 (3)	5·6 (2)
C4	−0·3627 (2)	0·270 (1)	0·1396 (5)	9·6 (3)
C5	−0·3337 (2)	0·5087 (8)	0·1302 (4)	7·2 (2)
C6	−0·2993 (2)	0·5915 (9)	0·1247 (5)	8·6 (3)
C7	−0·3032 (2)	0·7626 (8)	0·1227 (4)	8·3 (2)
C8	−0·2689 (2)	0·8624 (8)	0·1223 (4)	7·0 (2)
C9	−0·2757 (2)	1·0315 (7)	0·1364 (3)	4·8 (2)
C10	−0·2852 (2)	1·1476 (9)	0·2338 (4)	6·6 (2)
C11	−0·2441 (2)	1·1412 (7)	0·1529 (4)	5·4 (2)
C12	−0·2074 (2)	1·0761 (6)	0·1633 (3)	4·4 (2)
C13	−0·1783 (2)	1·1792 (7)	0·1712 (3)	5·0 (2)
C14	−0·1436 (2)	1·1214 (7)	0·1747 (3)	4·3 (2)
C15	−0·1384 (1)	0·9554 (7)	0·1713 (3)	3·9 (1)
C16	−0·1008 (2)	0·8967 (7)	0·1656 (3)	4·4 (2)
C17	−0·0759 (2)	0·5358 (7)	0·0381 (3)	4·8 (2)
C18	−0·0706 (3)	0·646 (1)	−0·0188 (4)	9·0 (3)
C19	−0·0491 (2)	0·3989 (8)	0·0317 (4)	7·5 (2)
C20	−0·1138 (2)	0·4718 (8)	0·0335 (4)	6·8 (2)
C21	−0·0238 (2)	0·7437 (7)	0·1226 (3)	4·1 (2)
C22	−0·0201 (2)	0·8858 (8)	0·0893 (4)	6·0 (2)
C23	0·0117 (2)	0·9686 (8)	0·0915 (4)	6·8 (2)
C24	0·0401 (2)	0·9162 (8)	0·1257 (4)	7·2 (2)
C25	0·0376 (2)	0·7759 (9)	0·1594 (4)	7·6 (2)
C26	0·0059 (2)	0·6941 (8)	0·1574 (4)	5·8 (2)
C27	−0·0725 (2)	0·4990 (6)	0·1858 (3)	4·0 (2)
C28	−0·0479 (2)	0·3811 (7)	0·2024 (4)	5·7 (2)
C29	−0·0536 (2)	0·2813 (8)	0·2547 (4)	6·8 (2)
C30	−0·0824 (2)	0·2970 (8)	0·2912 (4)	6·7 (2)
C31	−0·1075 (2)	0·4113 (8)	0·2755 (4)	6·4 (2)
C32	−0·1029 (2)	0·5094 (7)	0·2236 (3)	4·9 (2)
H9	−0·295 (1)	1·067 (6)	0·111 (3)	4*
H11	−0·245 (1)	1·211 (6)	0·125 (3)	4*
H12	−0·208 (1)	1·006 (6)	0·183 (3)	4*
H13	−0·181 (1)	1·274 (6)	0·164 (3)	4*
H14	−0·124 (1)	1·187 (7)	0·170 (3)	4*
H15	−0·155 (1)	0·901 (6)	0·191 (3)	4*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{\rm eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

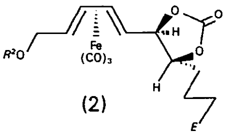
93·59 (5)°, $V = 3244$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 5{\cdot}47$ cm^{-1}, $F(000) = 1360$, $T = 293$ K, $R = 0{\cdot}052$ for 894 reflections. The structure of (2) presents a statistically disordered substituent.

Introduction. The *erythro* (1) and *threo* carbonates (2) and (3) are key intermediates during the preparation of the biologically important fatty acid metabolites lipoxin A and 5,6-dihetes (Gigou, Lellouche, Beaucourt, Toupet & Grée, 1989). In order to establish their stereochemistry unambiguously, X-ray diffraction studies were carried out.



