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Oxidation potential of benzylferrocenes and related compounds: effects of the *ortho*-methoxy substituent in the phenyl group

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Abstract

Oxidation potentials of some ferrocenyl derivatives of type Fc-CHΦOH, Fc–CΦΦ′OH, Fc–CH_2Φ, Fc–CHΦΦ′ [Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4); Φ, Φ′ = 2,4,6-$(MeO)_3C_6H_2$, 2,6-$(MeO)_2$·C_6H_3, 2,5-$(MeO)_2$·C_6H_3, 2,4-$(MeO)_2$·C_6H_3, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, C_6H_5] were measured in acetonitrile. All of them exhibited a reversible one-electron oxidation–reduction wave based on the ferrocene–ferrocenium redox couple with a wide range of shift. Compounds having *ortho*-methoxy groups showed lower redox potentials than those of compounds having *para*-methoxy groups. The X-ray crystal structure of Fc–CHΦ^a_2 showed that the *ortho*-methoxy oxygens was situated very close to the central carbon, and there is a possibility that one of the oxygen lone-pairs interacts with the antibonding orbital of C–Fc σ-bond. Some other possibilities are also discussed.

Keywords: Benzylferrocenes; Ferrocenyl derivatives; *o*-Methoxyphenyl; Oxidation potential; X-ray crystal structure

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1. Introduction

Due to the electronic and steric effects of *ortho*-methoxy groups, 2,6-dimethoxyphenyl derivatives often exhibit unusual properties. As part of our systematic investigation on the chemistry of 2,6-dimethoxyphenyl derivatives of a variety of elements, we have recently reported the preparation and reactions of ferrocenyl(phenyl)carbenium salts, [Fc–CHΦ]X[Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4); Φ = 2,4,6-$(MeO)_3C_6H_2$(Φ^a), 2,6-$(MeO)_2C_6H_3$(Φ^b)], which have very high stabilities, pK_{R+} = 3.0(Φ^a), 1.6(Φ^b) [1]. Although we were also interested in the preparation and properties of tertiary carbenium salts, [Fc–$C\Phi_2$]X, we have not yet succeeded in their isolation because these salts are unstable and decompose to give 6-diphenylfulvene, C_5H_4=$C\Phi_2$. On the other hand, ferrocene derivatives are well known to exhibit reversible one-electron oxidation [2–6], and recent years have seen developments in their applications as oxidizing agents [7], redox catalysts [8], sensors [9–12], organic magnets [13], modifiers of electrode [14–16], and second-order non-linear optical materials [17,18]. In the present study, we report unique effects of the *ortho*-methoxy substituent in ferrocenyl-(phenyl)methanols and the related ferrocenyl derivatives, Fc–CHΦOH (**1**), Fc–CΦΦ′OH (**2**), Fc–CH_2Φ (**3**), Fc–CHΦΦ′ (**4**), on the oxidation potential [Φ, Φ′ = (a) Φ^a, (b) Φ^b, (c) 2,5-$(MeO)_2C_6H_3$, (d) 2,4-$(MeO)_2C_6H_3$, (e) 2-$MeOC_6H_4$, (f) 4-$MeOC_6H_4$, (g) C_6H_5]. We abbreviate here some methoxyphenyl groups, Φ, as shown in Scheme 1.

2. Experimental

2.1. Physical measurements

^1H- and ^{13}C-NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX 270 spectrometer. IR spectra were recorded for Nujol® mulls using a Shimadzu FTIR-4200 spectrophotometer. GC–MS spectra were recorded for acetone or toluene

