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SYNTHESIS AND MOLECULAR STRUCTURE OF TETRABRIDGED FERROCENOPHANE[1]

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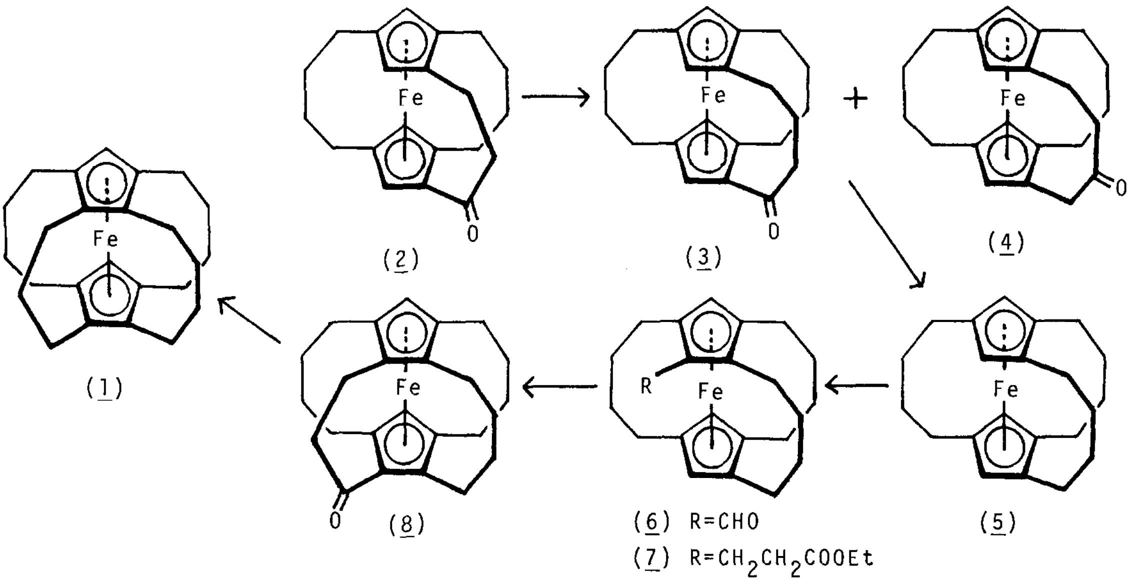
Synthesis of [4](1,1')[4](3,3')[4](5,5')[3](4,4')ferrocenophane (1) is described and its molecular structure was confirmed by X-ray diffraction.

Perferrocenophanes are very interesting as novel spherical cage compounds, a package wrapped iron in the center of molecule. Several attempted syntheses of tetrakis(trimethylene)ferrocenes had been unsuccessful because rearrangement took place during the fourth bridging reaction.[2,3] We previously reported[4] synthesis of two [4][4][4][3]ferrocenophane derivatives, but their structure must be revised from our further examination.[5]

We will report here the synthesis of the correct structure of [4](1,1')[4](3,3')[4](5,5')[3](4,4')ferrocenophane (1) and its molecular structure was confirmed by X-ray diffraction. Treatment of [4][4]-α-oxo[3]ferrocenophane[6] (2) in benzene with ether solution of diazomethane, in the presence of BF_3-OEt_2 complex afforded the ring-enlarged ketone (3), mp 140-141°, as orange prisms [53%; MS *m/e*: 362.1301, M^+; IR 1644 cm^{-1}] and (4), mp 110-110.5°, as yellow needles [21%; MS *m/e*: 362.1311, M^+; IR 1690 cm^{-1}]. Reduction of 3 with $LiAlH_4$-$AlCl_3$ in a mixture of ether-benzene in N_2 atmosphere for 1.5 hr gave [4](1,1')[4](3,3')[4](5,5')ferrocenophane (5), mp 89-91°, as orange prisms [96.6%; MS *m/e*: 348.1544, $C_{22}H_{28}Fe$ requires 348.1539; ^1H-NMR δ: 1.6-2.1 (12H, m, β-CH_2), 2.1-2.5 (12H, bs, α-CH_2), 3.95 (4H, s, Cp ring H)].



Formylation of 5 gave 6, mp 102.5-105°, as deep red granules (96.4%). Condensation of 6 and ethyl bromoacetate in Zn-I$_2$ and then catalytic reduction of the product with Pd-C catalyst gave an ester (7), as yellow oil [87%; MS *m/e*: 448.2064, M$^+$; IR 1730 cm^{-1}]. After hydrolysis of 7 with 20% NaOH-EtOH, treatment of the resulting acid with ClCOOEt-Et$_3$N and then with AlCl$_3$ afforded [4][4][4]-α-oxo[3]ferrocenophane (8), mp 175° (decomp.), as yellow needles [17%; IR 1659 cm^{-1}]. Reduction of 8 with LiAlH$_4$-AlCl$_3$ in ether in N$_2$ atmosphere yielded [4](1,1')[4](3,3')[4](5,5')[3](4,4')ferrocenophane (1), mp 234-236°, as yellow needles [64.5%; MS *m/e:* 388.1862, $C_{25}H_{32}Fe$ requires 388.1852; ^{1}H-NMR δ: 1.5-2.1 (18H, m, CH$_2$), 2.1-2.6 (12H, m, CH$_2$), 3.91 (2H, s, Cp ring 2,2'-H); ^{13}C-NMR δ: 18.8, 21.3, 21.9, 26.2, 27.5, 28.9, 29.2, 35.0 (bridged carbons); 69.8, 81.4, 84.0, 86.4, 87.7 (Cp ring carbons)].

