Journal of Organometallic Chemistry, 421 (1991) 75–90
Elsevier Sequoia S.A., Lausanne
JOM 22162

Redox potential and substituent effects at ferrocene derivatives. Estimates of Hammett σ_p and Taft polar σ^* substituent constants

M. Emília N.P.R.A. Silva [a], Armando J.L. Pombeiro [a,*],
João J.R. Fraústo da Silva [a], Rudolf Herrmann [b], Norbert Deus [b],
Tânia J. Castilho [a] and M. Fátima C.G. Silva [a]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex (Portugal)*
[b] *Organisch-Chemisches Institut, Technische Universität München, Lichtenbergstr. 4, W-8046 Garching (Germany)*

(Received April 25th, 1991)

Abstract

The anodic behaviour of 34 ferrocene derivatives (8 of which have been prepared for the first time) of the general type Fc-CHYZ [Y = R (hydrogen, alkyl or aryl), Fc or Fc^+; Z = amino or related functionalized groups, various unsaturated N-moieties (such as cyano, isocyano, imidazoyl, azide or triazene derivative), alkylammonium, hydroxy, alkoxy, thiolate, acyloxy, phosphinyl or thiocarbonyl groups] has been studied by cyclic voltammetry (and, in some cases, also by controlled-potential electrolysis and differential pulse polarography) at a Pt electrode in an aprotic solvent. The compounds undergo a one-electron reversible or quasi-reversible oxidation centred at each iron centre and the effect of the substituents on the half-wave oxidation potential is discussed in terms of their electronic properties. Linear correlations have been recognized between this potential and the Hammett σ_p constant or the Taft polar σ^* constant for the substituent, and have been used, in the cases they were not known, to estimate the values of these constants for the above-mentioned substituents and of the latter constant for a total of 73 of these substituents or their Z groups. The anomalous behaviours of complexes with an hydroxy, a carbonyl, an acylamido, a thiocarbonyl, or a phosphinyl group are discussed.

Introduction

Since its first synthesis, ferrocene has played a key role in the stimulation of the development of organometallic chemistry, and its redox properties, and those of its derivatives, have been widely studied by electrochemical methods [1–4].

Ferrocene complexes, when containing a single ring substituent (X), may be formulated as FcX [where Fc denotes the ferrocenyl group $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$], and thus can typically undergo a one-electron (reversible) anodic process whose oxidation potential is dependent on the substituent(s). Linear correlations have been found between the redox potential and the Hammett's σ constants (or related ones, such as the Taft σ^*) or, but less satisfactorily, between the redox potential and the shifts of bands in the electronic spectra of the substituted ferrocenes [5–11]. However, most of the electrochemical research has either been performed on ferrocene derivatives with substituents whose electron donor/acceptor properties were derived from other studies or was not oriented towards the elucidation of such properties. The aim of the present study is to gather information on a variety of substituents whose electronic features are not yet well documented, although the corresponding ferrocene derivatives may also be valuable in organic or organometallic syntheses e.g., in asymmetric synthesis, in catalytic hydrogenations by rhodium complexes [12] or in peptide syntheses by four component condensations [13].

In the ferrocene derivatives FcX of this study, the substituents are generally bonded to the cyclopentadienyl ring through a sp^3 hybridized carbon atom (which may be asymmetric), commonly with an heteroatom attached to such a carbon, i.e.: X = –CHYZ [Y = R(hydrogen, alkyl or aryl), Fc or Fc^+; Z = $NRR'NMe_3^+$, NHOH, NHCHO, NHCOR, OR, SR, OCOR, $(CH_2)_3COOH$, –CN, –NC, $-NCCr(CO)_5$, N_3, $-\overline{\mathrm{NCH{=}NCH{=}C}}\mathrm{H}$, $-\overline{\mathrm{NN{=}NC(CO_2Me){=}C}}\mathrm{(CO_2Me)}$, P(O)(OMe)OH or $\mathrm{C(S)}\overline{\mathrm{NCH_2CH_2OCH_2C}}\mathrm{H_2}$].

Preliminary results of this study were presented previously [14].

Results and discussion

The redox properties of the substituted ferrocenes were mainly studied by cyclic voltammetry at a Pt electrode, in 0.2 *M* $[N^nBu_4][BF_4]$/tetrahydrofuran (THF), dichloromethane or acetonitrile. They exhibit a one-electron reversible or quasi-reversible oxidation, which is believed to be localized mainly at the iron(II) centre; for complexes with electroactive substituents, a second, commonly irreversible, anodic or a cathodic wave may be observed, but the corresponding redox processes have not been investigated.

The values of the half-wave oxidation potential are quoted relative to that of ferrocene (Table 1), thus corresponding to an electrochemical substituent constant, Δ_X, defined (eq. 1) as the shift of the half-wave oxidation potential ($E_{1/2}^{ox}$) of the complex relative to that of ferrocene. Normally, only slight variations of Δ_X are observed with change in the solvent (THF, CH_2Cl_2 or NCMe).

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

For the substituted ferrocenes, the values of $E_{1/2}^{ox}$ versus SCE, $E_{1/2}^{ox}[FcX]$, can easily be estimated by using this equation and the known value (see below) of $E_{1/2}^{ox}[FcH]$ versus SCE. The oxidation potentials were measured by using as internal reference any of the following redox couples (with $E_{1/2}^{ox}$ values vs. SCE, in 0.2 *M* $[NBu_4][BF_4]$/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)].

Under our experimental conditions, with the high resistance THF solvent, although the ratio of the anodic and cathodic peak current for the reversible anodic wave (i_p^{ox}/i_p^{red}) is usually close to unity, the anodic process does not meet the criterion for electrochemical reversibility based on the separation of the anodic and cathodic peak potential (ΔE_p = 59 mV for a single electron reversible process).

Table 1

Oxidation potentials (measured in this study) of ferrocene derivatives FcCHYZ relative to that of ferrocene, Taft σ^* substituent constants (for CHYZ, Y and Z) and Hammett σ_p substituent constants (for CHYZ)

