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# Synthesis of [0]Orthocyclo[2]orthocyclo[0](1,1′)ferrocenophane and [0]Paracyclo[2]paracyclo[0](1,1′)ferrocenophane

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*syn-* and *anti-*[0]Orthocyclo[2]orthocyclo[0](1,1′)ferrocenophan-7-enes were synthesized *via* an intramolecular reductive coupling of 1,1′-bis(*o*-formylphenyl)ferrocene with low valent titanium reagents. *syn-* and *anti-*[0]Orthocyclo[2]orthocyclo[0](1,1′)ferrocenophanes and [0]paracyclo[2]paracyclo[0](1,1′)ferrocenophane were prepared by the reaction of 1,1′-bis[*o*-(bromomethyl)phenyl]ferrocene and 1,1′-bis[*p*-(bromomethyl)phenyl]ferrocene with butyllithium. The transannular π-electronic interactions between two aromatic rings in these compounds were examined on the basis of the NMR and electronic spectra.

Recently a wide variety of cyclophane compounds containing benzene or heteroaromatic rings has been synthesized in order to study the effect of transannular π-electronic interactions on their physical and chemical properties.[1] Many ferrocenophanes of [*m*] (1,2)-, [*m*]-(1,1′)- or [*m.n*] (1,1′)-type are known in which one or more intramolecular bridges link homo- or heteroannular positions within one or two ferrocene moieties,[2] but there have been only a few investigations of ferrocenophanes having transannular π-electronic interactions: [2.2]ferrocenophane-1,13-diyne,[3] [2.2]ferrocenophane-1,13-diene,[4] [3.3]- and [5.5] (1,1′)ferrocenophane derivatives,[5] and [2]paracyclo[2]paracyclo[2] (1,1′)ferrocenophane derivatives.[6] Moreover, as a part of our studies on metallocenophane chemistry, we have reported the synthesis of [0]metacyclo[2]metacyclo[0](1,1′)ferrocenophan-7-ene, in which substantial repulsive interactions exist between the two aryl rings.[7] These results have encouraged us to study the synthesis of [0]orthocyclo[2]orthocyclo[0]-(1,1′)ferrocenophanes (**1**) and [0]paracyclo[2]paracyclo[0] (1,1′)ferrocenophane (**2**).

## Results and Discussion

*Synthesis.* Although a number of synthetic methods have recently been developed for [2.2]paracyclophanes,[8] a reductive coupling of carbonyl compounds with low valent titanium reagents[9] is still very convenient and advantageous for the synthesis of cyclophane compounds because of the availability of the intermediary compounds.[5—7,10] In the present work, we attempted to synthesize by the same method the unsaturated ferrocenophanes: [0]orthocyclo[2]orthocyclo[0] (1,1′)ferrocenophan-7-enes (**3s** and **3a**) and [0]-paracyclo[2]paracyclo[0] (1,1′)ferrocenophan-7-ene (**4**). In connection with the synthesis of **3s**, **3a**, and **4**, it became desirable to synthesize 1,1′-bis(*o*-formylphenyl)ferrocene (**5a**) and 1,1′-bis(*p*-formylphenyl)ferrocene (**5b**) in quantity.

The syntheses of the intermediates, **5a** and **5b**, were carried out by the Gomberg's arylation of ferrocene with diazonium salts (**6a** and **6b**) derived from methyl anthranilate and ethyl *p*-aminobenzoate, subsequent reduction with $LiAlH_4$, and oxidation with $MnO_2$ in chloroform.

The reductive coupling of **5a** to the ferrocenophanes (**3s** and **3a**) with low valent titanium reagents was carried out according to Mukaiyama's procedure ($TiCl_4$–Zn).[9a] Separation of the reaction products by silica-gel column chromatography gave 1,1′-di-*o*-tolylferrocene (**8a**), **3s**, and **3a**, and 1,1′-bis[*o*-(hydroxymethyl)phenyl]ferrocene (**7a**). On the other hand, the intramolecular reductive coupling of **5b** with $TiCl_4$–Zn for preparing the unsaturated ferrocenophane **4**, was unfortunately unsuccessful and led to the formation of reduction products: 1,1′-bis[*p*-(hydroxymethyl)phenyl]ferrocene (**7b**) and 1,1′-*p*-tolylferrocene (**8b**).