The crystals of [4][4][4][3]ferrocenophane (1) grown from hexane solution were yellow thin plates. A specimen of the approximate dimensions of 0.22 x 0.02 x 0.53 mm was amounted on a Philips PW-100 diffractometer. Intensities were measured by the θ-2θ scan method, with the scan speed of 6°/sec in θ, using MoKα radiation monochromated by a graphite plate. The scans were repeated twice when the total counts received in a scan were less than 3000. The unit cell dimensions were determined as a=17.883(10), b=8.521(5), c=12.305(6) Å, β=97.11(3)° and space group P2$_1$/a with four molecules in a cell. Intensities of 3121 reflexions were measured within a

2θ range from 6° to 60° as above the 2σ(I) level which corresponds to 53% of the theoretically possible reflexions in the same angular range.

The crystal structure was solved by the heavy atom method and refined by the method of block-diagonal least-squares. The R value was reduced to 0.078 including hydrogen atom contributions and dispersion correction of Fe atom for MoKα radiation.

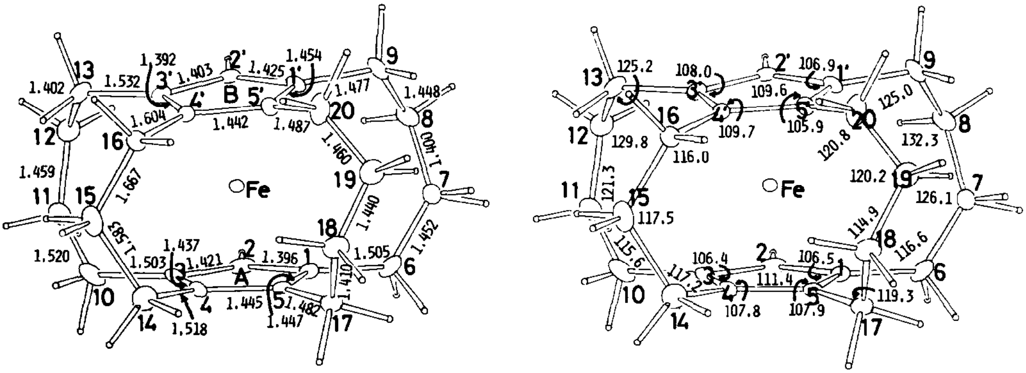


Fig. 1. ORTEP drawing of 1 with bond length (Å) and valency angle (°)

The molecular structure is illustrated in Fig. 1 by an ORTEP[7] drawing with 20% probability thermal ellipsoids. The C-C bond length and C-C-C valency angle of the A[C(1)~C(5)] and B[C(1')~(5')] cyclopentadienyl rings lie in the range of 1.396-1.447 Å and 106.4-111.4° in the A ring and 1.392-1.454 Å and 105.9-109.7° in the B ring, with average values of 1.429(10) Å and 108.0(6)° in A ring and 1.423(10) Å and 108.0(6)° in B ring. The average lengths are slightly longer than those found in ferrocene and biferrocenyl but in good agreement with bridged ferrocenes.[8] The distance between Fe and ring carbon atoms ranges from 2.012 to 2.032 Å for A ring and from 1.998 to 2.027 Å

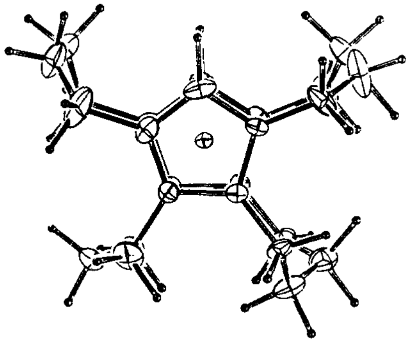


Fig. 2. ORTEP drawing of 1 projected on cyclopentadienyl rings (ORTEP diagram, 20% probability thermal ellipsoids as in Fig. 1.)

for B ring. The average distance 2.023(6) Å and 2.024(7) Å for A and B rings and the perpendicular distance from Fe to the least-squares planes of A and B rings, 1.617 and 1.618 Å, respectively, are both slightly shorter than those found in ferrocenes having no or only one bridge but agree well with two-bridged ferrocenes.[8] It has been found that the tilt angle between the two rings varies greatly with the type of the bridge.[8] The angle 5.68° found in the present structure lies in the range reported for ferrocenes with three trimethylene bridges.

The conformations of the bridge methylene chains are shown in Fig. 2. The tetramethylene bridges takes different conformations to each other. Distortions in bond lengths and angles in these bridge methylene chains are quite large. The average C-C lengths and C-C-C angles found in the above three tetramethylene bridges are 1.456(15), 1.483(15), and 1.456(13) Å, and 125.0(10), 123.0(10), and 118.8(9)°, respectively. In the trimethylene bridge, they are 1.593(14) Å and 117.1(8)°.

The last step towards synthesis of [4][4][4][4][4]-pentabridged ferrocenophane is now in progress.

References and Notes

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