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BRIDGED FERROCENES

IV *. THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1′,2,2′,3,3′,4,5,4′,5′-PENTAKIS(TRIMETHYLENE)FERROCENE

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Summary

The title compound (molecular formula $C_{25}H_{30}Fe$) forms prismatic crystals from hexane which belong to the monoclinic space group $P2_1/n$ with lattice constants a 9.486(2), b 12.134(2), c 16.024(2) Å, β 93.12(1)°, and $Z = 4$. The structure was solved by the heavy atom method and refined by full-matrix least squares against 3839 F^2 terms to yield $R = 0.08$ and $R_w = 0.12$. The Fe to cyclopentadienyl ring-carbon distances range from 1.985(3) to 2.042(4) Å. The two cyclopentadienyl rings are eclipsed, they are slightly non-planar, and the angle between their least-squares planes is 12.5°.

Introduction

In the course of the study of the multi-bridged ferrocenes, one compound of interest is the completely bridged compound 1,1′,2,2′,3,3′,4,4′,5,5′-pentakis-(trimethylene)ferrocene (I). In an attempt to synthesize [1] this compound, the step that was used to form the fifth bridge gave a very low yield. A compound presumed to be the five-bridged ferrocene (I) was then isolated in the subsequent step. Because of the extremely small amount of material available, characterization of the compound was undertaken using X-ray diffraction. Instead of the expected five-bridged ferrocene, the molecule was found to be 1,1′,2,2′,3,3′,-

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[*] For part III see ref. 11.

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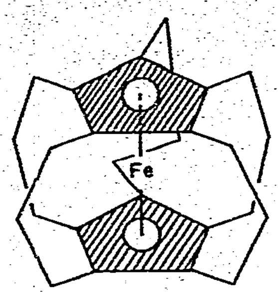
4,5,4′,5′-pentakis(trimethylene)ferrocene (Fig. 1), a ferrocene derivative with three adjacent trimethylene bridges and two homoannular trimethylene groups.



Experimental

A pale yellow prism was mounted along its long axis and the diffraction symmetry ($2/m$) determined photographically. Intensity data were collected on an Enraf—Nonius CAD4 diffractometer and examined for systematic absences. The reflections $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$ were systematically absent and the space group was uniquely determined as $P2_1/n$. The intensity data were reduced with application of appropriate Lorentz and polarization terms and absorption corrections calculated by the procedure of Busing and Levy [2] were applied. A total of 3839 unique and space-group-permissible reflections

TABLE 1

CRYSTALLOGRAPHIC DETAILS

Unit cell [a]: space group; monoclinic; $P2_1/n$	
a 9.486(2) Å	β 93.12(1)°
b 12.134(2) Å	V 1842 Å^3
c 16.024(2) Å	Z 4
Crystal dimensions (mm):	$d(001) = 0.29$, $d(00\bar{1}) = 0.26$, $d(10\bar{1}) = 0.17$, $d(\bar{1}01) = 0.12$, $d(010) = 0.04$, $d(0\bar{1}0) = 0.04$.
Data collection:	
Diffractometer	Enraf—Nonius, CAD4
Radiation	Cu-K_α-graphite monochromated (assumed ideally mosaic)
Attenuator	Nickel foil, I_0/I_{Att} 15.55
Linear absorption coefficient	μ 65.9 cm^{-1}
Two theta range	$0 \leqslant 2\theta \leqslant 140°$
Number of reflections	12560; 3839 unique
Scattering factors	Doyle and Turner [3a], Stewart, Davidson and Simpson [3b]
Anomalous dispersion	Cromer and Liberman [4]
Refinement: Full-matrix least squares against F^2s.	
$R_w = 0.12$ and $R = 0.08$	
$R = (\Sigma\|F_0^2 - k^2F_c^2\|)/\Sigma F_0^2$	$R_w = ((\Sigma w(F_0^2 - k^2F_c^2)^2)/\Sigma wF_0^4)^{1/2}$
where $w = 1/\sigma^2$ and $\sigma^2 = \sigma_c^2 + (0.02F_0^2)^2 + (0.02(F_0^2 - F_0^2/A))^2$	
Programs used: Absorption correction and averaging, BNLABS/AVSORT [5], least squares analysis, FLIN80 [5], Plotting, ORTEP [6]	

[a] Based on λ 1.54051 Å.

