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Hydrophilic tetrachloroferrate(III) salts of ferricenyl-substituted carboxylic acids

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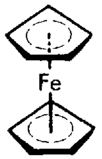
As part of a project to provide hydrophilic ferricenium compounds for biomedical investigations, several ferrocenyl-alkanoic and -alkanedioic acids, including ferrocenylacetic, β-ferrocenylpropionic and γ-ferrocenylbutyric acids, ferrocylmalonic acid, and the two thioether derivatives, *S*-ferrocyl-β-mercaptopropionic acid and *S*-ferrocylthiomalic acid, are chemically oxidized to the respective ferricenium salts. While oxidation with the nitromethane/tetrafluoroboric acid system affords poorly crystallizing tetrafluoroborate salts, for the most part possessing unsatisfactory solubility characteristics, more hydrophilic salts containing the tetrachloroferrate(III) ($FeCl_4^-$) counterion, albeit contaminated with $FeCl_2$, are obtained by treatment of the substrate acids with excess iron(III) chloride. The most promising method of ferricenium generation investigated in this study involves oxidation by means of the *p*-benzoquinone–HCl–$FeCl_3$ system, which directly provides the respective ferricenium tetrachloroferrate salts. The IR and Mössbauer spectra confirm the expected ferricenium structures. The method appears attractive enough to be utilized in future investigations involving more complex, notably polymeric, derivatives of the ferrocene parent compound.

Keywords: Ferrocenylalkane acids, ferricenium salts, oxidation

INTRODUCTION

Reports of the antineoplastic properties of certain oxidation products of ferrocene (**1**), notably ferricenium tetrachloroferrate(III) and ferricenium hydrogen bis(trichloroacetate),[1] have opened up a challenging field of research into the functioning of these radical cations in the biological environment. In our ongoing investigation of ferricenium compounds with biomedically useful properties, the need arose for the synthesis of hydrophilic ferricenium-containing carboxylic acids. In this paper we report on the preparation and properties of a series of carboxy- and dicarboxy-alkylferricenium tetrachloroferrate(III) salts by oxidation of the respective ferrocenyl-substituted acid precursors.



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RESULTS AND DISCUSSION

In view of the need for satisfactory *in vivo* stability of the ferricenyl-substituted target compounds in future biomedical application studies, it was considered imperative that the selection of substrate ferrocenes be restricted to those possessing electrochemical potentials similar to that of the parent complex **1**. For the ferricenium/ferrocene couple, the reduction potential (in acetonitrile) is known to be in the range 0.31–0.33V (versus s.c.e.).[2,3] In a preceding electrochemical investigation[3] we determined the potentials of a number of ferrocenyl-substituted carboxylic acids with a view to selecting suitable substrates for the present oxidation study. While ferrocenoic acid, in reasonable accord with earlier literature reports,[4] possessed an $E_{1/2}$ value (0.58V versus s.c.e.) too high for inclusion in our program, acceptable potentials ($E_{1/2}$(compound) $-E_{1/2}$(ferrocene) $\leq |0.06|$V) were determined for the ω-ferrocenylalkanoic acids **2a–2c** (ferrocenylacetic acid, β-ferrocenylpropionic acid, and γ-ferrocenylbutyric acid), the diacid **2d** (ferrocylmalonic acid; ferrocyl = ferrocenylmethyl), and the two carboxylated thioethers **2e** (*S*-ferrocyl-*β*-mercaptopropionic acid) and **2f** (*S*-ferrocylthiomalic acid), which were thus selected as suitable candidate compounds and were prepared for the present work by published procedures.[3] The half-wave potentials of the selected acids are given in Table 1, which also contains the data for the parent complex, ferrocene (**1**). Compounds **2a**–**2f** and their oxidized derivatives **3a**–**3f** are shown in Scheme 1.

In a preliminary series of experiments aimed at examining the oxidizability of acids **2a**–**2f** the BF_4^- anion was chosen as the counterion, and the substrate acids were oxidized with nitromethane and fluoroboric acid etherate by the procedure elaborated by Schumann[5] for the oxidation of ferrocene proper. The oxidation proceeded to completion under these conditions; the fluoroborates, obtained in nearly quantitative yields by precipitation with suitable non-solvents, gave a broad, multicomponent singlet Mössbauer resonance at $\delta = 0.3$–$0.5\,\mathrm{mm\,s^{-1}}$ (295 K; versus iron foil) in accord with the ferricenium cation structure and showed the characteristic ferricenium features (see below) in the infrared spectrum. Elemental analysis indicated the presence of complexed ether and, occasionally, contamination with fluoroboric acid. However, the compounds showed poor crystallization behavior and unsatisfactory solubility characteristics; no further work was therefore performed with these fluoroborates.

In subsequent experiments the counterion employed was the tetrachloroferrate(III) anion ($FeCl_4^-$). Tetrachloroferrates are known to be moderately-to-strongly hydrophilic. Excellent water solubility is observed, for example, with alkyl and aralkylammonium tetrachloroferrates,[6] a titanocene tetrachloroferrate,[7] and with the unsubstituted ferricenium tetrachloroferrate,[8] as well as the polymeric ferricenium salt, poly(ferricenylenemethylene tetrachloroferrate).[9] The preparation of the last-named polysalt by electron transfer to ferricenium tetrachloroferrate(III) ($FcFeCl_4$; $Fc = C_{10}H_{10}Fe^+$) was made possible by the fact that the reduction potential of the metallocene unit in poly(ferrocenylenemethylene) is lower (less positive) than that of ferrocene, thus providing the thermodynamic driving force for a shift of the equilibrium of reaction [1] (written here for a monosubstituted ferrocene substrate; R = electron donor substituent) to the right (Eqn [1]).