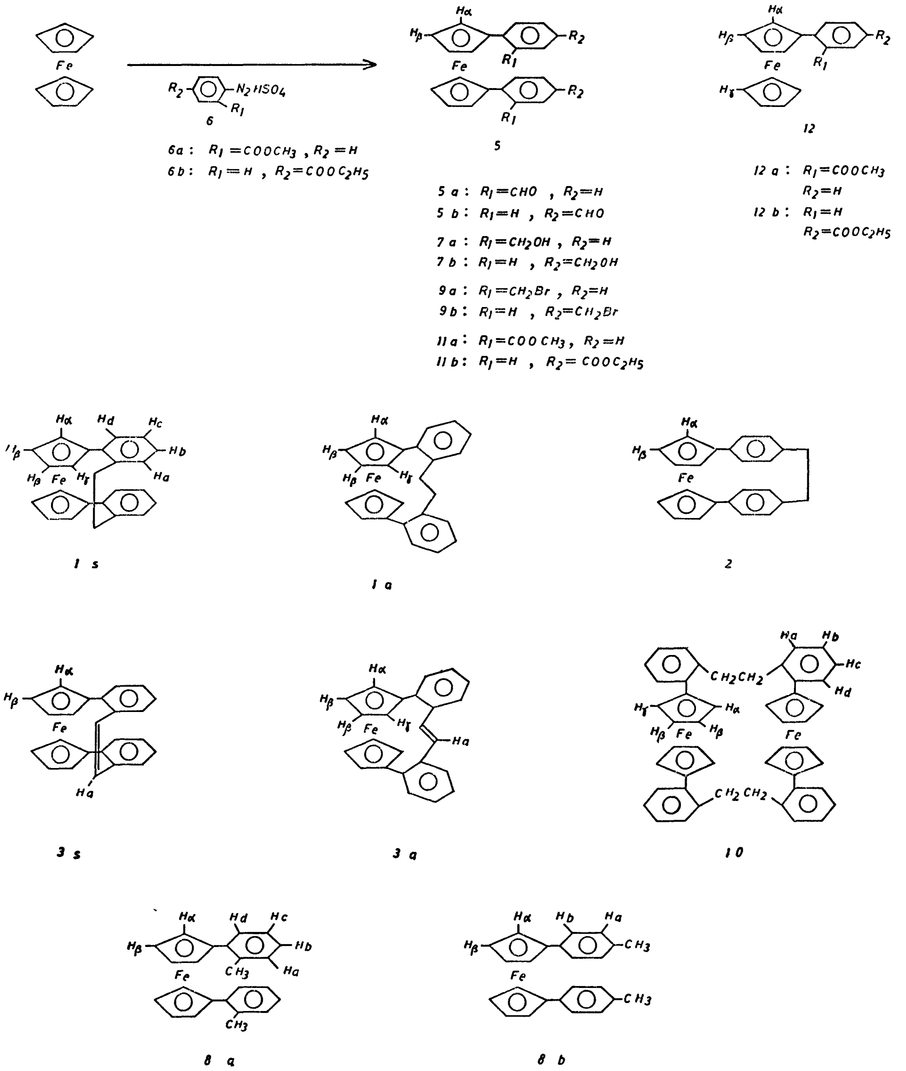
The ferrocenophanes, **3s** and **3a**, are exceedingly insoluble in common solvents and olefinic bond of the compounds is sterically hindered. Therefore, attempts to reduce catalytically to saturated ferrocenophanes, **1s** and **1a**, were made without results. Thus, the **1s** and **1a**, were prepared by the ring closure of 1,1′-bis[*o*-(bromomethyl)phenyl]ferrocene (**9a**) with butyllithium according to Trampe's procedure.[11] The separation of the reaction products by silica-gel column chromatography led to the isolation of **1s**, **1a**, and the dimer: [0]orthocyclo[2]orthocyclo[0] (1,1′)-ferroceno[0]orthocyclo[2]orthocyclo[0] (1,1′)ferrocenophane (**10**). The reaction of 1,1′-bis[*p*-(bromomethyl)-phenyl]ferrocene (**9b**) with butyllithium afforded the saturated ferrocenophane **2**.

The synthesis of the intermediates, **9a** and **9b**, were carried out by the reaction of the alcohols, **7a** and **7b**, with chlorotrimethylsilane and lithium bromide.[12]

*Structures.* The structures of the ferrocenophanes, **1s**, **1a**, **2**, **3s**, and **3a**, were determined on the basis of the IR, NMR, and mass spectra, and the elementary analyses. The NMR and IR spectra data of all ferrocenophanes and the reference compounds are summarized in Tables 1 and 2, respectively.

In the unsaturated ferrocenophanes (**3s** and **3a**), the mass spectra show the pattern containing a molecular ion peak at *m/e* 362, indicating that the two are isomeric. The configuration of olefinic bond in **3s** was confirmed to be *cis*, because the IR spectrum of **3s** exhibited a band of 730 cm$^{-1}$ which was characteristic of *cis* vinylene linkage and the characteristic C–H out of deformation modes of *trans* vinylene linkage at near 960 cm$^{-1}$ were absent. On the other hand, the configuration of olefinic bond in **3a** was confirmed to be *trans*, because the IR spectrum of **3a** exhibited a band of 960 cm$^{-1}$ which was characteristic of *trans* vinylene linkage.

In ferrocene, the distance between the two cyclo-



Scheme 1.

pentadienyl rings is 3.32 Å,[13] while the van der Waals separation between parallel π-system is 3.4 Å.[14] Thus, in **3s**, substantial repulsive interactions exist probably between the two aromatic rings which are bound together by vinylene bridges at both *ortho*-positions. In the NMR spectrum of **3s**, the aromatic protons (δ, 6.87) appear at higher fields than the corresponding protons of **3a** (δ, 7.18—7.33) and the reference compound **8a** (δ 7.13 and 7.60). This phenomenon indicates that the two benzene rings in **3s** are held face to face in close proximity by a vinylene bridge and the *syn*-conformation for **3s** can be accommodated. The aromatic proton signals of **3a** were observed at nearly the same positions as those of the reference compound **8a**. This suggests that the two benzene rins in **3a** are not held in a face to face conformation and the *anti*-conformation for **3a** can be accommodated.

