April, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 1143—1148 (1983) 1143

The Synthesis and Studies of Several [2.2.2]Ferrocenophane Derivatives[1)]

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(Received September 7, 1982)

Several ferrocenophanes, in which the two cyclopentadienyl rings are linked by acetylenic and olefinic bonds and aromatic rings, have been synthesized *via* the titanium-induced reductive coupling of the corresponding formyl compounds. The structures of these ferrocenophane compounds were determined by means of their IR and NMR spectra. The transannular π-electronic interactions between the two chromophores were examined on the basis of the electronic spectra.

Because of the topology and the mostly rigid molecular structure, a large number of layered compounds have been synthesized and their physical and chemical properties studied.[2)] Many ferrocenophanes of [*m*](1,1′)- or [*m.n*](1,1′)-type are known in which one or more intramolecular bridges link heteroannular positions with one or more ferrocene moieties; however, there have been only a few investigations of ferrocenophanes with interactions between the bridging elements. Tanner and Wennerstrom[3)] have recently reported the synthesis of [2.2.2.2]ferrocenophanetetraenes. Moreover, as a part of our studies of metallocenophane chemistry, we ourselves have reported the synthesis of [0]metacyclo[2]metacyclo[0](1,1′)ferrocenophan-7-ene,[4)] in which substantial repulsive interactions exist between the two aromatic rings. These results have prompted us to study the synthesis of [2.2.2]ferrocenophane derivatives (**1**—**4**), in which the ferrocene moiety is linked by acetylenic and olefinic bonds and aromatic rings.

Results and Discussion

Although a number of synthetic methods have recently been developed for [2.2]cyclophane,[2)] the reductive coupling of carbonyl compounds with low-valent titanium reagents[5)] is still very convenient and advantageous for the synthesis of cyclophane because of the availability of the intermediary compounds.[3,4,6)]

In the present work, we applied the same method for the synthesis of [2.2.2]ferrocenophane derivatives; [2]paracyclo[2]paracyclo[2](1,1′)ferrocenophan-9-ene-1,17-diyne (**1**),[7)] [2]metacyclo[2]metacyclo[2](1,1′)ferrocenophan-9-ene-1,17-diyne (**2**), [2]orthocyclo[2]orthocyclo[2](1,1′)ferrocenophan-9-ene-1,17-diyne (**3**), and [2]paracyclo[2]paracyclo[2](1,1′)ferrocenophane-1,9,17 triene (**4**) were synthesized *via* the titanium-induced coupling of dialdehyde (**5a**—**d**). The syntheses of the intermediate dialdehydes; 1,1′-bis(*p*-formylphenylethynyl)ferrocene (**5a**), 1,1′-bis(*m*-formylphenylethynyl)ferrocene (**5b**), and 1,1′-bis(*o*-formylphenylethynyl)ferrocene (**5c**) were carried out by means of the palladium-catalyzed substitution[8)] of 1,1′-diiodoferrocene (**6**) with acetylenic compounds (**7a**—**c**), whereas another dialdehyde, 1,1′-bis(*p*-formylstyryl)ferrocene (**5d**), was prepared by the palladium-catalyzed substitution[9)] of **6** with *p*-formylstyrene (**7d**).

The reductive coupling reactions of dialdehyde (**5a**—**d**) with low-valent titanium reagents ($TiCl_4$–Zn[5a)] or $TiCl_3$–$LiAlH_4$[5b)]) using a high-dilution method led to the formation of ferrocenophanes (**1**—**4**), accompanied by the formation of the reduction products of **5a**—**d**. The structures of ferrocenophanes (**1**—**4**) were determined on the basis of the IR, NMR, and mass spectra and the elementary analyses.

The IR spectrum of **1** reveals the presence of triple and *cis* olefinic bonds, and the NMR spectrum includes the proposed structure. In the NMR spectrum of **1**, it is noteworthy that the vinylene protons (H_c), which can be easily assigned by means of their relative intensities, appear at a lower field than the aromatic protons, by analogy with the case of [2.2.2](1,3,5)cyclophane-1,9,17-triene (vinylene protons $\delta=7.37$ ppm).[10)] In ferrocene, the distance between the two cyclopentadienyl rings is 3.32 Å.[11)] On the other hand, in **1** the molecule probably exists in the conformation illustrated by Structure 1, with the phenylethynyls approximately parallel to one another and approximately coplanar to the plane of the cyclopentadienyl ring. Thus, in **1**, substantial repulsive interactions must exist between the two phenylethynyl groups, which are bound together by a vinylene bridge at both ends. In the NMR spectrum of **1**, as expected, the aromatic protons ($\delta=6.47$ and 6.82) appear at higher fields than the corresponding protons of the reference compounds, 1,1′-bis(*p*-tolylethynyl)ferrocene (**8a**) ($\delta=7.10$ and 7.38). This phenomenon indicates that the two benzene rings in **1** are held face-to-face in close proximity by the vinylene bridge.

The NMR spectrum of **2** is also consistent with the proposed structure, and the stepped (*anti*) conformation is suggested by the large upfield shift ($\Delta\delta$, 0.59—0.76) for inner aryl protons (H_a) and the downfield shift of the outer aryl protons (H_b, H_c, and H_d) ($-\Delta\delta$, 0.08—0.13), compared with the corresponding signals of the reference compound, 1,1′-bis(*m*-tolylethynyl)ferrocene (**8b**).