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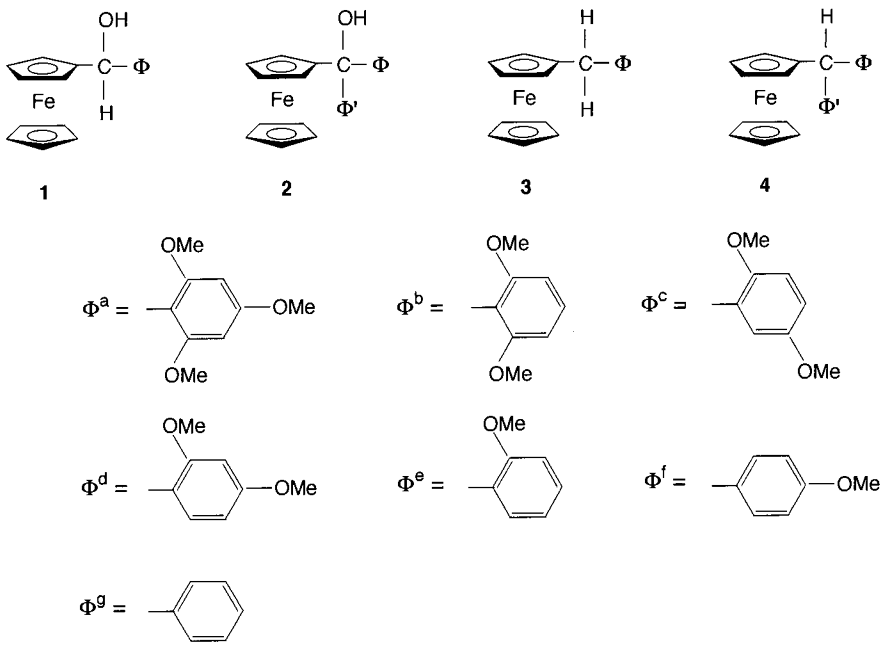
solutions using a Shimadzu QP-5000 mass spectrometer (gasified at 250°C). Visible spectra were recorded for 1,2-dichloroethane solutions using a Shimadzu UV-160 spectrophotometer. The ^{1}H- and ^{13}C-NMR spectral data are summarized in Tables 1 and 2, respectively.

2.2. Preparation of ferrocene derivatives

Compounds **1a**, **1b**, **1g**, **3a**, **3b**, **3g**, **4aa**, **4bd**, and **4dg**, were prepared as described elsewhere [1]. The following compounds were prepared essentially in an analogous manner.



Scheme 1.

Table 1
^{1}H-NMR spectral data for ferrocenyl (phenyl) methane derivatives [a]

	C_5H_5	C_5H_4	$C_{central}$–H	Others
1c	4.21s	4.25∼4.12m	5.74d[5]	6.94d[2] and 6.75d[2] (3,4-*H*), 6.77s (6-*H*), 3.79s and 3.75s (2,5-*MeO*), 2.85d[5] (*OH*)
1d	4.19s	4.27∼4.14m [b]	5.74d[5]	7.19d[9] (1H), 6.45∼6.43br (2H), 3.81s (3H), 3.78s (3H), 2.76d[5] (1H,*OH*)
1e	4.19s	4.27∼4.13m	5.79d[5]	7.35d[8], 7.22t[8], 6.93t[7], and 6.86d[8] (4H, 3,4,5,6-*H*), 3.84s (6H,*MeO*), 2.78d[5] (1H, *OH*)
1f	4.21s	4.21∼4.16m	5.44d[3]	7.30d[8] (2H), 6.85d[9] (2H), 3.79s (3H), 2.39d[3] (1H, *OH*)
2bb	4.03s	4.24br (2H), 4.08t[2] (2H)		7.08t[8] (2H), 6.54d[8] (4H), 6.27s (1H), 3.47br (12H)
2bb [c]	4.08s [b]	4.52s (1H), 4.17s (2H) [b],3.92s (1H)		7.24t[8] and 7.06t[8] (2H, 4-*H*), 6.78d[8], 6.61d[8], 6.53d[8], and 6.47d[8] (4H, 3,5-*H*), 6.00s (1H, *OH*), 4.08s[b], 3.42s, 3.37s, and 3.08s (3H+3H+3H+3H, *MeO*)
2bg	4.12s [b]	4.19∼4.09m [b]		7.25∼7.13m (6H, *Ph and 4-H*), 6.60d[8] (2H, 3,5-*H*), 6.11s (1H, *OH*), 3.47s (6H, *MeO*)
2gg	4.17s	4.27t[2], 4.04t[2]		7.31∼7.20m (12H, *Ph*), 3.44s (1H, *OH*)
3c	4.15s	4.15∼4.08m (4H)	3.63s (2H)	6.76∼6.62m (3H, *3,4,6-H*), 3.80s and 3.70s (6H, *2,5-MeO*)
3e	4.12s [b]	4.12 [b], 4.05br (2H)	3.68s (2H)	7,15t[7], 7.03d[7], 6.85d[7], and 6.82d[7] (4H, *3,4,5,6-H*), 3.85s (3H, MeO)
3f	4.12s	4.08s (4H)	3.63s (2H)	7.10d[9] (2H, *2,6-H*), 6.81d[9] (2H, *3,5-H*), 3.78s (3H, *MeO*)
4ae	4.03s	4.07br (4H)	5.98s	7.06∼7.01m (2H), 6.84d[8] and 6.74t[8] (2H), 6.14s (2H), 3.81s and 3.66s (12H)
4bg	3.98s	4.12br	5.90s	7.46br (2′,6′-*H*), 7.23t[8] (*4-H*), 7.26∼7.19m (3′,5′-*H*), 6.60d[8] (*3,5-H*), 3.73br (*2,6-MeO*), 3.10br (NMe_2)
4de	4.02s	4.11t[2] (2H), 3.98t[2] (2H)	5.86s	7.12td[8, 2] (1H); 6.95dd [8, 2] (1H), 6.88∼6.76m (2H), 6.43d[2] (1H), 6.34dd[8, 2] (2H), 3.81s (3H), 3.80s (3H), and 3.76s (3H)