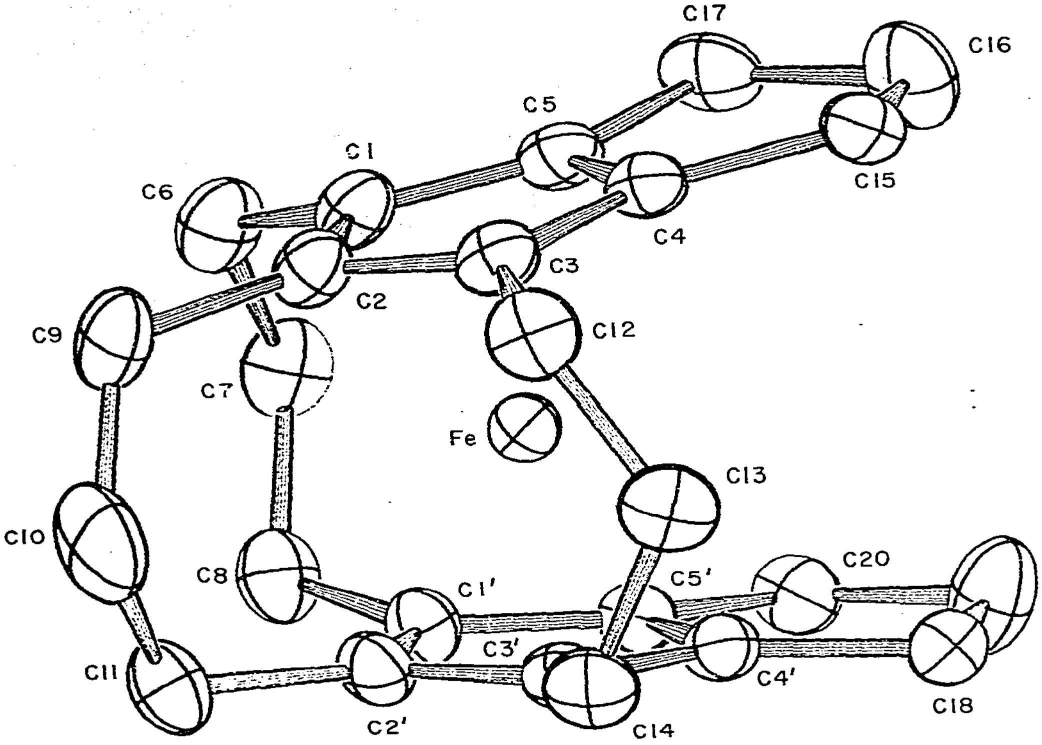


Fig. 1. A view of 1,1',2,2',3,3',4,5,4',5'-pentakis(trimethylene)ferrocene,

were obtained. Standard vector and electron-density syntheses were used to solve the structure which was refined by full-matrix least-squares. Positions for the hydrogen atoms were calculated and periodically updated. Further details of the experimental work are given in Table 1 *.

Results and discussion

The molecular structure and the aromic nomenclature are shown in Fig. 1. Final atomic coordinates and thermal motion factors are given in Tables 2 and 3. Bond distances and selected angles are found in Tables 4 and 5 respectively. A tabulation of structure factors was deposited in NAPS *.

Of the ferrocene derivatives with 3-carbon bridges, the one reported here has the largest ring—ring angle measured, Table 6. Apparently, placing bridges adjacent to each other requires a deformation that causes an increase in the ring—ring angle. The derivative [10] with two non-adjacent bridges displays a ring—ring angle of 9°, two adjacent [11] bridges 11°, and three adjacent bridges (this

(Continued on p. 114)

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* The table of structure factors has been deposited as NAPS Document No. 03264 (23 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

ATOMIC COORDINATES AND ANISOTROPIC THERMAL VIBRATION COEFFICIENTS FOR THE NONHYDROGEN ATOMS.