On the other hand, in the NMR spectrum of **3**, the aromatic proton signals are observed at nearly the same positions as those of the reference compound, 1,1′-bis(*o*-tolylethynyl)ferrocene (**8c**). This suggests that the two aromatic rings in **3** are not held in a face-to-face conformation and that the *anti*-conformation for **3** is accommodated.

In the IR spectrum, Compound **4** showed the presence of *trans* and *cis* vinylene groups at 950 and 730 cm^{-1} respectively. Moreover, the NMR spectrum of **4** indicated the presence of the signals of two A_2X_2 patterns due to *p*-disubstituted aromatic ($J=8$ Hz) and

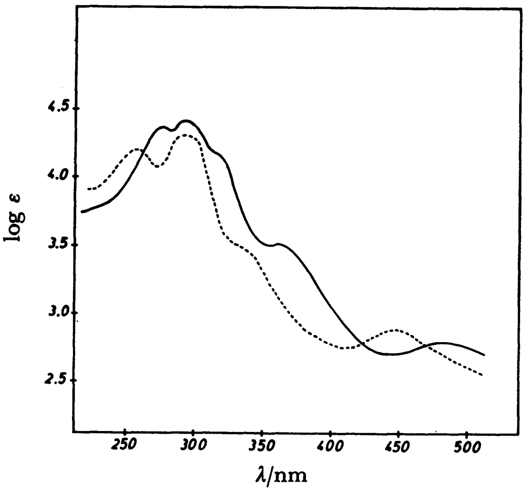


Fig. 1. Electronic spectra of **1** and **8a** in dioxane.
——: **1**, ------: **8a**.

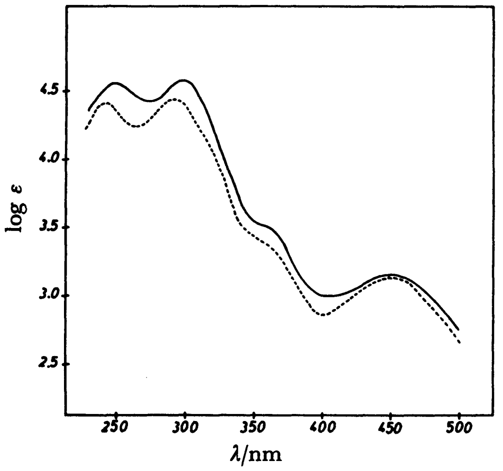


Fig. 2. Electronic spectra of **2** and **8b** in dioxane.
——: **2**, ------: **8b**.

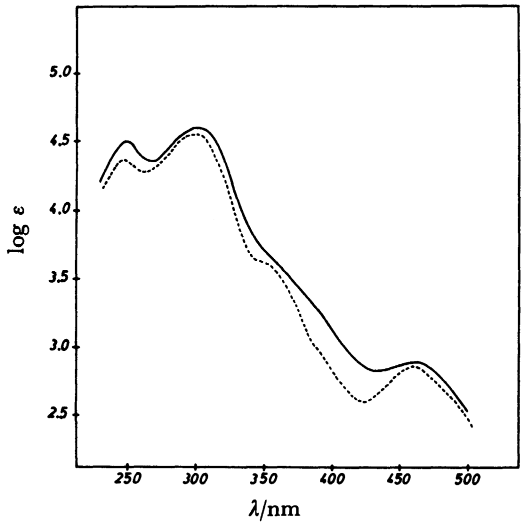


Fig. 3. Electronic spectra of **3** and **8c** in dioxane.
——: **3**, ------: **8c**.

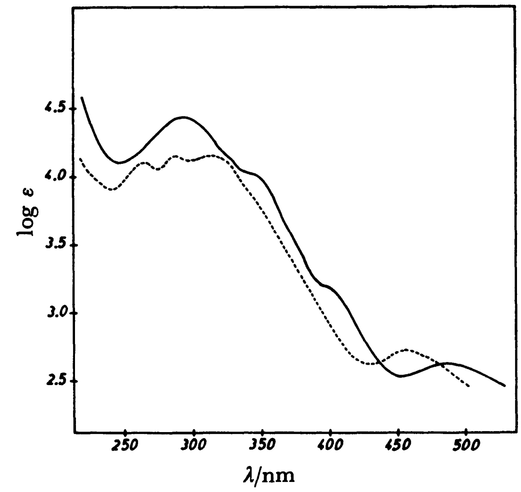


Fig. 4. Electronic spectra of **4** and **8d** in dioxane.
——: **4**, ------: **8d**.

trans vinylene protons (J=16 Hz), in addition to those attributable to 1,1′-disubstituted ferrocene and *cis* vinylene protons. These data are best explained by the parallel stacked configuration (**4**) rather than by the cross-stacked one (**4a**). The protons of aromatic and olefinic groups in **4** are shifted upfield by about 0.5 ppm compared with those of the reference compound, 1,1′-bis(*p*-methylstyryl)ferrocene (**8d**). This phenomenon may be caused by the diamagnetic shielding effect due to an overlapping of the two styryl groups.