[a] In $CDCl_3$ (δ), 270 MHz; coupling constants [J_{HH}/Hz] are given in parentheses; s, singlet; d, doublet; t, triplet; dd, double doublet; dt, double triplet; m, multiplet; br, broad.

[b] Overlapped.

[c] At −60°C.

Table 2
^{13}C-NMR spectral data for ferrocenyl (phenyl)methane derivatives [a]

	C_2H_5	C_5H_4	$C_{central}$	Others
1c	69.2	93.7, 68.5, 68.4, 68.3, 68.2	69.3	154.3 and 151.4 (2,5-C), 133.6 (1-C), 114.1, 113.4, and 112.2 (3,4,6-C), 56.6 and 56.4 (2,5-MeO)
1d	69.2	93.9, 68.4, 68.3, 68.1, 67.1	69.3	160.8 and 158.2 (2,4-C), 128.7, 125.2, 104.8, and 99.2 (1,3,5,6-C), 56.0 and (2,4-MeO) [b]
1e	69.3	93.7, 68.4, 68.4, 68.2, 67.2	[b]	157.1(2-C), 132.4 (1-C), 129.1 (6-C), 128.0 (4-C), 121.3 (5-C), 111.2 (3-C), 56.2 (MeO)
1f	68.4	94.3, 68.1, 68.0, 67.3, 65.9	71.7	158.9 (4-C), 135.6 (1-C), 127.4 (2,6-C), 113.5 (3,5-C), 55.2 (MeO)
2bb	69.0	100.5, 69.2, 66.9	78.2	158.8 (2,6-C), ---(1-C) [b], 127.7 (4-C), 107.8 (3,5-C), 57.1 (MeO)
2bg	69.3	98.8, 69.8, 69.8, 68.0, 67.2	79.7	158.8, 150.3, 129.1, 127.5, 127.2, 126.7, 125.7, 107.8, 57.0
3c	68.6	87.2, 68.9, 67.4	29.9	153.4 and 151.2 (2,5-C), 131.7 (1-C), 116.3, 110.9, 110.8, (3,4,6-C), 55.8 and 55.6 (2,5-MeO)
3e	68.6	87.5, 69.0, 67.3	29.8	156.9 (2-C), 130.4 (1-C), 129.5 (6-C), 127.0 (4-C), 120.3 (5-C), 110.0 (3-C), 55.2 (MeO)
3f	68.6	88.5, 68.5, 67.4	35.1	157.8 (4-C), 133.8 (1-C), 129.3 (2,6-C), 113.6 (3,5-C), 55.2 (MeO)
4ae	67.5	91.1, 69.5, 68.6, 66.9, 66.4	34.2	159.3 (2′,6′-C), 159.2 (4′-C), 156.7 (2-C), 134.7 (1-C), 131.3 (3-C), 125.9 (6-C), 119.2 (4-C), 113.9 (5-C), 110.2 (1′-C), 91.4 (3′,5′-C), 55.7, 55.5 and 55.1 (MeO)
4de	69.3	92.5, 69.6, 69.5, 68.0, 67.9	36.6	159.5 and 158.2 (2′,4′-C), 157.3 (2-C), 134.9 (1-C), 130.7 and 127.3 (5′,6′-C), 130.2 (6-C), 127.2 (4-C), 120.6 (5-C), 111.2 (3-C), 104.2 (1′-C), 99.0 (3′-C), 56.2, 56.1, and 55.9 (MeO)

