H-atoms fixed at calculated positions
$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 12.7786P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Re1	0.20300 (3)	0.13691 (2)	0.14701 (2)	0.0391 (2)
Mn1	0.32317 (12)	0.28031 (8)	0.09839 (8)	0.0401 (3)
C1	0.3896 (10)	0.2792 (7)	0.1895 (7)	0.065 (3)
O1	0.4290 (8)	0.2795 (7)	0.2433 (5)	0.101 (3)
C2	0.4195 (9)	0.2052 (7)	0.0649 (6)	0.056 (3)
O2	0.4783 (7)	0.1589 (6)	0.0427 (6)	0.083 (3)
C3	0.2124 (11)	0.3396 (8)	0.1376 (7)	0.066 (3)
O3	0.1415 (10)	0.3769 (7)	0.1618 (7)	0.103 (4)
C4	0.2414 (10)	0.2645 (6)	0.0157 (6)	0.053 (3)
O4	0.1940 (7)	0.2545 (6)	−0.0358 (5)	0.075 (3)
C5	0.3982 (12)	0.3613 (7)	0.0647 (7)	0.072 (3)
O5	0.4485 (9)	0.4142 (6)	0.0387 (5)	0.093 (3)
C6	0.1304 (9)	0.0427 (6)	0.1788 (6)	0.051 (2)
O6	0.0903 (8)	−0.0141 (5)	0.2001 (4)	0.076 (2)
C7	0.0623 (9)	0.1846 (6)	0.1132 (6)	0.051 (2)
O7	−0.0171 (7)	0.2137 (6)	0.0960 (5)	0.081 (3)
C8	0.3473 (9)	0.0958 (7)	0.1804 (6)	0.057 (3)
O8	0.4271 (8)	0.0759 (7)	0.2031 (6)	0.101 (3)
C9	0.1808 (9)	0.1859 (7)	0.2395 (5)	0.053 (3)
O9	0.1686 (8)	0.2150 (6)	0.2953 (4)	0.084 (3)
N1	0.2313 (7)	0.0878 (5)	0.0407 (4)	0.045 (2)
C10	0.2448 (8)	0.0657 (6)	−0.0159 (5)	0.042 (2)
C11	0.2706 (10)	0.0374 (7)	−0.0888 (5)	0.057 (3)
C12	0.1940 (19)	0.0740 (18)	−0.1459 (13)	0.154 (10)
C13	0.3939 (25)	0.0663 (17)	−0.1069 (15)	0.184 (10)
C14	0.2979 (25)	−0.0522 (23)	−0.0939 (19)	0.221 (15)

Table 2. *Selected geometric parameters* (Å, °)

Re1—N1	2.152 (8)	Mn1—C2	1.836 (12)
Re1—Mn1	2.969 (2)	Mn1—C1	1.862 (12)
Re1—C6	1.913 (11)	C1—O1	1.102 (13)
Re1—C7	1.999 (11)	C2—O2	1.137 (13)
Re1—C8	1.992 (11)	C3—O3	1.16 (2)
Re1—C9	1.912 (10)	C4—O4	1.124 (13)
Mn1—C3	1.832 (13)	N1—C10	1.119 (11)
Mn1—C4	1.840 (13)	C10—C11	1.458 (13)
C9—Re1—N1	176.9 (4)	C1—Mn1—Re1	86.4 (4)
C6—Re1—N1	91.9 (4)	O1—C1—Mn1	179.2 (12)
C8—Re1—N1	90.2 (4)	O2—C2—Mn1	178.6 (11)
C7—Re1—N1	90.6 (3)	O3—C3—Mn1	179.3 (12)
N1—Re1—Mn1	87.7 (2)	O4—C4—Mn1	178.2 (11)
C3—Mn1—Re1	87.7 (4)	C10—N1—Re1	176.7 (8)
C4—Mn1—Re1	82.1 (3)	N1—C10—C11	176.0 (12)
C2—Mn1—Re1	81.7 (3)		

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: AB1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-(Ferrocenylmethyl)-2,2,6,6-tetramethyl-3,5-heptanedione, a Non-Enolized 1,3-Diketone

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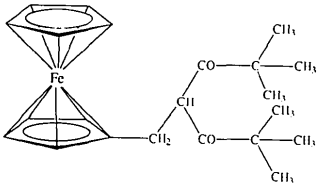
Abstract

The analysis of the title compound, (η^5-cyclopentadienyl){η^5-[2,2-bis(2,2-dimethylpropanoyl)ethyl]cyclopentadienyl}iron, $[(C_5H_5)Fe\{(C_5H_4)CH_2CH(COCMe_3)_2\}]$, shows that it exists in the solid state in the diketo form; there is no evidence at all for any keto–enol tautomeric contribution to the ground-state structure.

