Synthesis of Biphenyloferrocenophanes

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Some ferrocenophanes, in which the two cyclopentadienyl rings are linked by biphenyl rings, have been synthesized *via* intramolecular reductive coupling of the corresponding formyl compounds with a low-valent titanium reagent. The structures of these cyclophane compounds were determined by IR, NMR, and UV spectra analyses. Transannular π-electronic interactions between the two biphenyl rings were examined on the basis of electronic spectra.

In contrast to the active interest in cyclophane compounds, the ferrocenophane system having transannular π-electronic interactions has received little attention; the only compounds of this class which have been described are [2.2]ferrocenophane-1,13-diyne,[1] [2.2]-ferrocenophane-1,13-diene,[2] [2]paracyclo[2]paracyclo-[2](1,1′)ferrocenophane,[3] [3.3]- and [5.5](1,1′)ferrocenophane derivatives,[4] and [0]metacyclo[2]metacyclo[0](1,1′)ferrocenophane.[5] We wish to report the synthesis of some ferrocenophanes in which the two cyclopentadienyl rings are linked by biphenyl rings and an ethano or etheno bridge, using the low-valent titanium species.

Results and Discussion

Synthesis. Although a number of synthetic methods have been recently developed for [2.2]cyclophane,[6] a reductive coupling of carbonyl compounds with low-valent titanium reagents[7] is still very convenient and advantageous for the synthesis of cyclophane because of the availability of the intermediary compounds.[2,3,5,8]

In the present work, we applied the same method for the synthesis of [0](4,4′)biphenylo[2](4,4′)biphenylo[0](1,1′)ferrocenophan-13-ene (**1**), [0](4,3′)biphenylo[2](3,4′)biphenylo[0](1,1′)ferrocenophan-13-ene (**3**), and *syn*- and *anti*-[0](4,2′)biphenylo[2](2,4′)biphenylo-[0](1,1′)ferrocenophan-13-ene (**5s** and **5a**). The synthesis of an intermediate, 1,1′-bis(4′-formyl-4-biphenylyl)ferrocene (**13a**), was carried out by the cross coupling reaction[9] of 1,1′-bis(*p*-bromophenyl)ferrocene (**7**) with a Grignard reagent from *p*-bromobenzaldehyde ethylene acetal (**8**) in the presence of phosphino nickel complex. The synthesis of other intermediates, 1,1′-bis(3′-formyl-4-biphenylyl)ferrocene (**13b**) and 1,1′-bis-(2′-formyl-4-biphenylyl)ferrocene (**13c**), were carried out by the Gomberg's arylation of ferrocene with diazonium salt derived from 4′-aminobiphenyl-3-carboxylic acid (**10a**) and 4′-aminobiphenyl-2-carboxylic acid (**10b**), subsequent esterification in methanol, reduction with $LiAlH_4$, and oxidation with active MnO_2 in chloroform.

The reductive coupling reaction of dialdehyde, **13a** and **13b**, with low-valent titanium reagents were carried out according to Mukaiyama's procedure[7a] using a high dilution method. Silica gel column chromatography of the reaction products led to the isolation of **1** and **3**, respectively, accompanied by the formation of the reduction products of **13a** and **13b**. On the other hand, the $TiCl_4$–Zn reductive coupling of **13c** led to the formation of two isomers of **5s** and **5a**.

The catalytic hydrogenation of **1** and **3** with PtO_2 in ethanol–dioxane afforded [0](4,4′)biphenylo[2](4,4′)-biphenylo[0](1,1′)ferrocenophane (**2**) and [0](4,3′)biphenylo[2](3,4′)biphenylo[0](1,1′)ferrocenophane (**4**), respectively. The catalytic hydrogenation of **5s** and **5a** afforded the same product: [0](4,2′)biphenylo[2]-(2,4′)biphenylo[0](1,1′)ferrocenophane (**6**).

Structures. The structures of the cyclophanes, **1**—**6**, were determined on the basis of the IR, NMR, and mass spectra and the elementary analyses. The NMR and IR spectra data of all the cyclophanes and the reference compounds are summarized in Tables 1 and 2, respectively.

In the unsaturated cyclophane **1**, the configuration of –C–C– double bond was confirmed to be *cis*, because the IR spectrum of **1** exhibits a band at 740 cm^{-1} which is characteristic of *cis* vinylene linkage and the characteristic band near 960 cm^{-1} due to *trans* vinylene linkage is absent. In ferrocene, the distance between the two cyclopentadienyl rings is 3.32 Å,[10] while the van der Waals separation between parallel π-system is 3.4 Å.[11] On the other hand, in **1** and **2**, the molecules exist probably in the conformation with the biphenyl rings approximately parallel to one another and approximately coplanar to the plane of the cyclopentadienyl ring. Thus, in **1** and **2**, substantial repulsive interactions must exist between the two biphenyl rings which are bound together by an etheno or ethano bridge at each end. In the NMR spectrum of **1**, as expected, the aromatic protons (δ, 6.85—7.21 ppm) appear at higher fields than the corresponding protons of the reference compounds, 1,1′-bis(4′-methyl-4-biphenylyl)ferrocene (**15a**) (δ, 7.13—7.49 ppm) and (4′-methyl-4-biphenylyl)ferrocene (**16a**) (δ, 7.12—7.56 ppm). In the saturated cyclophane, the protons of biphenyl rings (δ, 6.88—7.21 ppm) are also shifted upfield compared with those of **15a** and **16a**. These phenomena are probably due to diamagnetic shielding effect of the facing biphenyl ring.