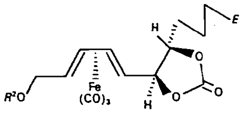
(1)

erythro



(2)

threo major



R² = SiPh₂ *tert*-Bu

E = CO₂Me

(3)

threo minor

Experimental. Single crystals of (1), (2) and (3) were obtained from an ether/hexane mixture. Data collected on an Enraf–Nonius CAD-4 diffractometer, $\omega/2\theta$ mode, variable scan rate ($t_{\max} = 60$s), graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions were obtained by a least-squares refinement of 25 reflections, and space group assignments are consistent with systematic absences and Laue symmetry. Lorentz and polarization corrections were applied but no absorption correction was made. The structures were solved with a Patterson map which allows the location of the Fe atom: after one or several scale-factor refinements and Fourier differences the remaining non-H atoms were found. In the case of (1) no particular problem was encountered: after refinements with isotropic, then anisotropic thermal parameters, many H atoms were found, the remainder were set in geometrical positions. During the resolution of (2), it appeared that the methoxycarbonyl substituent could have two positions, these positions correspond to a 180° rotation around the C8—C5—C4 axis, and are evaluated as 50/50 according to isotropic thermal parameters. Thus, there is statistical disorder in the crystal and

Table 3. *Atomic positional parameters and* $B_{\rm eq}$ *values for compound* (2)

