Tetrahedron Letters,Vol.24,No.51,pp 5757-5760,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

[2]METACYCLO- AND [2]PARACYCLO[2](1,3)FERROCENOPHANES[1-3]

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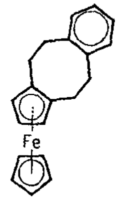
Summary: The title compounds, novel cyclophanes incorporating 1,3-disubstituted ferrocene moiety, have been synthesized and characterized by spectroscopies and X-ray diffraction.

There are several reports[4] on phanes containing benzenoid metal π-complex, but [2.2]phane with η^5-cyclopentadienyl (Cp) ring, a nonbenzenoid aromatic π-system, has not been described except for [2.2](1,2)ferrocenophane (1),[5] which is not an example of layered phane but of condensed-ring compound. Incorporation of η^5-Cp ring into [2.2]phane is of interest, since it would allow realization of a more strained system than benzenoid complexes and NMR spectral observation of magnetic anisotropy in the just above region of η^5-Cp ring. We now wish to report on the synthesis and characterization of [2.2]metacyclo- and paracyclo[2.2](1,3)ferrocenophanes (2 and 3) incorporating the η^5-Cp ligand of the π-complex into phane system.



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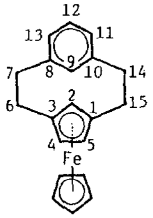

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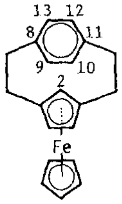

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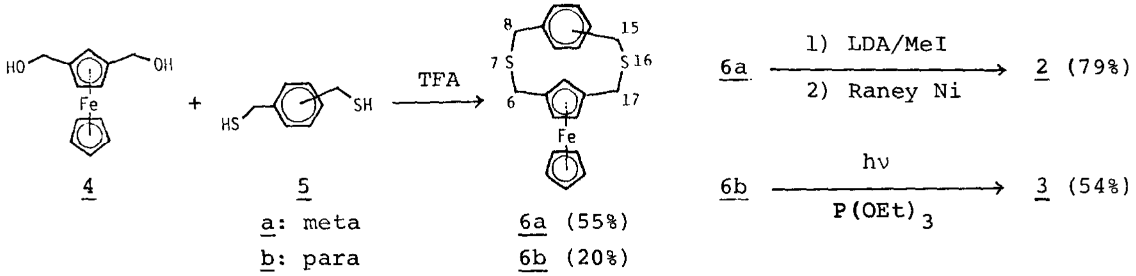
Among some attempts at preparation of cyclic sulfides which are precursors of [2.2]phanes, acid-catalyzed dehydration of diol and thiol was successful; treatment of bis(hydroxymethyl)ferrocene (4)[6] and bis(mercaptomethyl)benzene (5) with trifluoroacetic acid (TFA) in dichloromethane (conc., 10^{-3} mol/l) gave the corresponding sulfides (6).[7,8] Rearrangement[9] of 6a with LDA followed by addition of methyl iodide at room temperature yielded a mixture of isomeric methylthio[2.2]phanes, which was desulfurized with Raney nickel to give 2.[8] Irradiation[10] of 6b in triethyl phosphite/benzene (2/1) under an Ar atmosphere



at room temperature using a low pressure mercury lamp for 18 hr gave 3,[8] while the Wittig rearrangement and Stevens rearrangement of 6b were unsuccessful.

Both crystals of 2 and 3 used in the X-ray diffraction were grown from methanol solutions.[11] Intensity data were measured at room temperature on a Philips PW-100 diffractometer by means of the θ-2θ scan method by using graphite monochromated CuKα (2) and MoKα (3) radiations.[11] The crystal structures were resolved by the heavy atom method and refined by the method of block-diagonal least-squares. The final R values for 2 and 3 were reduced to 0.053 and 0.046, respectively, including hydrogen atom contributions and dispersion correction of Fe atoms. Final crystallographic coordinates and structural parameters can be found in reference 12.[12]

Molecular structural features of 2 and 3 in crystals are summarized as follows: (i) There lie the 2- and 9-hydrogens of 2 in the just above regions of the centres of benzene and Cp rings, respectively. (ii) Deformation of benzene rings of 2 and 3 are similar to those of meta- and paracyclophanes, respectively. (iii) The substituted Cp rings of the both are almost plane but 6- and 15-carbon atoms on the bridges fairly deviate from the least-squares planes of the Cp rings. (iv) The distance from the Fe atom to the substituted Cp ring in 2 is larger than that to the unsubstituted Cp ring, and perhaps 1.678 Å is the largest value among those of ferrocene derivatives except for ferricenium ions and complexes with acceptors. (v) The ferrocene moiety is more strained in 2 than in 3, and the difference is possibly due to less flexibility of meta-substituted benzene ring than that of para benzene.

