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XXVIII *. INTERMOLECULAR CARBON—CARBON BOND FORMATION BY OXIDATION OF (1-ARYLVINYL)FERROCENES WITH MOLECULAR OXYGEN IN THE PRESENCE OF SILICA GEL

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Summary

Treatment of (1-hydroxy-1-arylethyl)ferrocenes (VII) or (1-arylvinyl)ferrocenes (VIII) in hexane with O_2 gas in the presence of silica gel gave oxidative dimerization products; butadiene (XI), tetrahydrofuran (XII) and butan-1,4-diol (XIII) derivatives. It is suggested that the dimers were produced via six-membered cyclic peroxide formed by incorporation of a molecular oxygen into two olefin molecules.

Previously, we reported a novel oxidative cyclization of 1,1′-divinylferrocene derivatives (I) with molecular oxygen in the presence of hydrochloric acid or various Lewis acids [2]. The reaction involves intramolecular carbon—carbon bond formation accompanied by incorporation of a molecular oxygen. Six-membered cyclic peroxides (II) and their derivatives (III—VI etc.) were isolated in the oxidation (Scheme 1). Application of the above reaction mode to intermolecular reaction provides a method for head-to-head dimerization of vinyl compounds.

Wittig and Gauss [3] described in 1947 that autoxidation of 1,1′-bis(*p*-methoxyphenyl)ethylene in benzaldehyde for 1 year gave a six-membered cyclic peroxide by intermolecular reaction. However, further research for confirmation of the reaction and the structure of the resulting peroxide seems to have not yet been reported.

The present paper describes that oxidation of (1-arylvinyl)ferrocenes (VIII) with molecular oxygen in the presence of silica gel gave several head-to-head

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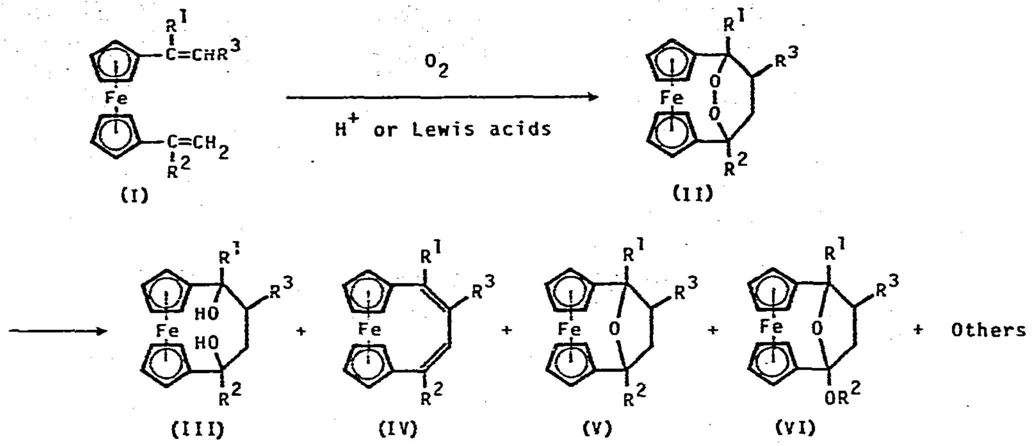
* For part XXVII, see ref. 1.

SCHEME 1



dimerization products formed via, undoubtedly, six-membered cyclic peroxides [4].

Results and discussion

(1-Hydroxyalkyl)ferrocenes (VII, XVI) and vinylferrocenes (VIII, XVII), the starting materials of the oxidation, were prepared by the Grignard reactions of acylferrocenes with alkyl or aryl halides. The Grignard intermediates were easily converted to the corresponding vinylferrocenes, due to unusual stability of ferrocenyl-1-carbocations [5]. Bozak et al. [6] have reported that no alcohol but an anomalous product (XIVa) resulted in the reaction of acylferrocenes with the Grignard reagents prepared from iodides. However, by re-examination of the reaction of benzoylferrocene (Xa) with methylmagnesium iodide, we obtained the corresponding alcohol (VIIa) (12%) and olefin (VIIIa) (47%) but no other product. The butene (XIVa), a head-to-tail dimerization product of the olefin (VIIIa), was produced on digestion of the Grignard intermediate with aq. HCl (74%), or on treatment of alcohol (VIIa) or olefin (VIIIa) with aq. HCl (see Table 1). Dimer XIVb (m.p. 153—155°C) was also obtained (39%) by quenching the Grignard intermediate with aq. HCl in the reaction of *p*-methoxybenzoylferrocene (Xb) with CH_3MgI. Treatment of the intermediate with aq. NH_4Cl yielded only a slight amount of the butene (XIVb) (2%). Careful work-up of the Grignard reaction mixtures could almost completely suppress formation of the acid-catalyzed dimerization products (XIV) and gave the corresponding hydroxyl and olefin derivatives.

(1-Hydroxy-1-phenylethyl)ferrocene (VIIa) or (1-phenylvinyl)ferrocene (VIIIa) was treated with O_2 gas or air under the same conditions (6 *N* HCl, benzene, 1 h) as the cyclization of 1,1′-divinylferrocenes (I) [2a—c] to give the olefin (VIIIa), butene (XIVa) and benzoylferrocene (Xa). However, the oxidation of the alcohol (VIIa) or olefin (VIIIa) in hexane in the presence of silica gel yielded three dimerization products, XIa (M^+, 574), XIIa (M^+, 592) and XIIIa (M^+, 610). The IR spectrum of the butadiene derivative (XIa) (m.p. 244—246°C), possessing a singlet signal of olefinic protons (2H) at δ 6.52 in the PMR spectrum, did not

