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**Preliminary communication**

# ORGANOMETALLIC COMPOUNDS

## XXXII*. SYNTHESES OF 1,3-DISUBSTITUTED FERROCENES AND INTERMOLECULAR (1,3)FERROCENOPHANES**

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**Summary**

1,3-Diformylferrocene (VI) and its derivatives, which are precursors for the syntheses of (1,3)ferrocenophanes, have been synthesized. [2.2.2](1,3)Ferrocenophane (X) and dithia[3.3](1,3)ferrocenophanes (XI and XII) are the first examples of intermolecular (1,3)ferrocenophanes and have been synthesized by coupling of 1,3-disubstituted ferrocenes.

A number of intramolecular ferrocenophanes [3] and intermolecular (1,1′)-ferrocenophanes [4,5] have already been reported, but there has been no paper on intermolecular (1,3)ferrocenophane, an analogue of *meta*- and *para*-cyclophanes. [2.2](1,2)Ferrocenophanes described recently by Benedikt and Schlögl [6] are examples of simple cyclic dimers. The reason why no (1,3)-ferrocenophane has been synthesized arises, possibly, from the difficulty of isolating 1,3-disubstituted ferrocenes, which are precursors for (1,3)ferrocenophanes, free from contamination of other regio-isomers on a preparative scale [7], while 1,2-disubstituted ferrocenes can easily be provided by regioselective lithiation of (*N*,*N*-dimethylaminomethyl)ferrocene at the 2-position [6,8,9]. In the present communication, we report syntheses of 1,3-diformylferrocene and its derivatives***, which are important intermediary compounds for syntheses of various 1,3-disubstituted ferrocenes; also formation of intermolecular (1,3)ferrocenophanes*** by coupling of the 1,3-disubstituted derivatives is described.

*For part XXXI, see ref. 1.
**Part of the results has been reported [2].
***The determination of all new compounds described was supported by satisfactory elemental analyses and/or high-resolution mass spectroscopy.

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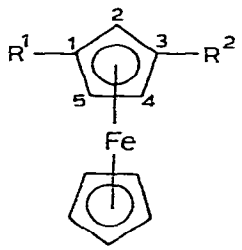
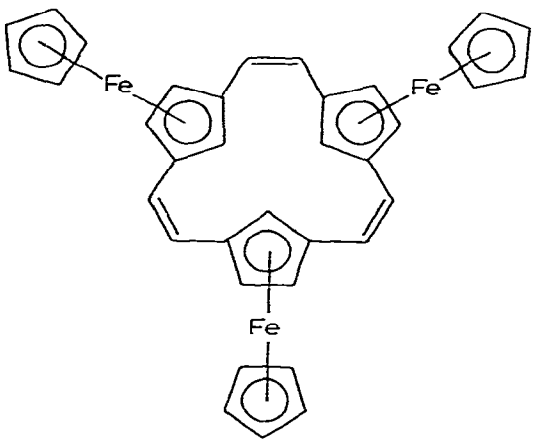
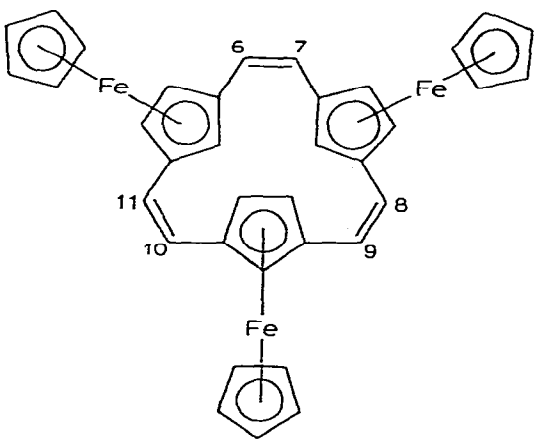