In the NMR spectra of **3** and **4**, the aromatic proton signals are observed at nearly the same positions as those of the reference compounds, 1,1′-bis(3′-methyl-4-biphenylyl)ferrocene (**15b**) and (3′-methyl-4-biphenylyl)ferrocene (**16b**). This suggests that the two biphenyl rings in both **3** and **4** are not held a face to face conformation and the *anti*-conformations for **3** and **4** are accommodated.

On the other hand, in two isomers of **5s** and **5a**, the mass spectra show the same pattern, which con-

Table 1. NMR spectra of the cyclophane and reference compounds (δ, in $CDCl_3$)[a)]

Compound	Biphenyl ring protons	Ferrocene ring protons	Other protons
1[a)]	6.85—7.21 (m, 16H)	4.34 (t, 4H, $\underline{H}_\beta$) 4.65 (t, 4H, $\underline{H}_\alpha$)	7.12 (s, 2H, -C$\underline{H}$=C$\underline{H}$-)
2[a)]	6.88—7.21 (m, 16H)	4.32 (t, 4H, $\underline{H}_\beta$) 4.63 (t, 4H, $\underline{H}_\alpha$)	2.67 (s, 4H, -C$\underline{H}_2$-)
15a	7.13—7.49 (m, 16H)	4.27 (t, 2H, $\underline{H}_\beta$) 4.56 (t, 4H, $\underline{H}_\alpha$)	2.39 (s, 6H, -C$\underline{H}_3$)
16a	7.18 (d, 2H, J=8 Hz) 7.33 (d, 2H, J=8 Hz) 7.38 (d, 2H, J=8.5 Hz) 7.55 (d, 2H, J=8.5 Hz)	4.02 (s, 5H, $\underline{H}_\gamma$) 4.33 (t, 2H, $\underline{H}_\beta$) 4.64 (t, 2H, $\underline{H}_\alpha$)	2.33 (s, 3H, -C$\underline{H}_3$)
3	7.07—7.78 (m, 16H)	4.44 (t, 4H, $\underline{H}_\beta$) 4.56 (t, 4H, $\underline{H}_\alpha$)	6.88 (s, 2H, -C$\underline{H}$=C$\underline{H}$-)
4	7.00—7.58 (m, 16H)	4.40 (t, 4H, $\underline{H}_\beta$) 4.56 (t, 4H, $\underline{H}_\alpha$)	2.84 (s, 4H, -C$\underline{H}_2$-)
15b	7.00—7.47 (m, 16H)	4.27 (t, 4H, $\underline{H}_\beta$) 4.54 (t, 4H, $\underline{H}_\alpha$)	2.36 (s, 6H, -C$\underline{H}_3$)
16b	7.08—7.78 (m, 8H)	4.02 (s, 5H, $\underline{H}_\gamma$) 4.30 (t, 2H, $\underline{H}_\beta$) 4.64 (t, 2H, $\underline{H}_\alpha$)	2.38 (s, 3H, -C$\underline{H}_3$)
5s	6.80 (b-s, 12H, $H_a+H_b+H_e+H_f$) 7.09—7.24 (m, 4H, H_c+H_d)	4.33 (t, 4H, $\underline{H}_\beta$) 4.64 (t, 4H, $\underline{H}_\alpha$)	7.22 (s, 2H, -C$\underline{H}$=C$\underline{H}$-)
5a	6.84 (m, 2H, H_a) 7.04—7·58 (m, 14H, $H_{a'}+H_b+H_c+H_d+H_e+H_f$)	4.36 (t, 4H, $\underline{H}_\beta$) 4.56 (t, 4H, $\underline{H}_\alpha$)	7.13 (s, 2H, -C$\underline{H}$=C$\underline{H}$-)
6	6.82 (m, 2H, H_a) 7.06—7.36 (m, 14H, $H_{a'}+H_b+H_c+H_d+H_e+H_f$)	4.31 (t, 4H, $\underline{H}_\beta$) 4.66 (t, 4H, $\underline{H}_\alpha$)	2.74 (s, 4H, -C$\underline{H}_2$-)
15c	7.08—7.34 (m, 16H)	4.24 (t, 4H, $\underline{H}_\beta$) 4.51 (t, 4H, $\underline{H}_\alpha$)	2.24 (s, 6H, -C$\underline{H}_3$)
16c	7·07—7.48 (m, 8H)	4.02 (s, 5H, $\underline{H}_\gamma$) 4.29 (t, 2H, $\underline{H}_\beta$) 4.62 (t, 2H, $\underline{H}_\alpha$)	2.26 (s, 3H, -C$\underline{H}_3$)

a) The spectra of **1** and **2** were observed in pyridine-d_5.