Table 1 Half-wave potentials of selected ferrocene compounds $C_{10}H_9Fe$—R[a]

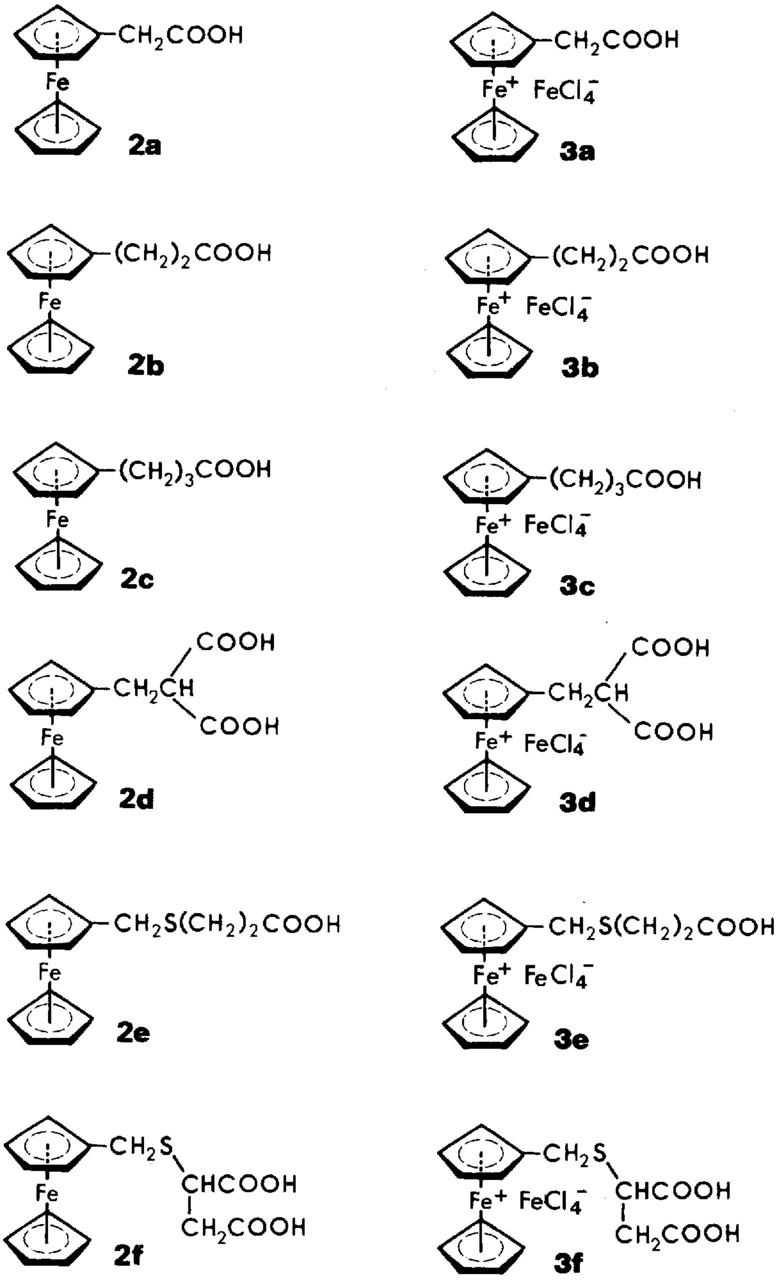
Compound	R	$E_{1/2}/V$[b]
1	H	0.33
2a	CH_2COOH	0.35
2b	$(CH_2)_2COOH$	0.32_5
2c	$(CH_2)_3COOH$	0.31
2d	$CH_2CH(COOH)_2$	0.34
2e	$CH_2S(CH_2)_2COOH$	0.36
2f	$CH_2SCH(COOH)CH_2COOH$	0.39

[a] From Ref. 3; $C_{10}H_9Fe$ = ferrocenyl. [b] Half-wave potential, versus s.c.e., determined by cyclic voltammetry in MeCN (Ref. 3).

$$[C_{10}H_9Fe{-}R] + [C_{10}H_{10}Fe]^+FeCl_4^- \rightleftharpoons [C_{10}H_9Fe{-}R]^+FeCl_4^- + [C_{10}H_{10}Fe] \quad [1]$$

Inspection of the electrochemical data of Table 1 shows that oxidation of the carboxylic acids **2a** and **2d**–**2f** by ferricenium cation is not thermodynamically favored.[10] Indeed, when treated in organic solvents with $FcFeCl_4$, these compounds underwent oxidation to an extent insufficient for preparative purposes, and, even with differences in solubility taken into account, separation of pure oxidation products from admixed electron transfer agent as the majority component was found to be economically impractical or outright unfeasible. Slightly more promising as a substrate was the ferrocenylpropionic acid **2b**. The oxidation product of **2b** was isolated as the tetrachloroferrate **3b** (Eqn [1], $R = (CH_2)_2COOH$), mildly contaminated with $FcFeCl_4$, and some, but not all, of this impurity could be removed by several carefully conducted, low-yield recrystallizations. Best results, as expected, were achieved with the butyric acid derivative **2c**; reasonably efficient oxidation by fericenium cation ensued (Eqn [1], $R = (CH_2)_3COOH$), and the resultant (3-carboxypropyl)ferricenium tetrachloroferrate (**3c**) was obtained in an analytically pure state after a single recrystallization.