-CHYZ		No.	Δ_X(THF) [a]	Δ_X(CH_2Cl_2) [a]	σ^*(CHYZ) [b]	σ^*(Y) [c]	σ^*(Z) [c]	σ_p [d]
Y	Z							
H	H	**1** [e]	−0.05	−0.05	0 [f]			−0.17 [f]
H	$(CH_2)_3COOH$	**2**	−0.04	−0.05	*−0.08* [g]			*−0.17*
H	P(O)(OMe)OH	**3**	−0.04	0.01	[h]		[h]	*−0.10*
^{t}Bu	NHMe	**4** [e]	−0.04	−0.05	−0.107 [i]	−0.30	0	*−0.20*
^{i}Pr	NMe_2	**5** [e]	−0.04	−0.06	−0.104 [i]	−0.19	−0.1	*−0.17*
Cy	$NH(CH_2)_2Ph$	**6** [e]	−0.04	−0.04	−0.05 [i]	−0.15	0	*−0.16*
^{t}Bu	$NH(CH_2C_6H_3Cl_2$-3,4)	**7**	−0.04	−0.03	*0.01*	−0.30	*0.33* [i]	*−0.14*
^{t}Bu	$NCH_2CH_2OCH_2CH_2$	**8**	−0.04	−0.04	*−0.04*	−0.30	*0.19* [i]	*−0.16*
^{t}Bu	NH_2	**9** [e]	−0.03	−0.04	−0.05 [i]	−0.30	0.15	*−0.15*
CH(Me)^{t}Bu	NH_2	**10** [e]	−0.03	−0.04	−0.05 [i]	−0.28	0.15	*−0.15*
^{i}Pr	NHBz	**11**	−0.03	−0.04	*0.01*	−0.19	*0.22* [i]	*−0.15*
Cy	NHBz	**12**	−0.03	−0.04	*0.01*	−0.15	*0.18* [i]	*−0.15*
^{i}Pr	NHCOCH(^{i}Pr)NHCOOBz	**13** [j]	−0.03	−0.04	0.47 [i]	−0.19	1.5	*−0.15*
Ph	OH	**14** [j]	−0.03	−0.01	0.70 [i]	0.6	1.35	*−0.11*
Fc	OH	**15** [j]	−0.02	−0.05	0.36 [i]	−0.33 [k]	1.35	*−0.14*
Cy	NHCHO	**16** [j]	−0.02	−0.03	0.48 [i]	−0.15	1.5	*−0.12*
H	OCH_2Fc	**17**	0.00	0.02	*0.40*		*1.1* [l]	*ca. 0*
H	$C(S)NCH_2CH_2OCH_2CH_2$	**18**	0.00	0.04	[h]		[h]	*ca. 0*
Me	$S(CH_2)_2NMe_2$	**19**	0.02	0.00	*0.41*	0	*1.2* [i]	*ca. 0*
Fc	OMe	**20** [e]	0.02 [m]	0.00	*0.38* [i]	−0.33 [k]	1.4	*ca. 0*
^{t}Bu	OCOCH(^{i}Pr)NHCOPh	**21** [e,n]	0.03	0.03	*0.66* [i]	−0.30	2.15	*ca. 0*
^{t}Bu	-NCH=NCH=CH	**22**	0.03	0.03	*0.59*	−0.30	*1.9* [i]	*ca. 0*

Table 1 (continued)

-CHYZ		No.	Δ_X(THF) [a]	Δ_X(CH$_2$Cl$_2$) [a]	σ^*(CHYZ) [b]	σ^*(Y) [c]	σ^*(Z) [c]	σ_p [d]
Y	Z							
^{t}Bu	OCOMe	**23** [e]	0.04	0.04	0.66 [i]	−0.30	2.15	*0.02*
^{t}Bu	N$_3$	**24**	0.04	0.05	*0.72*	−0.30	*2.3* [i]	*0.03*
Fc	N$_3$	**25**	0.06 [m]	0.06	*0.87*	−0.33 [k]	*2.8* [i]	*0.06*
H	-NC	**26**	0.06 [o]		*0.87*		*2.4* [l]	*0.12*
Men	-NC	**27**	0.08 [o]		*1.05*	*0.1* [i]	*2.8* [p]	*0.10*
^{i}Pr	NHOH	**28**	0.08	0.04	[h]	−0.19	[h]	*0.06*
Cy	-NC	**29**	0.08 [o]	0.09	*1.07*	−0.15	*3.1* [i]	*0.11*
^{t}Bu	-NN=NC(CO$_2$Me)C(CO$_2$Me)	**30**	0.09	0.10	*1.16*	−0.30	*3.5* [i]	*0.13*
Men	-NCCr(CO)$_5$	**31**	0.11 [o]		*1.34*	0.1 [q]	*3.7* [i]	*0.17*
H	-NCCr(CO)$_5$	**32**	0.13 [o]		*1.53*		*4.3* [l]	*0.21*
NMe$_2$	-CN	**33** [e]	0.13	0.14	*1.32* [i]	−0.1	3.8	*0.22*
	-CHYZ$^+$							
Fc$^+$	OH	**15**$^+$ [r,j]		0.05	1.14 [i]	1.85 [k]	1.35	*0.03*
Fc$^+$	OMe	**20**$^+$ [r,e]		0.10	1.16 [i]	1.85 [k]	1.4	*0.14*
Fc$^+$	N$_3$	**25**$^+$ [r]		0.15	*1.58*	1.85 [k]	*2.6* [i]	*0.24*
H	NMe$_3$$^+$	**34** [e,s]	0.16	0.18	1.90 [f]		5.3 [l]	*0.29*

[a] $E^{ox}_{1/2}$ values (in volt ±0.01) relative to $E^{ox}_{1/2}$[FcH] (eq. 1), measured by cyclic voltammetry at a Pt electrode in solvent (THF or CH$_2$Cl$_2$)/0.2 *M* [N^{n}Bu$_4$][BF$_4$]. [b] Values in italics (±0.2) were estimated in this study from the relationship between Δ_X and σ^* (eqs. 6 and/or 7) (the average value is indicated when data are available for both solvents) unless stated otherwise. [c] Values in italics (±0.3) were estimated in this study; the others were taken from ref. 17 unless stated otherwise. [d] Values in italics (±0.06) were estimated in this study from the relationship between Δ_X and σ_p (eqs. 2 and/or 4). [e] Considered for the establishment of the correlation between Δ_X and σ^* (eqs. 6 or 7). [f] Taken from ref. 17. [g] Value comparable with those (0.05 or 0.04) estimated from the sequential application of eq. 11, in the form $\sigma^*(CH_2Z) = \sigma^*(Z)/2.8$, to -CH$_2$COOH ($\sigma^* = 1.05$) (ref. 17) or to -COOH ($\sigma^* \simeq 2.4$) (ref. 17), respectively. [h] There is disagreement between the values in thf and in CH$_2$Cl$_2$, due to anomalous behaviour (see text). [i] Estimated from eq. 9, $\sigma^*(CHYZ) = [\sigma^*(Y) + \sigma^*(Z)]/2.8$ (Y, Z $\neq$ H). [j] Anomalous behaviour (see text). [k] S.P. Gubin and A.A. Lubovick, *J. Organomet. Chem.*, 22 (1970) 183. [l] Estimated from eq. 11, in the form $\sigma^*(CH_2Z) = \sigma^*(Z)/2.8$. [m] Value not considered for the correlation between Δ_X and σ^* since it corresponds to the observed wave resulting from the overlap of two unresolved anodic waves (see text). [n] Two diastereoisomers. [o] Value measured in NCMe (ref. 21b). [p] Average of the values (2.4 and 3.1) estimated from the data for complexes **26** and **29**, respectively. [q] See complex **27**. [r] Complex derived from one-electron anodic oxidation of the parent neutral substituted ferrocene; therefore, the quoted oxidation potential (Δ_X) corresponds to that of the second anodic wave of the latter. [s] Iodide complex, [FcCH$_2$NMe$_3$]I; an irreversible anodic wave is observed at $E^{ox}_p = -0.15$ V relative to $E^{ox}_{1/2}$ [FcH] and is assigned to the oxidation of the iodide counterion, as confirmed by addition of [NBu$_4$]I (also in agreement with the reported oxidation of iodide in other systems—J.A. McCleverty and N. El Murr, *J. Chem. Soc., Chem. Commun.*, (1981) 960).

Indeed, a peak potential separation of > 100 mV is then observed for the anodic wave of ferrocene, and for its derivatives separations are usually in the 0.10–0.30 V range; similar peak separations have been reported by other authors for related ferrocenyl-compounds [15] and polynuclear ferrocenyl complexes [16]. This is possibly due to uncompensated solution resistance between the working and reference electrodes, a slow electron transfer rate on the Pt electrode, and poisoning of the latter.

The number of electrons involved was commonly estimated from the ratio of the current functions $i_p \nu^{-1/2} C^{-1}$ (i_p, peak current; ν, scan rate; C, molar concentration) of the complex and of ferrocene (which undergoes a one-electron reversible oxidation), assuming identical diffusion coefficients. Although accurate measurements are precluded by this simplification and, in some cases, by considerable electrode coating with lower currents in subsequent sweeps, this method generally appeared to provide unambiguous results which, in a number of cases, were confirmed by controlled potential electrolysis.