	x	*y*	*z*	$B_{\rm eq}$ (Å^2)
Fe1	−0·16863 (3)	1·0328 (1)	0·09770 (6)	3·93 (2)
Si1	−0·06560 (6)	0·6373 (3)	0·1187 (1)	3·68 (5)
O1	−0·1104 (2)	1·0405 (9)	0·0089 (3)	7·1 (2)
O2	−0·1913 (2)	0·6936 (8)	0·0760 (3)	7·3 (2)
O3	−0·2104 (2)	1·226 (1)	0·0088 (4)	11·1 (3)
O4′	−0·3252 (5)	0·369 (2)	0·1234 (9)	12·2 (6)*
O4	−0·3537 (4)	0·448 (2)	0·1408 (8)	10·1 (4)*
O5′	−0·3607 (5)	0·569 (2)	0·1225 (8)	11·3 (5)*
O5	−0·2991 (4)	0·396 (2)	0·1381 (8)	11·0 (5)*
O6	−0·2941 (1)	0·9926 (7)	0·1985 (3)	5·4 (1)
O7	−0·3039 (2)	1·1621 (9)	0·2789 (3)	8·1 (2)
O8	−0·2541 (1)	1·1770 (7)	0·2249 (3)	5·6 (1)
O9	−0·0966 (1)	0·7768 (6)	0·1203 (2)	4·0 (1)
C1	−0·1328 (2)	1·038 (1)	0·0439 (4)	5·0 (2)
C2	−0·1824 (2)	0·026 (1)	0·0839 (4)	5·0 (2)
C3	−0·1939 (2)	1·148 (1)	0·0439 (4)	6·3 (3)
C4	−0·3594 (3)	0·271 (1)	0·1385 (6)	9·6 (4)
C5	−0·3280 (3)	0·498 (2)	0·1295 (5)	10·0 (4)
C6	−0·3154 (5)	0·675 (3)	0·1233 (9)	6·7 (5)*
C6′	−0·2992 (5)	0·623 (3)	0·1171 (9)	6·4 (5)*
C7′	−0·2853 (5)	0·713 (3)	0·0893 (9)	6·5 (5)*
C7	−0·3105 (4)	0·796 (2)	0·0938 (8)	4·7 (4)*
C8	−0·2776 (3)	0·909 (1)	0·0923 (4)	6·2 (3)
C9	−0·2642 (2)	0·951 (1)	0·1586 (4)	4·2 (2)
C10	−0·2857 (2)	1·114 (1)	0·2375 (4)	5·8 (2)
C11	−0·2408 (2)	1·106 (1)	0·1661 (4)	4·5 (2)
C12	−0·2029 (2)	1·0642 (9)	0·1747 (4)	4·0 (2)
C13	−0·1766 (2)	1·186 (1)	0·1722 (4)	4·6 (2)
C14	−0·1417 (2)	1·136 (1)	0·1733 (4)	4·4 (2)
C15	−0·1342 (2)	0·996 (1)	0·1749 (3)	3·6 (2)
C16	−0·0968 (2)	0·911 (1)	0·1639 (4)	4·2 (2)
C17	−0·0731 (2)	0·524 (1)	0·0414 (4)	4·7 (2)
C18	−0·0644 (3)	0·635 (1)	−0·0191 (5)	7·9 (3)
C19	−0·0486 (3)	0·376 (1)	0·0375 (5)	6·8 (3)
C20	−0·1110 (2)	0·471 (4)	0·0351 (4)	6·3 (2)
C21	−0·0216 (2)	0·741 (1)	0·1233 (4)	4·1 (2)
C22	−0·0176 (2)	0·888 (1)	0·0898 (4)	5·3 (2)
C23	0·0148 (2)	0·969 (1)	0·0904 (5)	6·3 (2)
C24	0·0428 (2)	0·909 (1)	0·1244 (5)	6·6 (3)
C25	0·0398 (2)	0·768 (1)	0·1575 (5)	7·0 (3)
C26	0·0074 (2)	0·684 (1)	0·1580 (4)	5·4 (2)
C27	−0·0719 (2)	0·4984 (9)	0·1884 (4)	4·0 (2)
C28	−0·0480 (2)	0·374 (1)	0·2058 (4)	5·4 (2)
C29	−0·0548 (2)	0·271 (1)	0·2582 (5)	6·8 (3)
C30	−0·0845 (3)	0·298 (1)	0·2938 (5)	6·9 (3)
C31	−0·1081 (3)	0·416 (1)	0·2771 (4)	6·2 (2)
C32	−0·1023 (2)	0·516 (1)	0·2246 (4)	4·5 (2)
H9	−0·252 (2)	0·86 (1)	0·178 (3)	4·0*
H11	−0·248 (2)	1·18 (1)	0·136 (4)	4·0*
H12	−0·197 (2)	0·98 (1)	0·201 (3)	4·0*
H13	−0·181 (2)	1·30 (1)	0·165 (4)	4·0*
H14	−0·126 (2)	1·21 (1)	0·164 (4)	4·0*
H15	−0·150 (2)	0·89 (1)	0·197 (4)	4·0*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{\rm eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

because (2) crystallizes in two conformers there is a statistical repartition in the crystal. This result may be characteristic in the case of asymmetric compounds which present a non-linear optical behaviour. Furthermore, we have tested the possibility of the space group *Cc* with two molecules in the asymmetric unit: in addition to the problems of correlations owing to pseudo centrosymmetry we observe the same disorder for the methoxycarbonyl substituent. In the case of (3) there was a very low number

Table 4. *Atomic positional parameters and B values for compound* (3)