TABLE 1

OXIDATION OF (1-HYDROXY-1-ARYLETHYL)FERROCENES AND (1-ARYLVINYL)FERROCENES WITH MOLECULAR OXYGEN

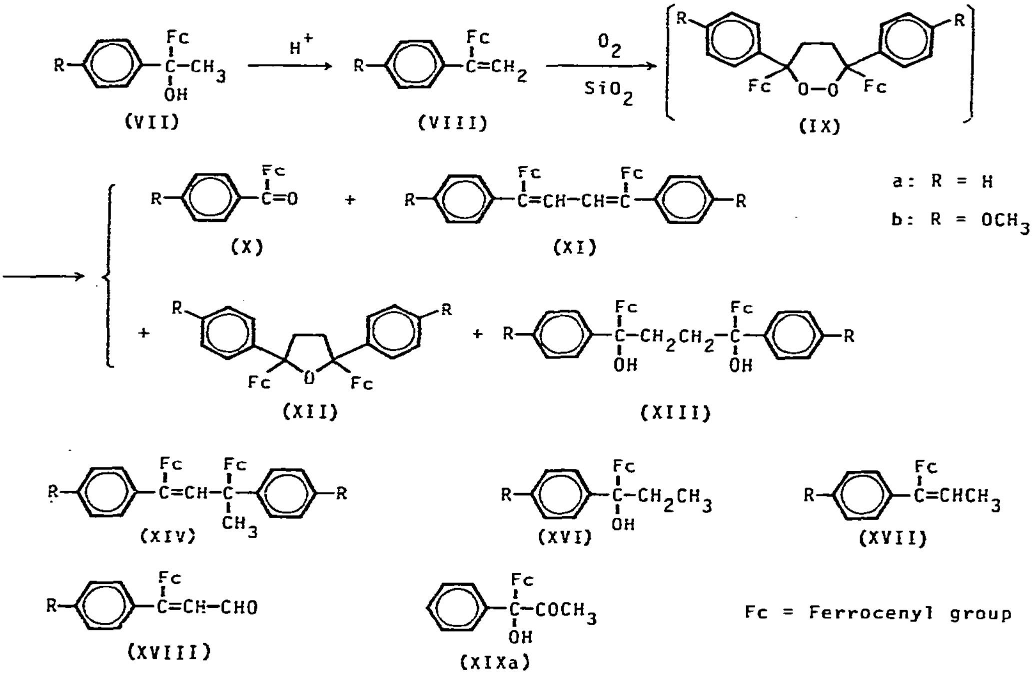
Starting material[a]	Conditions				Products (%)[b]							
	Catalyst	Atmosphere	Solvent	Reaction time (h)	VIII	XIV	X	Oxidative dimerization products				
								XI	XII-C	XII-T	XIII	Total
(R = H)												
VIIa	6 *N* HCl	O_2	benzene	1	82.0	1.6	2.2					
VIIIa	6 *N* HCl	air	benzene	1	73.9	5.3	1.9					
VIIa	SiO_2	air	benzene	5	70.0		2.3					
VIIa	SiO_2	air	hexane	5	50.6		2.8	15.4				15.4
VIIa	SiO_2	O_2	hexane	5	47.8		4.8	23.3	5.5	6.8	0.8	36.4
VIIa	H^+—Al_2O_3	O_2	hexane	5	48.5		5.7	5.9	1.0		5.0	11.9
VIIIa	SiO_2	O_2	hexane	5	22.0		7.9	11.4	1.6		3.1	16.1
VIIa	SiO_2	N_2	hexane	5	84.0		2.2		1.4			1.4
(R = OCH$_3$)												
VIIb	SiO_2	air	hexane	5	13.5		2.5	59.0				59.0
VIIb	SiO_2	O_2	hexane	0.25	32.7		8.7	30.6	2.3	1.1		34.0
VIIIb	SiO_2	O_2	hexane	1.5	15.4		5.6	32.3			9.0	41.3
VIIIb	SiO_2	O_2	hexane	0.25	51.0		2.4	17.1	1.8	1.8	15.5	36.2
VIIIb	SiO_2	O_2	CCl_4	0.25	66.5		1.8	5.5	0.5			6.0

[a] The reactions of alcohol (VIIa or VIIb) recovered the starting material in 2—3% yields. [b] Some unknown products and decomposition residues were found, except for the products shown in the table.

show a stretching band of the C=C bond in the region near 1600 cm^{-1} but only a weak band assigned to the Ph ring at 1601 cm^{-1}. However, in its Raman spectrum a strong stretching band of the conjugated C=C bond appeared at 1599 cm^{-1}. The inactivity and activity of the C=C bond in the two vibrational spectra are due to, possibly, a high symmetry of the diene (XIa). The spectra of butan-1,4-diol (XIIIa) (m.p. 190—192°C) indicated ν(OH) bands at 3512 and 3358 cm^{-1}, and a singlet of two hydroxyl protons. The singlet signal disappeared on addition of D_2O. The tetrahydrofuran derivative (XIIa) was separated into two isomers by further column chromatography over silica gel. On examination using a Dreiding stereomodel, the chemical shift difference ($\Delta\nu$) between two protons of a methylene group in the *cis* isomer should be larger than that of the *trans* isomer, due to the effectiveness of the paramagnetic anisotropy effect of two ferrocenyl groups. Therefore, the lower polar compound (XIIa-C) (m.p. 224—226°C, $\Delta\nu$ = 0.42 ppm) was assigned to the *cis* isomer and the higher polar compound (XIIa-T) (m.p. 168—168.5°C, $\Delta\nu$ = 0.03 ppm) to the *trans* isomer.

Oxidation of [1-hydroxy-1-(*p*-methoxyphenyl)ethyl]ferrocene (VIIb) or [1-(*p*-methoxyphenyl)vinyl]ferrocene (VIIIb) with O_2 gas and silica gel also gave four oxidative dimerization products (see Scheme 2); butadiene (XIb), *cis* and *trans* tetrahydrofuran (XIIb-C and XIIb-T), and butan-1,4-diol (XIIIb) derivatives. Butadiene (XIb) (m.p. 210—211°C) showed the PMR, Raman and mass spectra, respectively, involving a singlet of two olefinic protons at δ 6.53, a conjugated C=C stretching band at 1592 cm^{-1}, and a molecular ion peak at *m/e* 634. Two tetrahydrofuran derivatives XIIb-C (m.p. 211—213°C) and XIIb-T (m.p. 181.5—182°C) possessing molecular ions at *m/e* 652 were assigned to *cis* and