Oxidation potential versus Hammett σ_p constants

For the complexes containing substituents having known values of the Hammett σ_p constants (for *para* substituents) [17–20] and for which no anomalous influence on the redox potential is expected (see below), a linear correlation is observed between the half-wave oxidation potential and that constant. Hence $E_{1/2}^{ox}$ or Δ_X (see above) can be correlated linearly with σ_p for the substituent for monosubstituted ferrocene derivatives (or with the summation of the values of σ_p for disubstituted derivatives, in agreement with the additive nature of the effect of the substituents [7,9]), as reported by others [5,7–10]. The linear plots for the oxidation potential relative to that of ferrocene (Δ_X), measured in this study in THF or in CH_2Cl_2, versus Hammett σ_p constant is depicted in Fig. 1 for the following substituents: H (ferrocene), CH_3 (1), 1,1'-$(CH_3)_2$ (disubstituted ferrocene), Br, COMe, COPh and CN. It is evident that an increase in the electron-withdrawing ability of the substituent, as measured by the Hammett σ_p constant, is associated with an increase in the half-wave oxidation potential of the complex, as expected.

Numerical analyses of the available data, in THF and in CH_2Cl_2, gave the least squares eqs. 2 and 4 (with correlation coefficient, R, of 0.996 or 0.995, respectively) for the half-wave oxidation potential relative to that of ferrocene (Δ_X/V). The corresponding expressions for the half-wave oxidation potential versus SCE, $E_{1/2}^{ox}$/V, are given by eqs. 3 and 5.

$$\Delta_X(\mathrm{THF}) = 0.031 + 0.473\sigma_p \qquad (2)$$

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

$$\Delta_X(\mathrm{CH_2Cl_2}) = 0.034 + 0.479\sigma_p \qquad (4)$$

$$E_{1/2}^{ox}(\mathrm{CH_2Cl_2}) = 0.579 + 0.479\sigma_p \qquad (5)$$

The linear fit was not improved by considering the "calculated" $(\sigma_m + 2\sigma_p)/3$ constant [5] instead of σ_p, implying that a possible [5] decrease in the resonance effect of the substituent relative to that associated with σ_p is not detected for the above-mentioned substituents under our experimental conditions. The observa-

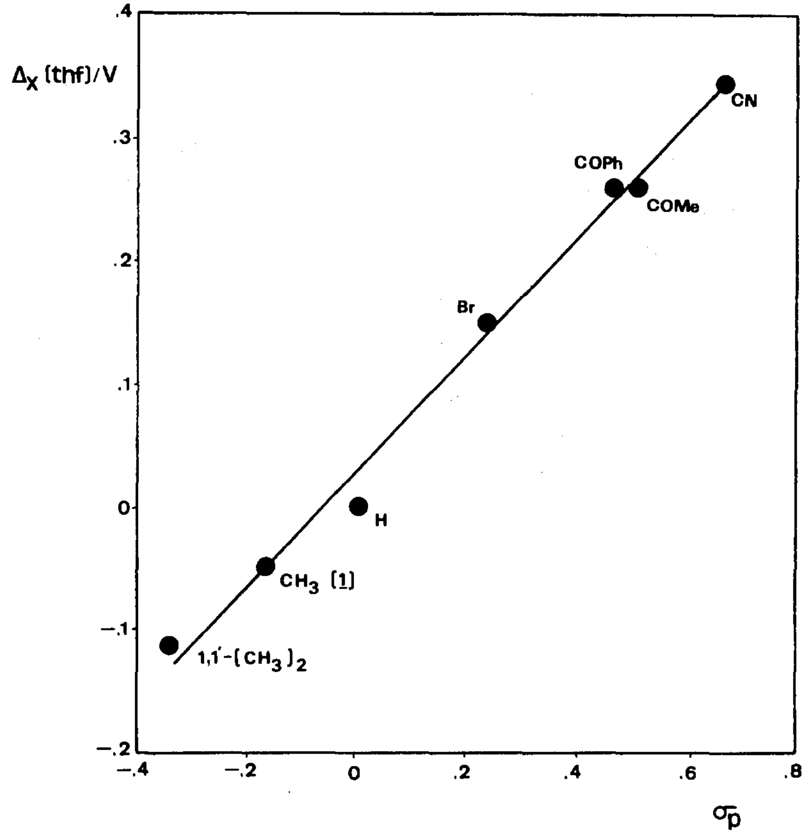

Fig. 1. Plot of Δ_X for substituted ferrocenes FcX (half-wave oxidation potential relative to that of ferrocene) versus the Hammett σ_P substituent constant. Δ_X values in volt, measured in this study, in THF/0.2 *M* $[Bu_4N][BF_4]$. Substituents 1,1'-$(CH_3)_2$, CH_3, Br, COMe, CN and σ_p taken from ref. 17; COPh and σ_p taken from ref. 19.

tions clearly indicate the importance of both the resonance and the inductive interaction, across the cyclopentadienyl ring, between the substituent and the iron redox centre.

Although the linear correlations were obtained from a rather limited number of data (only those corresponding to the complexes with substituents for which values of the Hammett constant were known could be considered), they are consistent with reported [5] regression lines for correlations of the chronopotentiometric quarter-wave potential ($E_{1/4}$) with σ_p or with $(\sigma_m + 2\sigma_p)/3$, for a higher number of substituted ferrocenes in an aprotic solvent (acetonitrile); the reported [5] $\Delta E_{1/4}/\Delta\sigma_p$ and $\Delta E_{1/4}[\Delta(\sigma_m + 2\sigma_p)/3]$ slopes of 0.493 and 0.517 V, respectively, are close to those found in the present study for the half-wave potential.

By applying eqs. 2 and/or 4 to the substituted ferrocenes included in the present study, σ_p values can be estimated for a variety of substituents for which values of this constant were previously unknown. The secondary σ_p constants thus derived from the half-wave oxidation potentials are listed in italics in the table, and will be discussed below. Since the point which represents ferrocene falls below the regression line (eqs. 2–5) (as also observed in earlier correlations [5,6]), there is a considerable uncertainty in the estimated σ_p values for substituents in complexes with values of $E^{ox}_{1/2}$ close to that of ferrocene. Hence substituents with Δ_X in the 0 to 0.031 V range in THF (i.e., in compounds with $E^{ox}_{1/2}$ values between those of ferrocene and of the corresponding point of the regression line) are considered to have a σ_p value of ca. zero.

The –CHYZ substituents with amino and hydroxy groups ($Z = NR_2$ or OH, respectively) usually correspond to complexes whose oxidation potentials fall in a narrow range, slightly below the value found for unsubstituted ferrocene (Δ_X ca. -0.04 to -0.02 V); these groups exhibit an inductive acceptor ($-$I) and a resonance donor ($+$R) effect, with predominance of the latter [17–20], and the corresponding –CHYZ substituents have estimated values of the Hammett σ_p constant (Table 1) that are negative and close to that of the methyl substituent.

However, as discussed below, substituents with an hydroxy (**14**, **15**, **15**$^+$ and **28**), a carbonyl (**13** and **16**), a thiocarbonyl (**18**) or a phosphinyl (**3**) group may confer an anomalous redox behaviour on the corresponding ferrocene complexes and so the estimated Hammett σ_p constants for such substituents should be regarded with caution.

