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STRUCTURAL CONSEQUENCES OF OXIDATION OF FERROCENE DERIVATIVES

II *. 1,1′,2,2′,4,4′-TRIS(TRIMETHYLENE)FERROCENIUM PERCHLORATE

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Summary

The crystal and molecular structures of 1,1′,2,2′,4,4′-tris(trimethylene)ferrocenium perchlorate (I) were determined by X-ray crystallography. Despite the rigidity imparted to the molecule by the three non-adjacent bridges, the iron-to-ring distance of the cation was 4.4(4) pm longer than in the neutral compound, in agreement with what was reported for non-bridged ferrocene derivatives. The increased separation of the rings was accommodated by an increase in angle between the α-carbon atoms and the ring-planes and by an increase in the ring–ring tilt angle.

Introduction

The ease with which certain structural features of ferrocene can be changed has been demonstrated by the formation of derivatives with ring tilts [2] of up to 26° and with iron-to-ring distances shorter than in ferrocene itself [2] by as much as 9 pm. These changes were introduced as a consequence of bridging the cyclopentadienyl rings with chains too short to span the original distance, i.e. a quasi-mechanical stress on the molecule. We are not aware of any similar stress that increases the iron-to-ring distance or that causes the tilting to open towards a bridge. The removal of one electron from ferrocene forming the ferrocenium cation, however, results in iron-to-ring distances longer than in ferrocene.

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* For part I see ref. 1.

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Originally, ferrocene was found [3] to have an iron-to-ring distance of 167 pm. Subsequently [4–6], refined methods gave the distance as 165 pm. Structures of ferrocenium with six different anions [7–13] and of the 1,1′-dimethylferrocenium triiodide [14] have been reported with iron-to-ring distances averaging 170 pm, 5 pm longer than in the parent neutral compounds. The accuracy of this comparison is limited by the disorder in the ferrocene structures.

In 1,1′,2,2′,4,4′-tris(trimethylene)ferrocene (II) the iron-to-ring distance is 9 pm shorter [2] than in ferrocene, and the molecule has been rendered rigid [15] as a consequence of the bridges. The existing strain in II is expected to make it much more difficult for the oxidation product, I, to accommodate an increase in iron-to-ring distance of the magnitude seen in other ferrocenes. It is of interest, therefore, to determine the structure of I.

Experimental section

Compound I was prepared by the oxidation [15] of II with $AgClO_4$. Crystals were grown from CH_2Cl_2 or from water by slow evaporation. The crystal used for the final analysis, 0.14 × 0.45 × 0.32 mm^3, was obtained by cleavage of a much longer crystal that had been grown from water.

A preliminary set of intensity data was collected on a modified Picker four-circle diffractometer at the National Research Council of Canada in Ottawa using a crystal grown from CH_2Cl_2. The final set of intensity data was collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation (λ 71.07 pm). The crystal data are summarized in Table 1. The space group was determined

TABLE 1

CRYSTAL DATA

Molecular formula	$C_{19}H_{22}ClFeO_4$
Molecular weight	405.68
Space group	$P2_1$
a (pm)	843.5(3)
b (pm)	1480.8(3)
c (pm)	728.9(3)
β (deg.)	108.54(2)
V (nm^3)	0.8631
Z	2
ρ_{calc} ($g\ cm^{-3}$)	1.561
Absorption coeff. (cm^{-1})	10.07
2θ-range (deg.)	2–70
Reflections collected	8069
Reflections used ($F > 3\sigma$)	5847
Scan width	$0.85 \pm 0.40 \tan\theta$
$R(F) = \Sigma\|F_0 - F_c\|/\Sigma\|F_0\|$	0.052
$R_w(F) = \Sigma\|F_0 - F_c\|w^{1/2}/\Sigma\|F_0\|w^{1/2}$	0.057
$w = 1/(\sigma^2(F) + cF^2)$	$c = 0.0010$
Maximum shift/error (Fe,C)	0.08
Maximum shift/error (Cl,O)	0.22
Maximum shift/error (H)	0.16
Res. electron dens. ($e\ nm^{-3}$)	1100

TABLE 2

FRACTIONAL COORDINATES[a]