In the saturated cyclophanes (**1s** and **1a**), the mass spectra also show the same pattern containing a molecular ion peak at *m/e* 364. This fact confirms that the two are isomeric, similar to the case of **3s** and **3a**. The structural difference between **1s** and **1a** is unequivocally realized in the NMR spectra. The aromatic protons of **1s** (δ, 6.58 and 7.06) exhibit an upfield shift, due to the diamagnetic shielding effect of the opposed aromatic ring, whereas the aromatic proton signals of **1a** were observed at nearly the same positions as those of the reference compound **8a**. These data are best accommodated by the *syn*-structure for **1s** and the *anti*-structure for **1a**.

In ferrocenophane **2**, the IR spectra revealed the presence of 1,1′-disubstituted ferrocene and *p*-disubstituted benzene rings. The molecule probably exists in the conformation with the phenyl rings approximately parallel to one another and approximately coplanar to the plane of the cyclopentadienyl ring. Thus, in **2**, substantial repulsive interactions must exist between the two benzene rings which are bound together by a methylene bridge at both *para*-positions. In the NMR spectra of **2**, as expected, the aromatic protons (δ, 6.62) appeared at higher fields than the corresponding protons of the reference compound, **8b** (δ, 6.98 and 7.18). This phenomenon is probably due to diamagnetic shielding effect due to opposed aromatic ring.

The electronic spectra of the ferrocenophanes (**1s**, **1a**, **2**, **3s**, **3a**, and **10**) and the reference compounds (**8a** and **8b**) are shown in Figs. 1 and 2. It is well known that the transannular electronic interactions in cyclophanes result in the bathochromic and hyperchromic shifts of absorption bands in electronic spectra.[1,8] Toluene shows no absorption in the long wavelength region above 270 nm.[15] The electronic spectra of **1s**, **3s**, and **2** showed somewhat bathochromic and hyperchromic shifts and unambiguous broadening in a range 220—300 nm, compared with those of the reference compounds, **8a** and **8b**. This may be due to transannular $\pi$-electronic interactions between the two benzene chromophores in **1s**, **3s**, and **2**; these phenomena are also explained by *syn*-structure, but not by *anti*-structure. On the other hand, in 240—300 nm region, the electronic spectra of **1a** and **3a**, are very similar to the spectra of the reference compound, **8a**. This phenomenon and the small shielding effects on aromatic protons in the NMR spectra of **1a** and **3a** indicate that the interactions between the two benzene rings in **1a** and **3a** are relatively weak and the *anti*-conformations are accommodated.

The IR, NMR, and mass spectra of the dimer **10** were all consistent with the proposed structure. The fragmentation pattern observed in the mass spectra of **10** consisted of only three predominant peaks: *m*/*e* 56, 364, and 728, corresponding to $Fe^+$, a doubly charged parent species, and a parent ion respectively. This fragmentation pattern is normally observed in [0.0]-,[16] [1.1]-,[17] [2.2]-,[3,4] and [3.3] (1,1′)ferrocenophanes.[5] The IR spectra revealed the presence of 1,1′-disubstituted ferrocene and *o*-disubstituted benzene rings. In the NMR spectrum of **10**, the aromatic proton signals were observed at nearly the same positions as those of the reference compound, **8a**. Moreover, in the 240—300 nm region of the electronic spectrum of **10**, the intensity was somewhat increased, but the shape of the spectrum was very similar to that of **8a**. These phenomena indicate that the interactions between the benzene rings in **10** are relatively weak.

The electronic spectrum of ferrocene have two main absorptions, *viz*., 325 and 440 nm. Both the position and the intensity of the 440 nm are particularly sensitive to ferrocene ring-tilt distortion.[18] In the 330—450 nm region, the intensity of the spectra of **1s**, **1a**, **3s**, **3a**, and **10** was somewhat increased, but the shape of the spectra was practically identical with that of the reference compound **8a** bearing an untilted ferrocene ring. These phenomena suggest that, due to the short length of the side chain which is bridging at the *ortho* position of the benzene ring, the planes of the cyclopentadienyl and benzene rings in these compounds have a nonplanar orientation, and accordingly the ferrocene ring tilt distortions are relatively weak. The electronic spectrum of **2** in the 330—450 nm region shows an increased intensity and a bathochromic shift to higher wavelength (475 nm), compared with that of **8b** bearing an untilted ferrocene ring. This suggests that, in **2**, a ferrocene ring-tilt distortion occurs due to the short length of the side chain which is bridging at the *para* position in benzene rings.