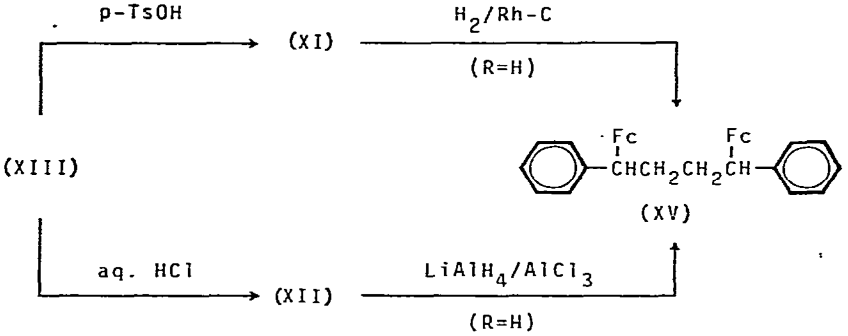
SCHEME 2



trans isomers, respectively, by comparison of chemical shift differences (XIIb-C: $\Delta\nu = 0.45$ ppm, XIIb-T: $\Delta\nu = 0.04$ ppm) between two kinds of methylene protons, according to the same consideration as described already in XIIa. Butan-1,4-diol (XIIIb) (m.p. 189.5—192.5°C) showed characteristic OH bands at 3555 and 3430 cm^{-1} and a singlet signal of two hydroxyl protons at δ 3.20, though no molecular ion peak at *m/e* 670 was found but only dehydrated ion peaks at *m/e* 652 and 634 in the mass spectrum. The diol (XIIIb) was easily dehydrated by heating or with contaminant acid. In fact, the diol was contaminated with XIIb formed by dehydration even in recrystallization from ethanol, benzene or AcOEt.

The structure of the oxidative dimerization products (XI, XII and XIII) were supported by the chemical correlation as shown in Scheme 3.

SCHEME 3



The alcohols (VII) and olefins (VIII) were treated with silica gel under an N_2 atmosphere to give hardly any oxidation product. The olefins (VIII) were converted into the oxidative dimers by treatment with acidic alumina and O_2 gas but could not be by neutral alumina and O_2 gas. Furthermore, the oxidative dimers were given neither by treatment with aq. HCl/O_2 gas nor by silica gel/O_2 gas in benzene.

Therefore, it is certain that the presence of molecular oxygen and acidic absorbent are required for the oxidative dimerization, and that non-polar solvent should be used in order to, possibly, make more effective the absorption of reactant molecules to the absorbent.

From the previous intramolecular cyclization [2] and the above experimental results, the intermolecular oxidative dimerization path can be summarized as follows. The alcohol (VII) is converted to the olefin (VIII) by dehydration with acidic catalyst. The olefin (VIII) is absorbed on the silica gel surface and this is followed by reaction with the oxygen molecule and the other olefin molecule absorbed on the silica gel. Six-membered cyclic peroxide (IX) is formed via a mechanism analogous to that presented already in the intramolecular cyclization [2d], though the peroxide (IX) could not be isolated in the present work. The peroxide (IX) is catalytically converted by silica gel or acid into butan-1,4-diol (XIII) via homolytic cleavage of the O—O bond followed by abstraction of hydrogens. Dehydration of one and two molecules, respectively, from the diol (XIII) gives tetrahydrofuran (XII) and butadiene (XI) derivatives. The three dimerization products XI, XII and XIII are, respectively, analogous to the ferrocenophane derivatives IV, V and III which were given by the oxidation of 1,1'-divinylferrocenes [2].

Benzoylferrocene (Xa) and *p*-methoxybenzoylferrocene (Xb) which were obtained in the oxidation are not contaminants from the starting materials in the Grignard reactions, because Xa and Xb were also given when alcohols (VII) and olefines (VIII) prepared by the Grignard reactions of acetylferrocene were used. The ketones (X) were produced even when no oxidative dimer was found, for example, in the oxidation of VIIIa in benzene with aq. HCl or silica gel. Therefore, the ketones (X) were possibly formed by oxidative cleavage of the double bond of olefins with molecular oxygen.

The oxidative dimerization products of the *p*-methoxyphenyl derivative (b: $R = OCH_3$) were obtained in better total yield than those of the phenyl derivative (a: $R = H$). This result suggests that the oxidation is accelerated by rich electron density in the double bond of the olefins. The strongly electron-donating character of the ferrocenyl group is already well-known [7]. Wittig and Gauss [3] obtained the six-membered cyclic peroxide just by autoxidation of the olefin possessing two *p*-methoxyphenyl groups, strong electron donors.

On the other hand, Keans [8] indicated theoretically that the concerted addition of ground state molecular oxygen ($^3\Sigma$) to olefins and dienes is allowed when the π-ionization potential of the acceptor is unusually low, and that the reaction of singlet molecular oxygen ($^1\Delta$) with dienes is predicted to be allowed. Therefore, the oxidative dimerization of the present compounds with ground state molecular oxygen may occur via a process similar to that of reaction of 4π-electron system with singlet molecular oxygen. In fact, photosensitized oxidation of the olefins (VIII) in the presence of neutral alumina and sensitizer also afforded the oxidative dimerization products [9]. An acidic medium in the oxidation of the olefin (VIII) with ground state molecular oxygen is, possibly, required for activation of another olefin in dimerizing, in analogy with the effect of Lewis acids for dienophiles in Diels—Alder reactions [10].

The same oxidative dimerization as that of VII and VIII was expected for (1-hydroxypropyl)ferrocene (XVI) and propenylferrocene (XVII) derivatives. However, only small amounts of some oxidation products, acroleins (XVIII) *, acetyl derivatives (XIXa) (m.p. 109—111°C) and ketones (X) were given, but no dimerization product. It is considered that the inertness of the olefins (XVII) in oxidative dimerization is due to an electronic or steric effect of the methyl group.

The cyclic peroxide described by Wittig and Gauss in some additional remarks could not be isolated by our re-examination [11] of the oxidation of 1,1'-bis(*p*-methoxyphenyl)ethylene in benzaldehyde with O_2 gas for 1 week or 1 month. Oxidation of the ethylene in hexane with O_2 gas in the presence of silica gel for 5 h, i.e. under the same conditions as the reaction of the ferrocene derivatives, recovered only the starting material (84%) [11]. Furthermore, the reaction of the ferrocene derivatives (VIII) under the modified conditions described by Wittig and Gauss (in benzaldehyde, O_2 gas, 48 h) afforded no oxidative dimerization product of VIII [11].

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* The structures of the compounds (XVIIIa and XVIIIb) have not yet been confirmed.

Experimental

All melting points were determined on a Yanagimoto Micro-Melting Point Apparatus and are uncorrected. Column-chromatographic separations were carried out with Wako activated alumina (300 mesh), Wakogel C-200 and C-100 and Mallinckrodt silicic acid (100 mesh). Kanto Kagaku silica gel (100 mesh), Wakogel C-200 and C-100 were used as catalysts in oxidations. Acidic alumina employed in oxidations was prepared by treatment of Wako activated alumina (300 mesh) with aq. HCl and then by drying at over 150°C.