Atom	*x/a*	*y/b*	*z/c*
Fe	36016(4)	0	18451(4)
C(1)	3059(4)	327(2)	−929(4)
C(2)	3898(4)	−526(2)	−582(4)
C(3)	5505(4)	−357(3)	832(5)
C(4)	5634(4)	559(3)	1391(5)
C(5)	4135(4)	988(4)	201(5)
C(1′)	1312(4)	−94(3)	2167(6)
C(2′)	2173(4)	−942(2)	2563(5)
C(3′)	3698(5)	−809(3)	4132(5)
C(4′)	3822(5)	118(4)	4663(5)
C(5′)	2328(6)	547(3)	3508(7)
C(6)	1246(5)	504(4)	−2123(7)
C(7)	177(5)	823(3)	−939(8)
C(8)	−181(5)	141(4)	474(9)
C(9)	3193(6)	−1446(3)	−1230(6)
C(10)	3020(6)	−2065(2)	388(7)
C(11)	1726(5)	−1777(3)	1342(6)
C(12)	6859(5)	951(3)	3191(5)
C(13)	6063(6)	1308(3)	4691(6)
C(14)	5412(8)	609(5)	5832(6)
Cl	8465(1)	−2000(1)	4986(2)
O(1)	9808(8)	−2589(4)	5691(15)
O(2)	7092(7)	−2397(4)	3803(14)
O(3)	8899(10)	−1160(5)	4580(18)
O(4)	7845(21)	−1811(15)	6372(23)
H(3)	635(7)	−89(4)	142(8)
H(5)	379(8)	161(5)	12(9)
H(3′)	459(12)	−124(8)	464(15)
H(5′)	215(8)	111(5)	339(9)
H(6A)	100(7)	8(6)	−248(8)
H(6B)	133(6)	82(4)	−316(7)
H(7A)	74(7)	148(4)	−33(8)
H(7B)	−87(6)	104(3)	−175(7)
H(8A)	−28(6)	−33(4)	−6(8)
H(8B)	−102(7)	34(4)	105(8)
H(9A)	201(7)	−138(4)	−214(8)
H(9B)	409(7)	−166(4)	−162(7)
H(10A)	396(9)	−221(4)	124(10)
H(10B)	287(5)	−258(3)	11(6)
H(11A)	171(7)	−221(4)	203(8)
H(11B)	65(6)	−165(4)	43(7)
H(12A)	768(7)	50(4)	365(8)
H(12B)	752(7)	133(4)	302(8)
H(13A)	512(5)	169(3)	394(6)
H(13B)	685(9)	172(6)	571(11)
H(14A)	509(6)	91(3)	673(7)
H(14B)	612(7)	21(4)	639(9)

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[a] The coordinates of the iron atoms are multiplied by 10^5. The coordinates of the carbon, chlorine and oxygen atoms are multiplied by 10^4. The coordinates of the hydrogen atoms are multiplied by 10^3. The iron atom was used to fix the origin on the *y* axis.

as $P2_1$ from the systematic absences. The cell constants were determined from twenty reflections of 31° < 2θ < 36.5°. The observed intensities were collected using θ–2θ scans and were corrected for absorption, Lorentz and polarization effects.

The atomic scattering factors for iron including components for anomalous dispersion were taken from tabulations of Doyle and Turner [16] and Cromer and Liberman [17]. Those for hydrogen are from Stewart et al. [18] The other atomic scattering factors are from Cromer and Mann [19].

Using the first set of data, the iron and chlorine atoms were located by direct methods using MULTAN-80 [20], and the other non-hydrogen atoms were found on difference Fourier maps using the NRC PDP-8e crystal structure system [21]. Final refinement of this data set was made using the Los Alamos crystal structure program [22]. These positions of the non-hydrogen atoms were then used in the analysis of the second set of data. The hydrogen atom positions were calculated after each least-squares refinement of the positions and thermal factors of the non-hydrogen atoms using [23] SHELX-76, and finally the positions and thermal factors of all the atoms were refined by full-matrix least-squares. The largest residual peaks were near the oxygen atoms of the perchlorate. Perchlorates are notoriously difficult to refine because of the potential for disorder. No special disorder was observed for the perchlorate in this structure, but one oxygen atom was found to have abnormally large thermal factors.

Results

The atomic coordinates are given in Table 2. The anisotropic thermal parameters for the non-hydrogen atoms, the isotropic thermal parameters for the hydrogen atoms, and the observed and calculated structure factors are included as supplemen-

