Crystal and Molecular Structures of 2,14-Dithia-5,8,11-trioxa[15](1,1′)ferrocenophane and 1,15-Dimethyl-2,14-dithia-5,8,11-trioxa[15](1,1′)ferrocenophane

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Structures of the title compounds have been determined by single-crystal X-ray crystallography. The crystals of 2,14-dithia-5,8,11-trioxa[15](1,1′)ferrocenophane (I) are orthorhombic with a = 8.626 (3) Å, b = 10.877 (5) Å, c = 22.080 (8) Å, space group $P2_12_12_1$, and D(calcd) (Z = 4) = 1.40 g cm^{-3}. The crystals of 1,15-dimethyl-2,14-dithia-5,8,11-trioxa[15](1,1′)ferrocenophane (II) are orthorhombic with a = 27.825 (9) Å, b = 35.66 (1) Å, c = 9.126 (4) Å, space group $Fdd2$, and D(calcd) (Z = 16) = 1.36 g cm^{-3}. Both structures were solved by the Patterson technique and refined by least-squares to final agreement factors of R_F = 0.027 (R_w = 0.029) for I and R_F = 0.024 (R_w = 0.025) for II. The two cyclopentedienyl rings of the ferrocenyl moieties are virtually parallel, the dihedral angles between the least-squares planes defined by the two rings being 0.3° and 1.8° for I and II, respectively. In both cases, the ferrocenyl moiety has an eclipsed conformation with twist angles of 3.1° and 0.6° for I and II, respectively. Configurations around the two asymmetric centers of II are identical (*R,R* and *S,S*), and the molecules pack as a racemic mixture. Differing steric arrangements of the bridging chains are discussed. The reduction potential of the ferrocenium cation derived from I is compared with those for analogous compounds that have one and two less ethyleneoxy units in the bridging chain.

Introduction

Polyoxa- and polythia[n]ferrocenophanes and analogous compounds with both oxygen and sulfur atoms in the bridging chains[1–10] provide the potential for interactions of a complexed metal ion with the iron atom of the ferrocene nucleus. Detailed structural information for such crownlike compounds is limited to three ferrocenophanes that have both sulfur and oxygen atoms in the bridging chains[11,12] and to one polyoxa[n]ferrocenophane metal ion complex.[13] Of the former grouping, one compound has two sulfur atoms and one oxygen in the bridging chains and two compounds have two sulfurs and two oxygens. We now report the crystals and molecular structures of 2,14-dithia-5,8,11-trioxa[15](1,1′)ferrocenophane (I) and the crystalline diastereomer of 1,15-dimethyl-2,14-dithia-5,8,11-trioxal[15](1,1′)ferrocenophane (II) which both have two sulfur atoms and three oxygen atoms in a longer bridging chain that should be more conducive to metal ion complexation. In addition, the electrochemical behavior of I in acetonitrile has been examined.

Experimental Section

Synthesis of Ferrocenophanes I and II. Ferrocenophane I with a melting point of 77–78.5 °C was prepared by the published procedure.[7] A mixture of diastereomeric ferrocenophanes II was synthesized and separated by preparative thin-layer chromatography according to the reported method[7] to give orange crystals with a melting point of 89–91 °C of the assumed[7] racemic stereoisomer.

Table I. Summary of Data Collection and Processing Parameters

	I	II
cryst color and shape	orange prism	same
cryst dimens, mm	0.25 × 0.22 × 0.20	0.31 × 0.26 × 0.20
space group	$P2_12_12_1$	$Fdd2$
a, Å	8.626 (3)	27.825 (9)
b, Å	10.877 (5)	35.66 (1)
c, Å	22.080 (8)	9.126 (4)
V, Å^{-3}	2071.5 (1)	9054.5 (1)
Z	4	16
mol formula	$FeS_2O_3C_{20}H_{28}$	$FeS_2O_3C_{22}H_{32}$
mol wt	436.4	464.5
D(calcd), g cm^{-3}	1.40	1.36
radiatn, Å	Mo Kα (λ = 0.710 73)	same
abs coeff, cm^{-1}	9.36	8.61
data collectn range	$4° \leq 2\theta \leq 60°$	$4° \leq 2\theta \leq 52°$
scan technique	$\theta/2\theta$	same
scan width, deg	$\Delta\theta = (0.9 + 0.35 \tan \theta)$	same
max scan time, s	180	same
scan speed range, deg min^{-1}	0.7–5.0	same
total (unique) data collected	3322	2682
data with $I \geq 3\sigma(I)$	2523	1985
no. of parameters refined	319	348
$R_F = \sum\|\|F_o\| - \|F_c\|\|\sum\|F_o\|$	0.027	0.024
$R_w = [\sum w(\|F_o\| - \|F_c)^2\|\sum w\|F_o\|^2]^{1/2}$	0.029	0.025
weighing scheme	$w = [\sigma(F_o)]^{-2}$	same
largest residual peak, e/Å^3	0.3	same
largest shift/esd, final cycle	0.31	0.28

Crystals of both I and II were prepared by diffusion of 95% ethanol into a solution of the ferrocenophane in diethyl ether.