In the ^{1}H-NMR spectra of 2 and 3, the Cp ring protons at 2-position appear at extremely high fields, and the shift differences of the 2-proton to the 4,5-protons (2, 2.57 ppm; 3, 1.00 ppm) reflect the degree of overlapping of benzene and Cp rings. The 9-protons of 2 and 3 also shift to high fields in comparison with the other benzene ring protons. Especially, the shift of the 9-proton of 2 which lies in the almost just above position of the centre of the Cp ring is exceedingly large (1.53 ppm to the corresponding proton of m-xylene). It is certain that the high field shifts of the 9-protons are caused by magnetic anisotropic effect of ferrocene. The result is the first example of the observation of the anisotropy in the just upper region of Cp ring in metallocene, which was predicted by Turbitt and Watts.[13] The low field shift of 9-carbon in the ^{13}C-NMR spectrum of 2 (δ139.07) is larger than those of the corresponding carbons of metacyclophane (δ136.3) and metaparacyclophane (δ133.0).

The electronic absorption spectra of 2 and 3 were measured and compared with reference compounds, 1,3-diethylferrocene (7) and 1,4-diethylbenzene. Discernible shoulders at 280-320 nm, possibly assigned to CT absorption, appeared in the both compounds. Bathochromic shifts of d-d* absorption band [2: 451 nm (ε=147), 3: 447 nm (ε=141), 7 438 nm (ε=112)] in visible region reflect the respective Cp-Cp distances (2: 3.327 Å, 3: 3.311 Å, ferrocene: 3.304 Å;[14] λ_{max}=440 nm[15]). The results suggest that the band does not only depend on tilting of two Cp rings[15] but also increase of Cp-Cp (or Fe-Cp) distance. The reasoning is supported by our investigation on the corelation between X-ray crystal structures and electronic spectra in intramolecular multibridged ferrocenophanes.[16]

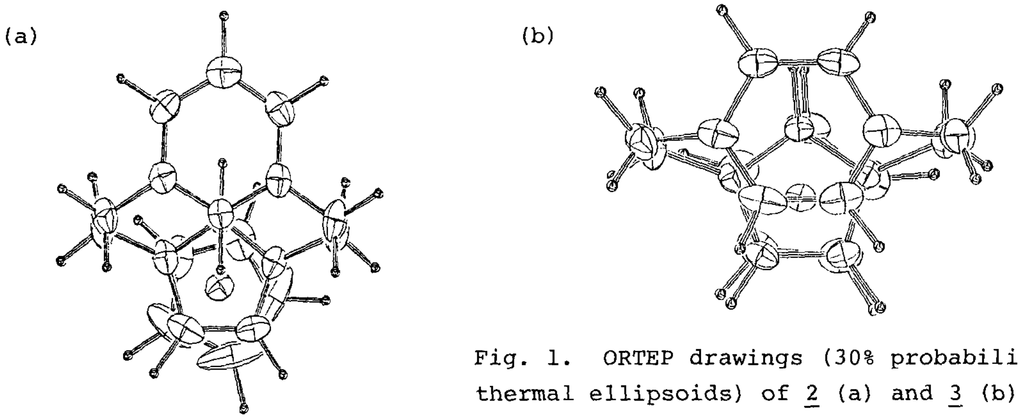


Fig. 1. ORTEP drawings (30% probability thermal ellipsoids) of 2 (a) and 3 (b).

