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Redox potential and substituent effects in ferrocene derivatives: II *

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Abstract

The anodic behavior of 31 ferrocene derivatives (FcX) (four of which have been prepared for the first time) of the types shown below has been investigated by cyclic voltammetry (and, in some cases, also by controlled-potential electrolysis and differential pulse polarography) at a Pt electrode, in an aprotic solvent: Fc–C(Y)=Z (class A; Y = R (hydrogen, alkyl or unsaturated-carbon moiety) or Cl; Z = CRR′, derived functionalized groups or {W(CO)$_5$}); Fc–C(Y)=O (class B; Y = R or OH); other types (class C, including azide, other unsaturated N moieties, acyloxy or phosphino); disubstituted ferrocenes (class D, with alkyl, aminoalkyl, phosphino, B(OH)$_2$ or –HgCl substituents, or the S–S–S bridge). All these substituted ferrocenes exhibit a one-electron reversible oxidation centered at iron and the effect of the substituents on the half-wave oxidation potential is discussed in terms of electronic properties. Using the accepted linear correlations between the half-wave oxidation potential and the Hammett constant σ_p of the substituent, σ_p was estimated for the first time for 29 of the substituents in the ferrocenes listed above. The anomalous behavior of complexes with a hydroxy or a carbonyl group is discussed. No correlation was observed between the oxidation potential and either the energy of the electronic absorption bands or the ^{1}H NMR chemical shift of the unsubstituted cyclopentadienyl ring, although there are rough correlations for class A compounds. This behaviour is compared with those of [Fc-CHYZ].

Key words: Iron; Redox potentials; Ferrocenes; Electrochemistry; Substituent effects

1. Introduction

The electrochemical study of sandwich complexes, in particular derivatives of ferrocene, has developed since the early 1950s and is still attracting wide interest [1–6]. Examples include the investigation of the electrochemical behaviour of ferrocenes in non-conventional conditions, *e.g.* by using ultramicroelectrodes [7] or in molten-salt mixtures [8], their use as electron-transfer mediators with enzymes [9], and the electrochemistry of inclusion complexes of ferrocenes [10].

Substituent effects on the redox properties have also been investigated [11–18], but such studies in general involve substituents whose electron-donor or electron-acceptor properties have been previously well evaluated by other methods.

Therefore, we embarked upon a systematic study of the redox properties of ferrocenes with a variety of substituents whose electronic properties have not yet been fully established, even though such complexes are much used in organic or organometallic synthesis [19,20]. We have already reported [21] the results of our investigation of the redox properties of ferrocene derivatives FcX (where Fc denotes the ferrocenyl group Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)) whose substituents bond to the cyclopentadienyl ring through an sp^3 hybridized

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* For part I, see ref. 21.

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carbon atom, commonly with an heteroatom attached to it, *i.e.* $-X = -CHYZ$ (Y = R(hydrogen, alkyl or aryl), Fc or Fc^+; Z = group with an heteroatom (N, P, O or S)). In particular, linear correlations have been recognized between the half-wave oxidation potential and the Hammett constant σ_p or the Taft polar constant σ^* for the substituent (see equations below) and have been applied to estimate the values of those constants for such substituents or their Z groups [21].

We now report the extension of this work to other types of substituent (X) which, according to their general structural features, can be grouped into the following classes:

class A $-C(Y)=Z$ (Y = R or Cl; Z = CRR′ and related groups, $C(COR)R'$, $C(CO_2Et)NHCHO$, CHCHO, $CHCOCF_3$, $-C=C(Fc)C=N-SO_2-C_6H_4CH_3$-4 or $\{W(CO)_5\}$);

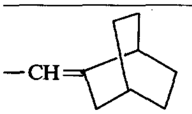
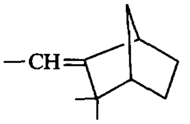
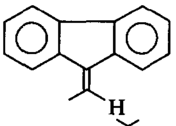
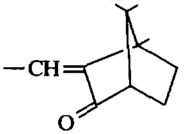
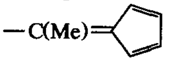
class B $-C(Y)=O$ (Y = R (forming ferrocenylketones) or OH);

class C (comprising those which do not fall within the previous classes): OCOR, –NC, N_3, $-\overline{NC(CO_2Me)=C(CO_2Me)N=N}$, $-\overline{NC(O)(1,2\text{-}C_6H_4)C(O)}$ or PPh_2;

class D (disubstituted homo- and hetero-annular ferrocenes): 1-HgCl-2-CH_2NMe_2, 1-PPh_2-2-CH_2NMe_2, 1-$CHMeNMe_2$-2-$B(OH)_2$ or 1,1′-S–S–S bridge.

For classes A and B, the substituent binds to the

TABLE 1. Oxidation potentials for ferrocene derivatives of the type Fc–C(Y) = Z (class A) relative to that of ferrocene, Hammett substituent constants σ_p, electronic spectroscopy data and ^1H NMR chemical shifts for the unsubstituted cyclopentadienyl ring

