Synthesis and Crystal Structure of 1-Ethoxyferrocenylmethyl-3-ferrocenylmethylene-1-cyclohexene, $C_{30}H_{32}OFe_2$

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The title compound was formed when 2,5-di(ferrocenylmethylene)cyclohexanone was variously treated with $NaBH_4$ in ethanol. The first step was probably a reduction to the corresponding alcohol. This was followed by nucleophilic attack on the vinylic carbon by ethanol, with subsequent elimination of water.

Its structure was determined by X-ray diffraction from data collected at 95 K. The orange crystals are monoclinic with $a = 11.597(2)$, $b = 7.436(1)$, $c = 13.689(2)$ Å, $\beta = 92.50(1)°$, $Z = 2$, space group Pa. The molecule consists of two ferrocenyl groups connected by a 1,3-pentadienyl chain. The three central carbon atoms of the chain are members of a cyclohexene ring. In addition an ethoxy group is substituted at the 1-position of the chain. The ferrocenyl group at the other end displays disorder in the unsubstituted ring.

With 2 mol of aromatic aldehyde and 1 mol of cyclic, aliphatic ketone, a cross-conjugated dienone such as 1 is obtained in the Claisen reaction. The same reaction also takes place when Ar is a ferrocenyl group.[1]

1   2
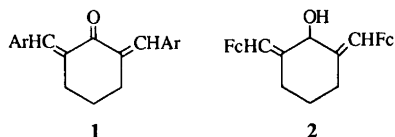
Upon reduction of the diferrocenyl derivative with $NaBH_4$ in ethanol, and subsequent heating with 95% ethanol the expected product, 2, could not be isolated (Fc-ferrocenyl). In order to establish the identity of the unknown species that resulted and to try to elucidate the mechanism for its formation it was decided to solve the structure of the product.

Experimental

Synthesis. To a stirred solution of 0.60 g (1.2 mmol) of diferrocenyl ketone, 1, in 25 ml of warm 95% ethanol was added 0.15 g (3.6 mmol) of fresh $NaBH_4$. The mixture

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was maintained at 60°C for 0.5 h and then at room temperature for another 24 h. During this period, the color changed from purple to pale orange with a deposit of beige solid.

The reaction mixture was suction-filtered, and the resultant solid was washed with cold 95% ethanol to yield 0.54 g (90%) of yellow powder, m.p. 80–90°C (uncorr.). This material was refluxed with 80 ml of 95% ethanol for 0.5 h and then allowed to cool to room temperature. Orange crystals of compound 3 (the title compound) resulted, m.p. 115–117°C. Thin-layer chromatography of a chloroform solution of this material on silica gel (acetone/petroleum ether; 1:3) showed only one spot, $R_f = 0.54$. This may be compared to the starting ketone at 0.34. Elementary analysis; found: C 69.3; H 6.2. Calc. for $C_{30}H_{32}OFe_2$: C 68.9; H 6.3.

Structure determination. Cell dimensions were obtained from setting angles of 25 carefully centered reflections, using a least-squares procedure. The structure was solved by standard Patterson and Fourier methods. Hydrogen atoms were positioned and constrained at their estimated geometrical positions with fixed C–H bond lengths of 0.95 Å. The structure was refined by a full-matrix least-squares procedure, the function minimized was $\Sigma w (\Delta F)^2$. The unsubstituted cyclopentadienyl ring in one of the ferrocenyl groups was disordered. Two such rings, one

nearly eclipsed (60% occupancy) and one nearly staggered (40% occupancy) relative to the substituted ring, seemed to give the most correct picture of the structure.

Crystallographic data and structural refinement parameters are listed in Table 1. Three standard reflections were remeasured every 2 h for scaling purposes. There was no significant decrease in intensity for these reflections. Intensity data were corrected for Lorentz, polarization and absorption effects.

Supplementary material. Further details of the structural work is deposited with the Cambridge Crystallographic Data Centre, UK. Computer programs were supplied by Enraf-Nonius.[2]

Results and discussion

The structure of the compound is shown in Fig. 1. Bond lengths and angles are listed in Tables 3 and 4 and least-squares planes are listed in Table 5.