In the next series of experiments, an iron(III) salt was used as the oxidant. The standard reduction potential (in water) for the Fe^{3+}/Fe^{2+} couple is $E^\circ = 0.771$ V,[11] corresponding to ~0.53 V versus s.c.e. Hence, even in non-aqueous media, all acids **2a**–**2f** were expected to be readily oxidized by iron(III) chloride. In the present



Scheme 1

work, Nesmeyanov's procedure[8a] was used, employing two equivalents of $FeCl_3$, one of which served to generate the $FeCl_4^-$ anion complex (Eqn [2]; H_2O from moisture traces in the reaction system,[8b,c] $x = 1–2$).

$$\underset{\mathbf{2a\text{–}2f}}{[C_{10}H_9Fe\text{—}R]} + 2FeCl_3 + xH_2O \rightleftharpoons \underset{\mathbf{3a\text{–}3f}}{[C_{10}H_9Fe\text{—}R]^+FeCl_4^-} + FeCl_2 . xH_2O \quad [2]$$

The experiments were performed by allowing compounds **2a–2f**, dissolved or dispersed in toluene, nitromethane or other media, to react with excess ferric salt at ambient temperature. The isolated crude product salts invariably constituted mixtures or coordination products of the desired tetrachloroferrates with hydrated iron(II) chloride ($FeCl_2$) (Eqn [2]), typically containing 0.8–1.0 equivalents of $FeCl_2.2H_2O$. Complete removal of the ferrous salt by extraction with ethanol was not practicable because of appreciable solubility of the tetrachloroferrates in this alcohol. Recrystallization from the same alcohol, as recommended in Nesmeyanov's work[8a] for ferricenium tetrachloroferrate purification, proved unsuccessful, as this treatment caused only minimal elimination of the ferrous contaminant, possibly because of ionic or coordinative bonding to the carboxyl functions. In addition, massive losses of material were incurred owing to a shallow temperature gradient of solubility and high susceptibility of ferricenium species to reductive degradation in this solvent. Only marginal improvements resulted from use of acetonitrile–ethanol (MeCN–EtOH) as the recrystallization medium. A moderate, yet by no means efficacious, purification of the crude salt was eventually brought about by brief washing with ethanol for partial removal of the ferrous salt (along with appreciable quantities of **3a–3f**) and subsequent multiple recrystallization from nitromethane ($MeNO_2$). Alternatively, the crude salt was subjected to several incomplete freeze-drying cycles in aqueous medium with intermittent removal of water-insoluble material, followed by recrystallization from nitromethane. With the exception of **3e**, which degraded substantially in the aqueous solution, this gave a reasonably pure **3**.

In view of the poor economy of the oxidation process involving ferric ion oxidant, a final set of experiments was conducted employing *p*-benzoquinone as the oxidizing agent. This quinone, with a standard reduction potential (in ethanol) $E^\circ = 0.715\,V$,[12] corresponding to $\sim 0.47\,V$ versus s.c.e., had earlier been used successfully in many ferrocene oxidations.[13] In our hands, successive treatment of acids **2a–2f**, suspended and partly dissolved in suitable non-polar organic media, with aqueous $10\,mol\,dm^{-3}$-HCl (2–3 equivalents), *p*-benzoquinone (0.55 equivalents),[14] and anhydrous iron(III) chloride (1.05–1.1 equivalents) at room temperature, preferentially aided by sonication, resulted in the nearly quantitative formation of tetrachloroferrates **3a–3f** (Eqn [3]; R = substituent on ferrocene; see Table 1). In this reaction, the ferric salt, in the presence of chloride ion, exclusively served the purpose of $FeCl_4^-$ anion generation, allowing the salts **3a–3f** to precipitate, whereas the hydroquinone byproduct remained essentially dissolved in the organic medium. With the exception of the particularly unstable **3e**, which gave persistently poor analytical results, recrystallization from nitromethane generally produced analytically pure compounds. (Possessing molecular geometries conducive to inner salt formation, the tetrachloroferrates **3a–3f** are prone to conversion into the respective simple salts of the type Fc^+  COO^-, of composition (**2a–2f**–H), comprising intramolecularly neutralized carboxyl groups. While we found no indication of this tendency with tetrachloroferrates formed directly as solids, product salts precipitated as liquid-phase constituents and manipulated over extended periods of time for eventual solidification occasionally did contain such zwitterions in low percentages. These were eliminated by repeated recrystallization from nitromethane.[15] The reaction of Eqn [3] clearly represents the most attractive synthetic approach toward the ferricenium salts **3a–3f**.

$$[C_{10}H_9Fe{-}R] + 0.5p{-}C_6H_4O_2 + H^+ + Cl^- + FeCl_3 \rightarrow [C_{10}H_9Fe{-}R]^+FeCl_4^- + 0.5p\text{-}C_6H_4(OH)_2 \quad [3]$$

The tetrachloroferrates **3a–3f**, black, microcrystalline solids, possess excellent solubility in dipolar aprotic solvents, although, once dissolved, they undergo rapid degradation even in the absence of dioxygen.[16] With the exception of **3e**, which possesses only moderate solubility, the salts dissolve readily in acetonitrile and nitromethane. Water is an excellent solvent for most of the salts, although slight, insoluble residues may occasionally be observed even with multiply recrystallized samples. When deaerated, such solutions are generally stable for half a day or longer. In several cases, extensive drying at 50–60°C or storage for several months at room temperature has been observed to cause some reduction in solubility, notably in water. This 'aging' effect is considerably retarded, however, with samples stored at temperatures below 0°C.