The electronic spectra data of the cyclophane (**1**—**4**) and the reference compounds (**8a**—**d**) are summarized in Figs. 1—4. It is well known that the transannular electronic interaction in cyclophane results in the bathochromic and hyperchromic shifts of the absorption bands in its electronic spectrum and that the magnitude of these shifts can simply be utilized as a measure of the interaction.2) Both phenylacetylene12) and styrene13) show no absorption in the long-wavelength region above 300 nm. The electronic spectra of **1**, **2**, and **4** show somewhat bathochromic and hyperchromic shifts and an unambiguous broadening in the range of 230—310 nm, especially as compared with those of the reference compounds, **8a**, **8b**, and **8d** respectively. This may be due to transannular π-electronic interactions between the two chromophores in **1**, **2**, and **4**. On the other hand, Compound **3** exhibits some hyperchromic shift in the 230—310 nm region; however the spectra are practically identical with those of the reference compound, **8c**. This indicates that the interaction between the two chromophores in **3** is relatively weak and that the *anti*-conformation for **3** is also accommodated.

On the other hand, the electronic spectrum of ferrocene has two main absorptions, 325 and 440 nm. In the case of the ring-tilted ferrocenophane, it has been found that the 440-nm band undergoes a bathochromic shift with a marked increase in intensity.14) In the electronic spectra of **1** and **4**, the 440-nm band undergoes a bathochromic shift and increases in intensity, compared with those of **8a** and **8d** bearing a no-tilt ferrocene ring. This may be caused by a ferrocene ring-tilt distortion due to an interaction between the two phenylethynyl or styryl groups in **1** or **4**.

In Compounds **2** and **3**, the electronic spectra in the

Table 1. NMR spectra of the cyclophane and reference compounds

Compound	δ, in $CDCl_3$		
	Aromatic-ring protons	Ferrocene-ring protons	Other protons
1	6.47 (d, J=8 Hz, 4H, $\underline{H}_a$) 6.82 (d, J=8 Hz, 4H, $\underline{H}_b$)	4.24 (t, 4H, $\underline{H}_\beta$) 4.47 (t, 4H, $\underline{H}_\alpha$)	7.18 (s, 2H, $\underline{H}_c$)
8a	7.10 (d, J=8 Hz, 4H, $\underline{H}_a$) 7.38 (d, J=8 Hz, 4H, $\underline{H}_b$)	4.30 (t, 4H, $\underline{H}_\beta$) 4.52 (t, 4H, $\underline{H}_\alpha$)	2.31 (s, 6H, –C$\underline{H}_3$)
2	6.44 (s, 2H, $\underline{H}_a$) 7.11—7.33 (m, 6H, $\underline{H}_b + \underline{H}_c + \underline{H}_d$)	4.29 (t, 4H, $\underline{H}_\beta$) 4.44 (t, 4H, $\underline{H}_\alpha$)	8.18 (s, 2H, –C$\underline{H}$=C$\underline{H}$–)
8b	7.03—7.20 (m, 8H, Ar–$\underline{H}$)	4.27 (t, 4H, $\underline{H}_\beta$) 4.49 (t, 4H, $\underline{H}_\alpha$)	2.22 (s, 6H, –C$\underline{H}_3$)
3	6.98—7.28 (m, 8H, Ar–$\underline{H}$)	4.22 (m, 4H, $\underline{H}_\beta$) 4.51 (m, 4H, $\underline{H}_\alpha$)	7.31 (s, 2H, –C$\underline{H}$=C$\underline{H}$–)
8c	7.01—7.33 (m, 8H, Ar–$\underline{H}$)	4.29 (t, 4H, $\underline{H}_\beta$) 4.49 (t, 4H, $\underline{H}_\alpha$)	2.40 (s, 6H, –C$\underline{H}_3$)
4	6.49 (d, J=8 Hz, 4H, $\underline{H}_e$) 6.71 (d, J=8 Hz, 4H, $\underline{H}_d$)	4.24 (t, 4H, $\underline{H}_\beta$) 4.42 (t, 4H, $\underline{H}_\alpha$)	5.98 (d, J=16 Hz, 2H, $\underline{H}_a$) 6.29 (d, J=16 Hz, 2H, $\underline{H}_b$) 7.17 (s, 2H, $\underline{H}_c$)
8d	7.06 (d, J=8 Hz, 4H, $\underline{H}_d$) 7.18 (d, J=8 Hz, 4H, $\underline{H}_c$)	4.24 (t, 4H, $\underline{H}_\beta$) 4.39 (t, 4H, $\underline{H}_\alpha$)	2.30 (s, 6H, –C$\underline{H}_3$) 6.67 (b-s, 4H, $\underline{H}_a + \underline{H}_b$)