[a] In $CDCl_3$ (δ), 68 MHz.

[b] Not detected or overlapped.

1c: by reaction of Fc–CHO with 2,5-dimethoxyphenyllithium in 78% yield; mp 87–88°C; IR 3580 cm^{-1} (OH); MS m/z (%) 214 (100, $[C_5H_4=CH\Phi^c]^+$). Calc. for $C_{19}H_{20}FeO_3$: C, 64.79; H, 5.72 Found: C, 65.02; H, 5.81%.

1d: by a reaction of Fc–CHO with 2,4-dimethoxyphenyllithium in 32% yield; m.p. 76–78°C;IR 3466 cm^{-1} (OH); MS m/z (%) 214 (100, $[C_5H_4=CH\Phi^c]^+$).

1e: by a reaction of Fc–CHO with 2-methoxyphenyllithium in 78% yield; m.p. 100–101°C; IR 3520 cm^{-1} (OH); MS (toluene) m/z (%) (1) 306 (100, 3e$^+$),(2) 320 (100, $[Fc\text{–}C\Phi^eO]^+$).

1f: by a reaction of Fc–CHO with 4-methoxyphenyllithium in 45% yield; m.p. 73–74°C (reported 72–74°C [19]); IR 3580 cm^{-1} (OH).

2bb: (1) by a reaction of Fc–COOEt with 2,6-dimethoxphenyllithium in 70 (crude) ~22% yield or (2) by a reaction of Φ^b_2CO [20] with ferrocenyllithium in 43 (crude) ~15% yield; m.p. 178–180°C; IR 3550 cm^{-1} (OH); MS m/z (%) 350 (100, $[C_5H_4=C\Phi^b_2]^+$).

2bg: by a reaction of Fc–CPhO with 2,6-dimethoxyphenyllithium in 78% yield; m.p. 144–145°C; IR 3500 cm^{-1} (OH); MS m/z (%) (82, $[C_5H_4=CPh\Phi^b]^+$).

2gg: by a reaction of Fc–CPhO with phenyllithium in 77% yield; m.p. 132–133°C (reported 130–131°C [21]); IR 3540 cm^{-1} (OH).

3c: by reduction of **1c** in 2-propanol in the presence of an acid in 27% yield; m.p. 64–65°C, MS m/z (relative intensity) 336 [100, M$^+$].

3e: by reduction of **1e** in 2-propanol in the presence of an acid in 32% yield; m.p. 57–59°C, MS m/z (relative intensity) 306 [100, M$^+$].

3f: by reduction of **1f** in 2-propanol in the presence of an acid in 36% yield; m.p. 74–75°C, MS m/z (relative intensity) 306 [100, M$^+$].

4ae: by a reaction of **1e** with 1,3,5-trimethoxybenzene in the presence of an acid in 86% yield; m.p. 157–158°C, MS m/z (relative intensity) 472 [100,M$^+$].

4de: by a reaction of **1e** with 1,3-dimethoxybenzene in the presence of an acid in 42% yield; m.p. 141–142°C, MS m/z (relative intensity) 442 (100, M$^+$). Calc. for $C_{26}H_{26}FeO_3$: C, 70.60; H, 5.92. Found: C, 70.88; H, 6.12%.