The IR spectra of [2.2]paracyclophane system have several obvious features.[19] One is the increase of the intensity of the band in 1530—1600 cm$^{-1}$, which is related to the increased double bond character due to the distortion of the benzene rings. The other is the appearance of a strong new maximum near the 710 cm$^{-1}$ region. Longgone and Warren[19b] reported that the strong maximum at 725 cm$^{-1}$ in [2.2]paracyclophane and at 710 cm$^{-1}$ in 4,7,12,15-tetramethyl[2.2]-paracyclophane might be a characteristic band associated with the distortion benzene ring in [2.2]paracyclophane system. Otsubo *et al*.[19c] also reported the same phenomena in the multilayered [2.2]paracyclophane system. In practice, besides the strong peak around 1600 cm$^{-1}$, the ferrocenophane **2** exhibits a strong new band around 710 cm$^{-1}$, whereas the reference compound **8b** bearing strain-free benzene rings exhibits no band in this region. This indicates that the compound **2** bears strained benzene rings due to the interactions between the two aromatic rings. On

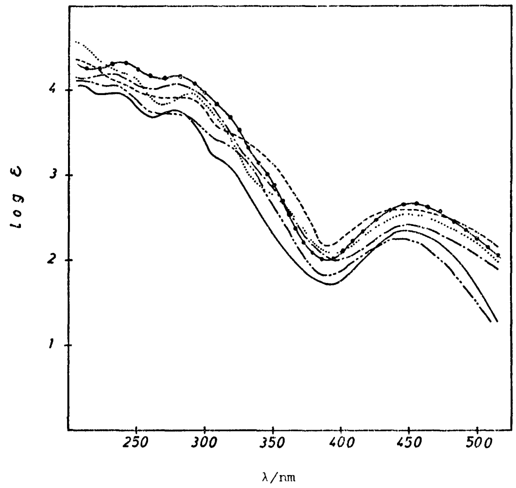


Fig. 1. Electronic spectra of **1s**, **1a**, **3s**, **3a**, **8a**, and **10** in dioxane.
······: **1s**, ——-: **1a**, ----: **3s**, ——–: **3a**, ——: **8a**, —•—•: **10**.

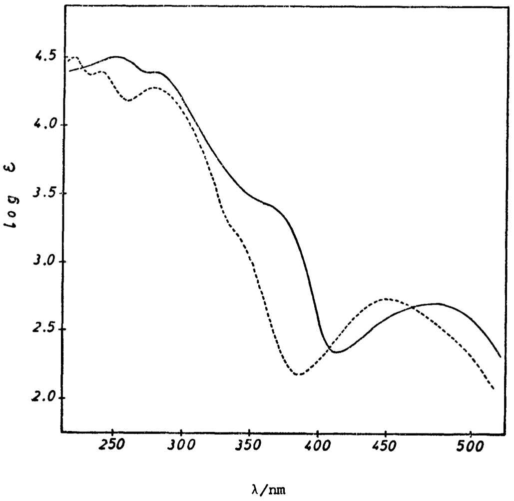


Fig. 2. Electronic spectra of **2** and **8b** in dioxane.
——: **2**, ······: **8b**.

Table 1. The $^1$H NMR spectra of the ferrocenophanes (**1s**, **1a**, **2**, **3s**, **3a**, and **10**) and the reference compounds (**8a** and **8b**) ($\delta$ from TMS, in $CDCl_3$)

| Compound | Aromatic ring protons | Ferrocene ring protons | Other protons |
|---|---|---|---|
| **1s** | 6.58 (m, 2H, $\underline{H}_a$)<br>7.06 (m, 6H, $\underline{H}_{b,c,d}$) | 4.27 (m, 4H, $\underline{H}_\beta$)<br>4.49 (m, 4H, $\underline{H}_\alpha+\underline{H}_\gamma$) | 4.15 (m, 2H, $\underline{H}_e$)<br>4.34 (m, 2H, $\underline{H}_f$) |
| **1a** | 7.20 (m, 8H) | 4.40 (m, 4H, $\underline{H}_\beta$)<br>4.51 (m, 4H, $\underline{H}_\alpha+\underline{H}_\gamma$) | 4.06—4.18 (m, 4H, $-C\underline{H}_2-$) |
| **3s** | 6.87 (m, 8H) | 4.41 (m, 8H, $\underline{H}_\alpha+\underline{H}_\beta$) | 6.98 (s, 2H, $\underline{H}_a$) |
| **3a** | 7.18—7.33 (m, 8H) | 4.31 (m, 4H, $\underline{H}_\beta$)<br>4.41 (m, 4H, $\underline{H}_\alpha+\underline{H}_\gamma$) | 7.46 (s, 2H, $\underline{H}_a$) |
| **10** | 7.08 (m, 6H, $\underline{H}_{a,b,c}$)<br>7.62 (m, 2H, $\underline{H}_d$) | 4.28 (m, 4H, $\underline{H}_\beta$)<br>4.51 (m, 4H, $\underline{H}_\alpha+\underline{H}_\gamma$) | 4.04—4.15 (m, 8H, $-C\underline{H}_2-$) |
| **8a** | 7.13 (m, 6H, $\underline{H}_{a,b,c}$)<br>7.60 (m, 2H, $\underline{H}_d$) | 4.22 (t, 4H, $\underline{H}_\beta$)<br>4.41 (t, 4H, $\underline{H}_\alpha$) | 2.31 (s, 6H, $-C\underline{H}_3$) |
| **2** | 6.62 (b-s, 8H) | 4.25 (t, 4H, $\underline{H}_\beta$)<br>4.62 (t, 4H, $\underline{H}_\alpha$) | 3.20 (s, 4H, $-C\underline{H}_2-$) |
| **8b**[23)] | 6.98 (d, 4H, $\underline{H}_a$)<br>7.18 (d, 4H, $\underline{H}_b$) | 4.17 (t, 4H, $\underline{H}_\beta$)<br>4.44 (t, 4H, $\underline{H}_\alpha$) | 2.28 (s, 6H, $-C\underline{H}_3$) |