	x	*y*	*z*	*B* (Å^2)
Fe	0·3048 (1)	0·1691 (2)	0·2410 (2)	2·98 (4)*
Si	0·1429 (2)	−0·1082 (5)	0·1222 (4)	3·2 (1)*
O1	0·2883 (5)	0·135 (1)	0·005 (1)	7·4 (4)*
O2	0·2015 (5)	0·262 (1)	0·297 (1)	6·6 (3)*
O3	0·3526 (6)	0·416 (1)	0·261 (1)	7·8 (4)*
O4	0·6322 (5)	0·223 (1)	0·5536 (9)	5·7 (3)*
O5	−0·6375 (5)	0·287 (1)	0·389 (1)	7·5 (4)*
O6	0·4994 (5)	0·100 (1)	0·0965 (9)	5·4 (3)*
O7	0·4710 (6)	0·229 (1)	−0·037 (1)	8·5 (4)*
O8	0·4208 (5)	0·200 (1)	0·1050 (9)	5·6 (3)*
O9	0·1948 (4)	−0·032 (1)	0·1739 (8)	4·1 (3)*
C1	0·2927 (7)	0·153 (2)	0·101 (1)	5·8 (5)*
C2	0·2427 (7)	0·228 (2)	0·272 (1)	4·1 (4)*
C3	0·3337 (7)	0·317 (2)	0·253 (1)	6·0 (5)*
C4	0·6708 (9)	0·311 (2)	0·591 (2)	8·3 (6)*
C5	0·6189 (7)	0·217 (2)	0·449 (1)	5·2 (5)*
C6	0·5811 (6)	0·116 (2)	0·419 (1)	3·9 (4)*
C7	0·5517 (7)	0·133 (2)	0·312 (1)	4·7 (4)*
C8	0·5149 (7)	0·020 (2)	0·282 (1)	4·4 (4)*
C9	0·4743 (6)	0·041 (1)	0·189 (1)	2·9 (4)*
C10	0·4625 (8)	0·180 (2)	0·053 (2)	6·5 (5)*
C11	0·4286 (6)	0·136 (1)	0·212 (1)	3·5 (4)*
C12	0·3790 (6)	0·071 (1)	0·241 (1)	3·3 (4)*
C13	0·3606 (6)	0·083 (1)	0·345 (1)	3·1 (4)*
C14	0·3095 (6)	0·041 (1)	0·363 (1)	3·2 (4)*
C15	0·2770 (6)	−0·016 (1)	0·275 (1)	3·4 (4)*
C16	0·2209 (7)	−0·049 (2)	0·281 (1)	3·9 (4)*
C17	0·1261 (6)	−0·036 (2)	−0·014 (1)	3·8 (4)*
C18	0·1679 (8)	−0·058 (2)	—0·092 (1)	5·9 (5)*
C19	0·1186 (8)	0·105 (2)	−0·001 (2)	6·6 (5)*
C20	0·0729 (8)	−0·087 (2)	−0·060 (2)	6·6 (5)*
C21	0·1649 (6)	−0·274 (1)	0·105 (1)	3·4 (4)*
C22	0·1308 (7)	−0·374 (2)	0·077 (1)	5·2 (5)*
C23	0·1486 (7)	−0·500 (2)	0·064 (1)	5·5 (5)*
C24	0·2032 (7)	−0·518 (2)	0·084 (1)	4·8 (4)*
C25	0·2391 (7)	−0·429 (2)	0·109 (1)	5·1 (5)*
C26	0·2187 (7)	−0·305 (2)	0·122 (1)	4·7 (4)*
C27	0·0878 (6)	−0·089 (2)	0·213 (1)	3·7 (4)*
C28	0·0839 (7)	0·019 (2)	0·275 (1)	4·3 (4)*
C29	0·0417 (8)	0·042 (2)	0·341 (1)	6·0 (5)*
C30	0·0024 (7)	−0·039 (2)	0·348 (1)	5·5 (5)*
C31	0·0049 (7)	−0·151 (2)	0·295 (1)	5·8 (5)*
C32	0·0455 (7)	−0·174 (2)	0·226 (1)	5·1 (4)*

Starred atoms were refined isotropically.