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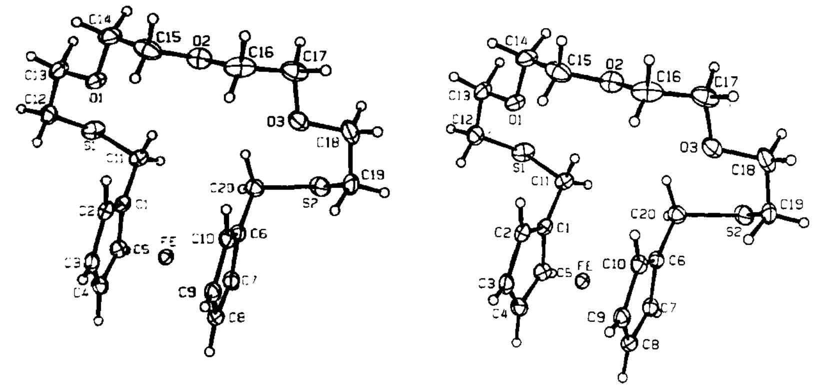

Figure 1. Stereoscopic view of I with the numbering system identified. Hydrogen numbers are the same as the carbons to which they are bonded.

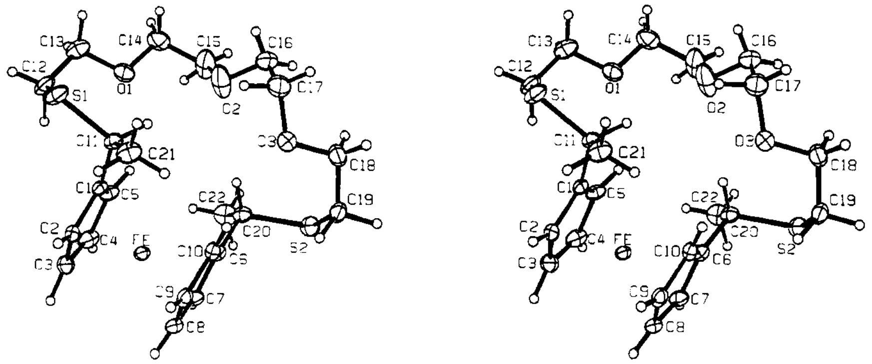

Figure 2. Stereoscopic view of II with the numbering system identified. Hydrogen numbers are the same as the carbons to which they are bonded.

Crystal Data, Structure Solutions, and Refinement. Intensity measurements for both crystals were carried out with an Enraf-Nonius CAD-4 computer-controlled diffractometer. Accurate cell constants were obtained by centering 25 strong, high angle reflections. A summary of pertinent crystal data and experimental parameters for data collection and processing is given in Table I. Intensities were measured with a scan rate depending on the net counts obtained by a rapid prescan of each reflection. Two standard reflections were monitored periodically during the course of data collection as a test of crystal stability and electronic reliability and did not vary significantly. Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_o|$. For both crystals an empirical absorption correction was also applied on the basis of azimuthal psi scans of several reflections have χ near 90 degrees.[14] Data processing and calculations were carried out by using the Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS system of programs. In both cases, a three-dimensional Patterson map was computed and the position of the iron atom determined. All the remaining non-hydrogen atoms were found from successive difference Fourier maps. Hydrogens were added at ideally calculated positions. Convergence was attained by anisotropic refinement of all the non-hydrogen atoms (the z coordinate of the Fe atom in space group $Fdd2$ was arbitrarily assigned and held constant) and by refinement of hydrogens (with their isotropic temperature factors fixed). The agreement factors thus obtained were $R_F = 0.039$ ($R_w = 0.041$) for I and $R_F = 0.024$ ($R_w = 0.025$) in the case of II. To check the absolute configuration of I, the atomic coordinates were inverted and refinement converged to the final values of $R_F = 0.027$ ($R_w = 0.029$). The much lower agreement factors thus obtained strongly suggests that the configuration obtained by inversion of coordinates was the correct one. Similarly, inversion of polarity in the case of II results in $R_F = 0.026$ and $R_w = 0.028$ which suggests that the initially chosen polarity of the crystal was correct.