2.3. Cyclic voltammetric measurements

Ferrocenyl derivatives were dissolved in acetonitrile containing 0.1 M (M = mol/dm^3) tetra-*n*-butylammonium tetrafluoroborate as a supporting electrolyte. Cyclic voltammetric measurements were carried out at 25°C in a conventional three-electrode cell with platinum wire working electrode, platinum plate counter electrode and aqueous Ag/AgCl reference electrode. Voltammograms were recorded with a Hokuto Denko model HA-501 potentiostat and a Function Generator HB-104 in connection with a Rika Denki RW-21TX-T recorder. The formal redox potentials of these compounds were estimated as the midpoint between the anodic and cathodic peak potentials, and were referred against the ferrocene–ferrocenium redox couple (+460 mV vs. aq. Ag/AgCl). All the relative current intensities (i_{ox}/i_{red}) were in the region of 1.0 ± 0.15. The redox potentials are summarized in Table 3, together with the electronic spectral data.

2.4. X-ray crystallography

Single crystals of **4aa** suitable for X-ray crystal structure analysis were obtained by recrystallization from hexane. The intensity data were collected at 173 K on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo–K_{α} ($\lambda = 0.71070$ Å) radiation from a rotating-anode generator operating at 50 kV and 100 mA to a maximum 2θ value of 55.2°. A total of 17 oscillation images, each being oscillated 6° and exposed for 40 min, were collected for **4aa**. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 3.55176e − 06). The structure was solved by direct methods (SIR92) [22] and expanded using Fourier techniques (DIRDIF94) [23]. Hydrogen atoms were included at calculated positions but not refined. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Crystal structure data for $C_{29}H_{32}O_6Fe$: approximate crystal dimensions = $0.8 \times 0.3 \times 0.1$ mm^3, triclinic, $a = 11.4013(9)$, $b = 13.405(1)$, $c = 8.3098(4)$ Å, $\alpha = 97.363(8)$, $\beta = 102.240(5)$, $\gamma = 81.491(4)°$, $V = 1221.2800$ Å^3, space group $P\bar{1}$ (No. 2), $Z = 2$, $D_{calc} = 1.45$ g cm^{-3}, $M_r = 532.42$, μ(Mo Kα) = 6.6 cm^{-1}, no. of observations ($I = 3.00\sigma(I)$) = 3116, no. variables = 326, residuals: R; R_w = 0.059; 0.087, goodness-of-fit = 1.22, max/min peak in final difference map = 0.77/ − 0.94 e Å^{-3}.

Table 3
The redox potentials and visible spectral data of ferrocene derivatives

Compounds	Φ	Φ'	Redox potentials [a]	Visible spectra [b]	
			E_0 (mV)	λ_{max} (nm)	log ε
Fc-CHΦOH (**1**)					
1a	Φ^a		−43	440	2.30
1b	Φ^b		−30	445	2.15
1c	Φ^c		−15	445	2.15
1d	Φ^d		−16	429	2.23
1e	Φ^e		−2.5	443	2.11
1f	Φ^f		−2	443	2.08
1g	Ph		+4	444	2.18
Fc-C$\Phi\Phi'$OH (**2**)					
2bb	Φ^b	Φ^b	−184	443	2.18
2bg	Φ^b	Ph	−98	450	2.30
2gg	Ph	Ph	+24	445	2.18
Fc-CH$_2\Phi$ (**3**)					
3a	Φ^a		−80	444	2.04
3b	Φ^b		−70	450	2.04
3c	Φ^c		−43	447	2.00
3e	Φ^e		−49	440	2.11
3f	Φ^f		−28	440	2.15
3g	Ph		−20	432 [c]	2.08
Fc-CH$\Phi\Phi'$ (**4**)					
4aa	Φ^a	Φ^a	−183	427	2.15
4ab	Φ^a	Φ^b	−179	445	2.23
4ae	Φ^a	Φ^e	−87	443	2.00
4ag	Φ^a	Ph	−62	445	2.11
4bd	Φ^b	Φ^d	−93	440	2.11
4de	Φ^d	Φ^e	−43	427	2.10
4dg	Φ^d	Ph	−18	442	2.08
4gg [d]	Ph	Ph	+10		
Fc–H			0	440	1.97

[a] Half-wave potentials versus ferrocene–ferrocenium measured in 1 mM acetonitrile solutions; potential sweep rate was 5 mV s^{-1}.

[b] Measured in 1,2-dichloroethane; d–d band.

[c] 22 400 cm^{-1} (446 nm) have been reported in Ref. [27].