IR spectra were measured using a Hitachi Perkin—Elmer model 225 or a Hitachi model 215 grating infrared spectrophotometer. Raman spectra were measured on a JASCO R-300 or JEOL JRS-400T Raser Raman spectrophotometer operating on the 5145 Å line of Argon ion laser. PMR spectra were measured on a JEOL JNM-4H-100 spectrometer at 100 MHz unless otherwise stated. The PMR spectra at 60 MHz were measured on a Hitachi R-24 spectrometer. All PMR spectra were recorded at room temperature with tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi RMU-7M double focussing mass spectrometer with a direct insertion probe. The spectra were recorded at an ionizing voltage of 70 eV unless otherwise stated. The numbers in parentheses in the mass spectral data indicate the relative intensities of each peak against the respective base peak. The high-resolution spectra were obtained using PFK as internal standard, and treated by a Hitachi Datalyser 002 system.

General procedures

The Grignard reactions of acylferrocenes

To a slowly stirred suspension of magnesium (24 mmol) in ether (5 ml) was added dropwise an ether solution (7 ml) of the corresponding bromide or iodide (20 mmol). Acylferrocene (4.1 mmol) in ether or ether/benzene (30 ml) was then added dropwise and the mixture was stirred at room temperature for 1 h. Saturated aq. NH_4Cl was added to the reaction mixture and the hydrolysate was extracted with ether. The extracts were washed with saturated aq. NaCl, dried and evaporated. Each reaction described below was carried out 1—5 times in the scale of the above procedure.

Dehydrations of (1-hydroxy-1-arylalkyl)ferrocenes (VII, XVI) with aq. HCl.

Nitrogen gas was bubbled in a benzene solution (500 ml) of VII or XVI (1.0 g), under stirring for 15 min. To the solution was added 3 *N* HCl and the mixture was vigorously stirred with a mechanical stirrer at room temperature under an N_2 atmosphere for 30 min. The reaction mixture was phase separated and the organic layer was washed with aq. $NaHCO_3$ and then saturated aq. NaCl, dried and evaporated. The residue was purified by column chromatography over alumina to give the corresponding (1-arylalkenyl)ferrocene (VIII, XVII) in 70—90% yields.

Oxidations with oxygen gas.

A suspension of a catalyst (5 times quantity of the alcohol or olefin) in a solution (30 ml) of alcohol (VII, XVI) or olefin (VIII, XVII) (0.5 mmol) was stirred while bubbling through dry O_2 gas or air at room temperature for the required reaction time. The reaction mixture was filtered and the products remaining on the catalyst were completely eluted with AcOEt until they were no longer appearing in the eluate. The combined solution of the filtrate and the eluate was evaporated under reduced pressure below room temperature. Each reaction described below was carried out 1—5 times in the scale of the above procedure.

Acylferrocenes

Acetylferrocene, m.p. 82—83°C (lit. [12]; m.p. 85—86°C), benzoylferrocene, m.p. 108—109°C (lit. [13] m.p. 108—109°C), and propanoylferrocene, m.p. 35—37°C (lit. [14], m.p. 38—39°C), were prepared according to the described procedures.

(p-Methoxybenzoyl)ferrocene (Xb)

To a powder (3.00 g) of *p*-anisic acid was slowly added, dropwise, PCl_3 (30 ml) under an N_2 atmosphere. The reaction mixture was stirred at 40—50°C for 5 h and the excess PCl_3 was then evaporated under reduced pressure. The unstable residue (IR spectrum (neat liq., cm^{-1}): ν(C=O) of —COCl 1780) was dissolved in CH_2Cl_2 (10 ml), and then the resultant solution was added dropwise to a CH_2Cl_2 suspension (20 ml) of $AlCl_3$ (1.00 g) and ferrocene (3.72 g) under an N_2 atmosphere. The reaction mixture was stirred at room temperature for 2 h, and then poured into ice-water. The hydrolysate was phase separated, and the organic layer was washed with aq. Na_2CO_3 and then saturated aq. NaCl, dried and evaporated. The residue was column-chromatographed over alumina to separate into the recovered ferrocene and two product bands. The band eluted with benzene/AcOEt (10 : 1) yielded (*p*-methoxybenzoyl)ferrocene (Xb) (642 mg), which was recrystallized from hexane/benzene to give reddish brown prisms, m.p. 84.5—85°C. (Found: C, 67.48; H, 5.00, $C_{18}H_{16}O_2Fe$ calcd.: C, 67.53; H, 5.04%). IR spectrum (KBr, cm^{-1}): ν(C=O) 1602. PMR spectrum (δ(ppm), $CDCl_3$): 3.85 (3H, s, —OCH_3), 4.18 (5H, s, unsubstituted Cp), 4.54 and 4.89 (each 2H, t, an A_2X_2 system, substituted Cp), 6.94 and 7.94 (each 2H, d, Ph). Mass spectrum (*m/e*): 320 (M^+, 100).

The last band eluted with benzene/AcOEt (5 : 1) yielded 1,1′-bis(*p*-methoxybenzoyl)ferrocene (20 mg), which was recrystallized from benzene/AcOEt to give reddish brown needles, m.p. 141.5—142°C. (Found: C, 69.08; H, 4.87. $C_{26}H_{22}O_4Fe$ calcd.: C, 68.74; H, 4.88%.) IR spectrum (KBr, cm^{-1}): ν(C=O) 1628 and 1613. PMR spectrum (δ, $CDCl_3$): 3.85 (6H, s, —OCH_3), 4.54 and 4.89 (each 4H, t, an A_2X_2 system, substituted Cp), 6.88 and 7.83 (each 4H, d, Ph). Mass spectrum (*m/e*): 454 (M^+, 100).

(1-Hydroxy-1-phenylethyl)ferrocene (VIIa) and (1-phenylvinyl)ferrocene (VIIIa)

The crude product given by the Grignard reaction of benzoylferrocene (Xa) with methylmagnesium iodide was separated into three bands by column chromatography over alumina. The first band eluted with benzene yielded (1-phenylvinyl)ferrocene (VIIIa) (47%), a reddish brown oil. (Found: M^+ 288.0595. $C_{18}H_{16}Fe$ calcd.: mol. wt. 288.0600.) IR spectrum (neat liq., cm^{-1}): ν(C=C) 1620. PMR spectrum (δ, CS_2): 3.92 (5H, s, unsubstituted Cp), 4.07 and 4.17 (each

2H, t, an A_2X_2 system, substituted Cp), 5.06 and 5.41 (each 1H, d, an AX system, J = 1.6 Hz, $=CH_2$), 7.1—7.4 (5H, m, Ph). Mass spectrum (m/e): 288 (M^+, 100).