Table 2. IR spectra of the cyclophane and reference compounds (KBr, cm^{-1})

Compound	
1	1600, 1500, 840 (*p*-disubstituted benzene ring), 1640, 740 (*cis* -CH=CH-, 810 (1,1′-disubstuted ferrocene ring), 720, and 690.
2	1600, 1500, 1450, 830 (*p*-disubstituted benzene ring), 810 (1,1′-disubstituted ferrocene ring), 725, and 690.
15a	1600, 1500, 840 (*p*-disubstituted benzene ring), and 805 (1,1′-disubstituted ferrocene ring).
16a	1600, 1500, 840 (*p*-disubstituted benzene ring), 1100, 1000, and 810 (monosubstituted ferrocene ring).
3	1600, 1500, 780, 750, 695 (aromatic ring), 815 (1,1′-disubstituted ferrocene ring), and 735 (*cis* -CH=CH-).
4	1600, 1500, 1480, 830, 795, 765, 705 (aromatic ring), and 815 (1,1′-disubstituted ferrocene ring).
15b	1605, 1500, 840, 775, 735, 690 (aromatic ring), and 810 (1,1′-disubstituted ferrocene ring).
16b	1600, 1500, 860, 825, 750, 735, 695 (aromatic ring), 1100, 995, and 810 (monosubstituted ferrocene ring).
5s	1600, 1500, 840, 770, 750 (aromatic ring), 800 (1,1′-disubstituted ferrocene ring), and 740 (*cis* -CH=CH-).
5a	1600, 1500, 840, 760, (aromatic ring), 810 (1,1′-disubstituted ferrocene ring), and 975 (*trans* -CH=CH-).
6	1605, 1500, 840, 765, 715 (aromatic ring), and 815 (1,1′-disubstituted ferrocene ring).
15c	1600, 1500, 880, 845, 820, 760, 740, 730 (aromatic ring), and 805 (1,1′-disubstituted ferrocene ring).
16c	1600, 1500, 845, 760, 740 (aromatic ring), 1100, 1000, and 810 (monosubstituted ferrocene ring).

tains the molecular ion peak at *m/e* 514. Thus we call them isomers. The configuration of double bond in **5s** was confirmed to be *cis*, because the IR spectrum of **5s** exhibits a band of 740 cm^{-1} which is characteristic of *cis* vinylene linkage. The configuration of double bond in **5a** exhibits a band of 975 cm^{-1} which is characteristic of *trans* vinylene linkage. The structural difference between **5s** and **5a** is unequivocal in the NMR spectra. In the NMR spectrum of **5s**, it is noteworthy that the vinylene protons of **5s**, which can be easily assigned by relative intensities, appear at lower field than the aromatic protons, in the analogy with the case of [2.2.2](1,3,5)cyclophane-1,9,17-triene.[12] The H_a, H_b, H_e, and H_f protons in **5s** are shifted to higher field than the corresponding protons of the reference compounds, 1,1′-bis(2′-methyl-4-biphenylyl)ferrocene (**15c**) and (2′-methyl-4-biphenylyl)ferrocene (**16c**), showing the strong shielding effect of the proximate aromatic ring. However, the H_c and H_d signals of **5s** were observed at nearly the same positions as those of **15c** and **16c**. These phenomena suggest that the two aromatic A rings in **5s** are approximately parallel and are held face to face with each other; however, the two aromatic B rings are not parallel, and the aromatic A and B rings have a non-planar orientation due to the short length of the side chain which is bridging at the ortho position of B rings. Consequently, the H_a, H_b, H_e, and H_f protons lie closer to the opposed biphenyl ring than do the H_c and H_d protons. The difference of the chemical shifts may be due to the difference in ring current effect of the biphenyl ring on the aromatic protons of **5s**. These data are best accommodated by the *syn*-conformation for **5s**. On the other hand, in **5a**, the shifts of H_a, H_b, H_b', and H_{c-f} protons are negligible, and the upfield shifts (0.24 ppm) of H_a protons are marked and roughly the same as those (0.28 ppm) of H_a protons of **5s**. Small shielding effects on H_a', H_b, H_b', and H_{c-f} protons are also explained by the *anti*-structure for **5a**.

In the NMR spectrum of the saturated cyclophane **6**, the aromatic protons H_a are shifted to higher field by about 0.26 ppm, compared with those of the reference compounds, **15c** and **16c**. However, the signals of H_a' and H_{b-d} were observed at nearly the same positions as those of **15c** and **16c**. These phenomena are also explained by an *anti*-structure for **6**, but not by a *syn*-structure.

The electronic spectra of the cyclophane and the reference compounds are shown in Figs. 1, 2, and 3. Biphenyl itself has no absorption in the long wavelength above 250 nm.[13] The electronic spectra of **1** and **2**, and **5s**, **5a**, and **6** show somewhat bathochromic and hyperchromic shifts and unambiguous broadening in a range 240—310 nm, compared with those of the reference compounds, **15a** and **16a**, and **15c** and **16c**, respectively. This may be due to transannular π-electronic interactions between the two chromopheres in **1**, **2**, **5s**, **5a**, and **6**. The stronger effect in **5s**, relative to that in **5a** or **6**, suggests that the two biphenyl rings in **5s** are closer to being vertically stacked than in the cases of **5a** and **6**. An examination of molecular modela also supports this conclusion.

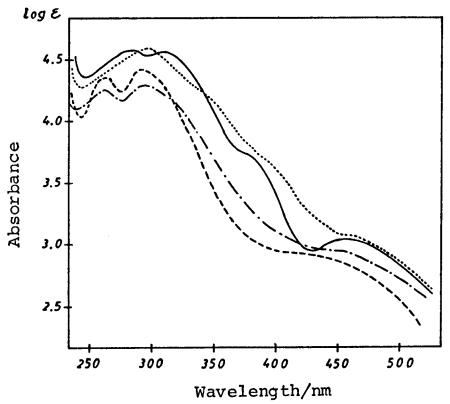


Fig. 1. Electronic spectra of **1**, **2**, **15a**, and **16a** in dioxane.
····· **1**, —— **2**, —·— **15a**, ---- **16a**.