[d] Data from Ref. [5].

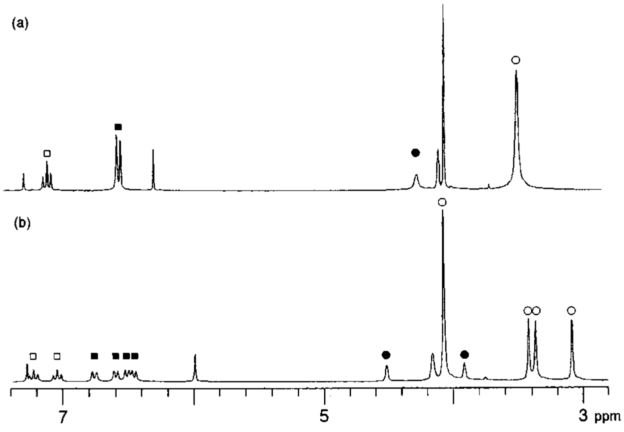


Fig. 1. Temperature-dependent ^{1}H-NMR spectra of **2bb** in $CDCl_3$; (a) at +50°C, (b) at −60°C.

3. Results and discussion

3.1. Preparation and general properties of ferrocenyl derivatives

Compounds of types **1**–**4** in Scheme 1 were prepared as described elsewhere [1] or were prepared essentially in an analogous manner. The new compounds were characterized by ^{1}H- and ^{13}C-NMR (Tables 1 and 2), IR, and GC mass spectra. The ^{1}H- and ^{13}C-NMR spectra are as expected for each compound except for **2bb** (see below). With a hope of isolating the carbenium salt, **2bb** was treated with acids under a variety of conditions, but it easily decomposed to give 6-bis(2,6-dimethoxyphenyl)fulvene, $C_5H_4=C\Phi^{b}_{2}$. We have also failed in the reductions of **1d**, **2bb**, **2bg** to **3** or **4** by the method reported previously [1], possibly because these compounds also decomposed to the fulvene in the presence of an acid.

The GC mass spectra of **1** showed thermal decompositions during the GC measurement to give the fulvene, $C_5H_4{=}CH\Phi$, or the disproportionation products, **3** and Fc–CΦO. The spectra of **2** also showed thermal decomposition to give $C_5H_4{=}C\Phi\Phi'$. Usage of acetone as the solvent for GC–MS measurement should be avoided, since it often reacted with **1** to give the adduct, Fc–$CH\Phi CH_2CMeO$. Related reactions with acetone have been reported [24,25]. Alcohols can also react with **1** and **2** to give the reduction product **3** or **4**.

All the compounds **3** and **4** studied here were thermally stable, showing only one GC peak, and the mass spectrum showed a very strong parent peak, respectively.

3.2. NMR spectra

The ^{1}H-NMR spectrum of **2bb** measured at ambient temperature showed the resonance due to only one kind of Φ^{b} group with a broad peak for the 2′,6′–dimethoxy protons. The resonances sharpened at +50°C with little chemical shift change (±0.01 ppm), as shown in Fig. 1. The C_5H_5 proton resonance was observed as a very sharp singlet at δ 4.03, and the C_5H_4 proton resonances were observed at δ 4.24 as a broad peak with 2H intensity and at δ 4.08 ($J_H = 2$ Hz) as a triplet with 2H intensity. The spectrum was also measured at −60°C, and it showed the presence of two kinds of Φ^{b} groups with all the four methoxy groups, all the four 3′,5′–protons, and both the two 4′-protons non-equivalent, as shown in Fig. 1. The C_5H_5 proton resonance was also observed as a singlet at δ 4.08 with stronger intensity due to overlapping with one of the methoxy proton resonances. The C_5H_4 proton resonances were observed at δ 4.52 (1H), 4.17 (2H) and 3.92 (1H) without magnetic coupling with each other. These results indicate that the free rotation around the C–Φ^{b} bonds is frozen in the compound at −60°C, and the compound takes an asymmetric structure. 1-Ferrocenylalcohols often aggregate by O–H···O hydrogen bonding, and they often involve intramolecular O–H···π(C_5H_5) interaction [26,27]. The OH proton resonance of **2bb** was observed at δ 6.27 (room temperature) or 6.00 (−60°C) as a sharp single peak, suggesting the absence of such hydrogen bondings. The ^{13}C-NMR spectrum measured at ambient temperature showed only one methoxy carbon resonance and is consistent with the compound having free rotation around the C–Φ^{b} bond.