The $-(CH_2)_4COOH$ (**2**) substituent behaves as a weak electron donor relative to hydrogen ($\Delta_X = -0.04$ V in THF, $\sigma_p = -0.17$), owing to the distance between the strong electron-acceptor –COOH group and the ferrocene nucleus, and to the combined effect of the four methylene groups that have donor properties. This result agrees with those reported by others [21a] for series of ferrocenylcarboxylic acids with interposed methylene groups, $Fc(CH_2)_nCOOH$ ($n = 1, 2$ or 3; $\Delta_X = 0.02$, -0.005 or -0.02 V, respectively); hence, the introduction of each methylene group in the bridge ($n = 1$ to 4) results in a cathodic shift of $E^{ox}_{1/2}$ of ca. 0.02 V and, for $n \geqslant 2$, the complex becomes easier to oxidize than ferrocene.

Like the amine and the hydroxy groups, the –OCOR substituents also display $-$I and $+$R effects; however, the electron-accepting inductive character predominates and, accordingly, the corresponding –CH(Y)OCOR-substituted ferrocenes have oxidation potentials that are slightly above that of ferrocene [$\Delta_X = 0.03$–0.04 V for **21** or **23**]; for such substituents of the type CH(Y)OCOR, the σ_p constant is close to zero.

Some compounds contain chiral elements and form diastereoisomers. These do not differ noticeably in their electrochemical properties; for example, the two diastereoisomeric valine derivatives $FcCH(^tBu)OCOCH(^iPr)NHCOPh$ (**21**) have the same redox potential, although the ^1H NMR chemical shifts of nearly all protons in the two compounds are quite different.

As expected, the groups containing two or three nitrogens [Z = imidazolyl (**22**) azide (**24**, **25**) or triazene derivative (**30**)] are electron withdrawing, and the corresponding substituted ferrocenes are less readily oxidized than ferrocene ($\Delta_X = 0.03$–0.10 V); the estimated values of the Hammett σ_p constant for the corresponding –CHYZ substituents lie in the 0 to 0.13 range.

The effect of –CN (a strong electron-withdrawing group mainly due to its inductive effect, as shown by the values of σ_p (0.66), Taft σ_I (0.52) and Taft σ^0_R (0.14) [17]) clearly predominates over that of the amino group in the $-CH(NMe_2)CN$ (**33**) substituent, whose ferrocenyl derivative has a relatively high oxidation potential ($\Delta_X = 0.14$ V in CH_2Cl_2), close to that of the cationic ammonium species, $FcCH_2NMe_3^+$ (**34**); both $-CH(NMe_2)CN$ and $-CH_2NMe_3^+$ have values of σ_p (0.22 and 0.29, respectively) comparable with that of Br (0.23) [18].

Also as a consequence of the strong electron withdrawal by the isocyano group, -NC, the complexes with substituents containing this functional group are harder to oxidize than ferrocene, particularly in the cases of FcCH(Men)NC (**27**) and $FcCH(Men)NCCr(CO)_5$ (**31**) (where CH(Men) = [(1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl]-(*R*)-methyl) which were previously described [21b]. For the isocyano substituents, σ_p values of 0.10 and 0.17, respectively, are now estimated. The increase in σ_p upon coordination of the isocyano substituent for the $\{Cr(CO)_5\}$ centre is a clear indication of the enhancing effect of the latter on the electron-acceptor character of the former.

The expected attenuation effect of the ligating sp^3 carbon atom of the -CHYZ substituent on the electronic effect of Z can also be clearly seen by comparing their σ_p values (or the $E^{ox}_{1/2}$ values of their ferrocenyl compounds), for example in the series: $-(CH_2)_4COOH$ (**2**) (−0.17) vs. −COOH (0.45), $-CH(^iPr)NMe_2$ (**5**) (−0.17) vs. $-NMe_2$ (−0.83), $-CH(^tBu)OCOMe$ (**23**) (ca. 0) vs. -OCOMe (0.31), $-CH(NMe_2)CN$ (**33**) (0.22) vs. -CN (0.66) and $-CH_2NMe_3^+$ (**34**) (0.29) vs. $-NMe_3^+$ (0.82), whose σ_p values are given in Table 1 (as estimated in this work or taken from the literature [17–20]).

An interesting group of complexes is that of the bridged ferrocenes in which two redox-active ferrocenyl moieties are joined by a bridge with one or more sp^3 carbon atoms, -CH(OH)- (**15**), -CH(OMe)- (**20**), $-CH(N_3)-$ (**25**) or $-CH_2OCH_2-$ (**17**). For $FcCH_2OCH_2Fc$ (**17**), with the longer bridge, in any of the used solvents (CH_2Cl_2, NCMe or THF) only one reversible oxidation wave is observed by cyclic voltammetry or by differential pulse polarography, at the expected range of potential, and this involves a two-electron process as indicated by controlled potential electrolysis. For all the other compounds two successive one-electron anodic waves are detected, with a potential gap of ca. 0.10 V (in CH_2Cl_2 or NCMe). This indicates that there is a considerable interaction between the two ferrocenyl groups in the complexes with just one sp^3 carbon bridge; the effect of the positive charge developed at one of the iron centres as a result of its oxidation is transferred through the bridge to the other metal site. For $FcCH_2OCH_2Fc$ (**17**), with a three atom bridge, the interaction is weak and the potential gap between the two corresponding anodic waves is so small that it cannot be detected under our experimental conditions. In THF, for both the above-mentioned bridged ferrocenes, only a single two-electron reversible anodic wave is observed, and the two single-electron transfer processes cannot be distinguished.

The electrochemical data for the bridged ferrocenes discussed above are in agreement with those reported by others for a number of related compounds containing two or more ferrocenyl groups, such as FcFc (biferrocene) [22], $FcCH_2Fc$ [23] and $FcCH_2OCH_2Fc$ [9c], although different experimental conditions were used. For these complexes, two successive one-electron oxidation waves have been detected, with a potential difference of 0.350 [22], 0.17 [23] and only 0.06 V [9c], respectively; when the two ferrocenyls are separated by a saturated $-CH_2CH_2-$ bridge, their weak interaction results in a common oxidation potential for both iron centres [23b].

From the potential of the first anodic wave of the bridged ferrocenes of the type discussed above, σ_p can be estimated for the substituents containing a ferrocenyl group—CH(Fc)OH (**15**) (−0.14), CH_2OCH_2Fc (**17**) (ca. 0), CH(Fc)OMe (**20**) (ca. 0) and $CH(Fc)N_3$ (**25**) (0.06)—whereas from the potential of the second anodic wave of these complexes, when available, σ_p can be calculated for the corresponding cationic substituents: CH(Fc$^+$)OH (**15**$^+$) (0.03), CH(Fc$^+$)OMe (**20**$^+$) (0.14) and CH(Fc$^+$)N_3 (**25**$^+$) (0.24). These values vary in the way expected in terms of the influence of the Z group. Moreover, the introduction of a positive charge at ferrocenyl (to give the ferrocenylium group) in those substituents of the type -CH(Fc)Z leads to an increase in their electron acceptor ability that appears to correspond to a positive shift of σ_p of ca. 0.15–0.20.

Oxidation potential and Taft polar σ^* constant

The above-mentioned overall correlation between the oxidation potential data and the Hammett σ_p constant indicates the importance of both the resonance and the inductive effect of the substituent on the redox potential of the iron centre. However, for the -CHYZ substituents, which have an *sp*^{3} hybridized ligating C atom [typically for α-aminoalkyls (Z = NR_2) but not for, for example, α-hydroxyalkyl or α-acylamido compounds (Z = OH or NHCOR, respectively)—see below], a linear correlation is observed between the oxidation potential of the corresponding ferrocene complexes and the Taft polar σ^* constant for the aliphatic series; this appears to indicate that for this type of substituent the changes in the oxidation potential are determined mainly by inductive effects.