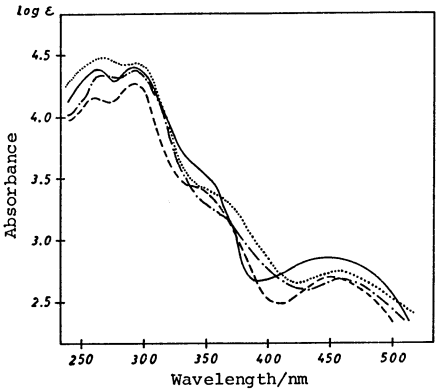


Fig. 2. Electronic spectra of **3**, **4**, **15b**, and **16b** in dioxane.
····· **3**, —— **4**, —·— **15b**, ----**16b**.

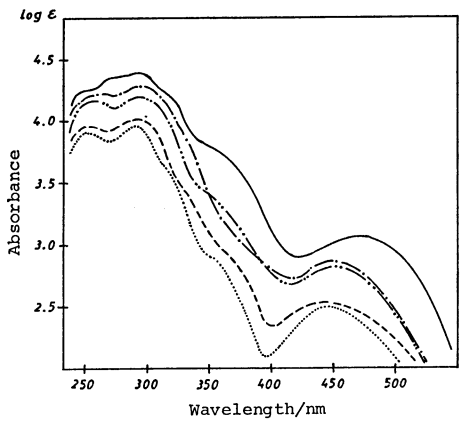
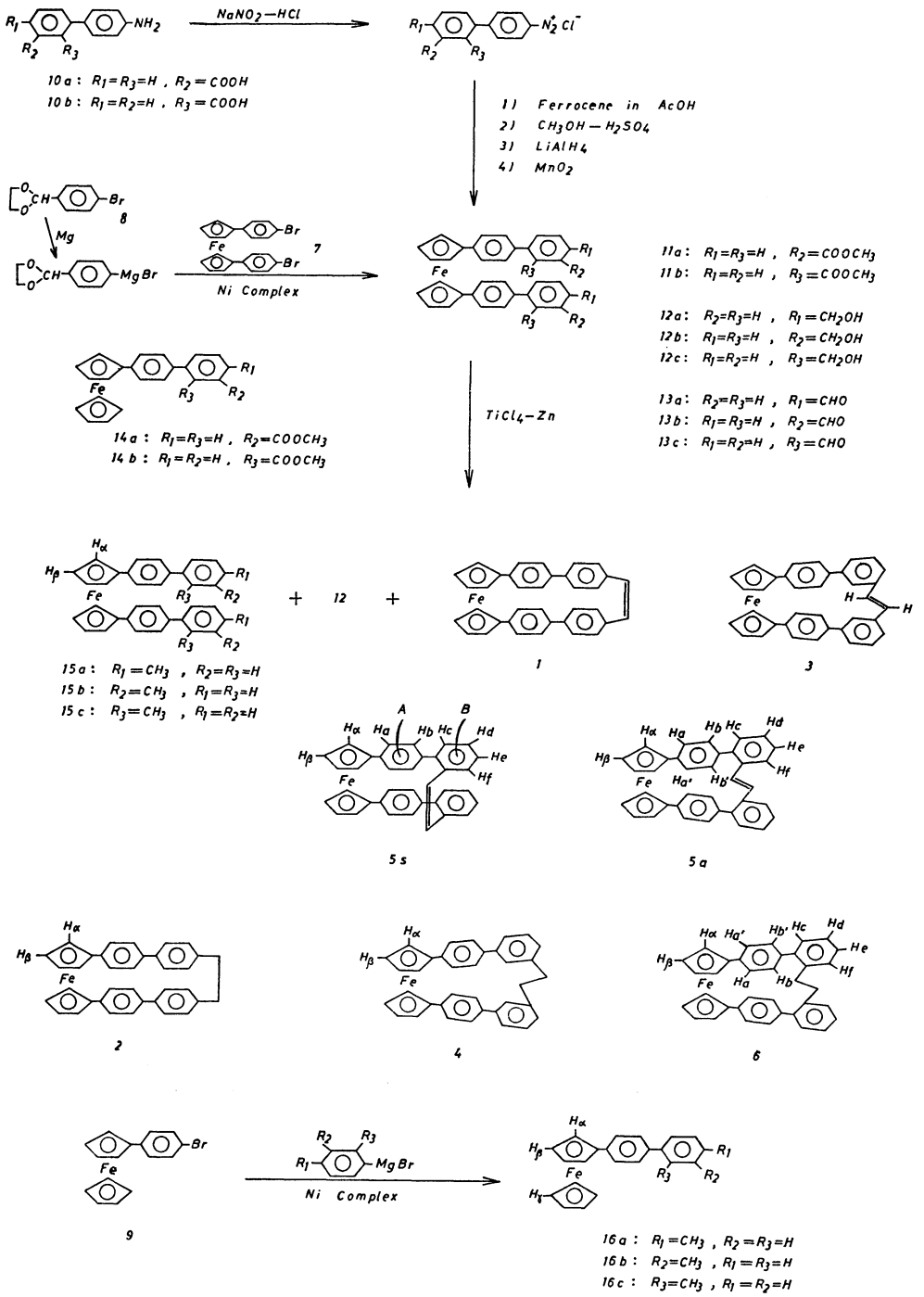


Fig. 3. Electronic spectra of **5s**, **5a**, **6**, **15c**, and **16c** in dioxane.
—— **5s**, —·— **5a**, —··— **6**, ---- **15c**, ····· **16c**.