The rotation barrier ($\Delta G^{\ddagger}$) around the central carbon atom in **2bb** was estimated by the temperature-dependent ^{1}H-NMR measurement in $CDCl_3$ to give 53.2 kJ mol^{-1} from the 2,5-proton resonances on the C_5H_4, or 52.8 or 54.9 kJ mol^{-1} from the methoxy protons resonances ($T_c = 0$°C).

3.3. Oxidation potentials

All of the substituted ferrocenes studied here exhibited a reversible one-electron diffusion-controlled oxidation–reduction wave (E_0, Table 3) based on the ferrocene–ferricenium redox couple ($i_{ox}/i_{red} = \sim 1.0$). It has been known that such an oxidation–reduction potential of substituted ferrocene depends on the electronic effects of the substituent group [3–5]. Little et al. have reported that successive replacement of the hydrogen of the methyl group in methylferrocene, Fc–CH_3, by phenyl groups changes the potential in the order Fc–CH_3 < **3g** < Fc–H < **4gg** < F–CPh_3 [5]. We also observed essentially the same order as seen in Table 1; **3g** < Fc–H ~ **1g** < **4gg** < **2gg**. In contrast, we observed a very different order for 2,4,6-trimethoxypheny substitution: **4aa** < **3a** < **1a** < Fc–H. These results may be because the phenyl group is electron withdrawing to the α-carbon, while 2,4,6-trimethoxyphenyl group is electron donating.

We were very interested in the difference of effects the between 2-methoxyphenyl group and 4-methoxyphenyl group on the oxidation potential: **1e** < **1f** < **1g**. An analogous difference was observed between the 2,6-dimethoxyphenyl group and 2,4-dimethoxyphenyl group: **1b** < **1d**. These results indicate that the *ortho*-methoxy group is more electron donating than the *para*-methoxy group. A series of **3a-g**, **3a** and **3b** bearing two *ortho*-methoxy substituents showed lower redox potentials (− 80 and − 70 mV) than **3c** and **3e** bearing only one *ortho*-methoxy substituent, and the latter showed much lower redox potentials than **3f** and **3g** (− 28 and − 20 mV, respectively). Fig. 2 visualizes the effect of the number of *ortho*-methoxy substituents on the redox potential of ferrocene derivatives.

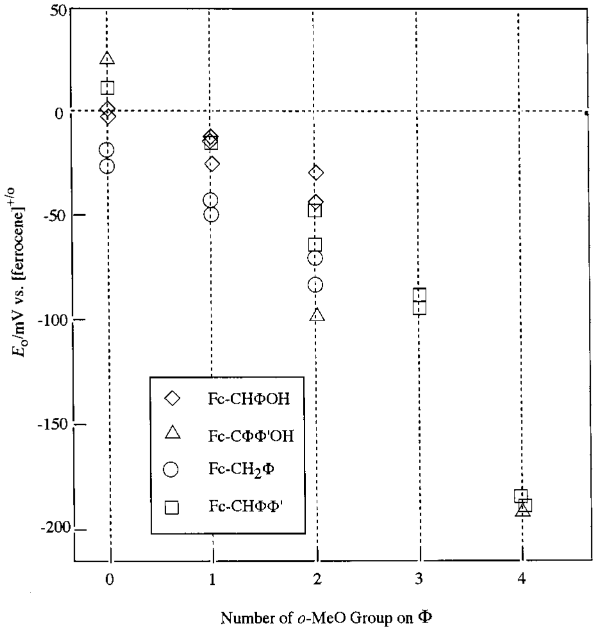


Fig. 2. Effect of the number and position of methoxy substituents on oxidation potentials of benzylferrocenes and the related compounds.