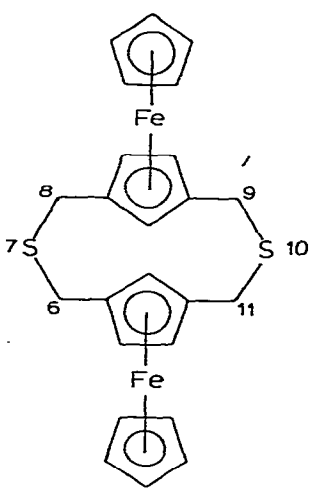

(I : $R^1 = CH_2CH_3$ , $R^2 = H$ ;
II : $R^1 = COCH_3$ , $R^2 = CH_2CH_3$ ;
III : $R^1 = R^2 = COCH_3$ ;
IV : $R^1 = R^2 = COOCH_3$ ;
V : $R^1 = R^2 = CH_2OH$ ;
VI : $R^1 = R^2 = CHO$ ;
VII : $R^1 = CHO$ , $R^2 = CH_2OH$ ;
VIII : $R^1 = R^2 = CH_2Br$ ;
IX : $R^1 = R^2 = CH_2SH$ )



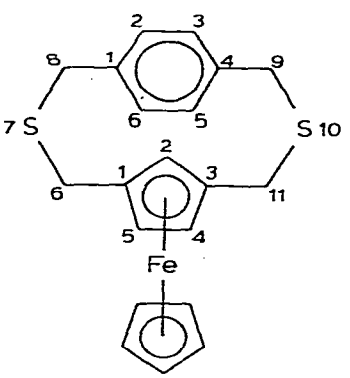

(X - S)




(X - A)




(XI)




(XII)

Acetylation products of ethylferrocene (I) with $Ac_2O$ and $BF_3 \cdot OEt_2$ [10] were chromatographed on silica gel with hexane/ether (1/1) using a long column (ca. 1 m, 40 mm diameter) yielding 1-acetyl-3-ethylferrocene (II) (30%) free from contamination with 1′- and 2-ethyl-1-acetylferrocenes. Oxidation of II with activated $MnO_2$ [7] in $CH_2Cl_2$ gave 1,3-diacetylferrocene (III) (82%, m.p. 187—188°C, lit. [11], m.p. 180—181°C). Acetylferrocene (III) was quantitatively converted into 1,3-bis(methoxycarbonyl)ferrocene (IV) (m.p. 160—161°C; mass spectrum *m/z* 302 ($M^+$); IR (KBr) 1705 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ (ppm) 3.81 (6H, s, $OCH_3$), 4.95 (2H, d, *J* 1.5 Hz, 4,5-H), 5.40 (1H, t, *J* 1.5 Hz, 2-H)) by reaction with aq. $NaOH/Cl_2$ in $C_2H_5OH/CH_2Cl_2$ (2/1) followed by treatment with $CH_2N_2$. Reduction of IV with $LiAlH_4$ gave quantitatively 1,3-bis(hydroxymethyl)ferrocene (V) (m.p. 115—117°C; mass spectrum *m/z* 246 ($M^+$); IR (KBr) 3270, 3350 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ (ppm) 4.31 (4H, s, $CH_2$)). Benzeneseleninic anhydride [12] in benzene containing a small amount of pyridine and of $MnO_2$ in benzene oxidized the diol (V) into 1,3-diformylferrocene (VI) (74% or 90%, respectively, m.p. 77—80°C; mass spectrum *m/z* 242 ($M^+$); IR (KBr) 1680 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 10.00 (2H, s, CHO)), while treatment of V with $CrO_3$/pyridine gave only a partially oxidized compound, 1-formyl-3-(hydroxymethyl)ferrocene (VII) (24%, brown oil; mass spectrum *m/z* 244 ($M^+$); IR (neat) 3400, 1660 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 4.44 (2H, s, $CH_2$), 9.95 (1H, s, CHO)).

On the other hand, the diol V was converted into 1,3-bis(bromomethyl)ferrocene (VIII) (m.p. 105°C (dec.); mass spectrum *m/z* 370, 372, 374 ($M^+$); IR (KBr) 497 $cm^{-1}$; $^1$H NMR ($CCl_4$) $\delta$ (ppm) 4.15 (4H, s, $CH_2$)) by bromination with $PBr_3$/pyridine in benzene. Reaction of the air sensitive dibromide VIII with thiourea in THF followed by hydrolysis with aq. NaOH gave 1,3-bis(mercaptomethyl)ferrocene (IX) (48% from V, yellow oil; mass spectrum *m/z* 278 ($M^+$); $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 1.75 (2H, t, *J* 7 Hz, SH), 3.48 (4H, d, *J* 7 Hz, $CH_2$)).

