Tetrahedron Letters,Vol.23,No.16,pp 1713-1716,1982 0040-4039/82/161713-04$03.00/0
Printed in Great Britain

A PACKAGE COMPOUND OF A METAL ATOM WITH A HYDROCARBON
[4][4][4][4][3](1,2,3,4,5)FERROCENOPHANE[1-3]

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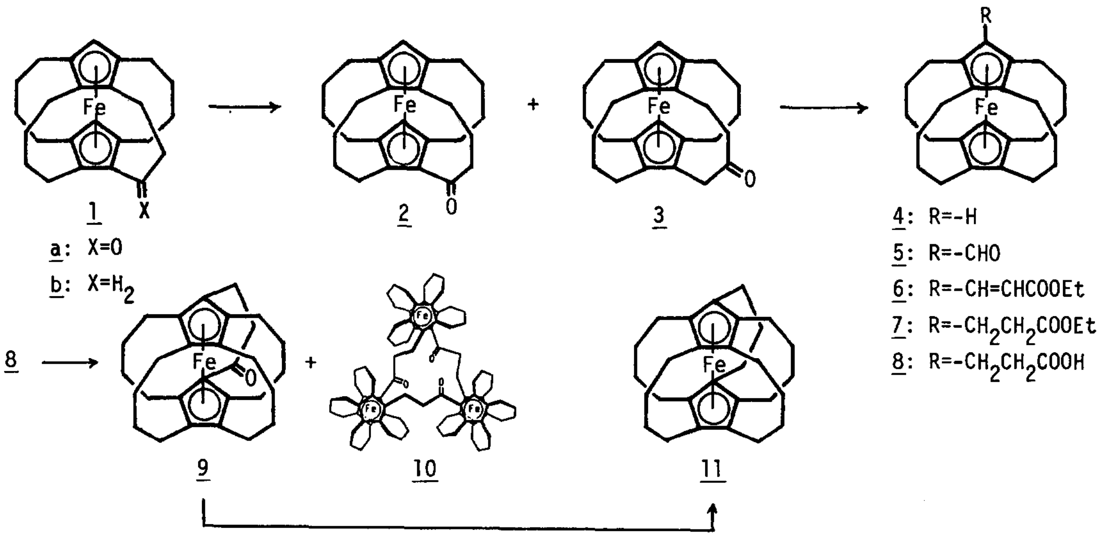
Summary: Perbridged ferrocenes (9 and 11: the title compound) have been synthesized and characterized by spectroscopies and X-ray diffraction, and an interesting rotational disorder has been found by the X-ray crystal analyses of both 9 and 11.

Pentabridged ferrocene is very interesting not only as a ferrocene analogue of Boekelheide's "superphane"[4] but also as a novel spherical cage compound packing an iron atom with a hydrocarbon. We previously reported the synthesis of tetrabridged [4][4][4][3]ferrocenophanes (1) and the molecular structure of 1b.[5] In the subsequent investigation, formation of the last bridge has been achieved by cyclization of propionic acid (8) derived from 1a. Although attempts to synthesize a D_5 symmetric ferrocenophane *via* bridge enlargement of 9 have been unsuccessful yet, we hasten to report the synthesis of [4][4][4][4][3]ferrocenophanes (9 and 11) and their characterization.[6]

Bridge enlargement of 1a[5] in benzene with CH_2N_2 in the presence of $BF_3 \cdot OEt_2$ gave α-ketone (2) [24%; mp. 262-264°(dec.); IR: 1650 cm^{-1}; PMR: δ3.95 and 4.19 (each 1H, s, ring-H)] and β-ketone (3) [37%; mp. 259-261°(dec.); IR: 1696 cm^{-1}; PMR: δ3.31 (2H, s, isolated methylene-H), 3.90 and 3.94 (each 1H, s, ring-H)]. Both ketones (2 and 3) were reduced with $LiAlH_4/AlCl_3$ to yield [4][4][4][4]ferrocenophane (4) [95 and 75%, respectively, from 2 and 3; mp. 258-259°(dec.); PMR: δ3.88 (2H, s, ring-H); CMR: δ26.765, 27.045, 27.386 and 27.825 (methylene-C), 68.417, 82.791 and 83.765 (ring-C)]. The molecular structure of 4 was determined by X-ray crystal analysis.[7]

Formylation of 4 with $DMF/POCl_3$ in $CHCl_3$ gave 5 [72%; mp. 236-238°; IR: 1655 cm^{-1}; PMR: δ4.01 (1H, s, ring-H), 10.57 (1H, s, -CHO)]. The Reformatsky reaction of the formyl derivative (5)



with ethyl bromoacetate/Zn/I_2 yielded acrylate (6) [87%; mp. 159-161°; IR: 1615 and 1700 cm^{-1}; PMR: δ3.71 (1H, s, ring-H), 6.80 and 7.95 (each 1H, an AB system, olefin-H)]. Hydrogenation of 6 with Pd/C catalyst gave propionate (7) [98%; mp. 122-124°; IR: 1730 cm^{-1}; PMR: δ3.57 (1H, s, ring-H)]. Hydrolysis of 7 with aq. NaOH/EtOH followed by treatment with neat polyphosphate ester (PPE) at 80°C for 20 min. afforded orange-yellow solid, which was chromatographed over preparative thin layer silica gel (benzene) to separate into several bands. The major two of these yielded intra- and inter-molecular cyclization products (9 and 10) in yields of 3.6 and 18% (from 7), respectively. The cyclization of propionic acid (8) under the conditions using a large excess of PPE gave 9 as the main product (9: 9%, 10: 7%). The trimeric structure of 10 was determined by X-ray crystal analysis and the result was already reported.[8]