The solid-state IR spectra of salts **3a–3f** (Table

Table 2 Prominent IR absorptions[a] of tetrachloroferrates **3**

Compound	ν(OH)[b]	ν(CH)[c]	ν(C=O)	ν(CC)[d]	ν(C—O), δ(OH)[e]	δ(CH)[f]	ν(FeCl)[g]
3a	3450v(br)	3100m	1707s, 1620w	1412m	1245ms	850s	380s, 290v
3b	3450v(br)	3110m	1707s, 1620w(sh)	1415m	1305m, 1230m	850s	380s, 292v
3c	—[h]	3100m	1702s, 1595w–m	1414m	—[h]	852s	379s, 290v
3d	3450v(br)	3100m	1710s(d), 1625wm	1418m	1302m, 1210m	852s	378s, 295v
3e	3480v(br)	3100m	1708s, 1615w	1416m	1230m	849s	380s, 295v
3f	3450v(br)	3105m	1707s(d), 1610w(sh)	1412m	1290	850s	378s, 292v

[a] In the solid state (KBr pellets). [b] Variable, partly merging with H_2O band; monomeric structures (dimer absorption not well defined). [c] Cyclopentadienyl ring; ν_8, ν_{17} in ferrocene. [d] Antisymmetric C—C stretching, cyclopentadienyl ring; ν_{20} in ferrocene. [e] C—O stretching, OH in-plane bending, monomeric and dimeric structures. [f] CH out-of-plane bending, cyclopentadienyl ring; ν_{19} in ferrocene. [g] Antisymmetric stretching, ν_3, in $FeCl_4$ anion; 290 cm^{-1} peak variable, generally ms. [h] Not prominent, generally weak.

2), displaying the typical ferricenium absorption pattern,[17] are characterized by the diagnostically useful, strong CH out-of-plane deformation band near 850 cm^{-1}. On the other hand, the 820 cm^{-1} CH deformation band, strong in the spectra of neutral ferrocene compounds, is entirely absent, and the composite peak near 490 cm^{-1} due to the skeletal modes ν_{11} and ν_{21}, which again is shown as a strong absorption by neutral ferrocenes, has completely or almost completely vanished, well in accord with the spectroscopic behavior of ferricenium salts.[17] The strong acid carbonyl absorption emerges in the vicinity of 1700 cm^{-1}. In two instances (**3d**, **3f**) the band is split into a doublet through vibrational coupling. The absorption is accompanied by a weak and broad signal (sometimes appearing as a shoulder) at 1620–1600 cm^{-1}, indicating partial intra- or inter-molecular hydrogen bonding in the solid state as observed with some of the unoxidized acids.[3] Occasionally the 1620 cm^{-1} band is found to increase in intensity on recrystallization of the sample, notably if the compound settles out as a liquid phase and has to be subjected to lengthy manipulations before solidification is complete (see the Experimental Section). The tetrahedral $FeCl_4^-$ anion complex is manifested in the infrared by the strong asymmetric Fe–Cl stretching peak (ν_3) at about 380 cm^{-1}; occasionally, especially with freeze-dried samples, distortion of tetrahedral symmetry leads to the emergence of a multiple-band pattern in the low-frequency region, with two bands dominant near 378 and 290 cm^{-1}. No μ-oxobis(trichloroferrate) pattern (365, 321 cm^{-1})[18] has been observed with our samples; the acidic conditions prevalent in the oxidation step, indeed, should have precluded the competitive generation of oxodiferrate anion.[8c] The salts give Mössbauer spectra (295 K) well in accord with the ferricenium oxidation state in **3a**–**3f**, showing a broad singlet in the vicinity of $\delta = 0.4$ mm s^{-1}, occasionally resolvable into two maxima at about $\delta = 0.25$ and 0.47 mm s^{-1}, i.e. near the velocity positions typical of the high-spin ferric iron in $FeCl_4^-$ and the low-spin (complexed) ferricenium iron species at that temperature.[8c]

The oxidation method utilizing the *p*-benzoquinone–hydrochloric acid–iron(III) chloride system, to which we have resorted in the present work, stands out for its efficaciousness, ease of product separation, and the added benefit that the ferricenium target salts are hydrophilic on account of the concurrently generated $FeCl_4^-$ counterion. The method thus appears promising enough to be applied to the challenge of oxidizing other, more complex ferrocene derivatives, including polymeric compounds.

EXPERIMENTAL

Instrumental and microanalytical work

Melting points, uncorrected, were obtained in sealed capillaries. Solid-state IR spectra were taken on KBr pellets; significant absorptions are in Table 2; in addition, carbonyl stretching bands (ν(CO)) of the carboxyl function are cited individually in the experimental text. Mössbauer spectra were recorded in transmission geometry at 295 K (^{57}Co/Rh source; velocity scale calibrated against hyperfine spectrum of metallic iron; isomer shifts, δ, referenced to α-iron foil at room temperature). Freeze-drying operations were performed on a Virtis Bench Top 3 instrument at $-50°C$, 0.03–0.04 Torr. Microanalyses were performed by Robertson Laboratory, Florham Park, NJ, USA, and by Galbraith Laboratories, Knoxville, TN, USA. As there was considerable scattering of analytical data (C, ± 0.6; Cl, ± 1.1; Fe, $\pm 1.4\%$, tending towards low values), all determinations were made in duplicate or triplicate and the results averaged.