Reductive coupling of formylferrocene (VI) with $TiCl_3/LiAlH_4$ in diglyme or $TiCl_4/LiAlH_4$/n-$Bu_3N$ in THF [13,14] afforded a mixture of *syn* (X-S) and *anti* (X-A) isomers of a cyclic trimer, [2.2.2](1,3)ferrocenophane-6,8,10-triene (3—6%, m.p. 74—80°C; mass spectrum *m/z* 630), besides 1,2-bis(3-methylferrocenyl)ethylene and a cyclic trimer (mass spectrum *m/z* 840 ($M^+$)). As yet each isomer of the interesting macrocyclic compound X has been isolated even though column and thin-layer chromatographies were repeatedly carried out, but the structures of the two isomers were confirmed by analysis of the NMR signals of the mixture taking the symmetric character of the two molecules and signal intensities into account. (X-S: $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 4.02 (s, unsubstd. Cp-H), 6.17 (s, olefin-H); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm) 126.259 (olefin-C). X-A: $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 4.17 (s, unsubstd. Cp-H), 6.01 and 6.12 (an AB system, *J* 10 Hz, 8,9,10,11-H), 6.16 (s, 6,7-H); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm) 124.699 and 124.992 (8,9,10,11-C), 126.453 (6,7-C)).

Recently, coupling of 1,1′-bis(hydroxymethyl)ferrocenes with dithiol in the presence of trifluoroacetic acid (TFA) synthesizing macrocyclic ring derivatives was reported by Czech and Ratajczak [4f]. This reaction was applied to the synthesis of (1,3)ferrocenophanes, because attempts at the coupling of IX with VIII in the presence of KOH according to usual preparative methods for

cyclophanes gave only a small amount of 7,8,11,12-tetrathia[4.4](1,3)ferrocenophane. The reaction of the diol V with the dithiol IX in $CH_2Cl_2$ (conc. $10^{-3}$ mol/l) in the presence of trifluoroacetic acid (TFA) at room temperature for 20 h afforded 7,10-dithia[3.3](1,3)ferrocenophane (XI) (21%, m.p. 215—218°C; mass spectrum *m/z* 488 ($M^+$); $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 3.55 (8H, s, $CH_2$), 3.85 (4H, d, 4,5-H), 3.90 (10H, s, unsubstd. Cp-H), 3.93 (2H, t, 2-H); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm) 32.941 (6,8,9,11-C), 67.930 (4,5-C), 68.756 (unsubstd. Cp-C), 73.095 (2-C), 84.740 (1,3-C)). Treatment of the diol V with *p*-bis(mercaptomethyl)benzene by the same procedure gave 7,10-dithia[3]paracyclo[3](1,3)ferrocenophane(XII) (82%, m.p. 187—190°C; mass spectrum *m/z* 380 ($M^+$); $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 3.36 (4H, bs, 8,9-H), 3.62 (4H, s, 6,11-H), 4.04 (5H, s, unsubstd. Cp-H), 3.90—4.20 (3H, m, 2,4,5-H), 7.17 (4H, m, Ph-H); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm) 30.822 (8,9-C), 35.226 (6,11-H), 68.691 (4,5-C of Cp), 69.454 (unsubstd. Cp-C), 70.276 (2-C of Cp), 84.895 (1,3-C of Cp), 129.045 (2,3,5,6-C of Ph), 136.912 (1,4-C of Ph).

The (1,3)ferrocenophanes (XI and XII) which have been synthesized can be precursors for the interesting [2.2](1,3)ferrocenophanes, an analogue of [2.2]-paracyclophane. Further experiments for the synthesis of the [2.2]ferrocenophanes from XI and XII are in progress.

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