The least squares fit is represented by eq. 6 for THF or eq. 7 for CH_2Cl_2 (Fig. 2), with correlation coefficients, *R*, of 0.989 or 0.993, respectively; the points considered are marked with superscripts *e* in Table 1. Expression 6 was derived from a smaller number of points than 7 because those involving the two oxidations of the diferrocenyl-type compounds are not available in THF since the two corresponding anodic waves are not resolved in this solvent.

$$\Delta_X(\mathrm{THF}) = -0.032 + 0.106\sigma^* \qquad (6)$$

$$\Delta_X(\mathrm{CH_2Cl_2}) = -0.041 + 0.121\sigma^* \qquad (7)$$

The values of the Taft σ^* constant were taken directly from the literature, when available, or obtained from the Thirot σ^H constant (eq. 8) [17], which corresponds essentially to the former constant except for a change in the origin (hydrogen for σ^H instead of methyl for σ^*).

$$\sigma^* = \sigma^H + 0.5 \qquad (8)$$

When neither σ^* nor σ^H values were available, as was the case for most of the substituents, they were estimated by use of eq. 9 derived from the combination of eqs. 10 (which expresses the additive nature of σ^*) and 11 (which gives the attenuation factor of a methylene group on the substituent effect) [17], taking account of the fact that $\sigma^*(\mathrm{CH_3}) = 0$.

$$\sigma^*(\mathrm{CHYZ}) = [\sigma^*(\mathrm{Y}) + \sigma^*(\mathrm{Z})]/2.8 \qquad (9)$$

$$\sigma^*(\mathrm{CXYZ}) = \sigma^*(\mathrm{CH_2X}) + \sigma^*(\mathrm{CH_2Y}) + \sigma^*(\mathrm{CH_2Z}) \qquad (10)$$

$$\sigma^*(\mathrm{CH_2X}) \simeq \sigma^*(\mathrm{X})/2.8 \qquad (11)$$

Expressions 6 and 7 were obtained from data covering a range of σ^*(–CHYZ) from −0.1 (**4** or **5**) to 1.9 (**34**) that corresponds to an even wider range of σ^*(Z), from ca. −0.1 (for Z = NR_2) to above 4 (for Z = isocyano derived groups or

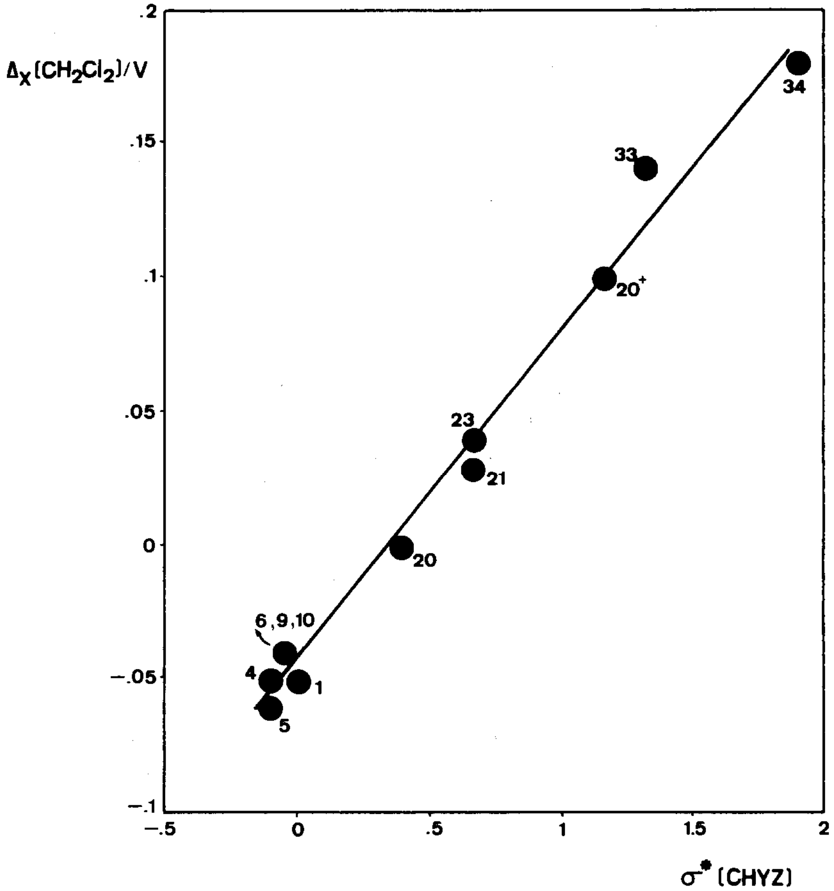

Fig. 2. Plot of Δ_X for substituted ferrocenes FcCHYZ (half-wave oxidation potential relative to that of ferrocene) versus the Taft polar σ^* substituent constant. Δ_X values in volt, measured in this study, in CH_2Cl_2/0.2 *M* [Bu_4N][BF_4] (Table 1). Substituent = $CH_2NMe_3^+$ (**34**), CH(NMe_2)CN (**33**), CH(Fc^+)OMe (**20$^+$**), CH(^{t}Bu)OCOMe (**23**), CH(^{t}Bu)OCOCH(^{i}Pr)NHCOPh (**21**, two diasteroisomers), CH(Fc)OMe (**20**), CH(Cy)NH(CH_2)$_2$Ph (**6**), CH(^{t}Bu)NH_2 (**9**), CH(CHMe^{t}Bu)NH_2 (**10**), CH_3 (**1**), CH(^{t}Bu)NHMe (**4**) or CH(^{i}Pr)NMe_2 (**5**).

tetramethylammonium); they also include Z groups with intermediate values of σ^*, such as –OMe (**22**) (1.4) or –OCOR (**21** or **23**) (ca. 2.2).

A linear relationship between the oxidation potential and σ^*, related to that observed in the present study, was reported [7] between the chronopotentiometric quarter-wave potential ($E_{1/4}$) and the Taft σ^* substituent constant for a considerable number of mono- or di-substituted ferrocenes (mostly with alkyl substituents); the slope of the correlation was 0.0978, although some data deviate from the overall trend. A better correlation, which include the latter data, was observed between $E_{1/4}$ and the Hammett σ_p constant, showing that resonance effects must also be taken into account. In related complexes of the type $FcCH_2X$, the formal oxidation potential also correlates linearly with the inductive constant of X (Hammett σ_I or Taft σ^* for aromatic or aliphatic substituents, respectively) [9a,24].

Our compounds with an amino group at C_α, i.e., $FcCH(Y)NR_2$, do not show the anomalous behaviour observed by others [25] for ferrocenylamines, $FcNR_2$, and ascribed to a marked resonance interaction between the N electron lone pair and ferrocene [25]. In our complexes there is no such resonance effect, and the normal linear correlation is observed between the oxidation potential and σ^*.

Interestingly, the points corresponding to the substituent with a ferrocenyl group -CH(Fc)OMe (**20**) (which has a modest resonance effect, as suggested by the value of $\sigma_p - \sigma_I = -0.05$ [26], close to zero) and to its derived oxidized moiety, $-CH(Fc^+)OMe$ (**20**$^+$) also fall on the Δ_X vs. σ^* correlation line. In contrast, the ferrocene derivatives with α-hydroxy (-OH) (**14**, **15** and **15**$^+$) or α-acylamido (-NHCOR) (**13** and **16**) groups are more readily oxidized than expected on the basis of that correlation, a fact that could possibly be ascribed to an interaction of the oxygen atom of the substituent with iron(III) in the oxidized species (as also suggested [5] for the case of ferrocenes with an acetamido (-NHCOMe) or a urethano (-NHCOOR) substituent, involving a possible interaction between the carbonyl oxygen and the iron(III) ion), or to a resonance contribution to the substituent effect. Nevertheless, this interpretation is open to criticism since the former hypothesis would require a close approach of the two interacting atoms, whereas the latter would imply the transmission of a resonance effect through an sp^3 carbon atom, which, if possible for those groups, would also be expected to occur for the amino group, a strong resonance electron donor.