Atomic coordinates and equivalent temperature factors for both compounds are given in Table II, parts A and B. Anisotropic thermal parameters have been deposited. The stereodrawings (Figures 1–4) were obtained with use of Johnson's ORTEP.[15]

Electrochemical Studies. Cyclic voltammetry was conducted with the apparatus and procedure reported previously.[12]

Results and Discussion

X-ray Crystallographic Study of Ferrocenophanes I and II. Both I and II contain two cyclopentadienyl rings η^5 bonded to iron. These rings are linked via a 2,14-dithia-5,8,11-trioxa[15] chain in I and by a 1,15-dimethyl-2,14-dithia-5,8,11-trioxa[15] chain in II. Thus I and II have the same chain length, but I has two hydrogens on each carbon which is attached to the Cp ring, whereas II has a hydrogen and a methyl group on each of the Cp-bound carbons.

Ferrocenophanes I and previously reported[12] III and IV provide a series of closely related compounds which differ only in the number of ethyleneoxy units in the bridging chain. Similarly II and the earlier investigated[11] V differ only by one ethyleneoxy unit in the bridging chain.

Both I and II exist in the crystal as discrete molecules held together by van der Waals forces. The atomic numbering systems employed are given in the stereodrawings of the molecules (Figures 1 and 2). The packing diagrams are shown in Figures 3 and 4. Bond distances and angles are given in Tables III and IV, and torsional angles are presented in Table V.

The two Cp rings in I and II are found to be planar with the largest deviation of any carbon from the best mean plane being 0.005 Å for both compounds. Details for the least-squares planes have been deposited. The two Cp rings are virtually parallel with dihedral angles between the least-squares planes of 0.3° for I and 1.8° for II. These

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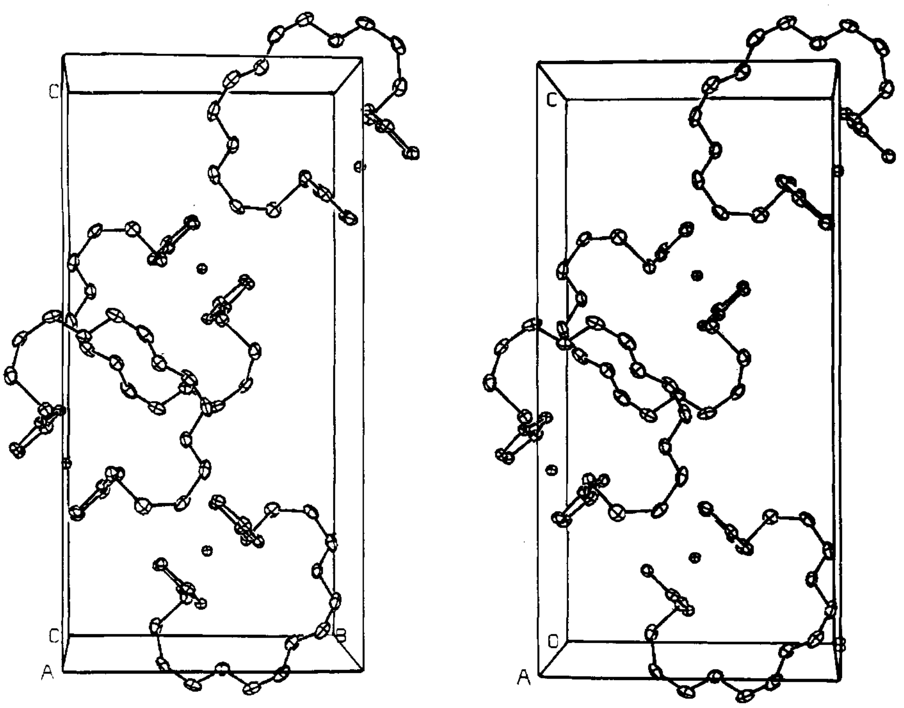


Figure 3. Stereoscopic view of the molecular packing for I. Hydrogen atoms are omitted for clarity.

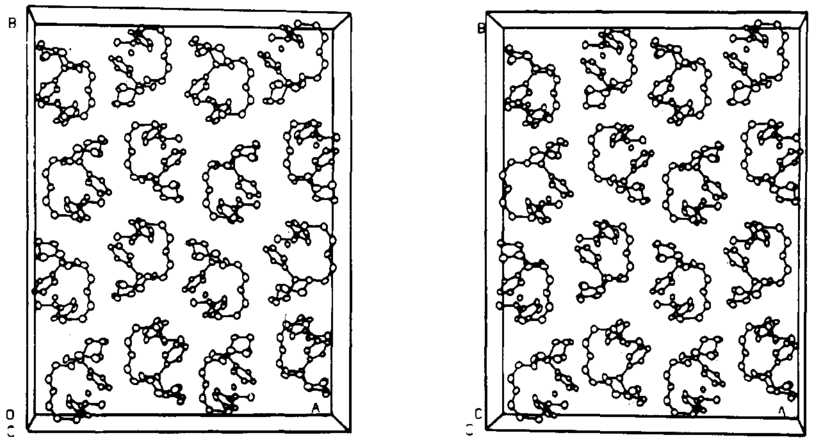
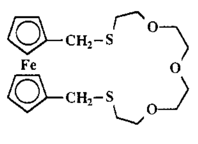
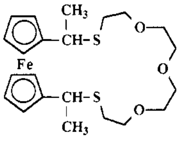


Figure 4. Stereoscopic view of the molecular packing for II. Hydrogen atoms are omitted for clarity.