Comment

Both in solution and in the vapour phase (Lowrey, George, D'Antonio & Karle, 1971), 1,3-diketones $R'COCH_2COR''$ generally exist as equilibrium mixtures of keto and enol tautomers where the enol tautomer contains a six-membered hydrogen-bonded ring. In the solid state, however, only a single form is generally observed. This is most frequently the enol form in which the hydrogen-bonded ring is virtually planar with the two C—O bonds necessarily *cis* (Tønnesen, Karlsen & Mostad, 1982; Tønnesen, Karlsen, Mostad, Pedersen, Rasmussen & Lawesson, 1983; Mostad, Pedersen, Rasmussen & Lawesson, 1983; Etter, Jahn & Urbanczyk-Lipkowska, 1987; Baxter, Blake, Heath & Stephenson, 1990). The enol H atom has been located accurately for several such enols (Jones, 1976*a*,*b*) using neutron diffraction data. However, there are several 1,3-diketones which in the solid state exist wholly in the dione form rather than in the enol form; a variety of factors may underlie this. For example, in 2-benzylidene-[3]ferrocenophane-1,3-dione (Gyepes, Glowiak & Toma, 1986) there are no H atoms available for enol formation, while in [3]ferrocenophane-1,3-dione itself (Gyepes, Glowiak, Toma & Soldánová, 1984) the ring containing the 1,3-diketone fragment is twisted severely as a result of the ring strain in the [3]ferrocenophane skeleton, so that enolization is again prevented. However, in the acyclic diketone 2-ethyl-1,3-diphenyl-1,3-propanedione, $(PhCO)_2CHC_2H_5$ (Mullica, Karban & Grossie, 1987), the solid-state structure again indicates a complete lack of enolization associated with a markedly non-planar O=C—C—C=O fragment, although 1,3-diphenyl-1,3-propanedione itself is wholly in the enol form in both crystalline modifications (Jones, 1976*a*; Etter, Jahn & Urbanczyk-Lipkowska, 1987).

In a study of the 1-ferrocenyldiketone $[(C_5H_5)Fe\{(C_5H_4)COCH_2COCH_3\}]$, it was found (Bell, Crayston, Glidewell, Mazid & Hursthouse, 1992) that in chloroform solution the enol:keto ratio was *ca* 17:1, but in the solid state both ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR and X-ray diffraction revealed only the enol form, 1-ferrocenyl-3-hydroxybut-2-en-1-one. In contrast, the 4-ferrocenylmethyl derivative $[(C_5H_5)Fe\{(C_5H_4)CH_2CH(COCMe_3)_2\}]$ (I) exhibits an enol:keto ratio in chloroform solution of 1:3 (Zakaria, Morrison, McAndrew, Bell & Glidewell, 1994), suggesting that, like $(PhCO)_2CHC_2H_5$, it might exist in the solid state solely in the diketo form. Here we report a single-crystal X-ray study of this compound which confirms that in the solid state it is indeed a non-enolized 1,3-diketone.



(I)