The occurrence of the intramolecular hydrogen-bonding which has been recognized [27–30] for ferrocenyl alcohols, either by OH interaction with iron or with the ring π-system, does not provide an explanation for their ready oxidation, particularly in the former case, in which the metal behaves as the Lewis base centre, which should lead to an increase in its oxidation potential; neither would intermolecular hydrogen-bonding with the solvent account for such behaviour, which is observed in all the solvents. Other substituents which also fail to follow the Δ_X vs. σ^* correlation will be considered below.

In addition, the presence of multiple aromatic rings in $-CPh_3$ corresponds to a point ($\Delta_X(FcCPh_3) = +0.057$ V [6]; $\sigma^*(CPh_3) = 0.64$ as estimated from eqs. 10 and 11 applied to $X = Y = Z = Ph$ where $\sigma^*(Ph) = 0.60$ [17]) which deviates from the correlation.

From the experimentally obtained expressions 6 and 7, which correlate Δ_X with σ^* in THF and in CH_2Cl_2, respectively, it is possible to estimate unknown σ^* constants for substituents with expected normal behaviour. For those substituents for which $\sigma^*(Y)$ or $\sigma^*(Z)$ is known, one can estimate $\sigma^*(Z)$ or $\sigma^*(Y)$, respectively, by applying eq. 9, although the uncertainty is considerable, whereas eq. 11 is better suited to estimate $\sigma^*(Z)$ for substituents $-CH_2Z$ ($X = Y = H$). The σ^* values estimated by these procedures are given in italics in Table 1.

The amino and the related morpholino groups (Z), for example, as well as the corresponding -CHYZ substituents (**7**, **11**, **12** and **8**, respectively) have values of σ^* close to zero (the known value [17] for methyl and the typical value for -NHR). However, stronger polar effects are associated with other groups (Z), such as $-S(CH_2)_2NMe_2$ (in **19**) ($\sigma^* = 1.2$, a value comparable with the typical 1.5 for thiolates, SR [17]), $-OCH_2Fc$ (in **17**) ($\sigma^* = 1.1$, close to the typical value, 1.4, for the related -OR groups [17]) and a variety of N-bonded groups ordered as follows: $-\overline{\mathrm{NCH{=}NCH{=}C}}\mathrm{H}$ (imidazolyl, in **22**, $\sigma^* = 1.9$), $-N_3$ [azide, 2.6, as the average of the values estimated for this group at $-CH(^tBu)N_3$ (**24**), $-CH(Fc)N_3$ (**25**) and $-CH(Fc^+)N_3$ (**25**$^+$)], $-NC$ [isocyano, 2.8, as the average of the values estimated for this group at $-CH_2NC$ (**26**) and $-CH(Cy)NC$ (**29**)], $-\overline{NN{=}NC(CO_2Me){=}C}(CO_2Me)$ (a triazene derivative, in **30**, $\sigma^* = 3.5$), the isocyano derived $-NCCR(CO)_5$ [4.0, as the average of the values estimated for this group at $-CH(Men)\{NCCr(CO)_5\}$ (**31**) and $-CH_2\{NCCr(CO)_5\}$ (**32**)] and $-NMe_3{}^+$ (trimethylammonium, 5.3).

The value estimated (2.8) for the isocyano group ($-NC$) is rather high, but smaller than that known (3.8) [17] for the cyano group ($-CN$), but the value for the latter is exceeded upon coordination of the $-NC$ group to $\{Cr(CO)_5\}$, and consequent enhancement of its electron-withdrawing ability.

In contrast to the above examples, anomalous behaviour was detected for the following groups (Z), when attempts were made to estimate their σ^* values by using eqs. 6 and 7: $-P(O)(OMe)OH$ (in **3**), $-C(S)\overline{NCH_2CH_2OCH_2CH_2}$ (in **18**) and $-NHOH$ (in **28**). For these species, the σ^* values obtained in THF do not agree with those estimated in CH_2Cl_2 and, for the first two groups, they appear to correspond to Δ_X values lower than expected; the corresponding $-CHYZ$ substituents, $-CH_2P(O)(OMe)OH$ (**3**) and $-CH_2C(S)\overline{NCH_2CH_2OCH_2CH_2}$ (**18**) have a phosphoryl and a thiocarbonyl moiety, respectively, in β-position, and their anomalous behaviour may be related to that observed [5], and mentioned above, for the acetamido and urethano substituents (which contain a β-carbonyl): this may conceivably be the result of interaction of the oxygen atom of the phosphoryl or of the sulphur atom of the thiocarbonyl groups, respectively, with the Fe^{III} centre of the oxidized species. The estimated σ^* values for $-NHOH$, in $-CH(^iPr)NHOH$ (**28**) appear to be too high (in comparison with for example the related $-NHCOR$ and $-NHNH_2$ groups [17]); this may tentatively be attributed to hydrogen bonding involving the central iron atom (see above).

Final comments

This study has indicated that the oxidation potential of ferrocene derivatives may be used as a probe in the study of the electronic properties of substituent groups, since their effects are transmitted through the carbocyclic ring to the iron redox active centre, conforming observations reported by others.

A linear correlation is observed between $E^{ox}_{1/2}$ and the substituent Hammett σ_p constant. For substituents attached to the cyclopentadinyl ring through a sp^3 carbon atom (with a limited resonance ability), the oxidation potential also usually correlates linearly with the Taft polar σ^* constant for the aliphatic series.

These correlations help in understanding and predicting the redox potentials of ferrocene derivatives or of electronic properties of substituents (as measured by the Hammett σ_p or the Taft polar σ^* constants, for which values may be estimated). However, such correlations fail in a number of cases, particularly for substituents with an hydroxy, a carbonyl, a thiocarbonyl, or a phosphinyl group; although interpretations based, for example, on interactions with the redox metal centre or on hydrogen-bonding effects may be proposed, the behaviour is irregular and not always understood. Such limitations should be taken into account when attempting to recognize and/or to apply correlations of the above-mentioned types.

Experimental

The electrochemical experiments were carried out with 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 carried out in a two-compartment three-electrode cell, at a platinum working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed.

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

The oxidation potentials of the complexes were measured in 0.2 *N* $[N^nBu_4][BF_4]$/tetrahydrofuran (dichloromethane or acetonitrile), by using as internal reference the following couples (with $E_{1/2}^{ox}$ values vs. SCE in 0.2 *N* $[N^nBu_4][BF_4]$/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*-$[ReCl(N_2)(Ph_2PCH_2CH_2PPh_20_2]^{0/+}$ [0.28 (THF) or 0.22 V (CH_2Cl_2)].

The ^1H-NMR spectra were recorded on Bruker WP 200 or Bruker AM 360 instruments.

Complex **1** is commercially available and the following compounds were prepared by published methods: **2** and **18** [31], **3** [32], **4**, **5**, **8** and **12** [33], **10** and **24** [34], **13** [35], **14** [36], **15** [37], **16**, **26**, **7**, **29**, **31** and **32** [21b], **17** [38], **22** [39], **23** [40], **28** [41], **33** [42] and **34** [43].