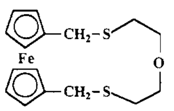
values compare with reported[11,12] angles of 2.4°, 3.4°, and 2.3° for compounds III, IV, and V, respectively. Although there are no large deviations from the ideal parallel geometry for the Cp rings in any of the ferrocenophanes I–V, it appears that the longer bridging chains in I and II allow for closer approach to a perfectly parallel arrangement. For ferrocenophanes I–V, the dihedral angle between the least-squares planes of the Cp rings is clearly the smallest in I. The near parallelism of the two Cp rings, as observed for I–V, is in contrast to the situation for strained ferrocenophanes which have one or more short (usually two or three bridging atom) chains. In such cases, strain is accommodated by ring tilting and dihedral angles as large as 23° have been observed.[16]



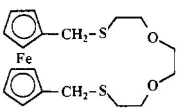
I



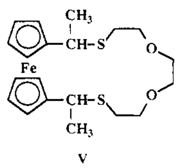
II



III



IV



V

The iron atom to ring-carbon atom distances are in the range of 2.034 (2)–2.046 (2) Å (average 2.040 Å) for I and 2.020 (2)–2.049 (2) Å (average 2.037 Å) in the case of II. For II the distance between the Fe atom and carbons C1 and C6 (those directly bonded to the bridging chain) are slightly, but significantly, longer than the remainder of the Fe–C(Cp) bonds. This difference is much less pronounced in I. This effect slightly perturbs the parallelism of the Cp rings in II (dihedral angle = 1.8°), more than in I (dihedral angle = 0.3°). The slight deviation from par-

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Table II. Atomic Coordinates, Equivalent Temperature Factors of the Non-Hydrogen Atoms, and Isotropic Temperature Factors of the Hydrogens for Compounds I and II