Compound (I) crystallizes in the triclinic system (space group $P\bar{1}$) with one molecule in the asymmetric unit. The structure comprises isolated molecules with no short intermolecular contacts. In the $—CH_2CH(COCMe_3)_2$ substituent, the C2—C3 and C2—C5 bond lengths (Table 2, Fig. 1) are typical of those in unenolized 1,3-diketones (range 1.507–1.537 Å; Gyepes, Glowiak, Toma & Soldánová, 1984; Gyepes, Glowiak & Toma, 1986; Mullica, Karban & Grossie, 1987), whereas in enolized 1,3-diketones the corresponding C—C distances lie in the range 1.34–1.43 Å (Bell, Crayston, Glidewell, Mazid & Hursthouse, 1992). The C3—O1 and C5—O2 distances are likewise typical of those in unenolized 1,3-diketones (range 1.212–1.221 Å) and are much shorter than C—O distances in enolized 1,3-diketones (range 1.27–1.34 Å). The absence of enolization in (I) is also demonstrated by (*a*) the location in a difference map of the H atom (H2) bonded to C2 and (*b*) the C—C—C bond angles around C2, all of which are close to the tetrahedral value. The intramolecular O1···O2 distance is 3.054 (2) Å while the shortest intermolecular O···O distance is 4.298 (2) Å. The lack of any enolization can be associated with the conformation of the $—CH_2CH(COCMe_3)_2$ fragment; the torsion angles C5—C2—C3—O1 and C3—C2—C5—O2 are 19.5 (2) and −88.4 (2)°, respectively, whereas in enolized 1,3-diketones forming intramolecular hydrogen bonds they are generally zero to within experimental error. The torsion angles C1—C2—C3—C4 and C1—C2—C5—C6 are 79.6 (2) and −145.5 (1)°, respectively; in a hydrogen-bonded enol these would both be close to zero. The net effect of the rotations about the C2—C3 and C2—C5 bonds is to move the bulky CMe_3 substituents away from the ferrocenylmethyl substituent on C2; it is probably the potential steric interference of the substituents on C2, C3 and C5 (Fig. 1) which prevents the formation of a planar *cisoid* O1—C3—C2—C5—O2 unit. In support of this, inspection of the structure of the enol tautomer of 1,3-diphenyl-1,3-propanedione (Jones, 1976*a*) indicates that, although the unique H atom on the central C atom is comfortably accommodated between the phenyl substituents in an essentially planar molecule, it is not possible to accommodate any substituent larger than an H atom at this site without destroying the skeletal planarity.

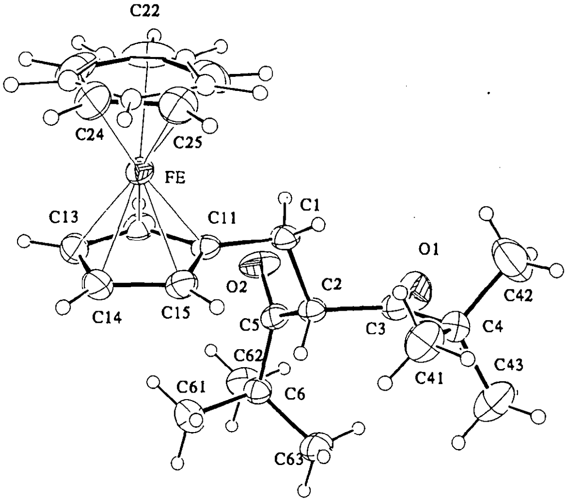


Fig. 1. A view of the $[(C_5H_5)Fe\{(C_5H_4)CH_2CH(COCMe_3)_2\}]$ molecule with the numbering scheme indicated. The non-H atoms are shown as displacement ellipsoids drawn at the 30% probability level. For clarity, H atoms and atoms of the minor component of the C_5H_5 ring are drawn as small spheres of arbitrary size.

Within the ferrocenyl nucleus, the unsubstituted ring exhibits orientational disorder; 78 (1)% of the molecules adopt an almost eclipsed conformation of the rings with an average torsion angle C1*n*—Cp1—Cp2—C2*n* (*n* = 1–5) of −6.1 (5)°, while 22 (1)% adopt a nearly staggered conformation with an average torsion angle C1*n*—Cp1—Cp3—C3*n* (*n* = 1–5) of 30.1 (2)° (Cp1, Cp2 and Cp3 are the centroids of the rings C11–C15, C21–C25 and C31–C35, respectively). The rings C11–C15 and C21–C25 are tilted away from a parallel arrangement by 1.1 (1)°; the corresponding tilt angle for the C11–C15 and C31–C35 rings is 3.2 (6)°. As frequently (but not always) observed in substituted ferrocenes (Bell, Crayston, Glidewell, Mazid & Hursthouse, 1992), the mean Fe—C distances for the two rings are identical within experimental uncertainty but the mean C—C distance in the substituted ring is greater than for the unsubstituted ring.

Experimental

Crystals of compound (I), synthesized by Zakaria, Morrison, McAndrew, Bell & Glidewell (1994), were grown by slow evaporation of a solution in dry acetone.