Table 2. IR spectra of the cyclophane and reference compounds

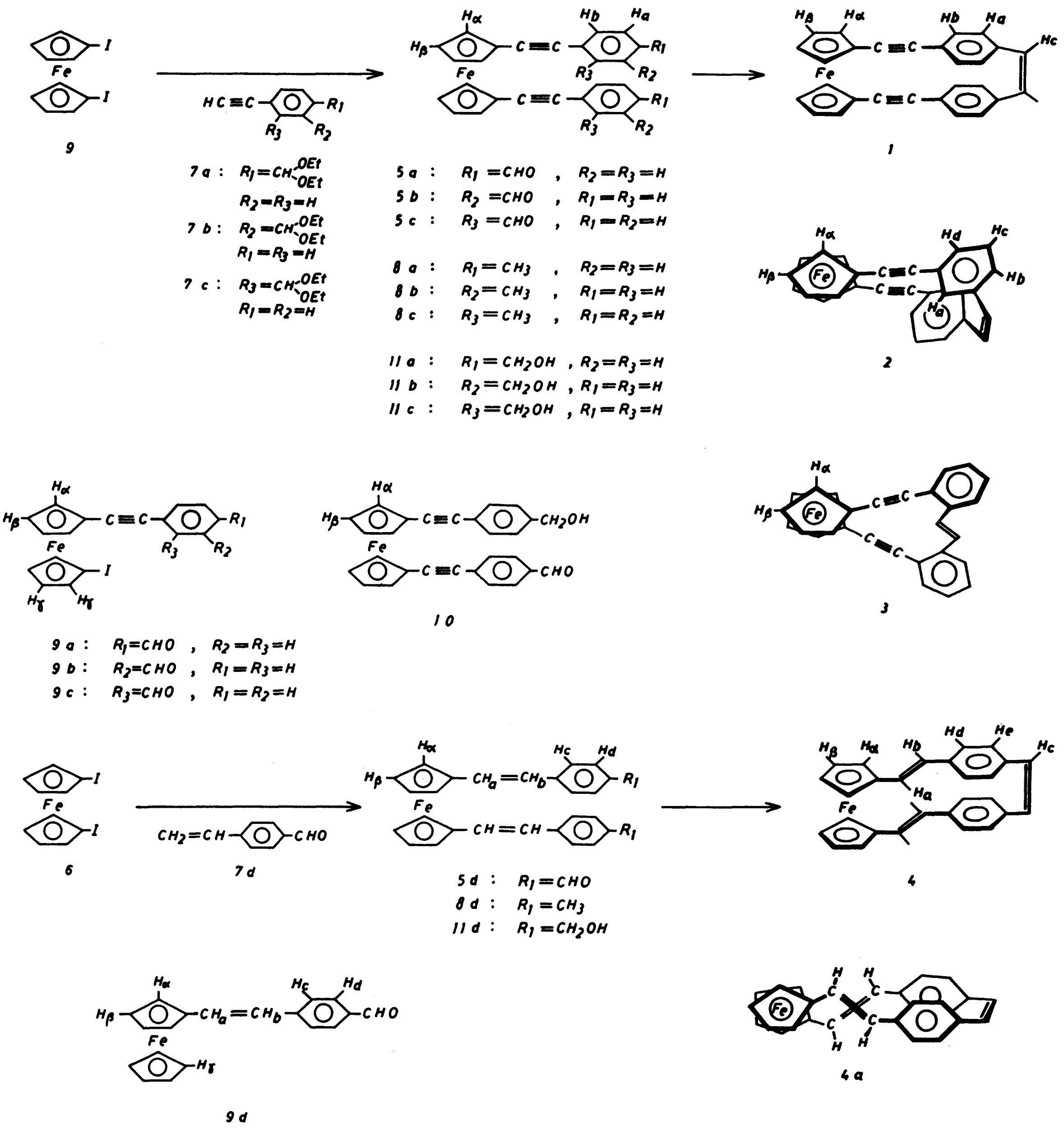
Compound	KBr, $\tilde{\nu}$/cm^{-1}
1	3100, 1400, 810 (1,1′-disubstituted ferrocene ring), 2200 (–C≡C–), 730 (*cis* –CH=CH–), 1600, 1580, 820 (*p*-disubstituted benzene ring), 710, and 690 (distorted benzene ring)
8a	3100, 1410, 805 (1,1′-disubstituted ferrocene ring), 2200 (–C≡C–), 1600, 1580, 1500, and 820 (*p*-disubstituted benzene ring)
2	3100, 1410, 810 (1,1′-disubstituted ferrocene ring), 2200 (–C≡C–), 1630, 720 (*cis* –CH=CH–), 1600, 1580, 1500, 845, and 765 (*m*-disubstituted benzene ring)
8b	3100, 1410, 810 (1,1′-disubstituted ferrocene ring), 2200 (–C≡C–), 1600, 1500, 850, and 770 (*m*-disubstituted benzene ring)
3	3100, 1410, 810 (1,1′-disubstituted ferrocene ring), 2200 (–C≡C–), 1640, 960 (*trans* –CH=CH–), 1600, 1500, and 740 (*o*-disubstituted benzene ring)
8c	3100, 1410, 810 (1,1′-disubstituted ferrocene ring), 2200 (–C≡C–), 1600, 1500, and 740 (*o*-disubstituted benzene ring)
4	3100, 1400, 805 (1,1′-disubstituted ferrocene ring), 1630, 950, (*trans* –CH=CH–), 730 (*cis* –CH=CH–), 1600, 1580, 1500, 820 (*p*-disubstituted benzene ring), 710, and 685 (distorted benzene ring)
8d	3100, 1400, 810 (1,1′disubstituted ferrocene ring), 1640, 960 (*trans* –CH=CH–), 1600, 1580, and 820 (*p*-disubstituted benzene ring)

330—450 nm region are closely similar to those of the reference compounds bearing a no-tilt ferrocene ring, **8b** and **8c**. This indicates that no ferrocene-ring distortion occurs in **2** and **3**.