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
A. Compound I									
Fe	0.92879 (4)	0.99757 (3)	0.82686 (1)	2.738 (5)	H3	1.149 (3)	0.851 (3)	0.785 (1)	5.0
S1	0.5119 (1)	0.73411 (9)	0.76818 (4)	5.60 (2)	H4	1.029 (3)	1.020 (2)	0.713 (1)	5.0
S2	0.6018 (1)	1.17458 (7)	0.97781 (4)	5.63 (2)	H5	0.735 (3)	1.003 (3)	0.731 (1)	5.0
O1	0.7011 (3)	0.5835 (2)	0.8728 (1)	4.66 (5)	H7	0.798 (3)	1.221 (2)	0.832 (1)	5.0
O2	0.7274 (2)	0.6772 (2)	0.9999 (1)	4.96 (5)	H8	1.091 (3)	1.211 (2)	0.820 (1)	5.0
O3	0.7504 (3)	0.9337 (2)	1.0446 (1)	4.88 (5)	H9	1.182 (3)	1.049 (2)	0.890 (1)	5.0
C1	0.7771 (3)	0.8706 (2)	0.7931 (1)	3.29 (5)	H10	0.975 (3)	0.947 (2)	0.948 (1)	5.0
C2	0.9192 (3)	0.8131 (2)	0.8104 (1)	3.48 (5)	H11A	0.634 (3)	0.800 (2)	0.859 (1)	5.0
C3	1.0391 (3)	0.8675 (3)	0.7765 (1)	4.17 (6)	H11B	0.550 (3)	0.899 (2)	0.819 (1)	5.0
C4	0.9748 (4)	0.9578 (3)	0.7382 (1)	4.19 (6)	H12A	0.597 (3)	0.552 (2)	0.735 (1)	5.0
C5	0.8120 (4)	0.9606 (3)	0.7489 (1)	3.93 (6)	H12B	0.747 (3)	0.614 (3)	0.759 (1)	5.0
C6	0.8227 (3)	1.0823 (2)	0.8985 (1)	3.37 (5)	H13A	0.500 (3)	0.509 (2)	0.839 (1)	5.0
C7	0.8678 (4)	1.1699 (2)	0.8543 (1)	3.72 (6)	H13B	0.660 (3)	0.445 (2)	0.820 (1)	5.0
C8	1.0303 (4)	1.1628 (2)	0.8455 (1)	3.87 (6)	H14A	0.733 (3)	0.434 (2)	0.918 (1)	5.0
C9	1.0867 (3)	1.0703 (3)	0.8852 (1)	3.80 (6)	H14B	0.593 (3)	0.512 (2)	0.945 (1)	5.0
C10	0.9606 (3)	1.0209 (2)	0.9178 (1)	3.51 (6)	H15A	0.796 (3)	0.521 (3)	1.006 (1)	5.0
C11	0.6204 (3)	0.8377 (3)	0.8173 (1)	4.01 (6)	H15B	0.900 (3)	0.585 (2)	0.962 (1)	5.0
C12	0.6316 (4)	0.5996 (3)	0.7689 (2)	5.42 (7)	H16A	0.837 (3)	0.664 (3)	1.081 (1)	5.0
C13	0.6234 (4)	0.5230 (3)	0.8250 (2)	5.47 (8)	H16B	0.909 (3)	0.741 (2)	1.033 (1)	5.0
C14	0.6951 (4)	0.5159 (3)	0.9280 (2)	5.96 (8)	H17A	0.628 (3)	0.809 (2)	1.088 (1)	5.0
C15	0.7958 (4)	0.5721 (3)	0.9743 (2)	5.94 (8)	H17B	0.802 (3)	0.845 (3)	1.119 (1)	5.0
C16	0.8199 (4)	0.7231 (3)	1.0486 (2)	6.07 (8)	H18A	0.591 (3)	1.044 (2)	1.088 (1)	5.0
C17	0.7417 (4)	0.8258 (4)	1.0798 (1)	5.76 (8)	H18B	0.761 (3)	1.054 (2)	1.110 (1)	5.0
C18	0.7084 (4)	1.0414 (4)	1.0763 (1)	5.42 (8)	H19A	0.724 (3)	1.220 (2)	1.060 (1)	5.0
C19	0.7381 (4)	1.1504 (3)	1.0382 (2)	5.46 (7)	H19B	0.855 (3)	1.139 (2)	1.024 (1)	5.0
C20	0.6631 (4)	1.0613 (3)	0.9218 (1)	4.25 (6)	H20A	0.593 (3)	1.075 (2)	0.891 (1)	5.0
H2	0.925 (3)	0.746 (2)	0.843 (1)	5.0	H20B	0.649 (3)	0.973 (2)	0.941 (1)	5.0
B. Compound II									
Fe	0.17793 (1)	0.05571 (1)	0.045	2.894 (6)	H4	0.098 (1)	0.0339 (8)	−0.031 (4)	5.0
S1	0.14640 (3)	0.00869 (3)	0.5233 (1)	5.34 (2)	H5	0.095 (1)	0.0694 (8)	0.194 (4)	5.0
S2	0.18044 (4)	0.18940 (2)	0.0315 (1)	5.37 (2)	H7	0.160 (1)	0.0969 (8)	−0.180 (4)	5.0
O1	0.07053 (8)	0.07617 (7)	0.4794 (3)	5.35 (6)	H8	0.226 (1)	0.0494 (7)	−0.197 (4)	5.0
O2	0.1282 (1)	0.13857 (7)	0.4666 (6)	10.6 (1)	H9	0.272 (1)	0.0522 (7)	0.023 (4)	5.0
O3	0.21947 (9)	0.15952 (6)	0.3628 (3)	4.65 (5)	H10	0.238 (1)	0.1052 (8)	0.169 (4)	5.0
C1	0.1571 (1)	0.03216 (8)	0.2393 (4)	3.17 (6)	H11	0.161 (1)	0.0702 (8)	0.413 (4)	5.0
C2	0.1784 (1)	0.00494 (8)	0.1459 (4)	4.01 (7)	H12A	0.074 (1)	0.0096 (8)	0.371 (4)	5.0
C3	0.1522 (1)	0.00257 (9)	0.0151 (5)	5.03 (8)	H12B	0.073 (1)	−0.0113 (8)	0.537 (4)	5.0
C4	0.1148 (1)	0.0282 (1)	0.0253 (4)	4.99 (8)	H13A	0.026 (1)	0.0416 (7)	0.557 (4)	5.0
C5	0.1168 (1)	0.04710 (9)	0.1628 (4)	3.86 (7)	H13B	0.069 (1)	0.0473 (8)	0.672 (4)	5.0
C6	0.1860 (1)	0.11218 (8)	0.0133 (3)	3.21 (6)	H14A	0.020 (1)	0.1124 (8)	0.577 (4)	5.0
C7	0.1822 (1)	0.09335 (9)	−0.1230 (4)	4.00 (7)	H14B	0.068 (1)	0.1090 (8)	0.656 (4)	5.0
C8	0.2199 (1)	0.06677 (8)	−0.1322 (4)	4.21 (7)	H15A	0.057 (1)	0.1269 (8)	0.429 (4)	5.0
C9	0.2472 (1)	0.06919 (8)	−0.0038 (4)	3.85 (7)	H15B	0.070 (1)	0.1604 (8)	0.485 (4)	5.0
C10	0.2265 (1)	0.09732 (8)	0.0855 (4)	3.21 (6)	H16A	0.148 (1)	0.1901 (7)	0.501 (4)	5.0
C11	0.1715 (1)	0.04224 (8)	0.3909 (4)	3.43 (6)	H16B	0.147 (1)	0.1599 (8)	0.621 (4)	5.0
C12	0.0828 (1)	0.0109 (1)	0.4908 (5)	5.46 (9)	H17A	0.224 (1)	0.1775 (7)	0.557 (4)	5.0
C13	0.0582 (1)	0.0435 (1)	0.5598 (5)	6.3 (1)	H17B	0.214 (1)	0.1315 (8)	0.540 (4)	5.0
C14	0.0570 (1)	0.1087 (1)	0.5515 (6)	6.4 (1)	H18A	0.202 (1)	0.2111 (8)	0.328 (4)	5.0
C15	0.0785 (2)	0.1407 (1)	0.4740 (8)	9.7 (2)	H18B	0.251 (1)	0.2102 (8)	0.348 (4)	5.0
C16	0.1542 (2)	0.1674 (1)	0.5349 (5)	7.1 (1)	H19A	0.249 (1)	0.2167 (8)	0.109 (4)	5.0
C17	0.2064 (2)	0.1594 (1)	0.5127 (5)	6.6 (1)	H19B	0.257 (1)	0.1696 (8)	0.113 (4)	5.0
C18	0.2265 (1)	0.19580 (9)	0.3039 (6)	5.20 (8)	H20	0.152 (1)	0.1401 (8)	0.172 (4)	5.0
C19	0.2338 (1)	0.19244 (9)	0.1413 (5)	5.18 (9)	H21A	0.233 (1)	0.0467 (8)	0.499 (4)	5.0
C20	0.1544 (1)	0.14272 (8)	0.0714 (4)	3.77 (7)	H21B	0.237 (1)	0.0163 (8)	0.393 (4)	5.0
C21	0.2256 (1)	0.0414 (1)	0.4174 (4)	5.06 (9)	H21C	0.241 (1)	0.0612 (7)	0.361 (4)	5.0
C22	0.1044 (1)	0.1436 (1)	0.0058 (5)	5.83 (9)	H22A	0.084 (1)	0.1628 (8)	0.045 (4)	5.0
H2	0.209 (1)	−0.0109 (8)	0.169 (4)	5.0	H22B	0.103 (1)	0.1489 (8)	−0.105 (4)	5.0
H3	0.159 (1)	−0.0128 (8)	−0.077 (4)	5.0	H22C	0.087 (1)	0.1219 (8)	0.029 (4)	5.0