New compounds were prepared as follows.

Ferrocene (10 mmol, 1.86 g) and the corresponding carbonyl compound (20 mmol) (cyclohexanecarboxaldehyde for **6**, 2,2-dimethylpropanal for **7** and **21**, 2-methylpropanal for **11** and acetaldehyde for **19**) were dissolved under nitrogen in a mixture of trichloroacetic acid (10.0 g) and acetic acid (1.5 ml). Fluorosulfonic acid (1.5 ml) was added dropwise with stirring at $-10\,^\circ$C, and the mixture was stirred for 40 min at $0\,^\circ$C to allow formation of the ferrocenylalkyl carbocations.

To obtain the amines, the solution of the corresponding carbocation was diluted with 15 ml of dichloromethane and added dropwise with very efficient stirring to a solution of an amine (100 mmol) (2-phenylethylamine for **6**, 3,4-dichlorobenzylamine for **7**, benzylamine for **11** and *N*-benzoyl-(*R*,*S*)-valine for **21**) and triethylamine (12.0 g, 120 mmol) in 30 ml of 2-propanol at $-78\,^\circ$C. The mixture was allowed to warm to room temperature, 100 ml of dichloromethane were added, and the mixture was extracted three times with water (100 ml). The extract was dried (Na_2SO_4), the solvent and excess triethylamine were evaporated off, and the residue was recrystallized from hexane.

6: Yield 35%, m.p. 92–94 °C. δ_H ($CDCl_3$) = 0.51–1.95 (m, 10H), 1.99–2.52 (m, 2H), 2.61–3.35 (m, 4H), 3.89 (s, 5H), 4.24 (m, 5H), 7.31 (m, 5H) ppm. Anal. Found: C, 74.7; H, 7.8; N, 3.8. $C_{25}H_{31}FeN$ calc.: C, 74.8; H, 7.8; N, 3.5%.

7: Yield 25%, m.p. 90–92 °C. δ_H ($CDCl_3$) = 0.85 (s, 9H), 1.93 (m, 1H), 2.93 (s, 1H), 4.13 (m, 11H), 7.37 (m, 2H), 7.56 (m, 1H) ppm. Anal. Found: C, 60.9; H, 5.9; N, 3.2; $C_{22}H_{25}Cl_2FeN$ calc.: C, 61.4; H, 5.9; N, 3.3%.

11: Yield 29%, m.p. 56–58 °C. δ_H ($CDCl_3$) = 0.88 (dd, 6H), 2.01 (m, 2H), 3.38 (d, 1H), 3.91–4.22 (m, 9H), 4.32 (m, 2H), 7.25–7.64 (m, 5H) ppm. Anal. Found: C, 72.6; H, 7.3; N, 4.0; $C_{21}H_{25}FeN$ calc.: C, 72.6; H, 7.3; N, 4.0%.

21: The two diastereoisomers were separated by fractional crystallization from diethyl ether/hexane. (*S*,*S* + *R*,*R*)-**21**: Yield 18%, m.p. 130–132 °C. δ_H ($CDCl_3$) = 0.81 (s, 9H), 1.14 (d, 3H, $J = 6.9$ Hz), 1.19 (d, 3H, $J = 6.9$ Hz), 2.52 (m, 1H), 4.07 (m, 2H), 4.12 (s, 5H), 4.15 (m, 2H), 4.99 (dd, 1H, $J_1 = 4.5$ Hz, $J_2 = 9.0$ Hz), 5.69 (s, 1H), 6.69 (d, 1H, $J = 9.0$ Hz), 7.49 (m, 3H), 7.88 (m, 2H) ppm. Anal. Found: C, 67.8; H, 7.0; N, 3.0; $C_{27}H_{33}FeNO_3$ calc.: C, 68.2; H, 7.0; N, 3.0%. (*R*,*S* + *S*,*R*)-**21**: Yield 29%, m.p. 173–175 °C. δ_H ($CDCl_3$) = 0.84 (s, 9H), 1.07 (d, 3H, $J = 6.7$ Hz), 1.15 (d, 3H, $J = 6.7$ Hz), 2.45 (m, 3H), 4.05 (s, 5H), 4.14 (m, 2H), 4.21 (m, 2H), 5.13 (dd, 1H, $J_1 = 3.8$ Hz, $J_2 = 9.0$ Hz), 5.66 (s, 1H), 6.81 (d, 1H, $J = 9.0$ Hz), 7.47 (m, 3H), 7.81 (m, 2H) ppm. Anal. Found: C, 67.9; H, 7.3; N, 2.9; $C_{27}H_{33}FeNO_3$ calc.: C, 68.2; H, 7.0; N, 3.0%.

To obtain **19**, 2-(*N*,*N*-dimethylamino)ethylmercaptane hydrochloride (40 mmol, 5.67 g) was added to a solution of the corresponding carbocation, and stirring was continued for 15 min at 0 °C. The mixture was slowly neutralized with saturated aqueous Na_2CO_3, and 200 ml of dichloromethane were added. The organic phase was washed with water, dried (Na_2SO_4), and evaporated, and the residue purified by chromatography (silica gel, hexane). Yield: 36%, oil. δ_H ($CDCl_3$) = 1.62 (d, 3H), 2.15 (s, 6H), 2.43 (m, 4H), 3.71 (q, 1H), 4.11 ("s", 9H) ppm. Anal. Found: C, 60.2; H, 7.1; N, 4.2; $C_{16}H_{23}FeNS$ calc.: C, 60.5; H, 7.3; N, 4.4%.

20 and **25** were prepared from diferrocenylmethylium tetrafluoroborate as follows. Ferrocene (2.2 g, 12 mmol) and ferrocenecarboxaldehyde (2.1 g, 10 mmol) were dissolved under nitrogen in 10 ml of trifluoroacetic acid. Trifluoroacetic anhydride (2.0 ml) was added and the mixture stirred for 30 min. Trifluoroacetic acid was removed at reduced pressure (1 mmHg) and the liquid residue was added dropwise very slowly to a solution of 5.0 ml of HBF_4 (54% in diethyl ether) in 100 ml of dry diethyl ether. Subsequently, 50 ml of pentane were added, and the black precipitate that separated was washed four times with ether/pentane 1:1 (30 ml), and dissolved in dichloromethane (25 ml). The solution was added dropwise at −40 °C with very efficient stirring to a mixture of triethylamine (5.0 ml) and a solution of lithium azide in dry methanol (saturated at room temperature) (40 ml). The mixture was allowed to warm to room temperature, dichloromethane (100 ml) was added, and the organic layer washed three times with water (100 ml), then separated and dried (Na_2SO_4). The solvent was evaporated off and the residue chromatographed on silica gel with hexane as eluant to give first the azide (**25**) and then the ether (**20**).

20: Yield 15%, m.p. 98–100 °C. δ_H = 4.07 (s, 18H), 4.38 (s, 3H), 4.50 (s, 1H) ppm. Anal. Found: C, 63.8; H, 5.6; $C_{22}H_{22}Fe_2O$ calc.: C, 63.8; H, 5.4%.

25: Yield 55%, m.p. 114–116 °C. δ_H = 4.17 (s, 18H), 5.10 (s, 1H). IR (KBr) 2070 cm^{-1}. Anal. Found: C, 59.6; H, 4.7; N, 9.5; $C_{21}H_{19}Fe_2N_3$ calc.: C, 59.3; H, 4.5; N, 9.9%.