The IR spectra of [2.2]paracyclophane system are known to reveal obvious features. One is the increase in the intensity of the band in the 1580—1600 cm^{-1} region, which is related to the increased double-bond character due to the distortion of the benzene rings.[15)] The other is the appearance of a strong new maximum in the 710-cm^{-1} region. Longone and Warren[15b)] reported that the strong maxima at 725 cm^{-1} in [2.2]-paracyclophane and at 710 cm^{-1} in 4,7,12,15-tetramethyl[2.2]paracyclophane might be characteristic bands associated with the distorted benzene ring in the [2.2]-paracyclophane system. Otsubo *et al.*[15c)] reported the same phenomenon in the multilayered [2.2]paracyclophane system. Besides the strong peak around 1600 cm^{-1}, the ferrocenophanes, **1** and **4**, exhibit the characteristic strong new band around 710 cm^{-1}, whereas the reference compounds bearing strain-free benzene rings, **8a** and **8d**, exhibit no band in this region. This phenomenon may be due to the distortion of the benzene rings in **1** and **4**. On the other hand, near 710 cm^{-1}, the IR spectra of **2** and **3** are closely similar to those of the open-chain models, **8b** and **8c**. This may be due to the lack of distortion of the benzene rings in **2** and **3**. (see Table 2).

Experimental

Materials and Measurements. All the melting points are uncorrected. The 1,1′-diiodoferrocene (**6**),[16)] *p*- (**7a**)[17)] and *o*-ethynylbenzaldehyde diethyl acetal (**7c**),[18)] and *p*-formylstyrene (**7c**)[19)] were prepared as has been described in the literature. The *m*-ethynylbenzaldehyde diethyl acetal (**7b**) was prepared from (*m*-bromophenylethynyl)trimethylsilane[20)]



Scheme 1.

by a modification of the method in the literature.[17] 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(p-formylphenylethynyl)ferrocene (5a). A mixture of **6** (4.37 g, 0.01 mol), **7a** (5.71 g, 0.28 mol), copper(I) iodide (0.19 g, 0.001 mol), dichlorobis(triphenylphosphine)palladium (II) (0.70 g, 0.001 mol), and diethylamine (80 cm³) was heated under nitrogen in an autoclave at 80 °C for 8 h. After the removal of the diethylamine under reduced pressure, chloroform and water were added to the residue. The chloroform layer was separated and washed thoroughly with 10% hydrochloric acid to hydrolyze the acetal to aldehyde. The resulting chloroform layer was washed with a saturated sodium hydrogen carbonate solution and a saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by silica-gel column chromatography.

The first fraction, eluted with hexane–benzene (1 : 1), gave 1-(*p*-formylphenylethynyl)-1′-iodoferrocene (**9a**) as reddish crystals (mp 139—141 °C) in a 45% yield based on **6** (1.98 g): IR (KBr): 2200 (–C≡C–), 1700 (–CHO), 1600, 1580, 820 (*p*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (CDCl$_3$): $\delta=4.22$ (m, 6H, $\underline{H}_\beta+\underline{H}_\gamma$), 4.51 (m, 2H, $\underline{H}_\alpha$), 7.56 (d, $J=8$ Hz, 2H, Ar–$\underline{H}$), 7.80 (d, $J=8$ Hz, 2H, Ar–$\underline{H}$), and 9.96 (s, 1H, –C$\underline{H}$O). Found; C, 51.62; H, 2.81%; M$^+$, 440. Calcd for $C_{19}H_{13}FeIO$: C, 51.85; H, 2.97%; M, 440.

The second fraction, eluted with benzene–chloroform (1 : 1), gave **5a**, as deep red crystals (mp 210 °C (decomp)) in a 27% yield (1.19 g): IR (KBr): 2200 (–C≡C–), 1690 (–CHO), 1600, 1580, 820 (*p*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (CDCl$_3$): $\delta=4.37$ (t, 4H, $\underline{H}_\beta$), 4.59 (t, 4H, $\underline{H}_\alpha$), 7.47 (d, 4H, $\underline{H}_a$), 7.71 (d, 4H, $\underline{H}_b$), and 9.98 (s, 2H, –C$\underline{H}$O). Found: C, 75.85; H, 3.96%; M$^+$, 442. Calcd for $C_{28}H_{18}FeO_2$: C, 76.03; H, 4.10%; M, 442.

*1,1′-Bis(*m*-formylphenylethynyl)ferrocene (5b).* In the presence of $(Ph_3P)_2PdCl_2$ and CuI, the palladium-catalyzed substituted of **6** with **7b** was carried out in the same way as has been described for **5a**; 1-(*m*-formylphenylethynyl)-1′-iodoferrocene (**9b**) (reddish crystals; mp 113—115 °C) and **5b** (reddish crystals; mp 164—165 °C) were thus obtained in 34 and 27% yields respectively.

9b: IR (KBr): 1700 (-CHO), 2200 (-C≡C-), 1600, 1580, 820, 780 (*m*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.20 (m, 6H, $\underline{H}_\beta+\underline{H}_\gamma$), 4.49 (m, 2H, $\underline{H}_\alpha$), 7.34—7.89 (m, 4H, Ar-$\underline{H}$), and 9.93 (s, 1H, -C$\underline{H}$O). Found: C, 51.73; H, 2.85%; M^+, 440. Calcd for $C_{19}H_{13}FeIO$: C, 51.85; H, 2.97%; M, 440.