On the other hand, in the 240—300 nm region, the cyclophanes **3** and **4** exhibit two absorption peaks and the intensity of these bands is somewhat increased; however, the spectra are practically identical with those of the reference compounds, **15b** and **16c**. These phenomena indicate that the interaction between the two biphenyl rings in both **3** and **4** is relatively weak and the *anti*-conformations for **3** and **4** can be accommodated.



Scheme 1.

The electronic spectra of ferrocene contain two broad absorptions at 325 and 440 nm.[14] It has been shown that both the position and the intensity of the 440 nm band are particularly sensitive to ferrocene ring-tilt distortion.[15] This is also true for [1]-[16] and [2]-ferrocenophanes;[15] the 440 nm band undergoes a bathochromic shift and increases in intensity. In Fig. 1, both **15a** and **16a**, which bear no tilted ferrocene ring, exhibit two weak absorptions near 335 and 450 nm; however, in the electronic spectra of **1** and **2**, both the 325 and 440 nm bands undergo a bathochromic shift and increase in intensity, compared with those of **15a** and **16a**. These phenomena may be due to ferrocene ring-tilt distortion in **1** and **2**.

The IR spectra of the [2.2]paracyclophane system show some obvious features. One is the increase of the intensity of a band in the 1580—1600 cm^{-1} region, which relates to the increased double bond character due to the distortion of the benzene rings.[17] The other is the appearance of a strong new maximum near the 710 cm^{-1} region. Longone and Warren[18] 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 characteristic bands associated with the distorted benzene rings in the [2.2]paracyclophane system. Furthermore, Otsubo

et al.[19] reported the same phenomena in the multilayered [2.2]paracyclophane system. The cyclophanes **1** and **2** also exhibit characteristic bands around 700 cm^{-1}, whereas the reference compounds bearing strain-free benzene rings, **15a** and **16a**, exhibit no bands in this region. This phenomenon may be due to the distortion of the benzene rings in **1** and **2**.

In the cyclophane, **3** and **4**, the electronic spectra in the 330—450 nm region are closely similar to those of the reference compounds bearing a no-tilt ferrocene ring: **15b** and **16b**. This indicates that, in **3** and **4**, the ferrocene ring is not tilted. Moreover, near the 710 cm^{-1} region, the IR spectra of **3** and **4** are closely similar to those of the open-chain models, **15b** and **16b**. This may be due to the non-distortion of benzene rings in **3** and **4**.

On the other hand, in the electronic spectra in the 300—400 nm region, **5s**, **5a**, and **6** show an increased intensity and a bathochromic shift at longer wave length, compared with those of **15c**. These phenomena suggest a ferrocene ring-tilt distortion due to the interaction between the two chromophores in **5s**, **5a**, and **6**. However, in the IR spectra near the 720 cm^{-1} region, the cyclophane, **5s**, **5a**, and **6**, and the open-chain models, **15c** and **16c**, have two absorption bands at approximately the same positions. It indicates that **5s**, **5a**, and **6** bear the no-tilt benzene rings.

Experimental

Materials and Measurement. All melting points are uncorrected. IR spectra were measured using a Hitachi 260-10 spectrophotometer. NMR spectra were obtained at 90 MHz with a Hitachi R-22 spectrometer using TMS as the internal standard. Mass spectra were recorded with a Hitachi RMU-6M spectrometer and electronic spectra with a Hitachi 200-10 spectrophotometer.

1,1′-Bis(*p*-bromophenyl)ferrocene (**7**),[20] *p*-bromobenzaldehyde ethylene acetal (**8**),[21] *p*-bromophenylferrocene (**9**),[22] 4′-aminobiphenyl-3-carboxylic acid (**10a**),[23] and 4′-aminobiphenyl-2-carboxylic acid (**10b**)[23] were prepared by the methods described in the literature.

*1,1′-Bis(4′-formyl-4-biphenylyl)ferrocene (**13a**).* Under a nitrogen atmosphere, the Grignard reagent prepared from **8** (9.16 g, 40 mmol) and magnesium turnings (1.19 g, 49 mmol) in dry THF (60 cm^3) was dropwise added to the mixture of **7** (3.52 g, 8 mmol) and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (0.9 g, 1.6 mmol) in dry THF (60 cm^3) at 0 °C with stirring over 2 h. The reaction mixture was stirred for 6 h at 0—5 °C and then was allowed to remain overnight at room temperature. The mixture was hydrolyzed with 10% hydrochloric acid under cooling with an ice bath and extracted with ether. The ether extracts were washed successively with 10% hydrochloric acid, water, aqueous sodium hydrogencarbonate, and brine. After drying over $MgSO_4$, the solution was evaporated *in vacuo*. The reddish residue was chromatographed on silica gel, using benzene as the eluent, to give **13a**, which was recrystallized from ethanol, mp 242—244 °C (decomp). IR (KBr): 1690 (–CHO), 1600, 1580, and 820 cm^{-1} (*p*-disubstituted benzene ring). NMR (pyridine-d_5): δ=4.03 (t, 4H, $\underline{H}_\beta$), 4.38 (t, 4H, $\underline{H}_\alpha$), 7.46—7.88 (m, 16H, Ar–$\underline{H}$), and 10.02 (s, 2H, –C$\underline{H}$O). Found: C, 79.04; H, 4.63%; M^+, 546. Calcd for $C_{36}H_{26}FeO_2$: C, 79.13; H, 4.79%; M, 546.