Molecular structure. From Fig. 1 it is seen that the backbone of the compound is a 1,3-pentadiene with a Fc substituent in the 1 position and with a Fc and an EtO substituent both in the 5 position. The three central pentadienyl atoms are also part of a cyclohexene ring:
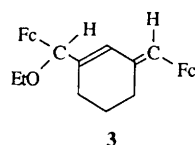
Fc\ /H   H
    C |
EtO/   \   C—Fc

3

Table 1. Crystal and experimental data.

| Compound	$C_{30}H_{32}OFe_2$
Diffractometer	Enraf-Nonius CAD-4
Radiation	MoKα
Wavelength/Å	0.71069
Crystal system	Monoclinic
a/Å	11.597 (2)
b/Å	7.436 (1)
c/Å	13.689 (2)
β/°	92.50
V/Å³	1179.4
Space group	Pa
Fomula wt	1.465
Z	2
D_{calc}/g cm^{-3}	1.465
μ(MoKα)/cm^{-1}	12.499
Crystal dim./mm	0.35×0.22×0.16
Scan mode/max θ/°	ω/28
Fudge factor, p	0.020
Scale factor	1.143
No. of independent measurements	2838
No. with $I > 2.0\sigma(I)$	2666
Transmission (max/min)	0.99/0.91
$R = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$	0.032
$R_w = [\Sigma_w (F_o - F_c)^2 / \Sigma_w F_o^2]^{1/2}$	0.035
$S = [\Sigma_w(\Delta F)^2/(N-n)]^{1/2}$	1.900
Max. in final diff. map/e Å^{-3}	0.55
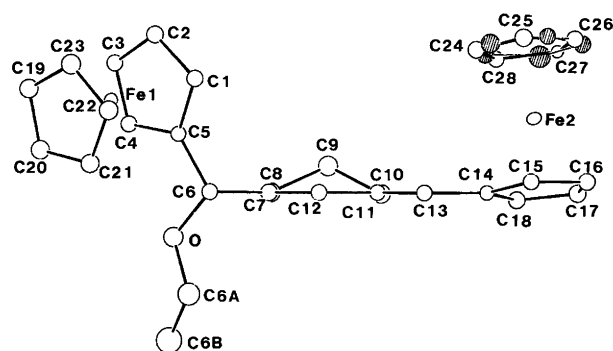
Fig. 1. The molecule, **3**, as seen at right angles to the normal of the central plane; i.e. plane 6 of Table 5. Atoms in the C24A–C28A ring are shaded to distinguish it from the C24–C28 ring, the two rings constituting the disordered cyclopentadienyl group.

All carbon atoms of the 1,3-pentadiene and the two carbons of the cyclohexene bound to it are essentially coplanar. Also C14 of the disordered Fc group lies in this plane. This agrees with sp²-hybridization of the doubly bonded carbons in the pentadiene backbone. The sixth carbon of the cyclohexene ring is 0.62 Å above this plane. Fc1 (connected via C5) has nearly eclipsed cyclopentadienyl rings, while Fc2 (C14) has the unsubstituted ring disordered such that the dominant structure (60%) is nearly eclipsed and the other is approximately staggered. Deviations from perfect eclipsed and staggered conformations are 8.0 and 3.7°, respectively. A similar disorder was earlier found by us in another monosubstituted ferrocene.[3] Again the structural work shows the tendency for ferrocene to prefer an eclipsed conformation.[4]

Bonding. The C⋯C bonds in the ferrocenes vary from 1.412 to 1.438 Å in the ordered cyclopentadienyl rings and from 1.37 to 1.48 Å in the disordered ring. The average bond lengths in the two types of rings are 1.423 and 1.41 Å, respectively. These values are quite normal.[3] The C⋯C⋯C bond angles in the rings vary from 106.4 to 109.0° in the ordered cyclopentadienyl rings and from 105 to 111° in the disordered; however, the average value is 108° for every cyclopentadienyl ring. The Fe–C distances have an average value of 2.045 Å, the iron atoms have an average distance from the ring planes of 1.65 Å.
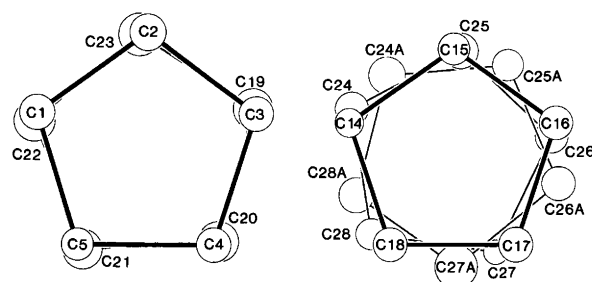

*Fig. 2.* The cyclopentadienyl rings of the ferrocenes, seen approximately along their plane normals.

Table 2. Positional and temperature parameters with estimated standard deviations.