The coordinates have been multiplied by 10^5 and the vibration coefficients by 10^4. The U_{ij} are coefficients in the expression $\exp\{-2\pi^2(U_{11}a^{*2}h^2 + \ldots 2U_{12}a^*b^*hh \ldots)\}$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	47823(5)	29891(4)	24280(3)	380(3)	455(3)	271(2)	1(2)	11(2)	−24(2)
C(1)	34292(36)	35380(30)	32472(19)	489(19)	511(19)	341(14)	58(16)	70(14)	−63(15)
C(2)	44561(37)	43744(29)	30537(20)	527(20)	479(19)	405(15)	4(16)	−29(15)	−102(15)
C(3)	43531(37)	45666(28)	21556(20)	519(20)	431(18)	432(16)	−48(15)	21(15)	5(15)
C(4)	32219(36)	38892(27)	18221(20)	474(19)	439(17)	397(15)	46(15)	−9(14)	−1(14)
C(5)	26717(35)	32724(27)	24794(21)	408(17)	449(18)	432(15)	36(14)	44(14)	−25(14)
C(1′)	57885(35)	18100(30)	30929(20)	416(17)	564(21)	382(15)	71(15)	−2(14)	87(14)
C(2′)	67198(35)	27164(31)	29146(21)	389(18)	621(23)	438(17)	13(15)	−26(15)	8(16)
C(3′)	67156(36)	28479(32)	20116(21)	392(17)	644(23)	460(17)	−21(17)	66(14)	28(17)
C(4′)	58472(35)	19923(31)	16605(19)	429(17)	590(20)	385(15)	76(17)	90(14)	−23(17)
C(5′)	52898(35)	13617(29)	23216(19)	526(17)	49(18)	566(15)	48(14)	13(15)	−9(15)
C(6)	32722(40)	29470(34)	40663(20)	636(22)	660(23)	340(15)	−2(14)	138(15)	−56(17)
C(7)	37283(42)	17355(32)	40621(20)	693(24)	626(24)	365(16)	19(19)	127(17)	68(15)
C(8)	52839(41)	14859(33)	39437(20)	651(24)	627(28)	338(15)	7(19)	−47(16)	87(16)
C(9)	55097(44)	48998(35)	36584(23)	772(28)	636(25)	492(20)	−104(22)	−104(20)	−139(19)
C(10)	66043(61)	41716(47)	40747(31)	1090(39)	966(38)	805(32)	−163(34)	−430(30)	−234(31)
C(11)	74825(42)	34508(42)	35436(25)	504(22)	914(33)	577(21)	−134(22)	−147(19)	−21(24)
C(12)	63401(43)	52271(33)	16468(25)	696(26)	537(22)	598(22)	−120(20)	−29(20)	104(19)
C(13)	62585(44)	45284(38)	10811(24)	694(26)	764(28)	544(21)	−144(22)	118(20)	168(2)
C(14)	73385(42)	37815(38)	15318(25)	547(23)	826(30)	561(21)	−121(22)	112(19)	47(21)
C(15)	24260(40)	36704(33)	10149(22)	616(23)	560(22)	473(18)	95(16)	−119(17)	−1(17)
C(16)	13925(47)	27577(80)	12356(28)	660(28)	1299(48)	609(25)	−237(30)	−102(22)	20(29)
C(17)	14348(37)	25781(32)	21732(23)	445(19)	545(20)	577(20)	13(17)	14(17)	−47(18)
C(18)	53855(45)	15236(37)	8295(21)	766(27)	733(25)	371(17)	123(23)	83(18)	−117(18)
C(19)	43115(41)	6198(41)	10308(24)	991(33)	912(34)	440(18)	−227(28)	79(22)	−183(22)
C(20)	43815(38)	4417(31)	19050(23)	526(21)	491(20)	566(20)	48(17)	13(18)	−94(17)

TABLE 3

CALCULATED HYDROGEN POSITIONS[a]

The coordinates have been multiplied by 10^5

Atom	*x*	*y*	*z*
H(6A)	38261	33237	44910
H(6B)	23097	29852	42044
H(7A)	21842	13746	36275
H(7B)	34854	14154	45774
H(8A)	58444	18585	43616
H(8B)	54349	7107	40142
H(9A)	49990	52415	40854
H(9B)	59763	54662	33707
H(10A)	61511	37075	44517
H(10B)	72423	46308	43950
H(11A)	80946	39119	32522
H(11B)	80500	29954	39099
H(12A)	59416	56462	20203
H(12B)	47912	57287	13063
H(13A)	67455	50180	7347
H(13B)	56466	40859	7353
H(14A)	79289	34789	11286
H(14B)	79057	42146	19115
H(15A)	30383	34156	6057
H(15B)	19289	43089	8228
H(16A)	16336	20952	9660
H(16B)	4588	29697	10491
H(17A)	5911	28270	24017
H(17B)	16015	18234	23021
H(18A)	61684	12233	5584
H(18B)	49280	20700	4855
H(19A)	46027	−553	7763
H(19B)	34190	−8169	8438
H(20A)	34564	4988	21848
H(20B)	47882	−2498	21326

[a] The hydrogens are given the numbers of the carbon atoms to which they are attached. An isotropic temperature factor of 5.0 Å² was assigned to each hydrogen atom.