Table 2. The IR spectra of the ferrocenophanes (**1s**, **1a**, **2**, **3s**, **3a**, and **10**) and the reference compounds (**8a** and **8b**) (KBr cm$^{-1}$)

| Compound | |
|---|---|
| **1s** | 3100, 815 (1,1′-disubstituted ferrocene ring), 1600, 1500, 760 (*o*-disubstituted benzene ring) |
| **1a** | 3100, 815 (1,1′-disubstituted ferrocene ring), 1600, 1500, 760 (*o*-disubstituted benzene ring) |
| **3s** | 3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1500, 740 (*o*-disubstituted benzene ring), 1635 730 (*cis* -CH=CH-) |
| **3a** | 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 750 (*o*-disubstituted benzene ring), 1640, 960 (*trans* -CH=CH-) |
| **10** | 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 760 (*o*-disubstituted benzene ring) |
| **8a** | 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 745 (*o*-disubstituted benzene ring) |
| **2** | 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 820 (*p*-disubstituted benzene ring), 710, 685 (distorted benzene ring) |
| **8b** | 3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1500, 825 (*p*-disubstituted benzene ring) |

the other hand, near the 700 cm$^{-1}$ region, the IR spectra of **1s**, **1a**, **3s**, **3a**, and **10** are quite similar to those of the open-chain model **8a**. This may be due to the non-distortion of benzene rings in these compounds.

## Experimental

*Measurements.* All the melting points are uncorrected. The IR, NMR, mass, and electronic spectra were recorded with Hitachi 260-10, Hitachi R-22, Hitachi RMU-6M, and Hitachi 200-10 spectrometers, respectively.

*1,1′-Bis[*o*-(methoxycarbonyl)phenyl]ferrocene (**11a**).* Methyl anthranilate (15.1 g, 0.10 mol) was diazotized in 10% sulfuric acid (300 cm$^3$) at 0—5 °C with sodium nitrite (7.1 g, 0.102 mol). After diazotization had been completed, the diazotized salt solution was added rapidly to a solution of ferrocene (7.44 g, 0.04 mol) in acetic acid (500 cm$^3$) under an atmosphere of nitrogen. The resulting dark brown solution was stirred overnight at room temperature, and was then poured into water. The reaction mixture was extracted with chloroform and the chloroform extract was washed with 5% aqueous sodium hydrogencarbonate solution, and brine, dried over anhyd $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (silica gel-benzene). First elution with benzene gave the starting material: ferrocene (1.23 g, 16.5%), mp 173 °C.

Second elution with benzene afforded 1.34 g (10.4% yield based on ferrocene) of [*o*-(methoxycarbonyl)phenyl]ferrocene (**12a**), raddish crystalls, mp 74—76 °C (lit,[20)] mp 74—75 °C). IR (KBr): 3100, 1100, 1000. 805 (monosubstituted ferrocene ring), 1720 (-COOMe), 1600, 1500, 760, 735 cm$^{-1}$ (*o*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta=3.68$ (s, 3H, $-C\underline{H}_3$), 4.02 (s, 5H, $\underline{H}_\gamma$), 4.26 (t, 2H, $\underline{H}_\beta$), 4.42 (t, 2H, $\underline{H}_\alpha$), 7.11—7.82 (m, 4H, Ar-$\underline{H}$). Found: C, 67.47; H, 4.87%; M$^+$, 320. Calcd for $C_{18}H_{16}FeO_2$: C, 67.52; H, 5.03%; M, 320.

Third elution with benzene gave 4.42 g of **11a** (23.3% yield based on ferrocene), reddish crystals, mp 92—94 °C. IR (KBr): 3100, 805 (1,1′-disubstituted ferrocene ring), 1720 (-COOMe), 1600, 1500, 760, 735 cm$^{-1}$ (*o*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta=3.69$ (s, 6H, $-C\underline{H}_3$), 4.19 (t, 4H, $\underline{H}_\beta$), 4.33 (t, 4H, $\underline{H}_\alpha$), 7.18—7.60 (m, 8H, Ar-$\underline{H}$). Found: C, 68.86; H, 4.95%; M$^+$, 454. Calcd for $C_{25}H_{22}FeO_4$: C, 68.73; H, 4.88%; M, 454.