Atom	x	y	z	$B/Å^2$
Fe1	0.000	0.14913(7)	0.000	0.876(8)
Fe2	−0.18678(5)	−0.28651(7)	−0.66219(4)	0.844(8)
O	0.2045(3)	0.2445(4)	−0.1919(2)	1.60(5)*
C1	−0.0507(3)	−0.0140(5)	−0.1148(3)	1.12(6)*
C2	−0.0465(3)	−0.1135(5)	−0.0260(3)	1.20(6)*
C3	0.0680(3)	−0.1040(5)	0.0140(3)	1.09(6)*
C4	0.1352(3)	0.0013(5)	−0.0493(3)	1.07(6)*
C5	0.0610(3)	0.0599(5)	−0.1290(3)	0.92(6)*
C6	0.0921(3)	0.1731(5)	−0.2152(3)	1.08(6)*
C6A	0.2302(4)	0.3943(6)	−0.2527(3)	2.07(8)*
C6B	0.3590(4)	0.4126(7)	−0.2566(4)	2.70(9)*
C7	0.0933(3)	0.0638(5)	−0.3081(3)	1.17(6)*
C8	0.1852(4)	−0.0766(6)	−0.3149(3)	1.53(6)*
C9	0.1475(4)	−0.2262(6)	−0.3853(3)	1.60(7)*
C10	0.1015(4)	−0.1504(6)	−0.4838(3)	1.47(6)*
C11	0.0094(3)	−0.0105(5)	−0.4730(3)	0.99(6)*
C12	0.0146(3)	0.0908(5)	−0.3815(3)	1.07(6)*
C13	−0.0732(3)	0.0285(5)	−0.5422(3)	1.04(6)*
C14	−0.0963(3)	−0.0528(5)	−0.6390(3)	0.87(6)*
C15	−0.2011(3)	−0.0200(5)	−0.6963(3)	1.06(6)*
C16	−0.1999(3)	−0.1241(5)	−0.7834(3)	1.19(6)*
C17	−0.0936(3)	−0.2212(6)	−0.7811(3)	1.26(6)*
C18	−0.0308(3)	−0.1786(5)	−0.6933(3)	1.20(6)*
C19	−0.0050(4)	0.2617(6)	0.1358(3)	1.44(7)*
C20	0.0681(4)	0.3639(6)	0.0763(3)	1.49(6)*
C21	0.0006(4)	0.4246(5)	−0.0067(3)	1.38(6)*
C22	−0.1134(4)	0.3597(6)	0.0030(3)	1.54(7)*
C23	−0.1169(4)	0.2597(6)	0.0908(3)	1.62(7)*
C24	−0.2316(5)	−0.3740(9)	−0.5273(5)	1.1(1)*
C25	−0.3291(6)	−0.3615(9)	−0.5895(5)	1.2(1)*
C26	−0.3139(5)	−0.4735(9)	−0.6709(5)	1.1(1)*
C27	−0.2037(5)	−0.5590(7)	−0.6563(4)	0.56(8)*
C28	−0.1521(5)	−0.4941(9)	−0.5680(4)	0.99(9)*
C24A	−0.2750(9)	−0.359(1)	−0.5434(7)	1.4(2)*
C25A	−0.3423(8)	−0.392(1)	−0.6258(7)	1.1(1)*
C26A	−0.2818(8)	−0.516(1)	−0.6871(7)	1.2(1)*
C27A	−0.171(1)	−0.554(2)	−0.6324(8)	2.0(2)*
C28A	−0.1745(8)	−0.460(1)	−0.5468(7)	1.3(2)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The two C⋯C bonds in the molecule have an average length of 1.349 Å.[5] Average C(sp²)–C(sp²) and C(sp³)–C(sp²) bond lengths (excluding the cyclopentadienyl rings) are 1.465 and 1.504 Å, respectively. These values may be compared with the sum of covalent radii of the appropriately hybridized carbons of 1.48 and 1.51 Å.[5]

Reaction mechanism. The first step is probably the reduction of the substituted cyclohexanone, **1a**, to the corresponding alcohol, **2**:
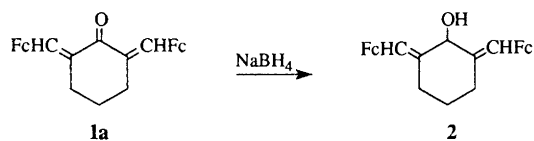
This diallylic system might be expected to easily undergo ionization to a resonance-stabilized species, **4**.

Table 3. Bond lengths (in Å) with estimated standard deviations.