$-C(Y)=Z$	No.	Δ_X [a] (V)	σ_p [b]	$1/\lambda_1$ (ϵ_1) [c] ($\times 10^3$ nm^{-1} (l mol^{-1} mm^{-1}))	$1/\lambda_2$ (ϵ_2) [c] ($\times 10^3$ nm^{-1} (l mol^{-1} mm^{-1}))	$\delta(C_5H_5)$ [d] (ppm)
	**1A**	−0.035 ± 0.01	−0.14 ± 0.06	2.22	[e]	4.05
	**2A**	−0.025	−0.12	2.25	[e]	4.05
$-CH = CMe_2$	**3A**	−0.025	−0.12	2.25 (7.5)	[e]	4.08
$-\overline{C=CHCH_2(CH_2)_2CH_2}$	**4A**	−0.005	−0.08	2.27 (33)	3.11 (80)	4.07
$-C(Me)=CMe_2$	**5A**	−0.005	−0.08	2.26	[e]	4.13
$-C(Me)=CHPh$	**6A**	0.005	0.0	2.24 (65)	3.14 (755)	4.13
	**7A**	0.075	0.09	2.09	2.94	4.19
	**8A**	0.085	0.11	2.15 (140)	3.13 (1015)	4.13
	**9A**	0.095	0.14	2.06	3.08	4.17
$-CH=C(CO_2Et)NHCHO$	**10A**	0.095	0.14	2.15	2.84 (195) [f]	4.17
$-C_6H_4NO_2$-*2*	**11A**	0.105	0.16	2.20 (44)	[e]	4.09
$-C(Me)=CHCOCF_3$	**12A**	0.185	0.31	1.92 (225)	3.07 (1420)	4.32
$-\overline{C=C(Fc)C}=NSO_2C_6H_4Me$-*4*	**13A**	0.215 [g]	0.39	2.09 (195)	2.86	4.22
$-C(Cl)=CHCHO$	**14A**	0.225	0.41	2.04	3.26	4.20
$-C(OCHMe)=W(CO)_5$ [h]	**15A**	0.405 [i]	0.79	1.96 (14)	2.50 (80)	4.38 [j]

[a] $E_{1/2}{}^{ox}$ values relative to $E_{1/2}{}^{ox}$ [FcH] (eqn. (1)), measured by cyclic voltammetry, at a Pt electrode, in THF–0.2M $[N^nBu_4][BF_4]$.
[b] Values estimated in this study from the relationship between Δ_X and σ_p (eqns. (2) and/or (3)).
[c] Values of wavenumbers for long-wavelength (λ_1 and λ_2) bands values of molar absorptivities ε are given in parentheses.
[d] Values relative to tetramethylsilane.
[e] Not clearly assigned.
[f] Another wave is observed at 3.33 (1652).
[g] A second anodic wave is observed at $\Delta_x = 0.325$ V ($\sigma_p = 0.62$); in NCMe, the two anodic waves occur at $\Delta_x = 0.25$ and 0.37 V *vs.* SCE.
[h] Disubstituted ferrocene but with predominant effect of the substituent with the carbene group.
[i] Same value for both diasteroisomers.
[j] 4.28 ppm for the other diasteroisomer.

ferrocenyl ring through an sp^2 hybridized carbon atom. Preliminary results of this study were presented previously [22].

2. Results and discussion

The redox properties of the ferrocene derivatives were studied mainly by cyclic voltammetry (in some cases also by controlled-potential electrolysis and by differential pulse polarography), at a Pt electrode, in 0.2 M $[N^nBu_4][BF_4]$-tetrahydrofuran (THF), dichloromethane or acetonitrile.

They show a one-electron reversible oxidation, localized at iron(II), as reported [1–18,21] for other ferrocenes; for complexes with electroactive substituents, a second, commonly irreversible anodic or cathodic wave may be observed, but these have not been investigated further. The values of the half-wave oxidation potential are quoted relative to that of ferrocene (see Tables 1–4). Thus, they correspond to an electrochemical substituent constant Δ_X defined by the following equation [21]:

$$\Delta_X = E_{1/2}^{ox}[FcX] - E_{1/2}^{ox}[FcH] \qquad (1)$$

Normally, only slight variations in Δ_X are observed upon changing the solvent (THF, CH_2Cl_2 or NCMe).

The values of $E_{1/2}^{ox}$ *vs.* a saturated calomel electrode (SCE), observed $E_{1/2}^{ox}[FcX]$, can be easily estimated using eqn. (1) and with the value of $E_{1/2}^{ox}[FcH]$ *vs.* SCE (see experimental section).

The observed anodic wave involves a single electron, as indicated by the ratio of the current function of the complex to that of ferrocene and confirmed, in some cases, by controlled-potential electrolysis. The ratio of the anodic to cathodic peak currents for this wave is close to unity, but, when using the high-resistance THF solvent, the peak potential separation is usually more than 100 mV, as observed for [Fc(CHYZ)] [21] and other ferrocenyl complexes [23,24]. This deviation from the criterion for electrochemical reversibility ($\Delta E_p = 59$ mV for a single-electron reversible process) possibly results from uncompensated solution resistance between the working and reference electrodes, a slow electron-transfer rate on the Pt electrode or its poisoning (a considerable electrode coating leading to decreased currents was often detected).

The values of Δ_X (eqn. (1)) obtained for the [FcX] complexes of this study allowed us to estimate the Hammett constant σ_p for the corresponding X substituents (see Tables 1–4), by using the linear correlations obtained under similar experimental conditions for other ferrocenes in THF, which assumes the form of the least-squares equation [21]

$$\Delta_X = 0.031 + 0.473\sigma_p \qquad (2)$$

If the oxidation potential is expressed relative to SCE (see eqn. (1)), eqn. (2) assumes the form [21]

$$E_{1/2}^{ox} = 0.576 + 0.473\sigma_p \qquad (3)$$

Substituents in complexes with $E_{1/2}^{ox}$ close to that of ferrocene (with Δ_X in the 0–0.03 V range) are considered to have a σ_p of about zero because the point which represents ferrocene ($\Delta_X = 0$; $\sigma_p = 0$) falls below the regression line expressed by eqn. (2), by a value of 0.031 V (intercept). An increase in the electron-withdrawing ability of the substituent X, as measured by the Hammett constant σ_p corresponds to an increase in the half-wave oxidation potential of [FcX].