TABLE 4

BOND DISTANCES

Bond	Distance (Å)	Bond	Distance (Å)
Fe—C(1)	2.000(3)	C(1)—C(6)	1.510(4)
Fe—C(1′)	1.996(3)	C(1′)—C(8)	1.521(4)
Fe—C(2)	1.990(3)	C(2)—C(9)	1.496(5)
Fe—C(2′)	1.985(3)	C(2′)—C(11)	1.501(5)
Fe—C(3)	2.000(4)	C(3)—C(12)	1.506(5)
Fe—C(3′)	1.993(3)	C(3′)—C(14)	1.508(5)
Fe—C(4)	2.042(3)	C(4)—C(15)	1.486(4)
Fe—C(4′)	2.033(3)	C(4′)—C(18)	1.492(5)
Fe—C(5)	2.038(3)	C(5)—C(17)	1.507(5)
Fe—C(5′)	2.042(4)	C(5′)—C(20)	1.493(5)
C(1)—C(2)	1.452(5)	C(6)—C(7)	1.533(5)
C(1′)—C(2′)	1.449(5)	C(7)—C(8)	1.528(5)
C(1)—C(5)	1.427(4)	C(9)—C(10)	1.493(7)
C(1′)—C(5′)	1.428(4)	C(10)—C(11)	1.504(7)
C(2)—C(3)	1.456(4)	C(12)—C(13)	1.545(6)
C(2′)—C(3′)	1.456(4)	C(13)—C(14)	1.523(6)
C(3)—C(4)	1.432(5)	C(15)—C(16)	1.533(6)
C(3′)—C(4′)	1.422(5)	C(18)—C(19)	1.543(6)
C(4)—C(5)	1.415(4)	C(16)—C(17)	1.517(6)
C(4′)—C(5′)	1.431(4)	C(19)—C(20)	1.542(5)

TABLE 5

C—C—C BOND ANGLES

Bond	Angle (°)	Bond	Angle (°)
C(2)—C(1)—C(5)	106.6(3)	C(4′)—C(18)—C(19)	104.4(3)
C(2′)—C(1′)—C(5′)	107.4(3)	C(15)—C(16)—C(17)	110.6(4)
C(1)—C(2)—C(3)	108.2(3)	C(18)—C(19)—C(20)	108.3(3)
C(1′)—C(2′)—C(3′)	108.1(3)	C(5)—C(17)—C(16)	102.6(3)
C(2)—C(3)—C(4)	106.5(3)	C(5′)—C(20)—C(19)	104.3(3)
C(2′)—C(3′)—C(4′)	106.5(3)	C(4)—C(5)—C(17)	111.5(3)
C(3)—C(4)—C(5)	109.0(3)	C(4′)—C(5′)—C(20)	111.2(3)
C(3′)—C(4′)—C(5′)	109.1(3)	C(1)—C(2)—C(9)	126.3(3)
C(1)—C(5)—C(4)	109.5(3)	C(1′)—C(2′)—C(11)	126.5(3)
C(1′)—C(5′)—C(4′)	108.8(3)	C(3)—C(2)—C(9)	125.3(3)
C(1)—C(6)—C(7)	114.2(3)	C(3′)—C(2′)—C(11)	125.3(3)
C(1′)—C(8)—C(7)	114.4(3)	C(2)—C(1)—C(6)	128.1(3)
C(2)—C(9)—C(10)	117.4(4)	C(2′)—C(1′)—C(8)	126.7(3)
C(2′)—C(11)—C(10)	117.6(3)	C(2)—C(3)—C(12)	127.6(3)
C(3)—C(12)—C(13)	114.4(3)	C(2′)—C(3′)—C(14)	127.5(3)
C(3′)—C(14)—C(13)	114.7(3)	C(5)—C(1)—C(6)	125.0(3)
C(6)—C(7)—C(8)	117.7(3)	C(5′)—C(1′)—C(8)	125.4(3)
C(9)—C(10)—C(11)	119.0(4)	C(4)—C(3)—C(12)	125.4(3)
C(12)—C(13)—C(14)	115.8(3)	C(4′)—C(3′)—C(14)	125.6(3)
C(15)—C(4)—C(5)	111.3(3)	C(1)—C(5)—C(17)	138.9(3)
C(18)—C(4′)—C(5′)	110.8(3)	C(1′)—C(5′)—C(20)	140.0(3)
C(4)—C(15)—C(16)	103.3(3)	C(3)—C(4)—C(15)	139.7(3)
		C(3′)—C(4′)—C(18)	140.1(3)

compound) 12.5°. The derivative with three non-adjacent bridges [12] is not comparable in this context, because the 4,4′-bridge requires those ring carbons to be closer together and the ring—ring angle 2.4°, is thus significantly smaller.