5b: IR (KBr): 1700 (-CHO), 2200 (-C≡C-), 1600, 1580, 850, 770 (*m*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.31 (t, 4H, $\underline{H}_\beta$), 4.53 (t, 4H, $\underline{H}_\alpha$), 7.29—7.75 (m, 8H, Ar-$\underline{H}$), and 9.83 (s, 2H, -C$\underline{H}$O). Found: C, 75.78; H, 4.01%; M^+, 442. Calcd for $C_{28}H_{18}FeO_2$: C, 76.03; H, 4.10%; M, 442.

*1,1′-Bis(*o*-formylphenylethynyl)ferrocene (5c).* In the presence of $(Ph_3P)_2PdCl_2$ and CuI, the palladium-catalyzed substitution of **6** with **7c** was carried out in the same way as has been described for **5a**; 1-(*o*-formylphenylethynyl)-1′-iodoferrocene (**9c**) (reddish oil) and **5c** (reddish crystals; mp 178—179 °C) were thus obtained in 40 and 14% yields respectively.

9c: IR (neat): 1690 (-CHO), 2200 (-C≡C-), 1600, 1580, 740 (*o*-disubstituted benzene ring), 3100, and 810 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.34 (m, 6H, $\underline{H}_\beta+\underline{H}_\gamma$), 4.55 (m, 2H, $\underline{H}_\alpha$), 7.21—7.74 (m, 4H, Ar-$\underline{H}$), and 10.24 (s, 1H, -C$\underline{H}$O). Found: C, 51.77; H, 2.90%; M^+, 440. Calcd for $C_{19}H_{13}FeIO$: C, 51.85; H, 2.97%; M, 440.

5c: IR (KBr): 1690 (-CHO), 2200 (-C≡C-), 1600, 1580, 1500, 740 (*o*-disubstituted benzene ring), 3100, and 810 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.36 (t, 4H, $\underline{H}_\beta$), 4.58 (t, 4H, $\underline{H}_\alpha$), 7.29—7.74 (m, 8H, Ar-$\underline{H}$), and 10.47 (s, 2H, -C$\underline{H}$O). Found: C, 75.92; H, 3.98%; M^+, 442. Calcd for $C_{28}H_{18}FeO_2$: C, 76.03; H, 4.10%: M, 442.

*1,1′-Bis(*p*-formylstyryl)ferrocene (5d).* A mixture of **6** (4.37 g, 0.01 mol), **7a** (3.70 g, 0.28 mol), palladium(II) acetate (0.04 g, 0.002 mol), triphenylphosphine (0.10 g, 0.004 mol), and triethylamine (2.83 g. 0.28 mol) in acetonitrile (60 cm^3) was heated under nitrogen in an autoclave at 90 °C for 10 h. After the removal of the solvent under reduced pressure, the residue was extracted with chloroform. The chloroform extracts were washed with 10% hydrochloric acid, a saturated sodium hydrogencarbonate solution, and a saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography on silica gel.

The first fraction, eluted with benzene, gave (*p*-formylstyryl)-ferrocene (**9d**); yellowish red crystals; mp 145—147 °C, 1.10 g (35% yield based on **6**). IR (KBr): 1690 (-CHO), 1635, 965 (*trans* -CH=CH-), 1600, 1500, 820, (*p*-disubstituted benzene ring), 3100, and 805 (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.12 (s, 5H, $\underline{H}_\gamma$), 4.32 (t, 2H, $\underline{H}_\beta$), 4.48 (t, 2H, $\underline{H}_\alpha$), 6.67 (d, J=15 Hz, 1H, $\underline{H}_b$), 7.04 (d, J=15 Hz, 1H, $\underline{H}_a$), 7.49 (d, J=8 Hz, 2H, $\underline{H}_c$), 7.78 (d, J=8 Hz, 2H, $\underline{H}_d$), and 9.93 (s, 1H, -C$\underline{H}$O). Found: C, 72.06; H, 4.95%; M^+, 316. Calcd for $C_{19}H_{16}FeO$: C, 72.17; H, 5.10%; M, 316.

The second fraction, eluted with benzene–chloroform (1 : 1), gave **5d** as reddish crystals (mp 218 °C (decomp)) in a 54% yield (2.41 g). IR (KBr): 1695 (-CHO), 1630, 960 (*trans* -CH=CH-), 1600, 1500, 830 (*p*-disubstituted benzene ring), 3100, and 810 (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.33 (t, 4H, $\underline{H}_\beta$), 4.48 (t, 4H, $\underline{H}_\alpha$), 6.53 (d, J=16 Hz, 2H, $\underline{H}_b$), 6.82 (d, J=16 Hz, 2H, $\underline{H}_a$), 7.28 (d, J=8 Hz, 4H, Ar-$\underline{H}$), 7.63 (d, J=8 Hz, 4H, Ar-$\underline{H}$), and 9.89 (s, 2H, -C$\underline{H}$O). Found: C, 75.19; H, 4.77%; M^+, 446. Calcd for $C_{28}H_{22}FeO_2$: C, 75.35; H, 4.96%; M, 446.