However, the following linear correlation [21] between $E_{1/2}^{ox}$ and the Taft polar σ^* substituent constant for the series [Fc–CHYZ] with an aliphatic α-carbon substituent does not apply to the cases of the present study with non-aliphatic substituents (at least for those with known σ^* values), indicating that polar effects are then not dominant:

$$\Delta_X = -0.032 + 0.106\sigma^* \qquad (4)$$

2.1. *Substituents of the type –C(Y)=Z (class A)*

The ferrocene derivatives with class A substituents (which are unsaturated at the α-carbon with a sp^2 hybridization) have oxidation potentials (Table 1) spread over a wider range ($\Delta_X = -0.04$ to $+0.41$ V) than those of the other classes, as well as those of the type [Fc(CHYZ)] [21] which have a substituent with an sp^3 α-carbon atom. This may be understood on the basis of the stronger substituent effect on the ferrocenyl redox center in this case as a result of the interaction of the p_z orbital of the sp^2 α-carbon atom with the ferrocenyl π system. The estimated values of σ_p for the substituents of this class, assuming that they follow eqn. (2), are also given in Table 1.

The oxidation potentials of the complexes with purely hydrocarbon substituents without extended π delocalization are usually not much different from that of ferrocene; hence, for **1A** to **6A**, Δ_X falls in the range from -0.04 to $+0.01$ V, which also includes the values observed for the complexes with the related substituents CH=CHMe (-0.025 V) [15] and CH=CHPh (-0.013 V) [14,15].

However, the effects of unsaturated electron-withdrawing (by resonance) functional groups are readily transmitted to the redox center, and **8A**, **10A**, **11A**, **12A** or **13A** with the CO, CO_2Et, NO_2, $COCF_3$ or SO_2R groups [25–28] have higher values of Δ_X (0.085–0.215 V range), corresponding to positive values of σ_p (about 0.1–0.4). Possibly as a result of the electron-acceptor character of both Cl and CHO in –C(Cl)=CHCHO (**14A**), the corresponding values of Δ_X (0.23 V) and σ_p (0.41) are considerably higher.

The highest electron-withdrawing ability is displayed by the carbene group $-\overset{|}{C}=W(CO)_5$ in **15A** and the corresponding substituted ferrocene is harder to oxidize than ferrocene by 0.405 V; this complex is a disubstituted ferrocene, but it is included in class A since the effect of the carbene substituent largely predominates over that of the OCHMe group. The anodic shift Δ_X relative to the ferrocene–ferricinium pair is even larger than those quoted [29] for related ferrocenyl-carbene and ferrocenyl-carbyne complexes, *e.g.* 0.315 V for [Fc–C(OEt)=W(CO)$_5$]. The estimated value (0.79) of σ_p (eqn. (2)) for the carbene substituent **15A** is higher than that [26] of the cyano group (0.660) and is close to those [26] of $-SO_2Me$ (0.72) and $-NO_2$ (0.778).

The complex **13A** has two redox active ferrocenyl centres joined by the unsaturated bridge $\diagdown\underline{C=C\diagup\!\!-C}=N$–tosyl and exhibits two successive single electron anodic waves, either in THF or in NCMe, with a potential difference of about 0.10 V, indicating a considerable interaction between the two ferrocenyl moieties through the unsaturated carbon bridge. This contrasts with the behaviour quoted [30] for the complex Fc–CH_2CH_2–Fc, with a saturated two-carbon bridge, which shows a single oxidation process for both iron centres as a result of their weak interaction. However, a separation (about 0.10 V) of the two anodic waves, similar to that of **13A**, has been observed [21] for bridged ferrocenes with a shorter saturated bridge with a single sp^3 carbon atom, *e.g.* –CH(OH)–, –CH(OMe)– or –CH(N$_3$)–, whereas a greater separation of 0.350 V has been reported [31] for biferrocene (Fc–Fc).

The two distinct anodic waves for **13A** occur at potentials (Δ_X = 0.215 and 0.325 V) which are higher than those of the above-mentioned compounds with two ferrocenyls bridged by a saturated carbon moiety, confirming the strong electron acceptance of the $\underline{>C=N\text{-tosyl}}$ group. The estimated σ_p values for $-\overline{C=C(Fc)C}=N$-tosyl and the derived cationic $-\overline{C=C(Fc^+)C}=$tosyl substituent are 0.39 and 0.62 respectively.

2.2. *Substituents of the type –COY (class B)*

The complexes of this class have $E_{1/2}{}^{ox}$ at considerably higher values than that of ferrocene, which fall within a narrow range ($\Delta_X \approx$ 0.20–0.30 V), corresponding to σ_p values from +0.36 to +0.56 (Table 2). This is consistent with the high electron-withdrawing ability of the COY substituent (*e.g.* σ_p(COMe) = 0.502 [26]) which binds directly to the aromatic ring through the carbonyl group, and it also shows that the electronic effect of the COY is only marginally affected by the Y moiety, consistent with data presented by other workers [13,17].

For Fc–CHO (**7B**), the observed value of Δ_X (0.27 V) is considerably higher than that expected (0.13 V) on the basis of the linear dependence upon σ_p but is consistent with data from the literature [14,32]. This may be ascribed to the ability of –CHO to conjugate with the reaction site and act as an electron acceptor (as revealed by its exceedingly high σ_p^- value of +1.126 [28]); this may be explained by overlap of a filled π-ferrocenyl orbital with a π^*-CO orbital, as suggested by others [15] for related groups.