Solvents and reactants, general preparative operations

Organic solvents used in preparative work were dried with Molecular Sieves 4A (3A for MeCN). In addition, in order to prevent partial reduction of ferricenium sites by oxygen, all solvents (incl. water) were saturated with nitrogen. Ferrocene was recrystallized from hexane. *p*-Benzoquinone was sublimed prior to use. Anhydrous iron(III) chloride ($FeCl_3$) (Merck) was used as received. Ferricenium tetrachloroferrate(III) ($FcFeCl_4$)[8c] and the carboxylic acids[3] **2a**, m.p. 166–169°C (Et_2O), **2b**, m.p. 114–117°C (Et_2O), **2c**, m.p. 119–121°C (Et_2O), **2d**, m.p. 147–149°C dec. (Et_2O), **2e**, m.p. 80–83°C (ethyl acetate), and **2f**, m.p. 176–179°C (ethyl acetate), were prepared by literature methods; they were dried prior to use at 50–70°C under reduced pressure. Abderhalden drying equipment (*ca* 0.5 Torr; bulb charged with P_4O_{10}) was employed routinely to dry preparative samples at ambient or elevated temperatures. In addition to conventional drying, samples prepared for microanalysis were dried in Abderhalden units for 1–2 days at 50°C, 0.1 Torr. Glassware employed in oxidation experiments was oven-dried. Although air was not rigorously excluded, cursory blanketing with nitrogen was routinely maintained in all preparative and purification steps. Small-scale filtrations (0.5–5 cm^3 filtration volume) were performed with the aid of a three-piece microfiltration assembly with a 1 cm^3 filtration area. Alternatively, samples were centrifuged at 4000 rpm. Volume reductions were made by rotatory evaporation at 5–20 Torr (diaphragm pump); solutions and system were prepurged with nitrogen. Solubility tests of ferricenium compounds **3a**–**3f** were performed under nitrogen on freshly prepared samples, and the synthesized ferricenium salts were stored at $-20°C$ to delay aging effects resulting in gradual reduction of solubility.

(1) Carboxymethylferricenium tetrachloroferrate(III) (3a)

(A) By oxidation of 2a with *p*-benzoquinone To the filtered solution of **2a** (245 mg, 1.0 mmol) in toluene (8 cm^3) was added successively, with shaking, *p*-benzoquinone (59 mg, 0.55 mmol) and aqueous 10 mol dm^{-3} HCl (0.2 cm^3, 2.0 mmol). This caused a color change from yellow to a dark brownish green. After several minutes, $FeCl_3$ (179 mg, 1.1 mmol) was added with vigorous shaking. The mixture was sonicated (alternatively shaken mechanically) for 4 h and stirred for another 20 h at ambient temperature in a stoppered flask. Vessel and contents were then stored overnight at $-20°C$. The black solid that had separated was collected by filtration, washed thoroughly with toluene, then briefly with Et_2O–pentane, and was dried at room temperature. The crude **3a** (0.45 g, 102% indicating solvent inclusion; 98–105% in repeat runs) was completely soluble in MeCN and almost completely soluble in H_2O; m.p. 90–100°C (75–85°C sintering; m.p. rising to 130–140°C after rigorous drying at elevated temperature).

IR(cm^{-1}): 1705s, 1625w. Analysis Found: C, 35.53; H, 3.09; Cl, 27.99. Calc. for $C_{14.4}H_{14.2}Cl_4Fe_{2.2}O_{2.4}$ [**3a** + 0.2 (**2a** − H)]: C, 35.27; H, 2.92; Cl, 28.92%.

Solvent removal from the combined toluene filtrate and washings left a residue predominantly composed of hydroquinone (IR, TLC). While most repeat runs gave solid product as described, several experiments yielded the salt as a sticky or oily bottom phase covered by a yellowish liquid supernatant. In these cases the top phase was removed by decantation, and the bottom phase was repeatedly washed with toluene and, ultimately, pentane until it had sufficiently solidified for further drying in the Abderhalden apparatus. The crude salt was dissolved in $MeNO_2$ (2 cm^3) with warming. To the filtered, dark green solution was added Et_2O–pentane (2:1; 8 cm^3), and the mixture, which slowly separated into two phases, was kept for 6 h at $-20°C$. The light-colored top layer was removed by decantation and further work-up (*vide infra*). The dark blue bottom phase was washed with Et_2O–pentane, then neat pentane and, having been covered with a layer of hexane, was left to stand in an open beaker overnight, allowing the hydrocarbon phase slowly to evaporate. The last-named step aided in the solidification of the product, which was subsequently dried for 24 h at ambient temperature. The solid so obtained, 280 mg, was immediately recrystallized in the same fashion. This gave **3a**, 180 mg, as a black salt, which dissolved fully in MeCN and $MeNO_2$ (bluish green) and DMSO (yellow–green, soon changing to yellow–brown); it dissolved almost completely in H_2O and EtOH (blue); m.p. 110–120°C (rising to 135–140°C on further extended drying at 50°C or lengthy storage at room temperature).

IR(cm^{-1}): 1707s, 1620w. Analysis Found: C, 32.94; H, 2.61; Cl, 31.76; Fe, 24.87. Calc. for $C_{12}H_{12}Cl_4Fe_2O_2$ (441.7) (**3a**): C, 32.63; H, 2.74; Cl, 32.10; Fe, 25.29%.

The combined top layer and Et_2O–pentane washings from the first recrystallization step were reduced in volume to 5 cm^3; the dark greenish solid precipitate, 50 mg after thorough washing (Et_2O, then pentane) and drying, consisted essentially of **3a** contaminated with hydroquinone. The solid obtained analogously from the top layer and washings of the second recrystallization step, 70 mg, was impure **3a.**

(B) By oxidation of 2a with $FeCl_3$ In a representative experiment, solid $FeCl_3$ (408 mg, 2.5 mmol) was added with manual shaking to the filtered solution of **2a** (245 mg, 1.0 mmol), in toluene (20 cm^3). The reaction flask was stoppered and was sonicated for 6 h (alternatively, a mechanical shaker may be used for agitation), followed by magnetic stirring of the contents for 40 h at room temperature. The mixture was filtered in Schlenk equipment under N_2 (to prevent autoxidation of admixed $FeCl_2$), and the greenish-black solid residue was washed thoroughly with toluene, ether and hexane. It was then dried for 2 days at 50°C. Yield 604 mg (99.9%; 93–105% in repeat experiments, indicating occasional solvent inclusion). The salt was soluble in MeCN, for the most part also in H_2O; it dissolved in DMSO with rapid degradation.