Table 5. *Selected bond distances* (Å) *for compounds* (1), (2) *and* (3), *with e.s.d.'s in parentheses*

	(1)	(2)	(3)
Fe—C1	1·775 (8)	1·782 (8)	1·73 (2)
Fe—C2	1·749 (7)	1·793 (9)	1·74 (2)
Fe—C3	1·830 (7)	1·740 (10)	1·73 (2)
C1—O1	1·154 (10)	1·134 (10)	1·19 (2)
C2—O2	1·165 (8)	1·143 (11)	1·15 (2)
C3—O3	1·105 (8)	1·149 (12)	1·16 (3)
C9—O6	1·429 (8)	1·461 (9)	1·47 (2)
C9—C8	1·492 (9)	1·509 (11)	1·49 (2)
C9—C11	1·532 (9)	1·555 (11)	1·56 (2)
C10—O6	1·319 (9)	1·323 (11)	1·34 (2)
C10—O7	1·195 (10)	1·188 (11)	1·25 (2)
C10—C8	1·294 (8)	1·332 (10)	1·27 (2)
C11—O8	1·471 (9)	1·460 (10)	1·48 (2)
C11—C12	1·480 (8)	1·486 (11)	1·48 (2)
C11—H11	0·83 (6)	0·93 (8)	0·97
C12—C13	1·397 (8)	1·413 (11)	1·39 (2)
C12—H12	0·71 (5)	0·92 (8)	0·98
C13—C14	1·380 (9)	1·383 (11)	1·38 (2)
C15—C14	1·428 (8)	1·417 (11)	1·44 (2)
C15—C16	1·491 (8)	1·509 (10)	1·45 (2)
C15—H15	0·88 (6)	0·96 (8)	0·98
O9—Si	1·657 (4)	1·638 (5)	1·624 (11)
O9—C16	1·429 (7)	1·426 (9)	1·44 (2)

Table 6. *Selected bond angles* (°) *for compounds* (1), (2) *and* (3) *with e.s.d.'s in parentheses*

	(1)	(2)	(3)
C1—Fe—C2	91·0 (3)	98·3 (4)	98·7 (8)
C2—Fe—C3	97·2 (3)	104·6 (4)	91·5 (8)
C1—Fe—C3	104·5 (3)	89·5 (4)	102·7 (9)
Fe—C1—O1	178·7 (7)	178·8 (8)	174·0 (2)
Fe—C2—O2	178·8 (6)	179·1 (8)	177·0 (2)
Fe—C3—O3	179·0 (6)	179·0 (9)	179·0 (2)
C8—C9—O6	107·4 (5)	109·4 (6)	111·0 (1)
C8—C9—C11	119·8 (5)	117·3 (7)	115·0 (1)
O6—C9—C11	103·0 (5)	101·5 (6)	103·0 (1)
O6—C10—O7	124·9 (7)	124·2 (8)	118·0 (2)
O6—C10—O8	110·0 (6)	119·9 (7)	118·0 (2)
O7—C10—O8	125·1 (7)	123·9 (8)	124·0 (2)
O8—C11—C9	100·8 (5)	101·7 (6)	101·0 (1)
O8—C11—C12	109·4 (5)	109·8 (6)	111·0 (1)
C9—C11—C12	120·0 (5)	111·7 (6)	112·0 (1)
O8—C11—H11	107·0 (4)	102·0 (5)	117·0
C9—C11—H11	107·0 (4)	110·0 (5)	110·0
C12—C11—H11	112·0 (4)	120·0 (5)	106·0
C11—C12—C13	109·1 (5)	120·8 (7)	121·0 (1)
C11—C12—C13	109·1 (5)	120·8 (7)	121·0 (1)
C13—C12—H12	119·0 (4)	114·0 (5)	122·0
C11—C12—H12	112·0 (4)	118·0 (4)	117·0
C12—C13—C14	120·0 (6)	117·5 (7)	118·0 (1)
C13—C14—C15	118·6 (5)	119·0 (7)	120·0 (1)
C14—C15—C16	117·7 (5)	118·7 (7)	124·0(1)
C16—C15—H15	122·0 (4)	118·0 (5)	117·0
C14—C15—H15	114·0 (4)	119·0 (5)	118·0
C15—C16—O9	108·8 (5)	110·3 (6)	108·0 (1)