The Reductive Coupling of 5a with $TiCl_4$–Zn. Under a nitrogen atmosphere, Zn dust (5.22 g, 0.08 mol) was added to a solution of $TiCl_4$ (7.58 g, 0.04 mol) in dry THF (150 cm^3) with cooling. The mixture was then refluxed for 1.5 h to give a deep black solution. To the metal complex solution thus obtained we added a solution of **5a** (3.53 g, 0.008 mol) and dry pyridine (0.60 g) in dry THF (550 cm^3) over 11 h under refluxing, followed by an additional 10-h period of reflux. The reaction mixture was then cooled to room temperature and quenched with a 20% aqueous K_2CO_3 solution. After filtration, the filtrate was extracted with chloroform. The chloroform extracts were washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvents, the residue was dissolved in benzene and chromatographed on silica gel.

The first fraction, eluted with benzene, gave **8a** as reddish crystals (mp 193—194 °C) in a 3.5% yield. Compound **8a** is identical in all respects with 1,1′-bis(*p*-tolylethynyl)ferrocene, which was prepared by the palladium-catalyzed substitution of **6** with *p*-tolylacetylene in the same way as has been described for **5a**. Found: C, 81.08; H, 5.29%; M^+, 414. Calcd for $C_{28}H_{22}Fe$: C, 81.16; H, 5.35%; M, 414.

The second fraction, eluted with benzene, gave **1** as deep reddish crystals (mp 260 °C (decomp)) in a 15% yield. Found: C, 81.83; H, 4.31%; M^+, 410. Calcd for $C_{28}H_{18}Fe$: C, 81.96; H, 4.42%; M, 410.

The third fraction, eluted with chloroform, gave 1-(*p*-formylphenylethynyl)-1′-[*p*-(hydroxymethyl)phenylethynyl]-ferrocene (**10**) as reddish orange crystals (mp 190 °C (decomp)) in a 6% yield. IR (KBr): 3300 (-OH), 1700 (-CHO), 2200 (-C≡C-), 1600, 1500, 820 (*p*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (DMSO-d_6): δ=4.36 (t, 4H, $\underline{H}_\beta$), 4.56 (t, 4H, $\underline{H}_\alpha$), 4.72 (s, 2H, -C$\underline{H}_2$-), 5.78 (b-s, 1H, -O$\underline{H}$), 6.91 (d, 2H, Ar-$\underline{H}$), 7.34—7.52 (m, 6$\underline{H}$, Ar-$\underline{H}$) and 9.88 (s, 1H, -C$\underline{H}$O). Found: C, 75.60; H, 4.44%; M^+, 444. Calcd for $C_{28}H_{20}FeO_2$: C, 75.69; H, 4.53%; M, 444.

The fourth fraction, eluted with chloroform–ethanol (10 : 1) gave 1,1′-bis[*p*-hydroxymethyl)phenylethynyl]ferrocene (**11a**) as reddish orange crystals (mp 195 °C (decomp)) in a 3% yield. IR (KBr): 3300 (-OH), 2200 (-C≡C-), 1600, 1500, 840 (*p*-disubstituted benzene ring), 3100, and 815 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (DMSO-d_6): δ=4.00 (b-s, 2H, -O$\underline{H}$), 4.36 (t, 4H, $\underline{H}_\beta$), 4.56 (t, 4H, $\underline{H}_\alpha$), 4.76 (s, 4H, -C$\underline{H}_2$-), 6.97 (d, 4H, Ar-$\underline{H}$), and 7.33 (d, 4H, Ar-H). Found: C, 75.17; H, 4.85%; M^+, 446. Calcd for $C_{28}H_{22}FeO_2$: C, 75.35; H, 4.96%; M, 446.

The Reductive Coupling of 5b with $TiCl_4$–Zn. The reductive coupling of **5b** was carried out in the same way as has been described for the reaction of **5a** with $TiCl_4$–Zn, and the products were separated by chromatography on silica gel.

The first fraction, eluted with benzene, gave as reddish orange crystals (mp 114—115 °C) in a 7% yield. Compound **8b** was found to be identical with 1,1′-bis(*m*-tolylethynyl)-ferrocene, which has been prepared by the palladium-catalyzed substitution of **6** with *m*-tolylacetylene in the way described for **5a**. Found: C, 81.10; H, 5.28%; M^+, 414. Calcd for $C_{28}H_{22}Fe$: C, 81.16; H, 5.35%; M, 414.

The second fraction, eluted with benzene, gave **2** as reddish crystals (mp 215—216 °C) in a 22% yield. Found: C, 81.88; H, 4.36%; M^+, 410. Calcd for $C_{28}H_{18}Fe$: C, 81.96; H, 4.42%; M, 410.

The third fraction, eluted with chloroform, gave 1,1′-bis[*m*-

(hydroxymethyl)phenylethynyl]ferrocene (**11b**) as reddish orange crystals (mp 245 °C (decomp)) in a 12% yield. IR (KBr): 3300 (-OH), 2200 (-C≡C-), 1600, 1500, 870, 770 (*m*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (acetone-d_6): $\delta=2.15$ (b-s, 2H, -O$\underline{\text{H}}$), 4.29 (t, 4H, $\underline{\text{H}}_\beta$). 4.51 (t, 4H, $\underline{\text{H}}_\alpha$). 4.72 (s, 4H, -C$\underline{\text{H}}_2$-), and 7.28—7.58 (m, 8H, Ar-$\underline{\text{H}}$). Found: C, 75.25; H, 4.90%; M$^+$, 446. Calcd for $C_{28}H_{22}FeO_2$: C, 75.35; H, 4.96%; M, 446.