The compound obtained from the second band was benzoylferrocene (Xa) (1.5%). The third band eluted with benzene/AcOEt (5 : 1) yielded (1-hydroxy-1-phenylethyl)ferrocene (VIIa) (12%), m.p. 112—114°C (lit. [15] m.p. 110—111°C).

When the above Grignard reaction mixture was hydrolyzed with 6N HCl, 1,3-diferrocenyl-1,3-diphenylbutene-1 (XIVa) (74%, m.p. 138—142°C, lit. [6a] m.p. 139—142.5°C) was obtained from the band eluted with hexane/benzene (1 : 1). Olefin (VIIIa) and benzoylferrocene (Xa) were afforded in 7 and 8% yields, respectively, but no alcohol (VIIa).

The Grignard reaction of acetylferrocene with phenylmagnesium bromide gave the olefin (VIIIa) and alcohol (VIIa) in 4.3 and 72% yields. A small amount of biphenyl (ca. 4%, based on bromobenzene), a by-product, was also produced.

[1-Hydroxy-1-(p-methoxyphenyl)ethyl]ferrocene (VIIb) and [1-(p-methoxyphenyl)vinyl]ferrocene (VIIIb)

The crude product given by the Grignard reaction of acetylferrocene with p-methoxyphenylmagnesium bromide was column-chromatographed over alumina. First, 4,4′-dimethoxybiphenyl was eluted with hexane until the biphenyl was not contained in the eluate. The band eluted with hexane/benzene (5 : 1) yielded [1-(p-methoxyphenyl)vinyl]ferrocene (VIIIb) (10%), a reddish brown oil. (Found: M^+ 318.0691. $C_{19}H_{18}OFe$ calcd.: mol. wt. 318.0705.) IR spectrum (neat liq., cm^{-1}): ν(C=C) 1605. PMR spectrum (δ, $CDCl_3$): 3.80 (3H, s, $-OCH_3$), 4.07 (5H, s, unsubstituted Cp), 4.22 and 4.32 (each 2H, t, an A_2X_2 system, substituted Cp), 5.12 and 5.46 (each 1H, an AX system, J = 1.7 Hz, $=CH_2$), 6.86 and 7.39 (each 2H, d, an A_2X_2 system, Ph). Mass spectrum (m/e): 3.18 (M^+, 100), 303 ($[M - CH_3]^+$, 9.1).

The next band eluted with benzene/AcOEt (5 : 1) gave a small amount of acetylferrocene. The last band eluted with AcOEt yielded [1-hydroxy-1-(p-methoxyphenyl)ethyl]ferrocene (VIIb) (69%), which was recrystallized from hexane/AcOEt to give yellow needles, m.p. 89.5—91.5°C. (Found: M^+ 336.0814. $C_{19}H_{20}O_2Fe$ calcd.: mol. wt. 336.0812.) IR spectrum (KBr, cm^{-1}): ν(OH) 3560. PMR spectrum (δ, $CDCl_3$): 1.80 (3H, s, $-CH_3$), 3.72 (3H, s, $-OCH_3$), 4.3—4.0 (4H, m, substituted Cp), 4.20 (5H, s, unsubstituted Cp), 6.76 and 7.27 (each 2H, d, an A_2X_2 system, Ph). Mass spectrum (m/e): 336 (M^+, 19), 318 ($[M - H_2O]^+$, 100), 253 ($[M - (H_2O + C_5H_5)]^+$, 23).

The crude product given by the Grignard reaction of (p-methoxybenzoyl)ferrocene (Xb) with methylmagnesium iodide was column-chromatographed over alumina. Besides olefin (VIIIb) (13%) and alcohol (VIIb) (81%), a small amount of 1,3-diferrocenyl-1,3-bis(p-methoxyphenyl)butene-1 (XIVb) (2%) was yielded from the second band eluted with benzene. The dimer (XIVb) was recrystallized from hexane/benzene to give orange-yellow prisms, m.p. 153—155°C. (Found: C, 71.99; H, 5.90. $C_{38}H_{36}O_2Fe_2$ calcd.: C, 71.72; H, 5.70%.) IR spectrum (KBr, cm^{-1}): ν(C=C) 1602. PMR spectrum (δ, $CDCl_3$): 1.48 (3H, s, $-CH_3$), 3.70 and 3.73 (each 3H, s, $-OCH_3$), 3.9—4.2 (8H, m, substituted Cp), 4.11 and 4.21 (each 5H, s, unsubstituted Cp), 6.55—7.10 (8H, m, Ph), 6.64 (1H, s, =CH—). Mass spectrum (*m/e*): 636 (M^+, 100), 450 ($[M - \text{FcH}]^+$, 67).

When the Grignard reaction mixture was treated with 6*N* HCl, the olefin (VIIIb) and the butene (XIVb) were yielded in 53 and 39%, respectively, but the alcohol (VIIb) not at all.

(1-Hydroxy-1-phenylpropyl)ferrocene (XVIa) and (1-phenyl-1-propenyl)ferrocene (XVIIa)

The crude product in the reaction of propanoylferrocene with phenylmagnesium bromide was column-chromatographed over alumina to separate into an olefin and an alcohol. The band eluted with hexane/benzene (1 : 1) yielded (1-phenyl-1-propenyl)ferrocene (XVIIa) (13%), a brown oil, which was a mixture of the *cis* and *trans* isomers (4 : 1). The isomer ratio was determined by means of PMR spectroscopy. [Found: M^+ 302.0750. $C_{19}H_{18}Fe$ calcd.: mol. wt. 302.0756.) IR spectrum (neat liq., cm^{-1}): ν(C=C) 1630. PMR spectrum (δ, CS_2): 1.45 and 1.97 (3H, intensity ratio = 4 : 1, each d, J = 7.0 Hz, —CH_3), 3.8—4.2 (9H, m, Cp), 5.55 and 5.90 (1H, intensity ratio = 1 : 4, each q, J = 7.0 Hz, =CH—), 7.0—7.3 (5H, m, Ph). Mass spectrum (*m/e*): 302 (M^+, 100), 275 ($[M - C_2H_3]^+$, 7.6).