Analysis: Found: C, 23.94; H, 2.76; Cl, 34.56; Fe, 27.11. Calc. for $C_{12}H_{16}Cl_6Fe_3O_4$ (**3a** $+FeCl_2.2H_2O$): C, 23.84; H, 2.67; Cl, 35.19; Fe, 27.72%.

No major compositional changes resulted from modification of the reaction conditions of the oxidation step, such as increasing the $FeCl_3$/**2a** ratio, varying overall concentrations, or removing moisture azeotropically.

Recrystallization of the crude salt from MeCN gave salts of very similar composition; specifically, this failed to eliminate admixed or coordinated $FeCl_2$. Use of MeCN–EtOH (1:1) as the solvent, with excess Et_2O–pentane (2:1) added as a non-solvent to the filtered solution, gave products with reduced $FeCl_2$ contents.

Typical analysis: Found: C, 24.76; H, 2.95; Cl, 32.47; Fe, 26.21. Calc. for $C_{12}H_{16.8}Cl_{5.6}Fe_{2.8}O_{4.4}$ [**3a** $+0.8$ $(FeCl_2.3H_2O)$]: C, 24.58; H, 2.89; Cl, 33.86; Fe, 26.67%.

Somewhat more effective removal of ferrous salt was brought about by washing of the crude salt with absolute EtOH and multiple recrystallization from $MeNO_2$, with Et_2O–pentane added as a non-solvent. The product recovered (10–20%) melted partially at 130–140°C (after drying at 50°C); it was completely soluble in MeCN and partly so in H_2O.

IR(cm^{-1}): 1708s, 1600 w–m. Analysis: Found: C, 33.20; H, 2.78; Cl, 39.96; Fe, 24.92. Calc. for **3a**: C, 32.63; H, 2.74; Cl, 32.10; Fe, 25.29%.

In these recrystallizations, the salt settled out as a solvent-containing liquid bottom phase, from which it was isolated in a semi-solid state by repeated washing and digestion with Et_2O–pentane (2:1), then neat pentane or hexane; it was dried at ultimately 40°C until completely solid and grindable.

Elimination of $FeCl_2$ from the crude salt was also accomplished by dissolution in H_2O, freeze-drying of the filtered (and conventionally N_2-saturated) solution to near-dryness, and pressing the moist solid between filter paper. The process was repeated, and the blackish product salt was dried at ultimately 40°C.

IR(cm^{-1}): 1708s, 1597ms. Analysis: Found: C, 32.43; H, 3.12; Cl, 29.86; Fe, 24.37; O, 9.68. Calc. for $C_{12}H_{14}Cl_4Fe_2O_3$ (**3a** $+H_2O$): C, 31.35; H, 3.07; Cl, 30.84; Fe, 24.30; O, 10.44%.

Recrystallization from $MeNO_2$ afforded **3a** essentially free from H_2O.

(2) 2-Carboxyethylferricenium tetrachloroferrate(III) (3b)

(A) By oxidation of 2b with *p*-benzoquinone *β*-Ferrocenylpropionic acid (**2b**) (258 mg, 1.0 mmol), was dissolved in toluene (5 cm^3), and the solution was filtered. After the addition of *p*-benzoquinone (59 mg, 0.55 mmol), and aqueous 10 mol dm^{-3} HCl (0.25 cm^3, 2.5 mmol), the mixture was shaken for several minutes. $FeCl_3$ (171 mg, 1.05 mmol) was added to the resulting solution. The mixture was sonicated for 5 h and magnetically stirred for another 15 h in a stoppered flask at room temperature. The suspended blackish solid was allowed to settle at -20°C, the yellow–green supernatant liquid was siphoned off, and the solid was washed with toluene, then Et_2O–pentane (2:1); it was dried at room temperature. The crude **3b** (409 mg, 90%), possessed complete solubility in MeCN and was almost completely soluble in H_2O; it melted over the range 80–110°C.

IR(cm¯1): 1708s. Analysis: Found: C, 36.84; H, 3.26; Cl, 28.73. Calc. for $C_{15.6}H_{16.6}Cl_4Fe_{2.2}O_{2.4}$ [**3b**+0.2 (**2b**−H)]: C, 36.94; H, 3.30; Cl, 27.96.

Repeat oxidation runs performed with the amount of benzoquinone raised to 1.0 mmol gave higher product yields (95–99%) but caused decreased purity. In one out of eight repeat experiments, the product salt separated as a dark blue, oily bottom phase rather than as a solid. The oily phase was worked up as described in Section 1A for the acetic acid analog.

For purification, the crude salt (0.4 g) was dissolved in $MeNO_2$ (2 cm^3) with warming. Et_2O–pentane (2:1; 8 cm^3) was added with shaking, and the mixture was allowed to stand overnight at -20°C. Two phases developed. The dark blue lower one was washed repeatedly with Et_2O and pentane until solidification occurred, and the solid product (285 mg) was recrystallized twice more and was dried at ultimately 40°C. The black salt dissolved readily in MeCN and $MeNO_2$ (bluish green) and, with traces of residue, in H_2O or EtOH (blue; complete dissolution observed with material dried at room temperature); it was soluble in dipolar aprotic solvents (yellow green, rapidly turning to yellow); m.p. 105–120°C (90–95°C observed with samples dried at room temperature).