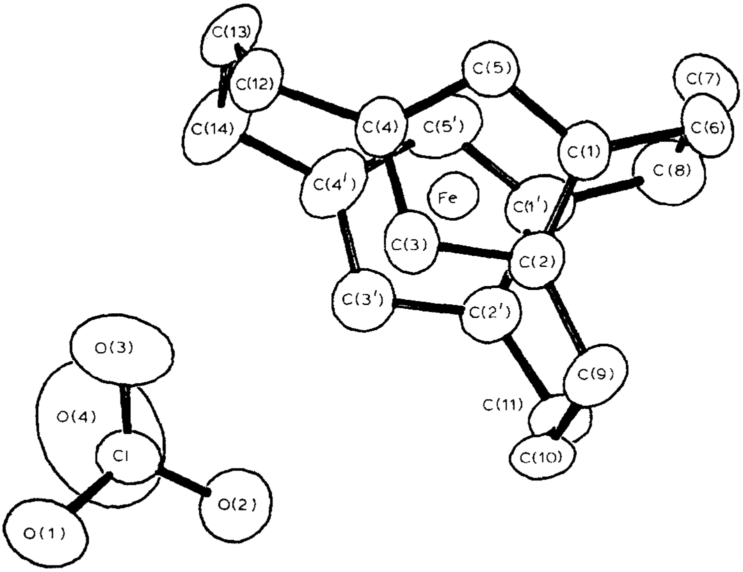

Fig. 1. ORTEP diagram of I showing 50% ellipsoids.

TABLE 3

SELECTED BOND DISTANCES (pm)

Atom	Distance	Atom	Distance
Fe(1)-C(1)	201.3(3)	Fe(1)-C(1′)	202.3(3)
Fe(1)-C(2)	202.0(3)	Fe(1)-C(2′)	201.8(3)
Fe(1)-C(3)	203.9(3)	Fe(1)-C(3′)	203.3(3)
Fe(1)-C(4)	202.4(3)	Fe(1)-C(4′)	201.0(3)
Fe(1)-C(5)	203.0(3)	Fe(1)-C(5′)	202.6(4)
C(1)-C(2)	143.1(5)	C(1′)-C(2′)	143.3(6)
C(2)-C(3)	144.0(5)	C(2′)-C(3′)	143.7(5)
C(3)-C(4)	140.9(6)	C(3′)-C(4′)	142.1(6)
C(4)-C(5)	143.5(5)	C(4′)-C(5′)	142.3(7)
C(5)-C(1)	142.0(5)	C(5′)-C(1′)	143.4(6)
C(1)-C(6)	151.6(5)	C(1′)-C(8)	149.7(6)
C(6)-C(7)	150.8(8)	C(7)-C(8)	154.0(7)
C(2)-C(9)	150.1(5)	C(2′)-C(11)	150.0(5)
C(9)-C(10)	153.7(7)	C(10)-C(11)	152.9(7)
C(4)-C(12)	150.5(5)	C(4′)-C(14)	152.5(6)
C(12)-C(13)	154.6(6)	C(13)-C(14)	153.4(7)
Cl-O(1)	139.2(5)	Cl-O(2)	134.0(5)
Cl-O(3)	135.6(6)	Cl-O(4)	130.7(15)
C(3)-H(3)	106(6)	C(3′)-H(3′)	96(11)
C(5)-H(5)	96(7)	C(5′)-H(5′)	85(7)
C(6)-H(6A)	68(8)	C(6)-H(6B)	92(5)
C(7)-H(7A)	111(6)	C(7)-H(7B)	95(5)
C(8)-H(8A)	78(6)	C(8)-H(8B)	97(6)
C(9)-H(9A)	102(6)	C(9)-H(9B)	94(6)
C(10)-H(10A)	86(7)	C(10)-H(10B)	79(5)
C(11)-H(11A)	81(6)	C(11)-H(11B)	96(5)
C(12)-H(12A)	94(6)	C(12)-H(12B)	83(6)
C(13)-H(13A)	99(4)	C(13)-H(13B)	102(8)
C(14)-H(14A)	90(5)	C(14)-H(14B)	85(6)

tary material. These are available from NAPS *. An ORTEP diagram of the two ions is given in Fig. 1. Selected bond distances and bond angles are given in Tables 3 and 4.

The structure of the ferrocene part of I is qualitatively similar [2] to that of II except that no disorder was observed in I for the β-methylene of the 4,4′-trimethylene bridge. This is probably due to the presence of the perchlorate in the neighborhood of that bridge. The shortest intermolecular non-bonding distances found were between O(3) and H(12A), 267 pm, and between O(1) and H(12B), 268 pm.

Discussion

Although, according to the available data, the removal of an electron from ferrocene expands the iron-to-ring distance by 5 pm, such an expansion might be

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expected to be inhibited in II where the rings have been pulled 9 pm closer to the iron by the short bridges. On the other hand, the ring–ring breathing vibrations of I appear to have the same energy as in ferrocene. The fine structure [15] in the room temperature electronic spectrum of I and the fine structure in the electronic spectrum of ferrocenium at low temperatures [24] have the same spacing. Both have been attributed to the ring–ring breathing vibration since the energy is in the expected range, but this interpretation is not conclusive.