The band eluted with benzene/AcOEt (30 : 1) yielded (1-hydroxy-1-phenylpropyl)ferrocene (XVIa), (70%), m.p. 110—111°C (lit. [15] m.p. 110—111°C).

[1-Hydroxy-1-(p-methoxyphenyl)propyl]ferrocene (XVIb) and [1-(p-methoxyphenyl)propenyl]ferrocene (XVIIb)

On chromatography over alumina, 4,4′-dimethoxybiphenyl, a by-product, was eluted with hexane/benzene (20 : 1) until the biphenyl was not contained in the eluate. The band eluted with hexane/benzene (5 : 1) yielded [1-(*p*-methoxyphenyl)propenyl]ferrocene (XVIIb) (12%), which was recrystallized from hexane to give reddish brown crystals, m.p. 80—82°C. The olefin was a mixture of *cis* and *trans* isomer (3 : 1). (Found: M^+ 332.0870. $C_{20}H_{20}OFe$ calcd.: mol. wt. 332.0862.) IR spectrum (KBr, cm^{-1}): ν(C=C) 1605. PMR spectrum (δ, CS_2): 1.47 and 1.98 (3H, intensity ratio = 3 : 1, each d, J = 7.0 Hz, —CH_3), 3.68 and 3.72 (3H, intensity ratio = 1 : 3, each s, —OCH_3), 3.8—4.2 (9H, m, Cp), 5.53 and 5.89 (1H, intensity ratio = 1 : 3, each q, J = 7.0 Hz, =CH—), 6.6—7.1 (4H, m, Ph). Mass spectrum (*m/e*): 332 (M^+, 100), 305 ($[M - C_2H_3]^+$, 4.2).

The band eluted with benzene/AcOEt (30 : 1) yielded [1-hydroxy-1-(*p*-methoxyphenyl)propyl]ferrocene (XVIb) (61%), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 86.5—87°C. (Found: M^+, 350.0942. $C_{20}H_{22}O_2Fe$ calcd.: mol. wt. 350.0967.) IR spectrum (KBr, cm^{-1}): ν(OH) 3565. PMR spectrum (δ, $CDCl_3$): 0.84 (3H, t, J = 7.5 Hz, —CH_3), 2.09 (2H, q, J = 7.5 Hz, —CH_2—), 2.52 (1H, s, —OH), 3.76 (3H, s, —OCH_3), 3.99, 4.17 4.32 (4H, each m, substituted Cp), 4.18 (5H, s, substituted Cp). 6.30 and 7.28 (each 2H, an $AA'XX'$ system, Ph). Mass spectrum (*m/e*): 350 (M^+, 12), 332 ($[M - H_2O]^+$, 100).

Oxidation of (1-hydroxy-1-phenylethyl)ferrocene (VIIa) or (1-phenylvinyl)ferrocene (VIIIa)

The crude product given by oxidation of VIIa or VIIIa was column-chromatographed over alumina. An oily compound afforded from the band eluted with hexane/benzene (4 : 1) was olefin (VIIIa).

The part eluted with hexane/benzene (1 : 1) was re-chromatographed several times over silicic acid with hexane/benzene (4 : 1) to separate into three products. The first eluted band yielded 1,4-diferrocenyl-1,4-diphenyl-1,3-butadiene (XIa), which was recrystallized from AcOEt to give deep red needles, m.p. 244—246°C. (Found: C, 75.15; H, 5.43; M^+ 574.1028. $C_{36}H_{30}Fe_2$ calcd.: C, 75.29; H, 5.27%; mol. wt. 574.1043.) Raman spectrum (KBr, cm^{-1}): ν(C=C) 1599. PMR spectrum (δ, $CDCl_3$): 4.02 (10H, s, unsubstituted Cp), 4.05—4.15 (8H, m, substituted Cp), 6.52 (2H, s, =CH—), 7.42 (10H, bs, Ph). Mass spectrum (*m/e*): 574 (M^+, 100), 287 (M^{2+}, 24).

The second band in the re-chromatography over silicic acid yielded *cis*-2,5-diferrocenyl-2,5-diphenyltetrahydrofuran (XIIa-C), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 224—226°C. (Found: C, 72.73; H, 5.48; M^+ 592.1154. $C_{36}H_{32}OFe_2$ calcd.: C, 72.99; H, 5.45%; mol. wt. 592.1150.) IR spectrum (KBr, cm^{-1}): ν(C—O—C) 1044 and 1027. PMR spectrum (δ, $CDCl_3$): 2.35 and 2.77 (4H, an $AA'XX'$ system, $—CH_2—$), 3.62, 3.68 and 3.95 (8H, each m, substituted Cp), 4.01 (10H, s, unsubstituted Cp), 7.35—7.90 (10H, m, Ph). Mass spectrum (*m/e*): 592 (M^+, 97), 574 ($[M-18]^+$, 71), 186 (FcH^+, 44), 105 ($PhCO^+$, 100).

The third band in the re-chromatography yielded *trans*-2,5-diferrocenyl-2,5-diphenyltetrahydrofuran (XIIa-T), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 168—168.5°C. (Found: M^+ 592.1179. $C_{36}H_{32}OFe_2$ calcd.: mol. wt. 592.1150.) IR spectrum (KBr, cm^{-1}): ν(C—O—C) 1046 and 1023. PMR spectrum (δ, $CDCl_3$): 2.55 and 2.58 (4H, an $AA'BB'$ system, $—CH_2—$), 3.87, 5.04 and 4.16 (8H, each m, substituted Cp), 4.00 (10H, s, unsubstituted Cp), 7.20—7.90 (10H, m, Ph). Mass spectrum (*m/e*): 592 (M^+, 100), 574 ($[M-H_2O]^+$, 24), 186 (FcH^+, 26), 105 ($PhCO^+$, 65).