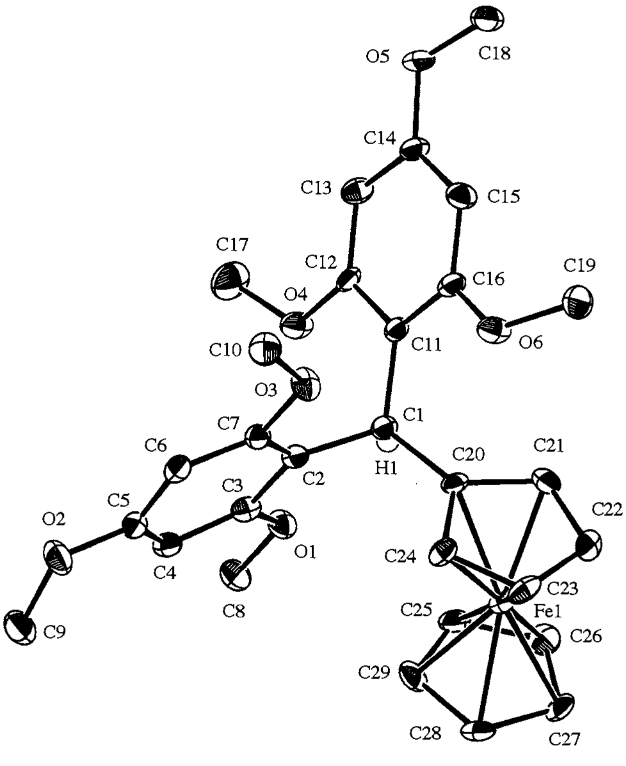


Fig. 3. X-ray crystal structure of Fc-CHΦ$^a_2$[Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4); Φ^a = 2,4,6-$(MeO)_3C_6H_2$] drawn at 50% probability level. All hydrogen atoms are omitted for clarity except for H1.

Table 4
Selected interatomic distances (Å) for **4aa**

O(1)···C(1)	2.749(4)	O(4)···C(1)	2.679(5)
O(3)···C(1)	2.831(5)	O(6)···C(1)	2.981(4)
Fe(1)···O(1)	3.934(3)		

In contrast to the wide range of shift in the redox potentials, the visible spectra of the derivatives **1**–**4** (Table 3) showed a band with λ_{max} at the analogous region (427–450 nm) to that of ferrocene and **3g**. This may be because the presence of *ortho*-methoxy substituent leads to destabilization of both HOMO (a_{1g}) and LUMO (e_{1g}) levels [28] of **1**–**4** by approximately equal amount.

In the hope of obtaining further information concerning the effect of the *ortho*-methoxy substituent, the X-ray crystallographic analysis of **4aa** was performed.

3.4. Crystal structure of bis-(2,4,6-trimethoxyphenyl)methylferrocene

The molecular structure derived from an X-ray structure analysis of **4aa** is shown in Fig. 3 and the selected interatomic distances are summarized in Table 4. The two Φ^a groups were nonequivalent in the crystal, and the fact that *ortho*-methoxy oxygens situated very close to the central carbon (C1) is characteristic; 2.749 (O1), 2.831(O3), 2.679 (O4), 2.981 (O6) Å, respectively. These distances are much shorter than the sum [3.22 Å] of the van der Waals radii of these two atoms, and there is a possibility, for example, that one of the oxygen (O4) lone pairs interacts with the antibonding orbital of C(1)–Fc σ-bond. In solution the molecule should be mobile, and the other methoxy oxygens may also take part in such an interaction. Such an interaction can increase the energy levels of ferrocenyl group to decrease the oxidation potential, as observed.

One of the methoxy oxygens (O6) of the four methoxy oxygens is also situated very close above the C_5H_4 ring with the interatomic distances of 2.768 Å (O(6)···C(20)) and 2.912 Å (O(6)···C(21)). Thus, it may also be possible to assume that there is an interaction between the oxygen lone pairs and the π-electron orbitals of the cyclopentadienyl group.

It may also be expected that *ortho*-methoxy groups can coordinate to the ion atom. However, the shortest intramolecular O···Fe interatomic distance was 3.934 Å (O(1)···Fe), which precluded the presence of such an interaction.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 132015 for **4aa**. Copies of this information may be obtained free of charge from: The Director CCDC, 12 Union Road Cambridge, CB2 1EZ, UK. Fax: +44-1223-336033 or e-mail:deposit @ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk

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