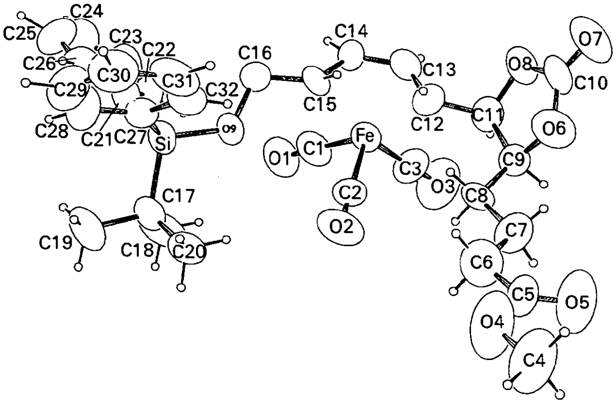


Fig. 1. An *ORTEP* (Johnson, 1965) view of (1).

of reflections owing to the size of the available sample: so it was not possible to refine the structure with anisotropic thermal parameters and the H atoms were set in geometrical positions according to an sp^2 hybridization: under these conditions, if the *R* values are good enough, the e.s.d. values are rather large.

The best full-matrix least-squares refinements (use of *F* magnitudes) of these structures [x, y, z, β_{ij} for Fe, Si, C and O atoms, x, y, z for H atoms for (1); x, y, z, β_{ij} for Fe, Si, C and O atoms, x, y, z for H atoms but disordered substituent CH_2—CH_2—CO_2—CH_3 isotropic for (2); x, y, z, B for Fe, Si, C and O atoms, H atoms fixed for compound (3)] gives the *R*, *wR* and *S* values presented in Table 1.* Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a Digital PDP11/60 computer with the *SDP-Plus* package (Frenz, 1985).

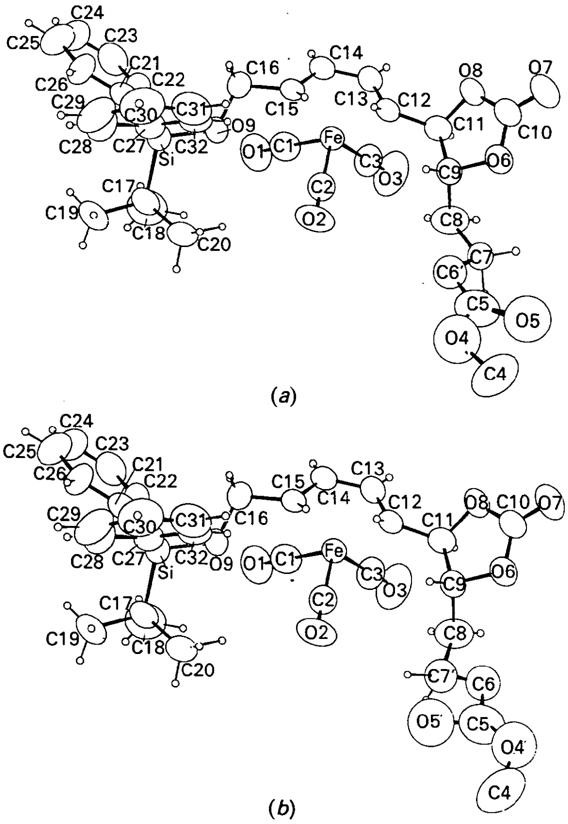


Fig. 2. *ORTEP* (Johnson, 1965) views of (*a*) the first form of (2) and (*b*) the second form of (2).

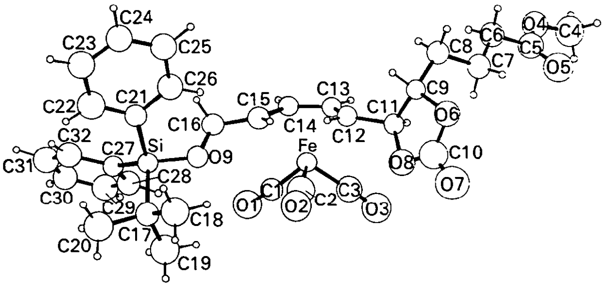


Fig. 3. An *ORTEP* (Johnson, 1965) view of (3).