The eluate with AcOEt in the first chromatography over alumina was evaporated and then the residue was re-chromatographed over alumina several times. The band eluted with benzene/AcOEt (15 : 1) yielded benzoylferrocene (Xa), which was identical with the authentic sample. The starting material in the reaction of VIIa was recovered from the band eluted benzene/AcOEt (5 : 1). The last band eluted with benzene/AcOEt (1 : 1) yielded 1,4-diferrocenyl-1,4-diphenylbutan-1,4-diol (XIIIa), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 190—192°C. (Found: M^+ 610.1287. $C_{36}H_{34}O_2Fe_2$ calcd.: mol. wt. 610.1256.) IR spectrum (KBr, cm^{-1}): ν(OH) 3512 and 3358. PMR spectrum (δ, $CDCl_3$, 60 MHz): 2.1—2.4 (4H, m, $—CH_2—$), 3.40 (2H, s, —OH), 3.9—4.4 (18H, m, Cp), 7.2—7.5 (10H, m, Ph). Mass spectrum (at 30 eV, *m/e*): 610 (M^+, 3.5), 592 ($[M-H_2O]^+$, 77), 574 ($[M-2H_2O]^+$, 49), 186 (FcH^+, 32), 105 ($PhCO^+$, 100).

Small amounts of several ether products were also given but their structures have not yet been determined.

Oxidation of [1-hydroxy-1-(p-methoxyphenyl)ethyl]ferrocene (VIIb) or [1-(p-methoxyphenyl)vinyl]ferrocene (VIIIb)

The oxidation product of VIIb or VIIIb was column-chromatographed over alumina. The olefin (VIIIb) was afforded from the band eluted with hexane/benzene (5 : 1). The part eluted with benzene was re-chromatographed over silica gel to separate into two bands. The first band eluted with hexane/benzene (1 : 1) yielded 1,4-diferrocenyl-1,4-di(*p*-methoxyphenyl)-1,3-butadiene (XIb), which was recrystallized from AcOEt to give red flakes, m.p. 210—211°C. (Found: C, 72.17; H, 5.45; M^+ 634.1263. $C_{38}H_{34}O_2Fe_2$ calcd.: C, 71.95; H, 5.40%, mol. wt. 634.1256.) Raman spectrum (KBr, cm^{-1}): ν(C=C) 1592. PMR spectrum (δ, $CDCl_3$): 3.90 (6H, s, —OCH_3), 4.04 (10H, s, unsubstituted Cp), 4.14 (8H, s, substituted Cp), 6.53 (2H, s, =CH—), 6.98 and 7.33 (each 4H, an $AA'XX'$ system, Ph). Mass spectrum (*m/e*): 63.4 (M^+, 100), 31.7 (M^{2+}, 23).

The yellow compound obtained from the band eluted with benzene/AcOEt (40 : 1) in the re-chromatography was the tetrahydrofuran derivative (XIIb), which was separated into two isomers by preparative thin-layer chromatography on silica gel (Merk silica gel HF_{254}) with benzene as a developing solvent. The lower polar isomer was *cis*-2,5-differrocenyl-2,5-bis(*p*-methoxyphenyl)tetrahydrofuran (XIIb-C), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 211—213°C. (Found: M^+ 652.1281. $C_{38}H_{36}O_3Fe_2$ calcd.: mol. wt. 652.1361.) IR spectrum (KBr, cm^{-1}): ν(C—O—C) 1045 and 1033. PMR spectrum (δ, $CDCl_3$): 2.30 and 2.75 (4H, an $AA'XX'$ system, —CH_2—), 3.58, 3.66 and 3.94 (8H, each m, substituted Cp), 3.87 (6H, s, —OCH_3), 4.02 (10H, s, unsubstituted Cp), 6.97 and 7.65 (8H, an $AA'XX'$ system, Ph). Mass spectrum (*m/e*): 652 (M^+, 8.7), 634 ($[M - H_2O]^+$, 100).

The higher polar isomer was *trans*-2,5-diferrocenyl-2,5-bis(*p*-methoxyphenyl) tetrahydrofuran (XIIb-T), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 181.5—182°C. (Found: M^+ 652.1340. $C_{38}H_{36}O_3Fe_2$ calcd.: mol. wt. 652.1361.) IR spectrum (KBr, cm^{-1}): ν(C—O—C) 1049 and 1032. PMR spectrum (δ, $CDCl_3$): 2.52 and 2.56 (4H, an $AA'BB'$ system, —CH_2—), 3.78 (6H, s, —OCH_3), 3.87, 4.03 and 4.14 (8H, each m, substituted Cp), 4.02 (10 H, s, unsubstituted Cp), 6.78 and 7.45 (8H, an $AA'XX'$ system, Ph). Mass spectrum (*m/e*): 652 (M^+, 16), 634 ($[M - H_2O]^+$, 100).

(*p*-Methoxybenzoyl)ferrocene (Xb) was obtained from the band eluted with benzene/AcOEt (10 : 1) in the first chromatography over alumina. The brown oil obtained from the band eluted with AcOEt was purified by column chromatography several times over alumina to afford 1,4-diferrocenyl-1,4-bis(*p*-methoxyphenyl)butan-1,4-diol (XIIIb), which was recrystallized from methanol to give yellow prisms, m.p. 189.5—192°C. The diol was easily converted to the tetrahydrofuran derivative (XIIb) in the solution so that it was difficult for purification by recrystallization. (Found: C, 68.87; H, 5.63. $C_{38}H_{38}O_4Fe_2$ calcd.: C, 68.08; H, 5.71%.) IR spectrum (KBr, cm^{-1}): ν(OH) 3555 and 3430. PMR spectrum (δ, $CDCl_3$): 1.8—2.3 (4H, m, —CH_2—), 3.20 (2H, s, —OH), 3.74 (6H, s, —OCH_3), 3.90—4.20 (8H, m, substituted Cp), 4.11 (10H, s, unsubstituted Cp), 6.75 and 7.22 (8H, an $AA'XX'$ system, Ph). Mass spectrum (15 eV, *m/e*): 652 ($[M - H_2O]^+$, 13), 634 ($[M - 2H_2O]^+$, 100).

Oxidation of (1-phenylpropenyl)ferrocene (XVIIa)

The starting material was only recovered (88%) in the reaction of olefin (XVIIa) in hexane with O_2 gas and silica gel for 5 h. In the oxidation in CH_2Cl_2 with O_2 gas and silica gel for 2 h, a slight amount of acetylphenylhydroxymethylferrocene (XIXa) was yielded besides the recovered olefin (XVIIa) (74%)

and benzoylferrocene (Xa) (3.4%). The ketol (XIXa) 1.8%), orange-yellow crystals (m.p. 109—111°C), was obtained from the band eluted with hexane/benzene (1 : 10) in column chromatography over alumina. (Found: M^+ 334.0638. $C_{19}H_{18}O_2Fe$ calcd.: mol. wt. 334.0655.) IR spectrum (KBr, cm^{-1}): ν(OH) 3520, ν(C=O) 1703. PMR spectrum (δ, $CDCl_3$): 2.17 (3H, s, —$COCH_3$), 4.13 (5H, s, unsubstituted Cp), 4.26 (4H, m, substituted Cp), 7.27 (5H, s, Ph). Mass spectrum (*m/e*): 334 (M^+, 40), 291 ($[M - COCH_3]^+$, 29), 213 ($[M - C_5H_5Fe]^+$, 61), 186 (FcH^+, 64), 105 ($PhCO^+$, 100).