Crystal data

$[Fe(C_5H_5)(C_{17}H_{25}O_2)]$
$M_r = 382.32$
Triclinic
$P\bar{1}$
$a = 5.8899\ (6)$ Å
$b = 11.7768\ (12)$ Å
$c = 15.2335\ (16)$ Å
$\alpha = 72.611\ (9)°$
$\beta = 88.277\ (12)°$
$\gamma = 82.632\ (12)°$
$V = 1000.00\ (18)$ Å^3
$Z = 2$
$D_x = 1.270$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.50–20.50°$
$\mu = 0.76$ mm^{-1}
$T = 293$ K
Block cut from needle
0.35 × 0.26 × 0.17 mm
Orange

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (five ψ scans, 4° steps)
$T_{min} = 0.705$, $T_{max} = 0.839$
4358 measured reflections
4358 independent reflections

3676 observed reflections $[I > 2.0\sigma(I)]$
$\theta_{max} = 26.90°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity variation: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0300$
$wR(F^2) = 0.0805$

$\Delta\rho_{max} = 0.216$ e Å^{-3}
$\Delta\rho_{min} = -0.295$ e Å^{-3}
Extinction correction: none

$S = 1.113$
4358 reflections
240 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.1339P]$
where $P = (F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

Cp1, Cp2 and Cp3 are the centroids of the rings C11–C15, C21–C25 and C31–C35, respectively. C21–C25 have occupancies of 0.781 (8); C31–C35 have occupancies of 0.219 (8). U_{iso} is given for C31–C35; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all other non-H atoms.

	x	*y*	*z*	U_{iso}/U_{eq}
Fe	0.22781 (4)	0.19138 (2)	0.133873 (15)	0.03842 (8)
Cp1	0.1832	0.0627	0.1198	
Cp2	0.2677	0.3197	0.1500	
Cp3	0.3003	0.3181	0.1463	
O1	0.5394 (2)	−0.31317 (14)	0.44434 (10)	0.0723 (4)
O2	0.6793 (2)	−0.22366 (13)	0.24307 (12)	0.0699 (4)
C11	0.2637 (3)	0.01084 (12)	0.19588 (11)	0.0394 (3)
C12	0.3855 (3)	0.03820 (14)	0.11150 (12)	0.0470 (4)
C13	0.2279 (4)	0.0995 (2)	0.03945 (12)	0.0550 (4)
C14	0.0092 (3)	0.1099 (2)	0.07807 (13)	0.0554 (4)
C15	0.0295 (3)	0.05522 (15)	0.17419 (12)	0.0470 (4)
C21	0.3243 (6)	0.2678 (2)	0.2272 (2)	0.0720 (11)
C22	0.4704 (5)	0.2902 (3)	0.1506 (3)	0.0796 (14)
C23	0.3346 (7)	0.3541 (2)	0.0729 (2)	0.0770 (12)
C24	0.1066 (5)	0.3695 (2)	0.1027 (2)	0.0659 (10)
C25	0.1027 (5)	0.3169 (2)	0.1967 (2)	0.0617 (10)
C31	0.4597 (5)	0.2652 (2)	0.1940 (2)	0.047 (2)
C32	0.4633 (5)	0.3158 (2)	0.0984 (2)	0.047 (2)
C33	0.2416 (5)	0.3695 (2)	0.0689 (2)	0.047 (2)
C34	0.1010 (5)	0.3521 (2)	0.1464 (2)	0.047 (2)
C35	0.2357 (5)	0.2876 (2)	0.2236 (2)	0.047 (2)
C1	0.3586 (3)	−0.05671 (13)	0.28948 (11)	0.0436 (3)
C2	0.3232 (3)	−0.19079 (12)	0.31441 (10)	0.0387 (3)
C3	0.3608 (3)	−0.25151 (14)	0.41737 (11)	0.0448 (4)
C4	0.1742 (3)	−0.2373 (2)	0.48727 (12)	0.0537 (4)
C5	0.4920 (3)	−0.25509 (14)	0.26099 (11)	0.0428 (3)
C6	0.4146 (3)	−0.35553 (14)	0.22951 (11)	0.0456 (4)
C41	−0.0356 (4)	−0.1480 (2)	0.4472 (2)	0.0715 (6)
C42	0.2847 (5)	−0.1985 (3)	0.5608 (2)	0.1037 (10)
C43	0.0954 (4)	−0.3612 (2)	0.5284 (2)	0.0856 (7)
C61	0.2639 (4)	−0.2935 (2)	0.14400 (14)	0.0679 (5)
C62	0.6234 (4)	−0.4297 (2)	0.2043 (2)	0.0699 (6)
C63	0.2748 (4)	−0.4363 (2)	0.30266 (14)	0.0610 (5)

Table 2. *Selected geometric parameters* (Å, °)