Ferrocene carboxylic acid Fc–COOH (**9B**) also appears to behave abnormally in THF, the corresponding point lying slightly above the Δ_X *vs.* σ_p line. Although such an anomaly has not been detected either in CH_2Cl_2 or by others in NCMe–MClO$_4$ (M = Li or Na) or in aqueous acidic medium [16b,17], other studies

TABLE 2. Oxidation potentials for ferrocene derivatives of the type Fc–COY (class B) relative to that of ferrocene, Hammett substituent constants σ_p, electronic spectroscopy data and ^{1}H NMR chemical shifts for the unsubstituted cyclopentadienyl ring

–COY	No.	Δ_X [a] (V)	σ_p [b]	$1/\lambda_1\ (\varepsilon_1)$ [c] ($\times 10^3$ nm^{-1}(1 mol^{-1} mm^{-1}))	$1/\lambda_2\ (\varepsilon_2)$ [c] ($\times 10^3$ nm^{-1}(1 mol^{-1} mm^{-1}))	$\delta(C_5H_5)$ [d] (ppm)
1,1′-$COCH_2CH_2$–	**1B** [e]	0.20	0.36 [f] ± 0.06	2.27	3.07	–
–$COCH_2{}^tBu$	**2B**	0.245	0.45	2.23 (37)	3.03 (205)	4.17
–CO^tBu	**3B**	0.255	0.47	2.21 (31)	3.11 (105)	4.17
–COCH(Me)Ph	**4B**	0.255	0.47	2.21 (48)	3.09 (138)	4.03
–COMe	**5B**	0.26 [g,h]	0.502 [i]	2.23 (32)	3.09 (115)	4.18
–COPh	**6B**	0.26 [g,h]	0.459 [j]	2.14 (75)	2.78 (140)	4.20
–CHO	**7B** [k]	0.27 [l]	0.216 [j]	2.20 (47)	3.05 (120)	4.26
–COC_6H_4Cl-*2*	**8B**	0.295	0.56	2.17 (85)	2.89 (190)	4.28
–COOH	**9B** [k]	0.31 [m]	0.45 [i]	2.26 (22)	3.00 (30)	4.25

[a] See footnote a to Table 1. [b] Values estimated in this study from the relationship between Δ_X and σ_p (eqns. (2) and/or (3)), unless stated otherwise. [c,d] See footnotes c and d respectively to Table 1. [e] The substituent bridges the two carbocyclic rings with predominant effect of the carbonyl group. [f] Value for hypothetical and equivalent substituent with the same effect on the redox potential as the overall substituent under consideration. [g] Considered for comparative purposes [21]. [h] The same value was obtained in CH_2Cl_2. [i] Ref. 25. [j] Ref. 27. [k] Anomalous behavior (see text). [l] 0.29 V in CH_2Cl_2. [m] 0.24 V in CH_2Cl_2.

TABLE 3. Oxidation potentials for miscellaneous ferrocene derivatives FcX (group C) relative to that of ferrocene, Hammett substituent constants σ_p, electronic spectroscopic data and ^1H NMR chemical shifts for the unsubstituted cyclopentadienyl ring

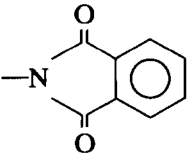
	No.	Δ_X [a] (V)	σ_p [b]	$1/\lambda_1 (\varepsilon_1)$ [c] ($\times 10^3$ nm^{-1}(1 mol^{-1} mm^{-1}))	$1/\lambda_2 (\varepsilon_2)$ [c] ($\times 10^3$ nm^{-1}(1 mol^{-1} mm^{-1}))	$\delta(C_5H_5)$ [d] (ppm)
$-\overline{NC(O)(1,2\text{-}C_6H_4)C}(O)$	**1C**	0.045	0.03 ± 0.06	2.26 (29)	3.07 (130)	4.20
–OCOMe	**2C** [e]	0.05 [f]	0.31 [g]	2.31 (10)	3.14	4.20
$-PPh_2$	**3C**	0.06	0.06			
$-N_3$	**4C**	0.125	0.20	2.47	[h]	4.27
–Br	**5C**	0.15 [i,j]	0.232 [k]	2.29 (12)	[h]	4.21
$-\overline{NN{=}NC(CO_2Me){=}C}(CO_2Me)$	**6C**	0.295	0.56	2.32 (33)	3.07 (105)	4.27
–NC	**7C**	0.305 [l]	0.58			
–CN	**8C** [i]	0.345 [l,m]	0.66 [k]	2.27 (15)	3.03 (15)	4.33

[a,b,c,d] See the corresponding footnotes to Table 2. [e] Anomalous behavior (see text); [f] 0.07 V in CH_2Cl_2; [g] Ref. 26; [h] not clearly assigned; [i] considered for comparative purposes [21]; [j] 0.16 V in CH_2Cl_2; [k] Ref. 25; [l] value in NCMe [34]; [m] 0.36 V in CH_2Cl_2.

have shown [33] that Fc–COOH (and $Fc-NH_2$) do not fit the linear relationship of $E_{1/4}{}^0$ *vs.* ^{57}Fe Mössbauer quadrupole splitting (QS) and of QS *vs.* $\sigma_R{}^+$, observed for a series of monosubstituted and disubstituted ferrocenes; these anomalies were rationalised [33] by hydrogen bonding.