*1,1′-Bis(3′-methoxycarbonyl-4-biphenylyl)ferrocene (**11a**) and (3′-Methoxycarbonyl-4-biphenylyl)ferrocene (**14a**).* The amine **10a** (10.66 g, 50 mmol) was diazotized in 10% sulfuric acid (300 cm^3) at 0—5 °C with sodium nitrite (3.45 g, 50 mmol). After diazotization was complete, the diazotized salt solution was added rapidly to a solution of ferrocene (3.72 g, 20 mmol) in acetic acid (150 cm^3) under a nitrogen atmosphere. The resulting dark brown solution was stirred overnight at room temperature, and was then poured into water. The precipitates which formed were filtered off, washed with water, dried at room temperature, and then were esterified in refluxing methanol (250 cm^3) containing 3 cm^3 of conc H_2SO_4 under a nitrogen atmosphere. After removal of the solvent *in vacuo*, the residue was extracted with $CHCl_3$ and the $CHCl_3$ extracts were washed with 5% sodium hydrogencarbonate solution and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (silica gel–benzene). First elution with benzene gave the starting materials; ferrocene (0.93 g, 25%), mp 173 °C.

Second elution with benzene afforded 0.82 g (10.3%) of **14a**, orange yellow crystals, mp 78—80 °C. IR (KBr): 1715 (ester), 1100, 1000, and 805 cm^{-1} (monosubstituted ferrocene ring). NMR ($CDCl_3$): δ=3.63 (s, 3H, –COOC$\underline{H}_3$), 4.01 (s, 5H, $\underline{H}_7$), 4.18 (b-s, 8H, $\underline{H}_\alpha+\underline{H}_\beta$), and 7.18—8.20 (m, 8H, Ar–$\underline{H}$). Found: C, 72.70; H, 4.97%; M^+, 396. Calcd for $C_{24}H_{20}FeO_2$: C, 72.74; H, 5.08%, M, 396.

Third elution with benzene gave 4.24 g (35%) of **11a**, reddish yellow crystals, mp 153—155 °C. IR (KBr): 1720 (ester), 1600, 1580, 880, 835 (*p*- and *m*-disubstituted benzene rings), and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=3.87 (s, 6H, –COOC$\underline{H}_3$), 4.08 (m, 8H, $\underline{H}_\alpha+\underline{H}_\beta$), and 7.21—8.12 (m, 16H, Ar–$\underline{H}$). Found: C, 75.18; H, 4.92%; M^+, 606. Calcd for $C_{38}H_{30}FeO_4$: C, 75.25; H, 4.98%; M, 606.

*1,1′-Bis(2′-methoxycarbonyl-4-biphenylyl)ferrocene (**11b**) and (2′-Methoxycarbonyl-4-biphenylyl)ferrocene (**14b**).* Gomberg's arylation of ferrocene with diazonium salts derived from **10b**, was carried out in the same way as described for **11a**, **11b** (reddish yellow crystals, mp 62—63 °C) and **14b** (reddish yellow crystals, mp 78—80 °C) were obtained in 18 and 22% yields, respectively.

11b: IR (KBr): 1720 (ester), 810 (1,1′-disubstituted ferrocene ring), 1600, 1500, 845, 820, and 730 cm^{-1} (aromatic ring). NMR ($CDCl_3$): δ=3.91 (s, 6H, –COOC$\underline{H}_3$), 4.22 (t, 4H, $\underline{H}_\beta$), 4.51 (t, 4H, $\underline{H}_\alpha$), and 7.11—7.85 (m, 16H, Ar–$\underline{H}$). Found: C, 75.14; H, 4.87%; M^+, 606. Calcd for $C_{38}H_{30}FeO_4$: C, 75.25; H, 4.98%; M, 606.

14b: IR (KBr): 1720 (ester), 1100, 1000, 805 (monosubstituted ferrocene ring), 1600, 1500, 840, 820, and 740 cm^{-1} (aromatic ring). NMR ($CDCl_3$): δ=3.86 (s, 3H, –COOC$\underline{H}_3$), 4.06 (s, 5H, $\underline{H}_7$), 4.22 (t, 2H, $\underline{H}_\beta$), 4.45 (t, 2H, $\underline{H}_\alpha$), and 7.15—8.12 (m, 8H, Ar–$\underline{H}$). Found: C, 72.66; H, 5.01%; M^+, 396. Calcd for $C_{24}H_{20}FeO_2$: C, 72.74; H, 5.08%; M, 396.

*1,1′-Bis(3′-hydroxymethyl-4-biphenylyl)ferrocene (**12b**).* To a solution of $LiAlH_4$ (1.41 g, 37 mmol) in anhydrous ether (200 cm^3) was added dropwise a solution of **11a** (10.90 g, 18 mmol) in dry benzene (100 cm^3) at room temperature during 1 h, and the reaction mixture was then heated under reflux for additional 5 h. After the reaction mixture was decomposed with a small amount of cold water, the organic layer was washed with 5% hydrochloric acid, 5% aqueous sodium hydrogencarbonate, and brine, and dried over anhydrous $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (benzene) to afford **12b** as reddish yellow crystals, which was recrystallized from ethanol, mp 166—168 °C, in 64% yield.