Column chromatographic separation (alumina) of the oxidation product of XVIIa in CH_2Cl_2 with acidic alumina for 2.5 h gave a slight amount of an acrolein derivative (deep red crystals, m.p. 112—115°C), which was eluted with benzene/AcOEt (30 : 1), besides the starting material (XVIIa) (51%) and benzoylferrocene (Xa) (8.6%). Though the structure of the acrolein derivative has not yet been confirmed because of its small amount (4.8 mg), its spectra can be explained by assuming 3-ferrocenyl-3-phenylpropenal (XVIIIa). (Found: M^+ 316.0548. $C_{19}H_{16}OFe$ calcd.: mol. wt. 316.0549.) IR spectrum (KBr, cm^{-1}): ν(C=O) and ν(C=C) of enone 1660 and 1582. PMR spectrum (δ, $CDCl_3$): 6.46 and 9.32 (an *AX* system, $J = 8.0$ Hz, =CH—CHO). Mass spectrum (*m/e*): 316 (M^+, 100), 288 ($[M - CO]^+$, 74), 251 ($[M - C_5H_5]^+$, 54).

Oxidation of [1-hydroxy-1-(p-methoxyphenyl)propyl]ferrocene (XVIb)

[1-(*p*-Methoxyphenyl)propenyl]ferrocene (XVIIb) (89%) was only obtained by oxidation of XVIb in hexane with silica gel and O_2 gas for 5 h. In the oxidation of XVIb in hexane with acidic alumina and O_2 gas for 5 h, a slight amount of an acrolein derivative was yielded together with the starting material (XVIb) (86%), olefin (XVIIb) (9.1%) and *p*-methoxybenzoylferrocene (Xb) (4.6%). The structure of the acrolein derivative (deep red oil), which was eluted with benzene/AcOEt (10 : 1), has not yet been confirmed because of its small amount (0.8 mg), but its spectra can be explained by assuming 3-ferrocenyl-3-(*p*-methoxyphenyl)-2-propenal (XVIIIb). (Found: M^+ 346.0659. $C_{20}H_{18}O_2Fe$ calcd.: mol. wt. 346.0655.) IR spectrum (neat liq., cm^{-1}): ν(C=O) and ν(C=C) of enone 1650 and 1610. Mass spectrum (*m/e*): 346 (M^+, 100), 318 ($[M - CO]^+$, 59), 281 ($[M - C_5H_5]^+$, 54).

Dehydrations of 1,4-diferrocenyl-1,4-diarylbutan-1,4-diol (XIII) with p-TsOH and aq. HCl

A benzene solution (5 ml) of XIIIa (3.0 mg) and *p*-TsOH (3.0 mg) was refluxed for 5 min. The reaction mixture was poured into saturated aq. NaCl and the organic layer was washed with saturated aq. NaCl, dried and evaporated. The residue was purified by column chromatography over alumina to give red crystals (2.5 mg), which were identified as 1,4-diferrocenyl-1,4-diphenyl-1,3-butadiene (XIa) by spectrometry.

By the same procedure as the above, dehydration of XIIIb (9.0 mg) with *p*-TsOH (10 mg) gave quantitatively 1,4-diferrocenyl-1,4-bis(*p*-methoxyphenyl)-1,3-butadiene (XIb).

A benzene solution (5 ml) of XIIIb (5.0 mg) was vigorously shaken with 10%

aq. HCl in a funnel flask for ca. 5 min. The organic layer was washed with aq. $NaHCO_3$ and then saturated aq. NaCl, dried and evaporated. The residue was purified by column chromatography over alumina to give yellow crystals (4.5 mg), which were identical with a mixture of two isomeric 2,5-diferrocenyl-2,5-bis(*p*-methoxyphenyl)tetrahydrofurans (XIIb) by spectrometry. The isomer ratio was not reproducible on repeated runs.

The dehydration of XIIIa was carried out by the same procedure as the above to give almost quantitatively the corresponding butadiene derivative (XIa).

Reductions of 1,4-diferrocenyl-1,4-diphenyl-1,3-butadiene (XIa) and 2,5-diferrocenyl-2,5-diphenyltetrahydrofuran (XIIa)

10% Rh—C (30 mg) was suspended in an AcOEt solution (20 ml) of XIa (60 mg) and AcOH (3 ml), and reduction was carried out in H_2 gas at 100 atm. at 80°C for 20 h. After filtration of the reaction mixture, the filtrate was washed with aq. $NaHCO_3$ and then saturated aq. NaCl, dried and evaporated. The residue was purified by column chromatography over alumina. The band eluted with hexane/benzene (4 : 1) yielded 1,4-diferrocenyl-1,4-diphenylbutane (XV) (19 mg), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 224—225°C. (Found: M^+ 578.1325. $C_{36}H_{34}Fe_2$ calcd.: mol. wt. 578.1356.) PMR spectrum (δ, $CDCl_3$): 1.70—2.00 (4H, m, $-CH_2-$), 3.54 (2H, m, $\geqslant$CH), 3.84 (10H, s, unsubstituted Cp), 3.98 (8H, m, substituted Cp), 7.10—7.35 (10H, m, Ph). Mass spectrum (*m/e*): 578 (M^+, 100), 275 ($FcCH^+Ph$, 71).

$LiAlH_4$ (8.0 mg) was suspended in a solution of $AlCl_3$ (30 mg) in dry ether/benzene (3 : 2, 5 ml). Crystals of XIIa (16 mg) was added to the suspension. After refluxing the reaction mixture for 1 h, wet ether was added for deactivation of the reagents. The hydrolysate was filtered and the filtrate was dried and evaporated. The residue was column-chromatographed over alumina to yield only one product (15 mg), which was identical with 1,4-diferrocenyl-1,4-diphenylbutane (XV).

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