2.3. Substituents of different types (miscellaneous, class C)

In this class of complex with miscellaneous types of substituent, $E_{1/2}{}^{ox}$ is spread over a considerable range greater than the value for ferrocene (Table 3). All the substituents studied behave as electron acceptors (relative to hydrogen) and the values of the Hammett constant σ_p were estimated as follows,



(**1C**, +0.03), $-PPh_2$ (**3C**, +0.06), $-N_3$(**4C**, +0.20) and $-\overline{N-N{=}N-C(CO_2Me){=}C}(CO_2Me)$ (**6C**, +0.56), as well as for the isocyano group, –NC (**7C**, +0.58), which appears to be a slightly stronger electron acceptor than $-CF_3$ ($\sigma_p = 0.54$) [26], although somewhat weaker than the much more common isomeric cyano form, –CN (**8D**, $\sigma_p = 0.66$) [26].

The observed electron-acceptor character of the diphenylphosphino group $-PPh_2$ is consistent with the known [32] redox behavior of the related diferrocenylphenylphosphine Fc_2PPh, which also has a higher oxidation potential than ferrocene and has been explained by the ability of vacant phosphorus 3d orbitals to accept electrons from ferrocene [35].

The ferrocene derivative with the –OCOMe (**2C**) is more readily oxidized than would be expected on the basis of the linear correlation between Δ_x and σ_p. Such anomalous behavior has also been observed [12] in the related acetamido (–NHCOMe) and urethano (–NHCOOR) substituents which also have a carbonyl group at a β position and it has been interpreted as the result of an interaction of the carbonyl oxygen atom with the Fe(III) in the oxidized complex.

2.4. Disubstituted ferrocenes (class D)

In this class, with the disubstituted ferrocene complexes of this study, only 1,1′-dimethylferrocene (included for comparative purposes) is more readily oxidized than ferrocene (Table 4).

On the assumption of the additive nature of the substituent effects (which has been recognized [12,16a,36] in a number of cases, provided that bond delocalization is irrelevant, and was also confirmed in this study for 1,1′-dimethylferrocene), the oxidation potential may be estimated for some complexes with two different substituents and compared with the observed value.

Hence, for the $-CH_2NMe_2$ substituent, with an aliphatic α-carbon, eqn. (4) should be valid [21] and the corresponding Δ_x value can be predicted, provided

TABLE 4. Oxidation potentials for disubstituted ferrocene derivatives (class D) relative to that of ferrocene, Hammett substituent constants σ_p and ^1H NMR chemical shifts for the unsubstituted cyclopentadienyl ring

Substituent	No.	Δ_X [a] (V)	$\Sigma\sigma_p$ [b]	$\delta(C_5H_5)$ [c] (ppm)
1,1′-dimethyl	**1D**	−0.115 [d,e] ± 0.01	−0.34 [f] ± 0.06	–
$1\text{-HgCl-2-}CH_2NMe_2$	**2D**	−0.02	−0.11	4.13
$1\text{-CHMeNMe}_2\text{-2-B(OH)}_2$	**3D** [g]	0.01	0.0	4.08
$1\text{-PPh}_2\text{-2-CH}_2\text{NMe}_2$	**4D**	0.06	0.06	3.92
1,1′-S–S–S bridge	**5D**	0.35	0.66	–

[a] See footnote a to Table 1. [b] Summation of the values of the Hammett constant σ_p for the two substituents or overall σ_p value for hypothetical substituent with identical effect on the redox potential to the combined effects of the substituents; estimated in this study from the Δ_X *vs.* σ_p correlation (eqns. (2) and/or (3)), unless stated otherwise. [c] See note d to Table 1; [d] considered for comparative purposes [21]; [e] −0.110 V in CH_2Cl_2; [f] Ref. 25; [g] anomalous behavior (see text).

that $\sigma^*(\text{-CH}_2\text{NMe}_2)$ is known. The latter has been estimated as −0.04 by considering the common attenuation factor (2.8) of a methylene group on the substituent effect [25], and the reported value [25] of −0.1 for $\sigma^*(\text{NMe}_2)$, *i.e.* $\sigma^*(\text{-CH}_2\text{NMe}_2) = \sigma^*(\text{NMe}_2)/2.8 = -0.1/2.8 = -0.04$. Using eqn. (4), the value of −0.04 V was estimated for $\Delta_X(\text{-CH}_2\text{NMe}_2)$.

Moreover, by considering the known Δ_X values for HgCl (0.033) [16b] and PPh_2 (**3C**, 0.06 V, obtained in the present study; see above), overall Δ_x values of $(0.033 - 0.04 = -0.01\ \text{V})$ and $(+0.06 - 0.04 = 0.02\ \text{V})$ would be expected for the disubstituted 1-HgCl-2-CH_2NMe_2 (**2D**) and 1-PPh_2-2-CH_2NMe_2 ferrocene (**4D**) complexes. These values are consistent with those observed (−0.02 V and 0.06 V respectively (Table 4)). The redox behavior of **4D** (which has a second anodic wave at $E_p^{ox} \approx 0.87$ V) has also been studied by others [23], who did not identify its anodic waves. We propose that the first wave corresponds to the oxidation of the ferrocenyl iron because of these estimates.

The oxidation potential of 1-$CHMeNMe_2$-2-$B(OH)_2$ (**3D**) is very close to that of ferrocene in spite of the supposed strong electron-acceptor character of the $B(OH)_2$ substituent ($\sigma_p = +0.454$ [27]). Although this anomalous behavior is not clearly understood, it may result from H bonding between the hydroxo and the amino groups, thus rendering the $B(OH)_2$ substituent a weaker electron acceptor than expected.