The intramolecularly cyclized constitution of 9 [orange prisms; mp.>300°; IR: 1670 cm^{-1}] was supported by disappearance of ring proton signal and by observation of the molecular ion peak at m/z 456 in the PMR and mass spectra, respectively. Reduction of 9 with $LiAlH_4/AlCl_3$ gave a crystalline product (11) [90%; orange-yellow plates, mp.>300°; MS: m/z 442 (M^+)], whose CMR spectrum indicated the presence of a C_{2v} symmetry in the molecule [δ18.419, 26.070, 26.850 27.289 and 37.863 (an approximate intensity ratio of 2:4:4:8:1, methylene-C), 80.697, 82.108 and 83.863 (a ratio of 1:2:2, ring-C)]. The PMR spectrum of 11 at 400 MHz is also consistent with that expected for the pentabridged structure which should possesses ten kinds of bridge methylene protons (9x4H and 1x2H); the proton signals centered at δ1.88, 1.99, 2.08, 2.46 and 2.55 appear in a ratio of 4:8:8:10:8.

The X-ray crystal analyses of 9 and 11 were carried out in order to confirm their penta-bridged structure.[9] Intensity data for both compounds were measured at room temperature on a Philips PW-1100 by means of the θ-2θ scan technique with a scan speed of 6° min^{-1} in 2θ by using graphite monochromated Mo *K*α radiation. Crystal data and the conditions for data collection are summarized in Table 1. As seen in Table 1, both crystals are isomorphous. Due to the platy shape of the crystal and to the difficulties in obtaining better *R* factor, absorption correction by crystal shape[10] was applied for the intensity data of 9 but not for 11. The crystal structures were solved by the heavy atom method. The Laue symmetry, $4/mmm$ and the absent reflections, $h+k+l \neq 2n$ for hkl and $2h+l \neq 4n$ for hhl, indicated the space group $I\bar{4}2d$ for both crystals. It was therefore concluded that the Fe atoms are located on the diad axis parallel to *b* and the molecules possess their own symmetry 2. The refinement was carried out by the full matrix least-squares procedure for 9 and by the brock-diagonal matrix procedure for 11. In both cases, the anisotropic thermal parameters were introduced for all non hydrogen atoms but the disorders of the trimethylene chains were not taken into account. The final *R* values including anomalous dispersion effect of the Fe atom were 0.079 for 9 omitting the contribution of carbonyl oxygen, and 0.060 for 11.

Fig. 1 shows a perspective drawing of the molecule of 11 by the ORTEP program.[11] For the

Table 1. Crystal data of 9 and 11.

	9	11
formula	$C_{30}H_{36}OFe$	$C_{30}H_{38}Fe$
M.W.	468.5	454.5
crystal system	tetragonal	tetragonal
space group	$I\bar{4}2d$	$I\bar{4}2d$
a (Å)	15.106(3)	15.127(2)
c (Å)	19.069(3)	18.905(2)
Z	8	8
μ(Mo *K*α) (cm^{-1})	7.4	7.3
$\exp(-d_{min}\cdot\mu)$	0.89	0.75(mean)
$\exp(-d_{max}\cdot\mu)$	0.71	
independent reflections (>3σ)	760	1143
$2\theta_{max}$ (°)	46	54
R (%)	7.9	6.0

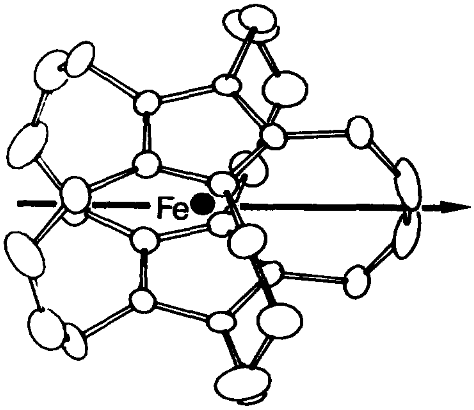


Fig. 1. ORTEP drawing of 11 (20% probability thermal ellipsoids). An arrow indicates the two fold rotation axis.

molecule of 9, there was no sign of existence of the carbonyl oxygen atoms in the electron-density map even if the refinement was attempted on the basis of space group *I*$\bar{4}$, and the ORTEP drawing was essentially the same as shown in Fig. 1. Furthermore, the five bridging methylene chains connecting the two Cp rings have very similar conformation and there seems to be almost no distinction between the tetra- and trimethylene chains. The electron-densities of these chains have a common feature that exhibits the bond distances between the second and the third carbon atoms in the tetramethylene chains are unacceptably short (∿1.40 Å). It is quite surprising to see that the crystal and molecular structures of both compounds are almost identical in spite of the difference in their chemical structures. The average difference in the atomic coordinates between the crystals of 9 and 11 is only 0.055 Å with maximum differences Δx_{max}=0.076 Å, Δy_{max}= 0.060 Å and Δz_{max}=0.107 Å. The facts strongly suggest that the both crystal structures contain such a rotational disorder about the axis of five fold symmetry through the two Cp rings of the molecules that the structures we obtained may reveal the weighted means of the bridging methylene chains consisting of 4/5 of tetramethylene and 1/5 of trimethylene chains. This kind of disorder together with the additional disorder about the two fold axis of the molecule may have the peaks of the electron-density maps for the carbonyl oxygen atom in the crystal of 9 so much obscured.

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(Received in Japan 27 January 1982)