The Reductive Coupling of **5c** *with $TiCl_4$–Zn.* The reductive coupling for **5c** with $TiCl_4$–Zn was carried out in the same way as has been described for the reaction of **5a** with $TiCl_4$–Zn, and the products were separated by chromatography on silica gel.

The first fraction, eluted with benzene, gave **8c** as reddish orange crystals (mp 97—98 °C) in a 9% yield. Compound **8c** was found to be identical with 1,1′-bis(*o*-tolylethynyl)ferrocene, which has been prepared by the palladium-catalyzed substitution of **6** with *o*-tolylacetylene in the same way as has been described for **5a**. Found: C, 81.03; H, 5.19%; M$^+$, 414. Calcd for $C_{28}H_{22}Fe$: C, 81.16; H, 5.35%; M, 414.

The second fraction, eluted with benzene, gave **3** as reddish crystals (mp 216—217 °C) in a 26% yield. Found: C, 81.87; H, 4.33%; M$^+$, 410. Calcd for $C_{28}H_{18}Fe$: C, 81.96; H, 4.42%; M, 410.

The third fraction, eluted with chloroform, gave 1,1′-bis[*o*-(hydroxymethyl)phenylethynyl]ferrocene (**11c**) as reddish orange crystals (mp 201—203 °C) in a 5% yield. IR (KBr): 3400 (-OH), 2200 (-C≡C-), 1600, 1500, 740 (*o*-disubstituted benzene ring), 3100, and 810 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (acetone-d_6): $\delta=2.06$ (b-s, 2H, -O$\underline{\text{H}}$), 4.30 (t, 4H, $\underline{\text{H}}_\beta$), 4.55 (t, 4H, $\underline{\text{H}}_\alpha$), 4.75 (s, 4H, -C$\underline{\text{H}}_2$-), and 7.28—7.71 (m, 8H, Ar-$\underline{\text{H}}$). Found: C, 75.19; H, 4.85%; M$^+$, 446. Calcd for $C_{28}H_{22}FeO_2$: C, 75.35; H, 4.96%; M, 446.

The Reductive Coupling of **5d** *with $TiCl_3$–$LiAlH_4$.* Under a nitrogen atmosphere, $LiAlH_4$ (0.76 g, 0.02 mol) was added to a stirred slurry of $TiCl_3$ (6.47 g, 0.0042 mol) in dry THF (150 cm^3) at 0 °C. After the resulting black suspension has been stirred for 20 min, a solution of **5d** (3.79 g, 0.0085 mol) in dry THF (100 cm^3) was added drop by drop to this mixture for 6 h under refluxing, followed by an additional 7-h period of reflux. After cooling to room temperature, the reaction was worked up in the way described for **5a**; the crude products were chromatographed on silica gel.

The first fraction, eluted with hexane, gave **8d** as reddish crystals (mp 143—144 °C) in a 1.4% yield. Compound **8d** was found to be identical with 1,1′-bis(*p*-methylstyryl)ferrocene, which has been prepared by the palladium-catalyzed substitution of **6** with *p*-methylstyrene in the same way as has been described for **5d**. Found: C, 80.30; H, 6.14%; M$^+$, 418. Calcd for $C_{28}H_{26}Fe$: C, 80.38; H, 6.26%; M, 418.

The second fraction, eluted with benzene, gave **4** as reddish crystals (mp 230 °C (decomp)) in a 2.2% yield. Found: C, 81.03; H, 5.35%; M$^+$, 414. Calcd for $C_{28}H_{22}Fe$: C, 81.16; H, 5.35%; M, 414.

The third fraction, eluted with chloroform–ethanol (10 : 1), gave 1,1′-bis[*p*-(hydroxymethyl)styryl]ferrocene (**8d**) as reddish yellow crystals (mp 152—154 °C) in 3.2% yield. IR (KBr): 3400, (-OH), 1635, 955 (*trans* -CH=CH-), 1600, 1500, 830 (*p*-disubstituted benzene ring), 3100, and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (DMSO-d_6): $\delta=2.65$ (b-s, 2H, -O$\underline{\text{H}}$), 4.28 (t, 4H, $\underline{\text{H}}_\beta$), 4.49 (t, 4H, $\underline{\text{H}}_\alpha$), 4.78 (s, 4H, -C$\underline{\text{H}}_2$-), 6.62 (d, $J=16$ Hz, 2H, -C=C$\underline{\text{H}}$-Ar), 7.01 (d, $J=16$ Hz, 2H, -C$\underline{\text{H}}$=C-Ar-), 7.43 (d, $J=8$ Hz, 4H, Ar-$\underline{\text{H}}$), and 7.75 (d, $J=8$ Hz, 4H, Ar-$\underline{\text{H}}$). Found: C, 74.56; H, 5.69%; M$^+$, 450. Calcd for $C_{28}H_{26}FeO_2$: C, 74.67; H, 5.81%; M, 450.

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