The redox behavior of a bridged ferrocene (**1B**) with a dominant electronic effect at one of the cyclopentadienyl rings, has already been mentioned.

There is one example of a ferrocene derivative (**5D**) with a symmetrical S–S–S bridge connecting the two rings and as a result of its strong electron-acceptor character, a high oxidation potential was observed, contrasting with the behavior [37] of ferrocenophanes

TABLE 5. Electronic spectroscopy data and ^{1}H NMR chemical shifts for ferrocene derivatives of the type Fc–CHYZ.

Y	Z	No. [a]	$1/\lambda_1\ (\varepsilon_1)$ [b] ($\times 10^3$ nm^{-1} (l mol^{-1} mm^{-1}))	$1/\lambda_2\ (\varepsilon_2)$ [b] ($\times 10^3$ nm^{-1} (l mol^{-1} mm^{-1}))	$\delta(C_5H_5)$ [c]
H	$(CH_2)_3COOH$	2	[d]	[d]	4.08
H	P(O)(OMe)OH	3	2.28 (27)	3.09 (12)	4.09
^{t}Bu	NHMe	4	2.27 (9.5)	3.05 (6)	4.18
^{i}Pt	NMe_2	5	2.28 (25)	[d]	4.13
Cy	$NH(CH_2)_2Ph$	6	2.31 (13)	[d]	3.83
^{t}Bu	$NH(CH_2C_6H_3Cl_2$-*3,4*)	7	2.27 (10)	3.13 (8)	4.11
^{t}Bu	$NCH_2CH_2OCH_2CH_2$	8	2.20 (15)	3.03 (9)	4.13
^{t}Bu	NH_2	9	2.30 (11)	3.10 (12)	4.15
CH(Me)^{t}Bu	NH_2	10	2.33 (14)	3.08	4.13
^{i}Pr	NHBz	11	2.30 (12)	3.13 (10)	4.04
Cy	NHBz	12	2.29 (5)	[d]	4.03
^{i}Pr	NHCOCH(^{i}Pr)NHCOOBz	13	2.27 (9)	3.09 (8)	4.09
Ph	OH	14	2.27 (11)	3.15 (11)	4.18
Fc	OH	15	2.29 (29)	[d]	4.27
Cy	NHCHO	16	2.32 (11)	3.09 (12)	4.13
H	OCH_2Fc	17	2.29 (29)	3.07 (21)	4.11
H	$C(S)NCH_2CH_2OCH_2CH_2$	18	2.31 (30)	[d]	4.16
Me	$S(CH_2)_2NMe_2$	19	2.27 (14)	3.13 (17)	4.14
Fc	OMe	20	2.27 (41)	3.13 (150)	4.15
^{t}Bu	OCOCH(^{i}Pr)NHCOPh	21 [e]	2.30 (11)	3.13 (12)	4.12
			(13)	(14)	4.05
^{t}Bu	-NCH=NCH=CH	22	2.27 (11)	3.05 (8)	3.79
^{t}Bu	OCOMe	23	2.29 (11)	3.11 (9)	4.14
^{t}Bu	N_3	24	2.28 (12)	3.13 (12)	4.23
Fc	N_3	25	2.28 (24)	[d]	4.16
^{i}Pr	NHOH	28	2.27 (26)	3.05 (45)	4.16
Cy	-NC	29	2.29 (10)	3.09 (7)	4.22
^{t}Bu	$-NN{=}NC(CO_2Me){=}C(CO_2Me)$	30	2.35 (14)	[d]	3.69
NMe_2	-CN	33	2.24 (22)	3.07 (43)	4.23
H	NMe_3^+	34	2.23	3.03	4.27

[a] Numbering is that given in ref. 21; for the redox potentials, see also this reference. [b] See footnote c to Table 1; [c] see footnote d to Table 1; [d] not clearly assigned; [e] two diasteroisomers.

which have a bridge of electron-donating methylene groups joining the two cyclopentadienyl rings and have $E_{1/2}{}^{ox}$ values less than that of ferrocene.

2.5. Oxidation potential and energy of electronic transitions

The interpretation of the electronic absorption spectra of ferrocene and its derivatives has been a matter of controversy [38]. In particular, the two long-wavelength bands of ferrocene at 440 and 325 nm (neglecting a less well-defined band at 528 nm) and the corresponding bands for substituted derivatives have been considered to correspond to a forbidden metal d–d transition and to a forbidden metal-to-ligand charge transfer respectively. A poor linear correlation has been suggested [13] between $E_{1/2}{}^{ox}$ and the wavelengths of these bands. However, a different assignment has also been proposed [39], suggesting that these bands result from spin-allowed d–d transitions, whereas a more intense L → M charge transfer occurs at a much shorter wavelength (200 nm for ferrocene). Less well-defined bands, not definitely characterized, in the UV region and ring- or substituent-localized transitions have also been assigned in the electronic spectra of ferrocene derivatives. Since substituent effects on these weak or poorly characterized bands would be difficult to assess, we selected the two long-wavelength (λ_1 and λ_2) bands and attempted to correlate $E_{1/2}{}^{ox}$ (or Δ_x) and the energy of these bands for ferrocenes with the various classes of substituent of Tables 1–3 as well as those of the type [Fc–CHYZ] (Table 5).