Another aspect of the crowding caused by the three adjacent bridges which is not evident in the compound with two adjacent bridges is in the variation of the torsion angles about the two bonds to each of the central carbon atoms in the bridges. The four torsion angles involving the C(6)—C(7), C(7)—C(8), C(12)—C(13) and C(13)—C(14) bonds range in magnitude from 66.5 to 67.9°. The angles at the central bridge (bonds C(9)—C(10) and C(10)—C(11)) are only 55.3 and

TABLE 6

RING TILTS OF FERROCENES WITH 3-CARBON BRIDGES

Compound	Ring tilt	Ref.
One 3-atom bridge		
α-Keto-1,1′-trimethyleneferrocene	8.8°	7
α-Keto-γ-phenyl-1,1′-trimethylene-2′-methylferrocene	10°	8
1,1′-Trimethylene-2-(α-phenyl-α-hydroxypropyl)ferrocene	10°	9
Two 3-atom bridges		
1,1′,3,3′-Bis(trimethylene)ferrocene	9°	10
1,1′,2,2′,3,4,4′,5′-Tetrakis(trimethylene)ferrocene	11.1°	11
Three 3-atom bridges		
1,1′,2,2′,4,4′-Tris(trimethylene)ferrocene	2.4°	12
1,1′,2,2′,3,3′,4,5,4′,5′-Pentakis(trimethylene)ferrocene	12.5°	This work

TABLE 7

LEAST SQUARES PLANES [a] OF CYCLOPENTADIENYL RINGS

Equation $pX + qY + rZ = s$

Coefficient	I	II	Deviations of atoms (Å) [b]	I	II
p	−0.669	0.788	C(1) or C(1′)	−0.013	0.015
q	0.728	−0.616	C(2) or C(2′)	0.017	−0.018
r	0.149	−0.006	C(3) or C(3′)	−0.014	0.013
s	1.928	2.747	C(4) or C(4′)	0.006	−0.004
			C(5) or C(5′)	0.005	−0.007

[a] Direction cosines of the plane refer to the orthogonal axis system a, b, c^*. [b] In ring I, negative deviations are toward the iron atom; in Ring II, positive deviations are toward the iron atom.

56.8°, however. This difference, of about 11°, may be sufficient to allow the carbon atoms of the central bridge greater sp^2 character and may also explain the shortness of the C(9)—C(10) and C(10)—C(11) bond distances, 1.499(6) Å. The average of the carbon—carbon bond distances to the middle carbon atoms for all other trimethylene bridged ferrocenes as well as for the outer bridges of this compound is 1.544(8) Å. (An alternative explanation of the bond shortening may reside in the high thermal motion of the C(10) atom which would yield apparent bond distances shorter than their actual value.)

A third aspect of the crowding is apparent in the slight non-planarity of the cyclopentadienyl rings (Table 7). The 2- and 2′-carbon atoms are displaced away from each other thereby increasing their separation distance. The larger ring-tilt associated with the introduction of the middle bridge and the non-planarity are seemingly counterproductive. However, there are numerous other interactions, besides the length of the carbon chain, which play a role, and these, such as the interaction of the homoannular trimethylene groups, have not been analyzed.

The iron to ring-carbon distances reflect the tilting of the two cyclopentadienyl rings. Thus, Fe—C(2) and Fe—C(2′) bond distances are quite short: 1.988(2) Å when compared to the value of 2.045(12) Å reported for ferrocene [13]. The average distance of the iron to the least squares plane of the cyclopentadienyl rings is 1.60 Å, also short compared to the 1.66 Å in ferrocene. The average carbon—carbon bond distances within the cyclopentadienyl rings are within experimental error of previously reported structures. The bond angles found in this structure are similar to those found in other bridged ferrocene structures.

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