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

allelism observed for II is probably due to steric interactions that result from the presence of the two methyl substituents on the carbons directly attached to the Cp rings.

The carbon–carbon bond distances in the Cp rings range from 1.406 (3) to 1.430 (2) Å (average 1.418 Å) for I and from 1.389 (4) to 1.426 (4) Å (average 1.411 Å) for II. Reported[11,12] average carbon–carbon bond distances in the Cp rings of III, IV, and V are 1.422, 1.415, and 1.418 Å, respectively, and mean bond lengths of 1.40 Å have been reported for both ferrocene[17] and bis(ferrocenyl).[18] The bond angles of the Cp rings are normal, ranging from 106.9 (2) to 109.2 (2)° for I and from 106.6 (2)° to 109.9 (2)° for II.

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Table III. Bond Lengths with Estimated Standard Deviations in Parentheses

	I	II
(a) Within the Fe–(C_5H_5) Moiety		
Fe–C1	2.043 (2)	2.049 (2)
Fe–C2	2.040 (2)	2.033 (2)
Fe–C3	2.035 (2)	2.043 (2)
Fe–C4	2.043 (2)	2.020 (2)
Fe–C5	2.034 (2)	2.038 (2)
Fe–C6	2.046 (2)	2.046 (2)
Fe–C7	2.039 (2)	2.038 (2)
Fe–C8	2.041 (2)	2.030 (2)
Fe–C9	2.035 (2)	2.035 (2)
Fe–C10	2.043 (2)	2.042 (2)
(b) Within the C_5H_5 Ring		
C1–C2	1.427 (2)	1.421 (3)
C2–C3	1.406 (3)	1.400 (4)
C3–C4	1.409 (3)	1.389 (4)
C4–C5	1.424 (3)	1.426 (4)
C5–C1	1.415 (2)	1.425 (3)
C6–C7	1.417 (2)	1.417 (3)
C7–C8	1.417 (3)	1.416 (3)
C8–C9	1.421 (2)	1.398 (4)
C9–C10	1.411 (2)	1.414 (3)
C10–C6	1.430 (2)	1.409 (3)
(c) Within the Bridging Chain		
C1–C11	1.497 (2)	1.485 (3)
C11–S1	1.823 (2)	1.838 (2)
S1–C12	1.791 (2)	1.796 (3)
C12–C13	1.494 (3)	1.488 (4)
C13–O1	1.412 (3)	1.419 (4)
O1–C14	1.425 (2)	1.385 (3)
C14–C15	1.475 (4)	1.471 (5)
C15–O2	1.405 (3)	1.388 (4)
O2–C16	1.429 (3)	1.408 (4)
C16–C17	1.476 (4)	1.495 (5)
C17–O3	1.410 (3)	1.415 (4)
O3–C18	1.412 (3)	1.414 (3)
C18–C19	1.476 (3)	1.503 (5)
C19–S2	1.797 (3)	1.793 (3)
S2–C20	1.824 (2)	1.851 (2)
C20–C6	1.488 (3)	1.497 (3)
C11–C21		1.523 (3)
C20–C22		1.516 (3)