No overall correlation was detected in the plots of Δ_X *vs.* $1/\lambda_1$ or *vs.* $1/\lambda_2$. The points representative of the type [Fc–CHYZ] and of the class B appear to fall randomly in two distinct regions (one a lower potential range and a narrower wavenumber range than the other). Points for class A substituents are spread over a wider range of both oxidation potential and wavenumber than those of other classes, indicating the greater ability of the sp^2 C to transmit substituent effect to the orbitals involved in the anodic process and in the electronic d–d transitions. Although there is no good linear correlation of Δ_X with $1/\lambda$, an overall gross tendency appears to occur for class A compounds; an increase in oxidation potential (as the result of an increase in the electron-acceptor character of the substituent) tends to correspond to a decrease in the d–d transition energy. A better correlation, possibly related to this suggested behavior of class A, has been reported for the isocyanide complexes *trans*-[M(CNR)$_2$(dppe)$_2$](M = Mo or W; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) [40] and *trans*-[ReCl(CNR)(dppe)$_2$] [41] where there is a linear relationship between $E_{1/2}{}^{ox}$ and the energy of the metal-to-ligand charge-transfer band.

2.6. Oxidation potential and cyclopentadienyl proton chemical shift

For most of the complexes of this study (Tables 1–5), the ^{1}H NMR spectra were recorded (in CDCl$_3$) and the variation in the proton chemical shift of the unsubstituted cyclopentadienyl ring was compared with that of the oxidation potential. No correlation was detected between Δ_X and $\delta(C_5H_5)$ although for closely related compounds with similar oxidation potentials a strong dependence of chemical shift upon substituent has been observed as with compounds of class [Fc–CHYZ] with an amino or an alkoxy moiety, as well as the ferrocenes of class B.

Other examples of the insensitivity of the oxidation potential to factors that determine $\delta(C_5H_5)$ are given by the pairs of diasteroisomers of [Fc-CH(^{t}Bu){OC-OCH(^{i}Pr)NHCOPh}] (**21**) (Table 5) and of **15A** (Table 1) which have similar redox potentials in spite of the observed differences (about 0.07 ppm and 0.10 ppm respectively) between their cyclopentadienyl proton chemical shifts.

However, for class A substituted ferrocenes, an overall gross increase in $E_{1/2}{}^{ox}$ with $\delta(C_5H_5)$ appears to occur, consistent with the expected decrease in the electron-richness of the ferrocenyl group (both the cyclopentadienyl ring and the metal center) with the increase in the electron-withdrawing ability of the substituent.

A similar but better defined relationship between $E_{1/2}{}^{ox}$ and $\delta(C_5H_5)$ has been observed [42] for a series of the substituted aromatic isocyanide complexes [Fe(η^5-C$_5$H$_5$)(CNC$_6$H$_4$X-4)$_2$Br] in which the substituent effect may also involve an extended conjugation.

3. Final comments

The sensitivity of the anodic potential of the ferrocene complexes to the substituent effect is highly dependent on the type of substituent. If its ligating α-carbon is sp^2 hybridised, with possible conjugation with the cyclopentadienyl ring (as in substituents of the type –C(Y)=Z, class A), the oxidation potential is much more sensitive to the effect of the substituent and the wavenumbers for the waves observed in their electronic spectra fall within a wider range than, *e.g.* when the substituents are bonded to the cyclopentadienyl ring through a sp^3 carbon atom.

Moreover, the linear correlations recognized [21] between the redox potential and the substituent Hammett constant σ_p (or the Taft polar constant σ^* for the substituents with a sp^3 aliphatic α-carbon) allowed estimates of the previously unknown values of these constants for over 100 groups (including those reported in the previous paper [21]).

4. Experimental section

The electrochemical experiments were carried out using an EG&G PAR 173 potentiostat–galvanostat, an EG&G PARC 175 universal programmer and an EG&G PAR 174A polarographic analyzer.

Cyclic voltammetry and differential pulse polarography were undertaken using a two-compartment three-electrode cell, at a platinum working electrode, probed by a Luggin capillary connected to a silver-wire pseudoreference electrode; a platinum or tungsten auxiliary electrode was employed.

Controlled-potential electrolyses were carried out using a three-electrode H-type cell with platinum-gauze working electrode and counterelectrode in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudoreference electrode.

The oxidation potentials of the complexes were measured in 0.2 M $[N^nBu_4][BF_4]$–THF (dichloromethane or acetonitrile), by using as internal reference the following couples (with $E_{1/2}{}^{ox}$ values *vs.* SCE in 0.2 M $[N^nBu_4]$–solvent indicated in parentheses): $[FcH]^{0/+}$ (0.54(5) (THF or CH_2Cl_2) or 0.40 V (NCMe)), *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]^{0/+}$ (−0.16 (THF) or −0.26 V (CH_2Cl_2)) or *trans*-$[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^{0/+}$ (0.28 (THF) or 0.22 V (CH_2Cl_2)).

The ^1H NMR spectra were obtained with a Bruker CXP 300, a Bruker AM 360, a Bruker WP 200 or a JEOL JNM-PS-100 instrument. Electronic spectra were recorded with a Perkin–Elmer λ9 spectrophotometer.

Compounds **5B**, **6B**, **7B**, **8B**, **9B** and **1D** are commercially available, and the following complexes were prepared according to methods in the literature: **4B** [43], **7C** [35], **1A**, **3A**, **4A** and **6A** [44], **5A** and **3B** [45], **2A** and **8A** [46], **7A** and **9A** [47a], **10A** [47b], **11A** [48], **14A** [49], **15A** [50], **1B** [51a], **2B** [51b], **1C**, **2C** and **8C** [52], **3C** [53], **4C** [54], **5C** [55], **2D** [56], **4D** [57] and **5D** [58]. For complexes of the type [Fc–CHYZ] (Table 5), see ref. 21.