Fe—Cp1	1.646	C11—C15	1.423 (2)
Fe—Cp2	1.648	C11—C1	1.495 (2)
Fe—Cp3	1.667	C12—C13	1.415 (3)
Fe—C11	2.038 (2)	C13—C14	1.406 (3)
Fe—C12	2.038 (2)	C14—C15	1.414 (2)
Fe—C13	2.042 (2)	C21—C22	1.409 (5)
Fe—C14	2.043 (2)	C21—C25	1.392 (4)
Fe—C15	2.040 (2)	C22—C23	1.406 (5)
Fe—C21	2.025 (2)	C23—C24	1.411 (5)
Fe—C22	2.021 (2)	C24—C25	1.380 (4)
Fe—C23	2.034 (2)	C1—C2	1.550 (2)
Fe—C24	2.044 (2)	C2—C3	1.527 (2)
Fe—C25	2.042 (2)	C2—C5	1.533 (2)
Fe—C31	2.078 (2)	C3—C4	1.536 (3)
Fe—C32	2.090 (2)	C4—C42	1.521 (3)
Fe—C33	2.046 (2)	C4—C41	1.528 (3)
Fe—C34	2.005 (2)	C4—C43	1.531 (3)
Fe—C35	2.025 (2)	C5—C6	1.526 (2)
O1—C3	1.206 (2)	C6—C62	1.523 (2)
O2—C5	1.206 (2)	C6—C63	1.529 (2)
C11—C12	1.424 (2)	C6—C61	1.534 (2)

Cp1—Fe—Cp2	178.6	O1—C3—C2	119.4 (2)
Cp1—Fe—Cp3	174.4	O1—C3—C4	119.3 (2)
C11—C1—C2	110.81 (12)	C2—C3—C4	121.30 (14)
C3—C2—C5	109.11 (12)	O2—C5—C6	121.7 (2)
C3—C2—C1	110.38 (13)	O2—C5—C2	119.7 (2)
C5—C2—C1	109.99 (13)	C6—C5—C2	118.58 (13)

Data collection and cell refinement: *Enraf–Nonius CAD-4/PC Software* (Enraf–Nonius, 1992). Data reduction, structure solution and refinement, and preparation of material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecule (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the successful refinement. It became obvious during the analysis of the data that the unsubstituted C_5H_5 ring was disordered over two sites. This was allowed for in the *SHELXL* (Sheldrick, 1994) refinement with the minor site constrained to be a regular pentagon with C—C 1.40 Å. The site occupancies refined to 0.781 (8) and 0.219 (8), respectively, for the major and minor sites, which are rotated by some 36° from an eclipsed conformation. The C atoms of the ring with 0.219 occupancy were allowed isotropic motion; all other non-H atoms were refined anisotropically. H atoms were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. Fig. 1 was prepared using *ORTEP*II (Johnson, 1976). Examination of the structures with *PLATON* (Spek, 1992) showed that there were no solvent-accessible voids in the crystal lattice.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Mn(salphen)(EtOH)$_2$](BPh$_4$) [salphenH$_2$ = *N*,*N*′-bis(salicylidene)-1,2-diaminobenzene], a Further Example of a Photosynthetic Model Compound Forming Dimers Linked by Hydrogen and π Bonds

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Abstract

The title molecule, bis(ethanol-*O*){2,2′-[*o*-phenylenebis(nitrilomethylidyne)diphenolato]-*N*,*N*′,*O*,*O*′}manganese(III) tetraphenylborate, $[Mn(C_{20}H_{14}N_2O_2)(C_2H_6O)_2]$-$(C_{24}H_{20}B)$, comprises a planar tetradentate Schiff base tightly bound to Mn^{III} *via* Mn—N bonds of 1.97 (1) and 1.99 (2) Å, and two Mn—O bonds of 1.85 (1) Å, with capping ethanol groups at the longer Mn—O distances of 2.27 (1) and 2.28 (1) Å completing a distorted octahedral arrangement. Pairs of molecules are linked across inversion centres by hydrogen bonds from the ethanol to the phenoxy O atoms [O···O 2.90 (2) Å], which are augmented by π-bonds between overlapping phenyl rings, resulting in an Mn···Mn separation of 4.995 (6) *cf.* 5.21 (1) Å for the salpn analogue [salpn = *N*,*N*′-bis(salicylidene)-1,3-diaminopropane] [Ashmawy, Beagley, McAuliffe, Parish & Pritchard (1990). *J. Chem. Soc. Chem. Commun.* pp. 936–937].

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