IR(cm^{-1}): 1707s, 1620w(sh). Analysis: Found: C, 34.32; H, 3.18; Cl, 30.69: Fe, 24.11. Calc. for **3b**: C, 34.26; H, 3.10; Cl, 31.11; Fe, 24.51%.

A portion of **3b** (80 mg) contaminated with hydroquinone was isolated from the combined supernatant phase and washings of the first recrystallization step after solvent removal by slow evaporation; the semi-solid residue was washed thoroughly with toluene, Et_2O and pentane, and was dried as above. In the same fashion, the subsequent recrystallization steps yielded impure **3b** from the supernatant phase and washings (ca. 20% recovery).

(B) By oxidation of 2b with ferricenium tetrachloroferrate Finely powdered $FcFeCl_4$ (388 mg, 1.01 mmol) was added to the solution of **2b** (258 mg, 1.0 mmol) in benzene (5 cm^3) prepared at 50–60°C and allowed to cool to ambient temperature. The suspension was sonicated (alternatively, shaken mechanically) for 4 h and stirred for a further 50 h in a stoppered flask at 20–25°C. The suspended material was allowed to settle, and the supernatant yellow–orange mother-liquor was decanted off. The solid, representing crude **3b**, was washed with benzene and Et_2O and was dried for 24 h at 40°C. Yield, 415 mg (91%; 88–95% in repeat experiments). The salt was completely soluble in H_2O, MeCN, and DMSO, undergoing rapid degradation in the last-named solvent; it melted partially at 100°C and underwent mild degradation near 120°C.

IR(cm^{-1}): 1709s. Analysis: Found: C, 33.63; H, 3.13; Cl, 32.40; Fe, 24.01. Calc. for $C_{15}H_{16}Cl_{4.8}Fe_{2.4}O_2$ (**3b**+0.2$FcFeCl_4$): C, 33.83; H, 3.03; Cl, 31.96; Fe, 25.17.

The contaminated **3b** (250 mg) was dissolved with warming in $MeNO_2$ (2 cm^3). Et_2O–pentane (2:1; 4 cm^3), was added to the filtered solution with shaking, and the mixture was left to stand for several hours at -20°C, whereupon it had separated into two liquid phases. The lower one, worked up as in Section 1A, gave a solid compound (180 mg), which was immediately recrystallized once more in the same fashion. The salt ultimately isolated (65 mg) showed the same solubility and spectroscopic behavior as did the crude salt mixture; m.p. 90–100°C (115–120°C after extended drying at 50°C).

Analysis: Found: C, 33.97; H, 3.05; Cl, 31.41; O, 6.50. Calc. for $C_{13.5}H_{14.5}Cl_{4.2}Fe_{2.1}O_2$ (**3b**+0.05 $FcFeCl_4$): C, 34.14; H, 3.08; Cl, 31.35; O, 6.74%.

Occasionally, in repeat recrystallization runs, the product salt gave a moderately strong 1600 cm^{-1} carboxylate band in addition to the strong peak at 1709 cm^{-1}, but this entailed no significant compositional changes.[19]

In a separate, more successful, purification Experiment, a sample (200 mg) of crude **3b** was dissolved in H_2O (3 cm^3), and the filtered solution was freeze-dried to near-dryness. The blackish wet solid which separated was pressed between filter paper for removal of $FcFeCl_4$ predominantly contained in the adhering mother-liquor, and was immediately subjected to the same freeze-drying treatment. The bluish-black hydrated product, after drying for 24 h at 50°C (90 mg), dissolved completely in MeCN and almost completely in H_2O.

Analysis: Found: C, 33.07; H, 3.15; Cl, 30.47; O, 9.72. Calc. for $C_{13}H_{16}Cl_4Fe_2O_3$ (**3b**+H_2O): C, 32.96; H, 3.40; Cl, 29.93; O, 10.13%.

(C) **By oxidation of 2b with $FeCl_3$** The propionic acid derivative **2b** (258 mg, 1.0 mmol) was dissolved in toluene (5 cm^3) with warming, and the solution was filtered. After the addition of $FeCl_3$ (359 mg, 2.2 mmol), the mixture was treated and worked up as described in Section 1B, giving greenish-black, $FeCl_2$-containing **3b** in 95–100% yield, m.p. 90–120°C. The salt dissolved readily in MeCN and, with a slight residue, in H_2O; it was completely soluble in DMSO with degradation.

IR(cm^{-1}): 1710s. Typical analysis: Found: C, 26.13; H, 2.87; Cl, 33.61; Fe, 25.98. Calc. for $C_{13}H_{17.6}Cl_{5.8}Fe_{2.9}O_{3.8}$ [**3b**+0.9 ($FeCl_2 . 2H_2O$)]: C, 25.92; H, 2.95; Cl, 34.14; Fe, 26.89%.

Very similar analytical results were obtained for a salt recrystallized from MeCN/Et_2O–pentane. Predominant elimination of bound $FeCl_2$ was brought about by washing of the crude salt with absolute EtOH and subsequent multiple recrystallization from $MeNO_2$ as described for the acetic acid analog in Section 1B. The product salt (12% recovery) dissolved almost completely in MeCN and H_2O.