12A: ferrocene (10 mmol, 1.86 g) and trifluoro-2,4-pentandione (20 mmol) were dissolved under dinitrogen in a mixture of trichloroacetic acid (10.0 g) and acetic acid (1.5 ml). At −10°C, fluorosulfonic acid (1.5 ml) was added dropwise with stirring, and the mixture was allowed to react for 40 min at 0°C to form the ferrocenylalkyl carbocation. This solution was made alkaline by the addition of 30% aqueous NaOH and diluted with 100 ml of water and 100 ml of dichloromethane. The organic layer was dried with Na_2SO_4, and the solvent was evaporated. The residue was recrystallized from hexane to give 1,1,1-trifluoro-4-ferrocenyl-3-penten-2-one (**12A**) as a 95 : 5 *E/Z* mixture, according to NMR spectroscopic (yield 48%, m.p. 84–85°C) *E*(**12A**): ^1H NMR ($CDCl_3$): δ 2.50 (s, 3H); 4.07 (s, 5H); 4.40 (m, 2H); 4.53 (m, 2H); 6.45 (m, 1H) ppm. *Z*(**12A**): ^1H NMR ($CDCl_3$); δ 2.05 (s, 3H) ppm, Anal. Found: C, 56.2; H, 4.3. $C_{15}H_{13}F_3FeO$ calc.: C, 55.9; H, 4.1%.

13A: diferrocenylcyclopropenone (prepared as described [59]) (10 mmol, 4.22 g) was dissolved in toluene (50 ml), and toluenesulfonyl isocyanate (11 mmol, 2.17 g) was added. The mixture was heated to reflux with exclusion of moisture for 16 h. After cooling to room temperature, hexane (80 ml) was added and the precipitate filtered off. The product crystallizes from the solution upon cooling to −10°C for about 10 h (yield, 85%; m.p., 168–170°C). ^1H NMR ($CDCl_3$); δ 2.35 (s, 3H); 4.23 (s, 10H); 4.63 (m, 4H); 5.05 (m, 4H); 7.22 (d, 2H,$J = 7.2$ Hz); 7.90 (d, 2H) ppm. Anal. Found: C, 62.5; H, 4.5; N, 2.7. $C_{30}H_{25}FeNSO_2$ calc.: C, 62.6; H, 4.4; N, 2.4%.

6C: this 1,2,3-triazole complex was obtained by 1,3-dipolar cycloaddition of the corresponding azide with dimethyl acetylenedicarboxylate. Thus, 5 mmol of the azide (**4C**) were dissolved in benzene (30 ml). Dimethyl acetylenedicarboxylate (20 mmol, 2.84 g) was added and the mixture was heated to reflux for 24 h. The solvent and excess dimethyl acetylenedicarboxylate were evaporated and the residue purified by chromatography ((silica gel)–dichloromethane), (yield, 80%; m.p., 65–67°C). ^{13}C NMR ($CDCl_3$): δ 52.5; 53.7 (Me); 159.9; 160.0 (C=O); 133.2; 138.1 (C=C); 70.8 (unsubstituted C_5H_5); 64.0; 67.3 (CH); 92.4 (C_{quart}) ppm. Anal. Found: C, 52.3; H, 4.2; N, 11.0. $C_{16}H_{15}FeN_3O_4$ calc.: C, 52.0; H, 4.1; N, 11.4%.

3D: (*S*,*R*)-2-(*N*,*N*-Dimethyl-1-aminoethyl)ferroceneboronic acid: the compound was prepared by analogy with other boron-containing ferrocenes [52,60,61]. To a solution of (*S*)-1-(*N*,*N* -dimethylamino)ethylferrocene [62] (10 mmol, 2.57 g; $[\alpha]_D^{22} = 14.4°$ ($c = 1$; ethanol)) in 40 ml of dry diethyl ether, *n*-butyllithium (10 mmol, 6.5 ml of 1.5 M solution in hexane) was added and the mixture was left stirring under dinitrogen for 4 h. The solution obtained was added dropwise with efficient stirring to a solution of triethyl borate (12.5 mmol, 1.8 g) in 150 ml of diethyl ether at −78°C. After warming to room temperature, the mixture was heated to reflux for 10 h. 60 ml of water were added, and the organic phase was dried with $MgSO_4$. The solvent was evaporated and the residue was purified by chromatography (neutral alumina; methanol: diethyl ether 1 : 1) (yield, 47%; m.p., 142–145°C). $[\alpha]_D^{22} = +98°$ ($c = 1$, ethanol). ^1H NMR ($CDCl_3$); δ 1.28 (d, 3H, 6.8 Hz); 2.15 (s, 6H), 4.12 (s, 5H), 4.23 (qua, 1H, $J = 6.8$ Hz), 4.27 (m, 1H); 4.30 (m, 1H); 4.50 (m, 1H); 8.80–9.90 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$), δ 7.36 (CH–CH_3), 37.5 (NMe_2^*), 59 (CH–Me), 69.4 (C_5H_5), 66.2*, 69.5, 70.1, 75.8 (CH), 92.1 (C_{quart}) ppm. The signals labelled with asterisks (*) could not be observed directly because of extreme broadening but were detected by integration of a spectrum with inverse-gated decoupling and a very long relaxation delay (12 s; flip angle, 30°). Anal. Found: C, 57.8; H, 7.0; N, 4.7. $C_{14}H_{20}BFeNO_2$ calc.: C, 58.0; H, 6.9; N, 4.8%.

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