*1,1′-Bis[*p*-(ethoxycarbonyl)phenyl]ferrocene (**11b**).* Gomberg's arylation of ferrocene with diazonium salts (**6b**) derived from ethyl *p*-aminobenzoate, was carried out in the same way as descrived for **11a**, and [*p*-(ethoxycarbonyl)-phenyl]ferrocene (**12b**, mp 87—88 °C, reddish crystals, (lit,[21)] mp 88—90 °C) and **11b** (reddish yellow crystals, mp 130—131 °C) were obtained in 14 and 26% yields, respectively.

**12b**: IR (KRr): 3100, 1100, 800 (monosubstituted ferrocene ring), 1715 (-COOEt), 1600, 820 cm$^{-1}$ (*p*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=1.33 (t, 3H, -$C\underline{H}_3$), 3.97 (s, 5H, $\underline{H}_\gamma$), 4.33 (t, 2H, $\underline{H}_\beta$), 4.37 (q, 2H, -$C\underline{H}_2$-), 4.65 (t, 2H, $\underline{H}_\alpha$), 7.44 (d, 2H, Ar-$\underline{H}$), 7.92 (d, 2H, Ar-$\underline{H}$). Found: C, 68.16; H, 5.26%; M$^+$, 334. Calcd for $C_{19}H_{18}FeO$: C, 68.28; H, 5.42%; M, 334.

**11b**: IR (KBr): 3100, 805 (1,1′-disubstituted ferrocene ring), 1720 (-COOEt), 1600, 820 cm$^{-1}$ (*p*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=1.36 (t, 6H, -$C\underline{H}_3$), 4.24 (t, 4H, $\underline{H}_\beta$), 4.37 (q, 4H, -$C\underline{H}_2$-), 4,49 (t, 4H, $\underline{H}_\alpha$), 7.22 (d, 4H, Ar-$\underline{H}$), 7.80 (d, 4H, Ar-$\underline{H}$). Found: C, 69.25; H, 5.37%; M$^+$, 482. Calcd for $C_{28}H_{26}FeO_4$: C, 69.37; H, 5.43%; M, 482.

*1,1′-Bis*[o-*(hydroxymehyl)phenyl*]*ferroccne* (***7a***). To a suspension of $LiAlH_4$ (1.41 g, 0.037 mol) in anhydrous diethyl ether (160 cm$^3$) was added dropwise a solution of **11a** (8.17 g, 0.018 mol) in dry benzene (100 cm$^3$) at room temperature during 1 h, and the reaction mixture was then heated under reflux for an additional 5 h. After the mixture had been decomposed with a small amount of cold water, the organic layer was washed successively with 5% hydrochloric acid, 5% sodium hydrogencarbonate solution, and brine, and dried over anhyd $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (chloroform) to afford **7a** as reddish yellow crystals, which were recrystallized from ethanol, mp 103—104 °C (6.73 g, 94% yield). IR (KBr): 3300, 1020 (-OH), 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 750 cm$^{-1}$ (*o*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=2.20 (br-s, 2H, -$O\underline{H}$), 4.24 (m, 4H, $\underline{H}_\beta$), 4.36 (m, 4H, $\underline{H}_\alpha$), 4.56 (s, 4H, -$C\underline{H}_2$-), 7.13—7.35 (m, 8H, Ar-$\underline{H}$). Found: C, 72.49; H, 5.67%; M$^+$, 398. Calcd for $C_{24}H_{22}FeO_2$: C, 72.37; H, 5.56%, M, 398.

*1,1′-Bis*[p-*(hydroxymethyl)phenyl*]*ferrocene* (***7b***). A reduction of **11b** with $LiAlH_4$ was carried out in the same way as described above, and **7b** (reddish crystals mp 210—212 °C) was obtained in 89% yield. IR (KBr): 3200 (-OH), 3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1500, 820 cm$^{-1}$ (*p*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=4.12 (t, 4H, $\underline{H}_\beta$), 4.47 (m, 8H, $\underline{H}_\alpha$+-$C\underline{H}_2$-), 5.07 (br-s, 2H, -$O\underline{H}$), 7.11 (d, 4H, Ar-$\underline{H}$), 7.26 (d, 4H, Ar-$\underline{H}$). Found: C, 72.31; H, 5.48%; M$^+$, 398. Calcd for $C_{21}H_{22}FeO_2$: C, 72.37; H, 5.56%; M, 398.

*1,1′-Bis(*o-*formylphenyl)ferrocene* (***5a***). At room temperature, active manganese(IV) oxide (100 g) was added to a solution of **7a** (6.76 g, 0.017 mol) in chloroform (200 ml) and the mixture was stirred in the dark for 12 h. After filtration to remove $MnO_2$, the reddish chloroform solution was evaporated to dryness and the residue was chromatographed by elution of benzene on silica gel to afford reddish crystals **5a** (5.88 g, 87% yield), mp 124—125 °C. IR (KBr): 2820, 1680 (-CHO), 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 740 cm$^{-1}$ (*o*-disusfituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=4.38 (m, 4H, $\underline{H}_\beta$), 4.47 (m, 4H, $\underline{H}_\alpha$), 7.33—7.85 (m, 8H, Ar-$\underline{H}$), 10.31 (s, 2H, -$C\underline{H}O$). Found: C, 73.27; H, 4.73%; M$^+$, 384. Calcd for $C_{24}H_{18}FeO_2$: C, 73.11; H, 4.60%; M, 384.