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* Lists of structure factors, anisotropic thermal parameters, complete distortions and angles, and H-atom parameters [for compound (3) only] have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53802 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

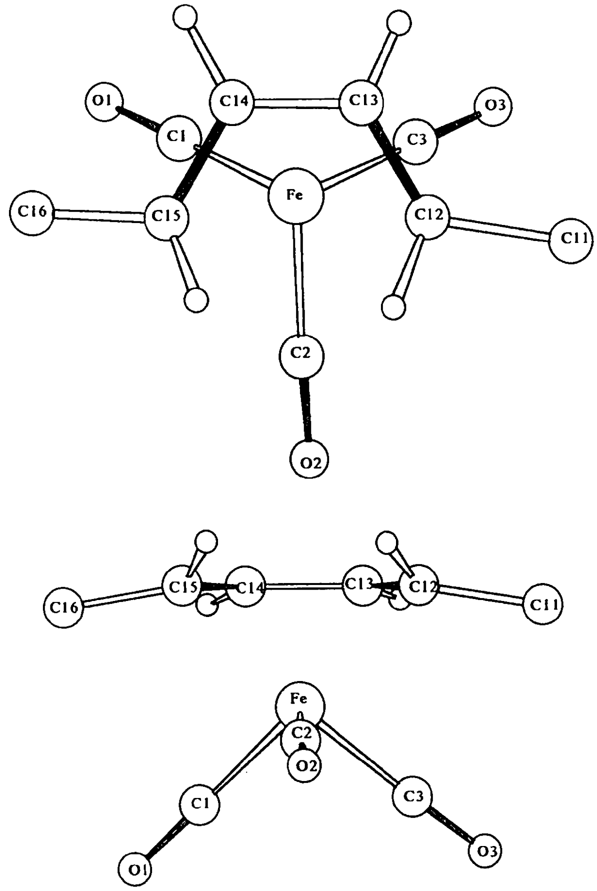

Fig. 4. Perpendicular and planar view of the butadienetricarbonyliron moiety.

Discussion. Table 1 contains crystal and refinement data for (1), (2) and (3), while Tables 2, 3 and 4 give the atomic positional parameters and B_{eq} values for the non-H atoms of the three compounds. Table 5 presents selected bond distances and Table 6 selected valence angles. Figs. 1, 2(*a*), 2(*b*) and 3 are *ORTEP* (Johnson, 1965) drawings of the three molecules. As can be seen from Tables 5 and 6, the three geometries are homogeneous, in particular for (1) and (2). In the butadiene–tricarbonyliron moiety, the two H atoms (H12 and H15) lie above the C12—C13—C14—C15 plane as shown in Fig. 4. The hybridization of the corresponding C atoms (C12 and C15) is intermediate between sp^3 and sp^2 as a result of complexation by the tricarbonyliron moiety (Messager & Toupet, 1986). With regard to the stereochemical outcome of this synthesis, in each case the first step of the reaction (the osmylation of the double bonds) occurs *anti* to the Fe(CO)$_3$ moiety. Thus, these results not only indicate the stereochemistry of the three compounds, but also show that stereocontrolled preparation of other natural product derivatives in this family is possible.

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β–α Photoisomerization of Cobaloxime Complexes in the Solid State. II. A Topochemically Controlled Reaction

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Abstract. (*β*-Cyanoethyl)bis(dimethylglyoximato)(pyridine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), [Co(C$_3$H$_4$N)(C$_4$H$_7$N$_2$O$_2$)$_2$(C$_5$H$_5$N)], crystallizes in two forms. The rates of *β–α* isomerization by exposure to visible light differ for the two forms. One of the two forms, form I, has been reported previously [Zangrando, Bresciani-Pahor, Randaccio, Charland & Marzilli (1986).

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