The 1,2,3-triazole (**30**) was obtained by 1,3-dipolar cycloaddition of the azide with dimethyl acetylenedicarboxylate. Thus to a solution of 5 mmol of the azide **24** in benzene (30 ml) was added dimethyl acetylenedicarboxylate (20 mmol, 2.84 g). The mixture was heated under reflux for 24 h, the solvent and excess of dimethyl acetylenedicarboxylate were evaporated off and the residue purified by chromatography (silica-gel/dichloromethane).

30: Yield 96%, oil. δ_H ($CDCl_3$) = 0.72 (s, 9H), 3.56 (s, 5H), 3.82 (s, 3H), 3.90 (s, 3H), 4.03 (m, 3H), 4.60 (m, 1H), 5.22 (s, 1H) ppm; δ_C ($CDCl_3$) = 26.6, 36.7 (^{t}Bu), 52.2, 53.2 (Me), 159.8, 160.2 (C=O), 131.1, 137.5 (C=C), 68.0 (unsubst. Cp), 66.6, 68.4, 68.7, 69.0, 71.1 (CH), 83.0 (C_{quart}) ppm. Anal.: Found: C, 57.3; H, 5.4; N, 9.4; $C_{21}H_{25}FeN_3O_4$ calc.: C, 57.4; H, 5.7; N, 9.6%.

Acknowledgements

This work was supported by the Instituto Nacional de Investigação Científica (INIC), the Junta Nacional de Investigação Científica e Tecnológica (JNICT) and the DAAD/Conselho de Reitores das Universidades Portuguesas. The authors also wish to thank Dr. G. Hübener for preparing some of the compounds.

References

1 J.C. Kotz, in A.J. Fry (Ed.), Topics in Organic Electrochemistry, Plenum, New York, 1986, chap. 3.
2 N.G. Connelly and W.E. Geiger, Adv. Organomet. Chem., 23 (1984) 1.
3 A.J.L. Pombeiro, Port. Electrochim. Acta, 1 (1983) 19.
4 C.J. Pickett, in D. Pletcher (Ed.), Electrochemistry, Vol. 8, Royal Society of Chemistry, London, 1983, p. 81.
5 D.W. Hall and C.D. Russel, J. Am. Chem. Soc., 89 (1967) 2316.
6 W.F. Little, C.N. Reilley, J.D. Johnson and A.P. Sanders, J. Am. Chem. Soc., 86 (1964) 1382, 1376.
7 G.L.K. Hoh, W.E. McEwen and J. Kleinberg, J. Am. Chem. Soc., 83 (1961) 3949.
8 S.P. Gubin, Pure Appl. Chem., 23 (1970) 363.
9 (a) É.G. Perevalova, S.P. Gubin, S.A. Smirnova and A.N. Nesmeyanov, Proc. Acad. Sci. USSR, 155 (1964) 328; (b) S.P. Gubin and É.G. Perevalova, ibid., 143 (1962) 346; (c) É.G. Perevalova, S.P. Gubin, S.A. Smirnova and A.N. Nesmeyanov, ibid., 147 (1962) 994.
10 J. Tirouflet, E. Laviron, R. Dabard and J. Komenda, Bull. Soc. Chim. Fr., (1963) 857; J. Boichard and J. Tirouflet, ibid., (1960) 1032.
11 H. Hennig and O. Gürther, J. Organomet. Chem., 11 (1968) 307.
12 T. Hayashi and M. Kumada, Acc. Chem. Res., 15 (1982) 395; T. Hayashi, in J. Streith, H. Prinzbach and G. Schill (Eds.), Organic Synthesis: Interdisciplinary Challenge, Blackwell, Oxford, 1985.
13 I. Ugi, in E. Gross and J. Meienhofer (Eds.), The Peptides, Vol. 2, Academic Press, New York, 1980; I. Ugi, D. Marquarding and R. Urban, in B. Weinstein (ed.), Chemistry and Biochemistry of Amino Acids, Peptides and Proteins, Vol. 6, Marcel Dekker, New York, 1982.
14 R. Herrmann, A.J.L. Pombeiro, M.E.N.P. Rodrigues and I. Ugi, Port. Electrochim. Acta, 2 (1984) 57.
15 J.C. Kotz, C.L. Nivert, J.M. Lieber and R.C. Reed, J. Organomet. Chem., 84 (1975) 255.
16 S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 2 (1983) 943.
17 C. Laurence and B. Wojtkowiak, Ann. Chim, 5 (1970) 163.
18 D.H. McDaniel and H.C. Brown, J. Org. Chem., 23 (1958) 420.
19 H.H. Jaffé, Chem. Rev., 53 (1953) 191.
20 J.J.R. Fraústo da Silva, Aplicação da Equação de Hammett às Reacções de Complexação, Lisbon, 1967.
21 (a) N.F. Blom, E.W. Neuse and H.G. Thomas, Transition Met. Chem., 12 (1987) 301; (b) T. El-Shihi, F. Siglmüller, R. Herrmann, M.F.N.N. Carvalho and A.J.L. Pombeiro, J. Organomet. Chem., 335 (1987) 239.
22 C. LeVanda, K. Bechgaard and D.O. Cowan, J. Org. Chem., 41 (1976) 2700; G.M. Brown, T.J. Meyer, D.O. Cowan, C. LeVanda, F. Kaufman, P.V. Roling and M.D. Rausch, Inorg. Chem., 14 (1975) 506.
23 (a) P. Shu, K. Bechgaard and D.O. Cowan, J. Org. Chem., 41 (1976) 1849; (b) W.H. Morrison, Jr., S. Krogsrud and D.N. Hendrickson, Inorg. Chem., 12 (1973) 1988.

24 S.P. Gubin and V.S. Khandkanova, J. Organomet. Chem., 22 (1970) 449.

25 W.E. Britton, R. Kashyap, M. El-Hashash, M. El-Kady and M. Herberhold, Organometallics, 5 (1986) 1029.

26 S.P. Gubin and A.A. Lubovich, J. Organomet. Chem., 22 (1970) 183.

27 J.C. Kotz and D.G. Pedrotty, Organomet. Chem. Rev. A, 4 (1969) 479.

28 A.N. Nesmeyanov, M.D. Reshetova and É.G. Perevalova, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1939 (English transl., p. 1795).

29 S.C. Chen and R.M. Elofson, Chem. Ind., (1978) 64.

30 A.W. Baker and D.E. Bublitz, Spectrochim. Acta, 22 (1966) 1787.

31 K.L. Rinehart Jr., R.J. Curby and P.E. Sokol, J. Am. Chem. Soc., 79 (1957) 3420.

32 V.I. Boev, Zh. Obsh. Khim., 48 (1978) 1594.

33 R. Herrmann and I. Ugi, Angew. Chem., 91 (1979) 1023.

34 R. Herrmann, G. Hübener, F. Siglmüller and I. Ugi, Liebigs Ann. Chem., (1986) 251.

35 R. Urban, Dissertation, TU München, 1975.

36 B. Misterkiewicz, J. Organomet. Chem., 224 (1982) 43.

37 V.I. Boev and A.V. Dombrovskii, Zh. Obsh. Khim., 50 (1980) 2520.

38 V.I. Boev and A.V. Dombrovskii, Zh. Obsh. Khim., 51 (1981) 2643.

39 R. Herrmann and I. Ugi, Tetrahedron, 37 (1981) 1001.

40 F.H. Hon and T.T. Tidwell, J. Org. Chem., 37 (1972) 1782.

41 H. Martin, R. Herrmann and I. Ugi, J. Organomet. Chem., 269 (1984) 87.

42 C.R. Hauser and J.K. Lindsay, J. Org. Chem., 22 (1957) 906.

43 J.K. Lindsay and C.R. Hauser, J. Org. Chem., 22 (1957) 355.