Distances of the iron atom from the planes of the two rings in I and II are 1.645, 1.645, 1.647, and 1.645 Å. These distances are close to those reported: 1.655 and 1.655 Å for III;[12] 1.649 and 1.645 Å for IV;[12] 1.649 and 1.655 Å for V;[11] similar results have been obtained for ferrocene[17] and bis(ferrocenyl).[18]

The two Cp rings in I and II exhibit conformations that are very close to totally eclipsed with mean twist angles[19] of 3.1° and 0.6°, respectively. The eclipsed conformation is usually found for substituted ferrocenyl compounds[16,20-23] and is in contrast to that observed in ferrocene itself which is staggered.[17] An intermediate situation was reported for [3](1,1′)-[4](3,2′)ferrocenophan-6-one[24] in which one Cp ring is rotated relative to the other by 27°. The mean twist angles decrease with increasing length of the bridging chain for the structural series of III (7.8°) > IV (6.7°) > I (3.1°).

Table IV. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

angle	I	II
C2–C1–C5	107.7 (2)	106.9 (2)
C1–C2–C3	107.8 (2)	109.6 (2)
C2–C3–C4	108.8 (2)	107.0 (2)
C3–C4–C5	107.7 (2)	109.9 (2)
C4–C5–C1	108.0 (2)	106.6 (2)
C10–C6–C7	106.9 (2)	107.0 (2)
C6–C7–C8	109.2 (2)	108.3 (2)
C7–C8–C9	107.0 (2)	108.1 (2)
C8–C9–C10	108.7 (2)	107.8 (2)
C9–C10–C6	108.1 (2)	108.8 (2)
C2–C1–C11	125.1 (2)	127.7 (2)
C5–C1–C11	127.1 (2)	125.3 (2)
C1–C11–S1	113.5 (1)	110.6 (2)
C11–S1–C12	101.7 (1)	103.7 (1)
S1–C12–C13	115.8 (1)	114.7 (2)
C12–C13–O1	109.7 (2)	108.1 (2)
C13–O1–C14	112.4 (2)	112.1 (3)
O1–C14–C15	111.0 (2)	108.2 (3)
C14–C15–O2	111.7 (2)	112.6 (3)
C15–O2–C16	110.6 (2)	116.8 (3)
O2–C16–C17	111.1 (2)	107.5 (3)
C16–C17–O3	110.4 (2)	112.3 (3)
C17–O3–C18	113.8 (2)	114.0 (2)
O3–C18–C19	109.9 (2)	108.7 (2)
C18–C19–S2	115.2 (1)	116.4 (2)
C19–S2–C20	102.4 (1)	105.6 (1)
S2–C20–C6	113.5 (1)	110.8 (2)
C20–C6–C7	126.5 (2)	127.7 (2)
C20–C6–C10	126.5 (2)	125.3 (2)
S1–C11–C21		105.0 (2)
C1–C11–C21		114.2 (2)
S2–C20–C22		105.3 (2)
C6–C20–C22		114.5 (2)

Table V. Torsional Angles (deg) within the Bridging Chain

angle	I	II
C1–C11–S1–C12	63.3	−57.2
C11–S1–C12–C13	76.0	−80.0
S1–C12–C13–O1	−73.1	73.4
C12–C13–O1–C14	179.0	−168.3
C13–O1–C14–C15	171.8	170.2
O1–C14–C15–O2	77.1	−58.3
C14–C15–O2–C16	174.4	−118.4
C15–O2–C16–C17	−174.3	−179.8
O2–C16–C17–O3	−75.5	62.4
C17–O3–C18–C19	173.6	−172.8
O3–C18–C19–S2	74.8	83.2
C18–C19–S2–C20	−77.0	−70.1
C19–S2–C20–C6	−62.6	−67.8

Thus the longer bridging chain in I appears to favor attainment of the eclipsed conformation.