IR (KBr): 3430 (-OH), 1605, 1500, 880, 840 (aromatic ring), and 810 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=1.50 (s, 2H, -OH), 4.08 (t, 4H, H_β), 4.29 (t, 4H, H_α), 4.57 (s, 4H, $-CH_2-$), and 7.07—7.76 (m, 16H, Ar-H). Found: C, 78.45; H, 5.35%; M^+, 550. Calcd for $C_{36}H_{30}FeO_2$: C, 78.55; H, 5.49%; M, 550.

*1,1′-Bis(2′-hydroxymethyl-4-biphenylyl)ferrocene (**12c**).* A reduction of **11b** with $LiAlH_4$ was carried out in the same way as described for **12b**, and **12c** (reddish yellow crystals, mp 152—153 °C) was obtained in 73% yield. IR (KBr): 3400 (-OH), 1600, 1500, 850, 820, 735 (aromatic ring), and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=1.58 (s, 2H, -OH), 4.25 (t, 4H, H_β), 4.48 (t, 4H, H_α), 4.56 (s, 4H, $-CH_2-$), and 7.11—7.56 (m, 16H, Ar-H). Found: C, 78.51; H, 5.40%; M^+, 550. Calcd for $C_{36}H_{30}FeO_2$: C, 78.55; H, 5.49%; M, 550.

*1,1′-Bis(3′-formyl-4-biphenylyl)ferrocene (**13b**).* An active manganese dioxide (100 g) was added to a solution of **12b** (6.47 g, 11.7 mmol) in $CHCl_3$ (200 cm^3) at room temperature, and the mixture was stirred in the dark for 20 h. After filtration to remove manganese dioxide and evaporation to dryness *in vacuo*, the residue was chromatographed in benzene on silica gel to afford reddish crystals **13b** (2.81 g, 44%), which were recrystallized from ethanol, mp 162—163 °C. IR (KBr): 2825, 1690 (-CHO), 1610, 1500, 875, 840 (aromatic ring), and 805 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=3.92 (t, 4H, H_β), 4.20 (t, 4H, H_α), 7.13—7.80 (m, 16H, Ar-H), and 9.98 (s, 2H, -CHO). Found: C, 79.11; H, 4.68%; M^+, 546. Calcd for $C_{36}H_{26}FeO_2$: C, 79.13; H, 4.79%; M, 546.

*1,1′-Bis(2′-formyl-4-biphenylyl)ferrocene (**13c**).* An oxidation of **12c** with active manganese dioxide was carried out in the same way as described for **13b**, and reddish crystals **13c** (mp 175—176 °C) were obtained in 57% yield. IR (KBr): 2820, 1690 (-CHO), 1600, 1500, 845, 820, 740 (aromatic ring), and 800 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR ($CDCl_3$): δ=4.28 (t, 4H, H_β), 4.56 (t, 4H, H_α), 7.15—7.95 (m, 16H, Ar-H), and 9.96 (s, 2H, -CHO). Found: C, 78.96; H, 4.64%; M^+, 546. Calcd for $C_{36}H_{26}FeO_2$: C, 79.13; H, 4.79%; M, 546.

*The Reductive Coupling of **13a** with $TiCl_4$–Zn.* Under a nitrogen atmosphere, Zn dust (1.56 g, 24 mmol) was added in small portions to a stirred solution of $TiCl_4$ (2.27 g, 12 mmol) in dry THF (60 cm^3) at 0—5 °C. After the resulting mixture was refluxed for 2 h, a solution of **13a** (1.31 g, 2.4 mmol) and dry pyridine (0.20 g) in dry THF (80 cm^3) was added to the refluxing solution over 18 h, followed by a further 10 h period of reflux. The reaction mixture was then cooled to room temperature and quenched by addition of 60 cm^3 of saturated aqueous K_2CO_3 solution. The black mixture was stirred for 0.5 h, diluted with $CHCl_3$, and filtered through celite. The filtrate was washed with brine and dried over $MgSO_4$. After removal of the solvents, the residue was dissolved in benzene and chromatographed on silica gel.

The first fraction, eluted with benzene, gave 0.25 g (20%) of compounds **15a**, reddish yellow crystals, mp 137—138 °C. Found: C, 83.26; H, 5.75%; M^+, 518. Calcd for $C_{36}H_{30}Fe$: C, 83.39; H, 5.83%; M, 518.

The second fraction, eluted with chloroform, gave 1,1′-bis(4′-hydroxymethyl-4-biphenylyl)ferrocene (**12a**), orange yellow crystals, mp 250—252 °C (dec), in 2.5% yield. IR (KBr): 3450 (-OH), 1600, 1500, 820 (*p*-disubstituted benzene ring), and 810 cm^{-1} (1,1′-disubstituted ferrocene ring). NMR (pyridine-d_5): δ=1.58 (s, 2H, -OH), 4.23 (t, 4H, H_β), 4.48 (t, 4H, H_α), 4.59 (s, 4H, $-CH_2-$), and 7.18—7.78 (m, 16H, Ar-H). Found: C, 78.52; H, 5.41%; M^+, 550. Calcd for $C_{36}H_{30}FeO_2$: C, 78.55; H, 5.47%; M, 550.

The third fraction, eluted with a mixture of chloroform and ethanol (10:1), gave **1**, reddish crystals, mp 238—240 °C (decomp), in 32% yield. Found: C, 83.87; H, 4.96%; M^+, 514. Calcd for $C_{36}H_{26}Fe$: C, 84.05; H, 5.09%; M, 514.