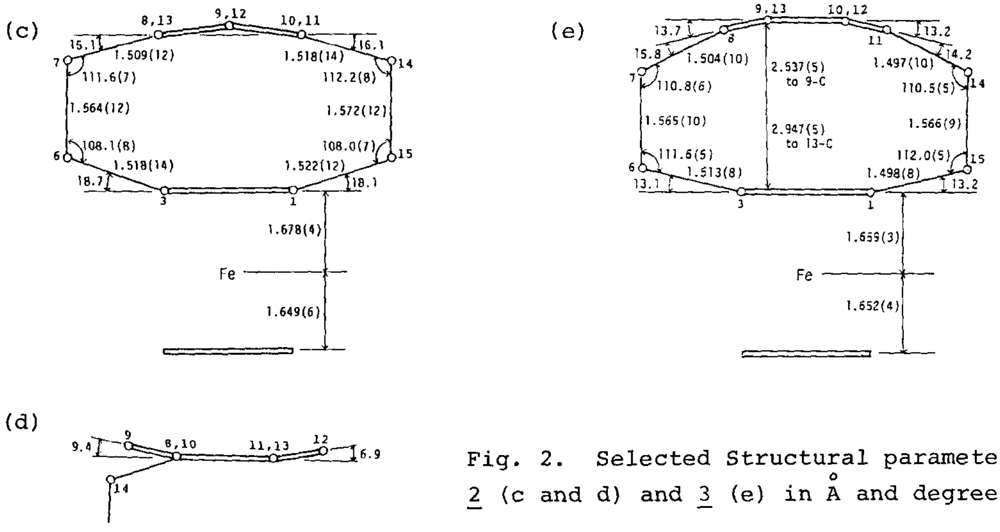


Fig. 2. Selected Structural parameters of 2 (c and d) and 3 (e) in Å and degree.[12]

References and Notes

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2. The nomenclature is according to the one presented by Vögtle and Neumann.[3]
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7. The reaction of 4 with 5b gave a tetramer as the major product (65%).
8. Conbustion elemental analyses gave sufficient results. 6a: yellow needles; mp. 136-137°C; FD-MS, m/z380(M^+); ^{1}H-NMR($CDCl_3$), δ3.51 and 3.71(4H, AB, J=14.5Hz, 6,17-H), 3.53 and 3.66(4H, AB, J=11.5Hz, 8,15-H), 3.65(2H, d, J=1.4Hz, 4,5-H), 3.93(5H, s, unsubstd. Cp-H), 3.97(1H, t, J=1.4Hz, 2-H), 6.79(1H, m, 10-H), 6.85-7.05(3H, m, Ph-H). 6b: yellow needles, mp. 172-173°C; FD-MS, m/z380(M^+); ^{1}H-NMR($CDCl_3$), δ2.89(1H, t, J=1.4Hz, 2-H), 3.22 and 3.46(4H, AB, J=14.5Hz, 6,17-H), 3.80(4H, s, 8,15-H), 3.92(2H, d, J=1.4Hz, 4,5-H), 6.96 and 7.01(each 2H, AA'BB', Ph-H). 2: orange-yellow needles, mp. 131-132°C; EI-MS, m/z316(M^+); ^{1}H-NMR($CDCl_3$), δ1.18(1H, t, J=1.5Hz, 2-H), 1.60-3.00(8H, m, methylene-H), 3.75(2H, d, J=1.5Hz, 4,5-H), 3.98(5H, s, unsubstd. Cp-H), 5.34(4H, m, 9-H), 6.80-7.15(3H, m, 11,12,13-H). 3: orange-yellow needles; mp. 106-107°C; EI-MS, m/z316(M^+); ^{1}H-NMR($CDCl_3$), δ2.00-3.18(8H, m, methylene-H), 2.37(1H, t, J=1.5Hz, 2-H), 3.37(2H, d, J=1.5Hz, 4,5-H), 3.87(5H, s, unsubstd. Cp-H), 6.23 and 6.93(each 2H, AA'XX', Ph-H).
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11. 2: dimensions, 0.015x0.060x0.30 mm; $C_{20}H_{20}Fe$, MW=316.23; monoclinic, space group $P2_1$, a=8.851(4), b=15.742(8), c=5.963(3) Å, β=109.76(5), Z=2, μ(CuKα)=76.5 cm^{-1}; scan speed 4° 2$\theta$$min^{-1}$; independent reflections 1326, $2\theta_{max}$ 156°. 3: dimensions 0.17x0.10x0.60 mm; $C_{20}H_{20}Fe$, MW=316.23; orthorhombic, space group *Pbca*, a=15.308(8), b=24.716(12), c=8.034(4); Z=8, μ(MoKα)=9.81 cm^{-1}; scan speed 6° 2$\theta$$min^{-1}$; independent reflections 1552, $2\theta_{max}$ 50°.
12. The data have been deposited with the Cambridge Crystallographic Data Centre.
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16. Unpublished results. The manuscript is in preparation.

(Received in Japan 17 September 1983)