*1,1′-Bis(*p-*formylphenyl)ferrocene* (***5b***). An oxidation of **7b** with active manganese(IV) oxide was carried out in the same way as described above, and reddish crystal **5b** (mp 220—221 °C) were obtained in 54% yield. IR (KBr): 2820, 1695, (-CHO), 3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1500, 820 cm$^{-1}$ (*p*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=4.33 (m, 4H, $\underline{H}_\beta$), 4.58 (m, 4H, $\underline{H}_\alpha$), 7.28 (d, 4H, Ar-$\underline{H}$), 7.61 (d, 4H, Ar-$\underline{H}$), 9.92 (s, 2H, -$C\underline{H}O$). Found: C, 73.02; H, 4.45%; M$^+$, 384. Calcd for $C_{24}H_{18}FeO_2$: C, 73.11; H, 4.60%; M, 384.

*1,1-Bis*[o-*(bromomethyl)phenyl*]*ferrocene* (***9a***). Under an atmosphere of nitrogen, chlorotrimethylsilane (5.43 g, 0.05 mol) was added to a solution of anhyd lithium bromide (3.48 g, 0.04 mol) in dry acetonitrile (50 cm$^3$) with stirring at room temperature. The alcohol **7a** (3.62 g, 0.01 mol) was then added and the reaction mixture was heated under reflux for 12 h. After cooling, the mixture was extracted with diethyl ether (300 cm$^3$), and the extract was washed successively with water, 5% sodium hydrogencarbonate solution, and brine, and dried over anhyd $MgSO_4$ Removal of the solvents and subsequent recrystallization from benzene-hexane afforded orange crystals **9a** (2.10 g, 40% yield), mp 150—152 °C. IR (KBr): 3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 760 cm$^{-1}$ (*o*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$=4.27 (m, 4H, $\underline{H}_\beta$), 4.34 (s, 4H, -$C\underline{H}_2$-), 4.51 (m, 4H, $\underline{H}_\alpha$), 7.11—7.64 (m, 8H, Ar-$\underline{H}$). Found: C, 54.87; H, 3.73%. MS: 364 (M$^+$ −2Br), 444 (M$^+$ −Br), 524 (M$^+$). Calcd for $C_{24}H_{20}Br_2Fe$: C, 55.00; H, 3.48%; M, 524.

*1,1′-Bis*[p-*(bromomcthyl)phenyl*]*ferrocene* (***9b***). The reaction of the alcohol **7b** with $Me_3SiCl$-LiBr in acetonitrile was carried out in the same way as described above, and the reaction product **7b** was purified by column chromatography on silica gel using benzene as eluent in 43% yield, reddish crystals, mp 136—138 °C (decomp). IR (KBr): 3100, 805 (1,1′-disubstiuted ferrocene ring), 1600, 1500, 825 cm$^{-1}$ (*p*-disubstituted benzene ring). $^1$H NMR ($CDCl_3$): $\delta$ =4.23 (t, 4H, $\underline{H}_\beta$), 4.48 (m, 8H, $\underline{H}_\alpha$+-$C\underline{H}_2$-), 7.17 (br-s, 8H, Ar-$\underline{H}$). Found: C, 54.87; H, 3.33%. MS: 364 (M$^+$ −2Br), 444 (M$^+$−Br), 524 (M$^+$). Calcd for $C_{24}H_{20}Br_2Fe$: C, 55.00; H, 3.48%; M, 524.

*The Intramorecular Reductive Coupling of* ***5a*** *with* $TiCl_4$*-Zn.* Under an atomosphere of nitrogen, zinc dust (7.8 g, 0.12 mol) was added in small portions to a stirred solution of $TiCl_4$ (11,3 g, 0.06 mol) in dry THF (180 cm$^3$) at 0—5 °C. After the mixture was refluxed for 2 h, a solution of **5a** (4.72 g, 0.012 mol) and dry pyridine (0.90 g) in dry THF (600 cm$^3$) was added over 21 h under refluxing, followed by an additional 10 h period of reflux and quenched by addition of 200 cm$^3$ of saturated $K_2CO_3$ solution. The mixture was stirred for 0.5 h, diluted with chloroform, and filtered through Celite. The chloroform layers were washed with brine and dried over anhyd $MgSO_4$. After removal of the solvents, the residue was dissolved in hexane and chromatographed on silica gel.

The first fraction, eluted with hexane and followed by evaporation and recrystallization from ethanol, gave yellow orange crystals (0.10 g, 2.3% yield). These were identified as 1,1′-*o*-tolylferrocene (**8a**, mp 67—68 °C), by a comparison of the IR, NMR, and mass spectra and by a mixed-melting-point determination with the authentic sample, which was prepared by Gomberg's reaction of ferrocene with diazonium salts derived from *o*-toluidine.22) Found: C, 78.55; H, 5.04%; M$^+$, 366. Calcd for $C_{24}H_{22}Fe$: C, 78.69; H, 6.05%; M, 366.