Compounds I and II attain the eclipsed conformation in different ways. For I, Cp ring carbons C1 and C6, through which the bridging chain is attached, face each other. On the other hand for II, C1 faces Cp ring carbon C10 which is *adjacent* to the attachment carbon for the bridging chain, C6. This rotation of 360/5° undoubtedly results from steric interactions between the two methyl groups in II. A similar rotation of the Cp ring carbons to which the bridging chain ends are attached has been noted in V.[11]

The geometrics of the bridging chains in I and II are normal. Values of the torsion angles (Table V) can be used to define conformations of the C1–C6 chain. In crown ethers,[25,26] the C–C and C–O bonds are gauche and anti, respectively. As can be seen from the data in Table V, this rule is observed for I and II except for the C14–C15–O2–

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(19) The angle of twist was calculated by averaging the five dihedral angles between planes defined by the two ring centroids and one carbon atom of the first Cp ring and the two ring centroids and the corresponding carbon of the second ring.

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C16 angle in II which is 118°. The conformation about the C–S bonds was found to be gauche in all cases.

Ferrocenophane II contains two carbon atoms, namely, C11 and C20, which are asymmetric centers. The priority sequence of the ligands around these carbons is S > C(Cp ring) > C(methyl) > H.[27] As can be seen from Figure 2, both asymmetric centers have identical *S* conformations. Thus, II packs as a racemic compound containing *SS* and *RR* molecules. This confirms the conjecture[7] made by analogy of thin-layer chromatographic behavior, that the crystalline diastereomer of II is the racemic compound. Thus II is shown to be different from V in which the two asymmetric centers are enantiomeric which gives the meso molecule.

Electrochemical Studies. The cyclic voltammogram of I in acetonitrile solution (0.10 M in tetrabutylammonium perchlorate), with initial anodic sweep, was as expected for a reversible, one-electron oxidation of the ferrocenophane to the corresponding ferricenium cation.[12] The reduction potential (vs SHE) of the ferricenium cation derived from I is +416 mV. Reduction potentials for previously studied ferrocenophanes III and IV were found to be +405 and +419 mV, respectively. Thus the reduction potentials for the ferricenium cations derived from I and IV are essentially the same, and both Fe (II) species are slightly weaker reductants than III, which has the shortest bridging chain of the series.

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Registry No. I, 80973-98-4; II, 71840-04-5.

Supplementary Material Available: Tables of anisotropic temperature factors and least-square planes for I and II (5 pages); listings of observed and calculated structure factors for I and II (23 pages). Ordering information is given on any current masthead page.

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A Dinuclear Bis(1,3-diene) Complex of Titanium: Crystal and Molecular Structure of μ-[o-$(CH_2)_2C_6H_4$](μ-Cl)$_2$[(η^5-C_5Me_5)Ti]$_2$, Containing an Unprecedented "*o*-Xylidene" Bridging Group

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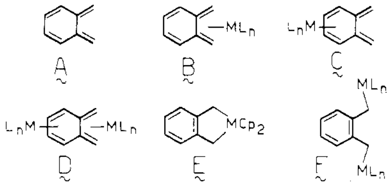
$(\eta^5\text{-}C_5Me_5)TiCl_3$ reacts with $[o\text{-}(CH_2)_2C_6H_4]Mg(THF)_2$ to give $(\eta^5\text{-}C_5Me_5)TiCl[o\text{-}(CH_2)_2C_6H_4]$ (**3**) or $\mu\text{-}[o\text{-}(CH_2)_2C_6H_4](\mu\text{-}Cl)_2[(\eta^5\text{-}C_5Me_5)Ti]_2$ (**4**) depending on the solvent. The crystal structure of **4** has been determined by X-ray diffraction methods. Crystals of **4** are monoclinic of space group $C2/c$ with $Z = 8$ in a unit cell of dimensions $a = 26.746$ (4) Å, $b = 11.832$ (3) Å, $c = 16.781$ (3) Å, and $\beta = 90.44$ (1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.080$ and $R_w = 0.095$ for 1089 observed reflections. The complex shows an *o*-xylidene ligand bridging two $Ti(\eta^5\text{-}C_5Me_5)$ fragments through its exo- and endocyclic conjugated diene systems which are bonded in different (σ^2 and π^2) modes to the titanium atoms.

Introduction

1,3-Diene complexes of the early transition group 4 and 5 metals (especially Zr, Hf, and Ta) are being actively investigated because of their particular bonding features and chemical reactivity.[1] In this context the lack of similar titanium derivatives is surprising, and just a few titanium diene compounds have been so far reported,[2] although no crystallographic characterization is available.

The "*o*-xylidene"[6b] group (A) coordinates to transition metals usually as a 1,3-diene through its exocyclic π system, as in B,[3] and less frequently through its endocyclic π system (C)[4] or both of them (D).[5] With the early transition metallocenes the bonding is more adequately described as a metallobenzocyclopentane (E)[6a] where the σ

Chart I



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