*The Catalytic Hydrogenation of **1** to **2**.* In the mixture of dioxane (100 cm^3) and ethanol (100 cm^3), compound **1** (0.50 g) was hydrogenated with PtO_2 (0.1 g) at room temperature under ordinary pressure. The reaction mixture was filtered to remove the catalyst and the filtrate was evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel with chloroform to give 0.35 g (70% yield) of **2**, reddish crystals, mp 240—242 °C (decomp). Found: C, 83.61; H, 5.38%; M^+, 516. Calcd for $C_{36}H_{28}Fe$: C, 83.72; H, 5.46%; M, 516.

*The Reductive Coupling of **13b** with $TiCl_4$–Zn.* The reductive coupling of **13b** with $TiCl_4$–Zn was carried out in the same way as described for the reductive coupling of **13a**, and the products were separated by column chromatography on silica gel.

The first fraction, eluted with benzene, gave compound **15b**, reddish yellow crystals, mp 199—200 °C, in 12.5% yield. Found: C, 83.31; H, 5.73%; M^+, 518. Calcd for $C_{36}H_{30}Fe$: C, 83.39; H, 5.83%; M, 518.

The second fraction, eluted with chloroform, gave **12b**, reddish yellow crystals, mp 166—168 °C, in 8.5% yield.

The third fraction, eluted with chloroform, gave **3**, reddish crystals, mp 215—216 °C, in 28% yield. Found: C, 83.92; H, 4.93%; M^+, 514. Calcd for $C_{36}H_{26}Fe$: C, 84.05; H, 5.09%; M, 514.

*The Catalytic Hydrogenation of **3** to **4**.* The catalytic hydrogenation of **3** was carried out in the same way as described for the catalytic hydrogenation of **1**, and the product was purified by column chromatography on silica gel with chloroform to give **4**, orange yellow crystals, mp 239—240 °C, in 80% yield. Found: C, 83.69; H, 5.40%; M^+, 516. Calcd for $C_{36}H_{28}Fe$: C, 83.72; H, 5.46%; M, 516.

*The Reductive Coupling of **13c** with $TiCl_4$–Zn.* The reductive coupling of **13c** was carried out in the same way as described for the reductive coupling of **13a** with $TiCl_4$–Zn, and the products were separated by column chromatography on silica gel.

The first fraction, eluted with benzene, gave compound **15c**, reddish crystals, mp 137—138 °C, in 11% yield. Found: C, 83.30; H, 5.71%; M^+, 518. Calcd for $C_{36}H_{30}Fe$: C, 83.39; H, 5.83%; M, 518.

The second fraction, eluted with chloroform, gave **12c**, reddish yellow crystals, mp 152—153 °C, in 8.5% yield.

The third fraction, eluted with chloroform, gave **5a**, reddish crystals, mp 287—288 °C, in 34% yield. Found: C, 83.91; H, 4.97%; M^+, 514. Calcd for $C_{36}H_{26}Fe$: C, 84.05; H, 5.09%; M, 514.

The fourth fraction, eluted with chloroform, gave **5s**, reddish crystals, mp >280 °C, in 25% yield. Found: C, 83.88; H, 4.91%; M^+, 514. Calcd for $C_{36}H_{26}Fe$: C, 84.05; H, 5.09%; M, 514.

*The Catalytic Hydrogenation of **5s** and **5a** to **6**.* The catalytic hydrogenation of **5s** was carried out in the same way as described for the catalytic hydrogenation of **1**, and the product was purified by column chromatography on silica gel with chloroform to give **6**, reddish crystals, mp 279—280 °C (decomp), in 54% yield. Found: C, 83.70; H, 4.38%; M^+, 514. Calcd for $C_{36}H_{28}Fe$: C, 83.72; H, 5.46%; M, 516.

The catalytic hydrogenation of **5a** also led to the formation of **6**, mp 279—280 °C (decomp), in 65% yield.

*(4'-Methyl-4-biphenylyl)ferrocene (**16a**).* In the presence of nickel complex, the reaction of **9** with the Grignard reagent prepared from *p*-bromotoluene was carried out in the same way as described for **13a**, and the product was purified by column chromatography on silica gel with benzene to give **16a**, reddish orange crystals, mp 174—176 °C, in 57% yield. Found: C, 78.29; H, 5.65%; M^+, 352. Calcd for $C_{23}H_{20}Fe$: C, 78.42; H, 5.72%; M, 352.

*(3'-Methyl-4-biphenylyl)ferrocene (**16b**).* The reaction of **9** with the Grignard reagent derived from *m*-bromotoluene was carried out in the same way as described for **13a**, and the product was purified by column chromatography on silica gel with benzene to give **16b**, reddish orange crystals, mp 106—108 °C, in 44% yield. Found: C, 78.33; H, 5.59%; M^+, 352. Calcd for $C_{23}H_{20}Fe$: C, 78.42; H, 5.72%; M, 352.

*(2'-Methyl-4-biphenylyl)ferrocene (**16c**).* The reaction of **9** with the Grignard reagent derived from *o*-bromotoluene was carried out in the same way as described for **13a**, and the product was purified by column chromatography on silica gel with benzene to give **16c**, reddish orange crystals, mp 137—138 °C, in 48% yield. Found: C, 78.32; H, 5.61%; M^+, 352. Calcd for $C_{23}H_{20}Fe$: C, 78.42; H, 5.72%; M, 352.

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