The second fraction, eluted with hexane-benzene (1:1) and followed by evaporation and recrystallization from ethanol, gave reddish crystals (0.62 g, 14.3% yield), mp 181—182 °C, which were determined to be *syn*-[0]orthocyclo[2]-orthocyclo[0](1,1′)ferrocenophan-7-ene (**3s**). Found: C, 79.65; H, 5,11%; M$^+$, 362. Calcd for $C_{24}H_{18}Fe$: C, 79.57; H, 5.03%; M, 362.

The third fraction, eluted with benzene and followed by evaporation and recrystallization from benzene-hexane gave yellowish red crystals (5.23 g, 5.3% yield), mp 230—231 °C, which were determined to be *anti*-[0]orthocyclo[2]orthocyclo-[0](1,1′)ferrocenophan-7-ene (**3a**). Found: C, 79.51; H, 5.08%; M$^+$, 362. Calcd for $C_{24}H_{18}Fe$: C, 79.57; H, 5.03%;

M, 362.

The fourth fraction, eluted with chloroform and followed by evaporation and recrystallization from ethanol gave reddish yellow crystals (0.79 g, 16.5% yield), mp 103—104 °C, which were identified as 1,1′-bis[*o*-(hydroxymethyl)phenyl]ferrocene (**7a**) by a comparison of the IR and NMR spectra and by a mixed-melting-point determination with **7a**.

*The Reaction of **5b** with $TiCl_4$-Zn.* The reaction of **5b** with $TiCl_4$-Zn was carried out in the same way as described above, and 1,1′-di-*p*-tolylferrocene [**8b**, reddish crystals, mp 167—169 °C (lit,[23] mp 168—169 °C)] and 1,1′-bis[*p*-(hydroxymethyl)phenyl]ferrocene (**7b**), mp 103—104 °C, were obtained in 47 and 24% yields, respectively.

*The Intramolecular Coupling of **9a** with Butyllithium.* Under an atmosphere of nitrogen, a 15% solution of butyllithium in hexane (8 $cm^3$) was added dropwise to a solution of **9a** (2.41 g, 0.0046 mol) in dry THF (320 $cm^3$) at −50 °C, followed by stirring at the same temperature for 2 h and then at 0 °C for 2 h. After a successive addition of water (20 $cm^3$) and 1 M hydrochloric acid (40 $cm^3$), the mixture was extracted with chloroform. The chloroform extracts were washed successively with 1 M hydrochloric acid, brine, 5% sodium hydrogencarbonate solution, and brine, and dried over anhyd $MgSO_4$. After removal of the solvents, the residue was dissolved in benzene-hexane (1:1) and chromatographed on silica gel.

The first fraction, eluted with benzene-hexane (1:1) and followed by evaporation and recrystallization from benzene-hexane, gave reddish crystalls (0.10 g, 6% yield), mp 164—165°C, which were determined to be *syn*-[0]orthocyclo[2]-orthocyclo[0](1,1′)ferrocenophane (**1s**). Found: C, 79.01; H, 5.39%; $M^+$, 364. Calcd for $C_{24}H_{20}Fe$: C, 79.13; H, 5.53%, M, 364.

The second fraction, eluted with benzene-hexane (1:1) and followed by evaporation and recrystallization from ethanol afforded reddish crystals (0.10 g, 6% yield), mp 182—183 °C, which were determined to be *anti*-[0]orthocyclo[2]-[2]orthocyclo[0](1,1′)ferrocenophane (**1a**). Found: C, 78.96; H, 5.41%; $M^+$, 364. Calcd for $C_{24}H_{20}Fe$: C, 79.13; H, 5.53%; M, 364.

The third fraction, eluted with benzene-hexane (1:1) and followed by evaporation and recrystallization from ethanol gave yellow orange crystals (0.70 g, 42% yield), mp 245—247 °C (decomp), which were determined to be [0]orthocyclo [2] orthocyclo [0] (1, 1′) ferroceno [0] orthocyclo [2] orthocyclo[0](1,1′)ferrocenophane (**10**). Found: C, 78.91; H, 5.44%. MS: 56 ($Fe^+$), 364 ($M^+/2$), 728 ($M^+$). Calcd for $C_{48}H_{40}Fe_2$: C, 79.13; H, 5.53%; M, 728.

*[0]Paracyclo[2]paracyclo[0](1,1′)ferrocenophane (2).* The intramolecular coupling of **9b** with butyllithium was carried out in the same way as described above, and the ferrocenophane **2** was separated by column chromatography on silica gel using benzene as eluent, followed by recrystallization from benzene (yield 20%), mp 230 °C (decomp), reddish crystals. Found: C, 78.98; H, 5.44%; $M^+$, 364. Calcd for $C_{24}H_{20}Fe$: C, 79.13; H, 5.53%; M, 364.

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