C1–C2	1.422(6)	C27–C28	1.41(1)
C1–C5	1.428(5)	C24A–C25A	1.37(2)
C2–C3	1.415(5)	C24A–C28A	1.39(2)
C3–C4	1.424(6)	C25A–C26A	1.44(2)
C4–C5	1.427(5)	C26A–C27A	1.48(2)
C19–C20	1.421(6)	C27A–C28A	1.37(2)
C19–C23	1.412(6)	C7–C8	1.498(6)
C20–C21	1.424(6)	C7–C12	1.343(5)
C21–C22	1.419(7)	C8–C9	1.524(7)
C22–C23	1.416(6)	C9–C10	1.535(6)
C14–C15	1.438(5)	C10–C11	1.502(6)
C14–C18	1.433(6)	C11–C12	1.460(5)
C15–C16	1.421(6)	C5–C6	1.560(5)
C16–C17	1.428(6)	C6–C7	1.510(5)
C17–C18	1.414(6)	C11–C13	1.349(5)
C24–C25	1.39(1)	C13–C14	1.471(5)
C24–C28	1.42(1)	O–C6	1.429(5)
C25–C26	1.41(1)	O–C6A	1.429(6)
C26–C27	1.43(1)	C6A–C6B	1.503(7)

Table 4. Bond angles (in°) with estimated standard deviations.

C2–C1–C5	108.6(4)	C8–C7–C12	121.3(4)
C1–C2–C3	107.5(4)	C7–C8–C9	111.2(4)
C2–C3–C4	108.7(4)	C8–C9–C10	111.5(4)
C3–C4–C5	107.8(4)	C9–C10–C11	112.9(4)
C1–C5–C4	107.4(3)	C10–C11–C12	116.0(3)
C20–C19–C23	108.5(4)	C7–C12–C11	124.5(4)
C19–C20–C21	107.8(4)	C1–C5–C6	124.8(4)
C20–C21–C22	107.4(4)	C4–C5–C6	127.8(4)
C21–C22–C23	108.6(4)	C5–C6–C7	111.7(3)
C19–C23–C22	107.7(4)	C6–O–C6A	111.8(3)
C15–C14–C18	106.4(3)	O–C6–C5	106.3(3)
C14–C15–C16	109.0(4)	O–C6–C7	110.2(3)
C15–C16–C17	107.3(4)	O–C6A–C6B	108.9(4)
C16–C17–C18	108.5(4)	C6–C7–C8	117.4(3)
C14–C18–C17	108.8(4)	C6–C7–C12	121.3(4)
C25–C24–C28	109.2(7)	C10–C11–C13	124.5(4)
C24–C25–C26	108.6(7)	C12–C11–C13	119.5(4)
C25–C26–C27	107.1(7)	C11–C13–C14	129.8(4)
C26–C27–C28	108.1(7)	C13–C14–C15	122.6(4)
C24–C28–C27	107.1(7)	C13–C14–C18	131.0(4)
C25A–C24A–C28A	109(1)		
C24A–C25A–C26A	109(1)		
C25A–C26A–C27A	105(1)		
C26A–C27A–C28A	106(1)		
C24A–C28A–C27A	111(1)		

4a ⟷ **4b**

(2 forms)
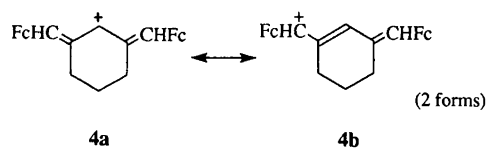
Table 5. Molecular planes.

No. of plane	Atoms in plane	Δ^a	Distance to other atoms/Å		Interplanar angles/°	
1	C1–C5	−0.008	Fe1	−1.653	1.2	0.91
2	C19–C23	0.21	Fe1	1.654	1.3	105.56
3	C14–C18	−0.003	Fe2	−1.648	1.6	101.13
4	C24–C28	−0.010	Fe2	1.648	3.4	1.76
5	C24A–C28A	−0.014	Fe2	1.652	3.5	1.20
6	C6, C7, C8, C10–C14	0.010	C9	−0.619	3.6	10.68
					4.5	2.48

^{a} Represents the maximum deviation from planarity.

A nucleophilic attack of ethanol at either of the carbons adjacent to the ferrocenyl groups then affords compound **3** as shown by the X-ray analysis (Fig. 1).

References

1. Bozak, R. E., Hicks, R. J., Rennels, R., Husebye, S. and Maartmann-Moe, K. *Synth. React. Inorg. Metalorg. Chem.* Submitted.
2. *SDP Users Guide*, B. A. Frenz Associates, Inc., College Station, Texas, and Enraf-Nonius, Delft, Holland 1987.
3. Bozak, R. E., Hadi, M., Husebye, S., Maartmann-Moe, K. and Shaieb, D. *Acta Chem. Scand. A42* (1988) 454.
4. Doman, T. N., Landis, C. R. and Bosnich, B. *J. Am. Chem. Soc. 114* (1992) 7264.
5. Bastiansen, O. and Trætteberg, M. *Tetrahedron 17* (1962) 147.