TABLE 4

SELECTED BOND ANGLES (deg.)

Atom	Angle	Atom	Angle
C(5)–C(1)–C(2)	108.0(3)	C(5′)–C(1′)–C(2′)	106.7(4)
C(1)–C(2)–C(3)	106.3(3)	C(1′)–C(2′)–C(3′)	107.9(3)
C(2)–C(3)–C(4)	110.1(3)	C(2′)–C(3′)–C(4′)	108.6(4)
C(3)–C(4)–C(5)	106.2(3)	C(3′)–C(4′)–C(5′)	107.2(3)
C(4)–C(5)–C(1)	109.2(3)	C(4′)–C(5′)–C(1′)	109.4(4)
C(2)–C(1)–C(6)	127.6(3)	C(2′)–C(1′)–C(8)	127.5(4)
C(5)–C(1)–C(6)	123.6(4)	C(5′)–C(1′)–C(8)	124.8(5)
C(1)–C(2)–C(9)	128.1(3)	C(1′)–C(2′)–C(11)	125.9(3)
C(3)–C(2)–C(9)	124.9(3)	C(3′)–C(2′)–C(11)	125.3(4)
C(2)–C(3)–H(3)	121(3)	C(2′)–C(3′)–H(3′)	128(6)
C(4)–C(3)–H(3)	128(3)	C(4′)–C(3′)–H(3′)	123(6)
C(3)–C(4)–C(12)	126.3(3)	C(3′)–C(4′)–C(14)	126.0(5)
C(5)–C(4)–C(12)	125.8(4)	C(5′)–C(4′)–C(14)	125.0(5)
C(4)–C(5)–H(5)	131(4)	C(4′)–C(5′)–H(5′)	126(4)
C(1)–C(5)–H(5)	120(4)	C(1′)–C(5′)–H(5′)	123(4)
C(1)–C(6)–C(7)	114.7(4)	C(1′)–C(8)–C(7)	114.3(3)
C(2)–C(9)–C(10)	115.1(3)	C(2′)–C(11)–C(10)	114.7(3)
C(4)–C(12)–C(13)	114.6(3)	C(4′)–C(14)–C(13)	114.9(4)
C(6)–C(7)–C(8)	117.2(4)	C(9)–C(10)–C(11)	116.1(3)
C(12)–C(13)–C(14)	117.6(4)		
O(1)–Cl–O(2)	113.5(4)	O(1)–Cl–O(3)	114.3(4)
O(1)–Cl–O(4)	109.1(9)	O(2)–Cl–O(3)	120.0(5)
O(2)–Cl–O(4)	96.6(10)	O(3)–Cl–O(4)	100.1(12)

TABLE 5

COMPARISON OF I WITH II

Distances (pm)	II	I
Fe–Ring	157.3(2)	161.7(4)
C–C (Ring)	143.9(2)	142.8(3)
Ring(C)–CH_2	151.5(5)	150.7(4)
CH_2–CH_2	154.6(8)	153.2(5)
C11(C13)–Ring	20.2(9)	23.5(4)
C14(C16)–Ring	22.6(9)	23.5(4)
C17(C19)–Ring	30.2(9)	39.8(1)
Angles (deg.)	**II**	**I**
C–C–C (Ring)	108.0(1)	108.0(4)
Ring(C)–CH_2–CH_2	113.2(2)	114.7(1)
CH_2–CH_2–CH_2	115.9(6)	117.0(4)
Ring–Ring	2.5(1)	4.3(1)

The results of the present work indicate that removal of an electron from II causes a 4.4(4) pm expansion of the iron-to-ring distance, about the same as in ferrocene. Table 5 compares the bond angles and distances of I with those of II. Since compound II is already under strain because the bridges are too short to span the rings, it is of interest to note how I accomodates the span of the bridges across an even larger distance. There is essentially no change in any of the bond distances and angles except for the angle that the α-carbons make with the rings. In I these carbon atoms are displaced toward the iron atom by an even greater distance than in II, and the 4,4′ α-carbons have a larger increase in displacement than the other α-carbons. This, in turn, causes the dihedral angle between the rings of I to be greater than in II. Displacement of an α-atom out of the plane of the ring appears to be a facile way that ferrocene derivatives use to relieve strain. The largest of such displacements are found in the [1]ferrocenophanes [25,26].

The driving force behind the expansion of the iron-to-ring distance is apparently the removal of a bonding electron. This is consistent with molecular orbital calculations [27] that find that removal of an electron is accompanied by an extensive orbital rehybridization. Orbitals that belong exclusively to the iron contribute about 0.1 of the removed electron.

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