IR(cm^{-1}): 1709s, 1600m. Analysis: Found: C, 32.73; H, 2.99; Cl, 30.87; Fe, 24.03. Calc. for $C_{13}H_{14.4}Cl_{4.2}Fe_{2.1}O_{2.2}$ [**3b**+0.1 ($FeCl_2 . 2H_2O$)]: C, 33.08; H, 3.08; Cl, 31.54; Fe, 24.25%.

In separate purification experiments the crude salt was subjected to a freeze-drying treatment in aqueous phase as in Section 1B, followed by recrystallization from $MeNO_2$. The product salt, completely soluble in MeCN and predominantly so in H_2O, essentially corresponded in elemental composition to **3b**.

(3) 3-Carboxypropylferricenium tetrachloroferrate(III) (3c)

(A) **By oxidation of 2c with *p*-benzoquinone** γ-Ferrocenylbutyric acid (**2c**) (271 mg, 1.0 mmol) was oxidized in toluene solution (5 cm^3) with *p*-benzoquinone (0.55 mmol), 10 mol dm^{-3} HCl (2.5 mmol), and $FeCl_3$ (1.1 mmol) as described in Section 1A for the acetic acid analog **3a**. Yield 410 mg (87.2%), m.p. 55–60°C (partial melting). The salt was completely soluble in MeCN and partly in H_2O.

IR(cm^{-1}): 1700s. Analysis: Found: C, 37.37; H, 3.33; Cl, 29.01; Fe, 23.20. Calc. for $C_{15.4}H_{17.5}Cl_4Fe_{2.1}O_{2.2}$ [**3c**+0.1 (**2c**−H)]: C, 37.22; H, 3.55; Cl, 28.54; Fe, 23.60%.

Recrystallization from $MeNO_2$ as described in Section 1A gave two fractions of black **3c**, both melting in the range 75–85°C and possessing complete solubility in H_2O (blue), MeCN and $MeNO_2$ (bluish green), as well as DMSO and other aprotic solvents (yellow–green, soon fading into yellow). (One sample out of six prepared independently was not entirely soluble in H_2O, but still dissolved completely in MeCN.)

IR(cm^{-1}): 1702s, 1595w–m. Analysis: Found: C, 36.26; H, 3.27; Cl, 29.81; Fe, 23.49. Calc. for $C_{14}H_{16}Cl_4Fe_2O_2$ (469.8) (**3c**): C, 35.79; H, 3.43; Cl, 30.19; Fe, 23.78%.

(B) **By oxidation of 2c with ferricenium tetrachloroferrate** To the filtered solution of **2c** (271 mg, 1.0 mmol) in benzene (10 cm^3) was added finely powdered $FcFeCl_4$ (388 mg, 1.01 mmol). The mixture was mechanically shaken for 8 h, and magnetically stirred overnight in a stoppered vessel at room temperature. The suspended solid was allowed to settle, the supernatant orange liquid was decanted, and the black powdery residue constituting crude **3c** was washed thoroughly with benzene and Et_2O, and finally with pentane, and dried for 24 h at 40°C. Yield, 469 mg (99.8%; 90–102% in other experiments). The crude salt dissolved readily in MeCN and, not quite completely, in H_2O; m.p. 85–90°C.

IR(cm^{-1}): 1700s, 1590m. Analysis: Found: C, 35.85; H, 3.45; Cl, 30.22; Fe, 22.11. Calc. for **3c**: C, 35.79; H, 3.43; Cl, 30.19; Fe, 23.78%.

A sample (150 mg) of crude **3c** was dissolved in $MeNO_2$ (1 cm^3). The deep-blue solution was filtered and the residue washed with $MeNO_2$ (1 cm^3). Et_2O–pentane (2:1; 6 cm^3) was added to the combined filtrates, and the resulting single-phase solution was stored for 6 h at −20°C, during which period it separated into two phases. Work-up of the bottom phase as in Section 1A afforded **3c** (50 mg), completely soluble in H_2O and MeCN, m.p. 75–78°C.

IR(cm^{-1}): 1700m, 1590s. Analysis: Found: C, 35.99; H, 3.76; Cl, 29.20; Fe, 23.19%.

From the upper phase, combined with all

washings, the solvents were allowed slowly to evaporate, and the semi-solid residue was washed with Et_2O–pentane (2:1), then pentane, until solidified. It was dried at room temperature overnight, followed by 8 h at 40°C. This left another portion of **3c** (45 mg), identical with the first fraction in composition, melting and solubility behavior.

IR(cm^{-1}): 1700s, 1590m.

(C) By oxidation of 2c with $FeCl_3$ To the filtered solution of **2c** (272 mg, 1.0 mmol), in toluene (6 cm^3) was added $FeCl_3$ (359 mg, 2.2 mmol). The mixture was sonicated for 6 h and stirred for another 20 h. It was worked up as described in Section 1A for the acetic acid analog **3a**, giving $FeCl_2$-containing tetrachloroferrate **3c** in a yield of 630 mg (99.6%; 96–105% in repeat runs). The greenish-black salt was completely soluble in H_2O and MeCN.

IR(cm^{-1}): 1700s. Analysis: Found: C, 27.01; H, 3.37; Cl, 31.98; Fe, 24.37. Calc. for $C_{14}H_{21.4}Cl_{5.8}Fe_{2.9}O_{4.7}$ (**3c**+0.9 ($FeCl_2.3H_2O$)]: C, 26.58; H, 3.41; Cl, 32.51; Fe, 25.61%.

The major portion of crude salt (410 mg) was purified by washing with EtOH and recrystallization from $MeNO_2$ as in analogous preceding experiments. This afforded material (65 mg) soluble with negligible residues in H_2O and MeCN, approximately corresponding in composition to **3c**+0.15 ($FeCl_2.2H_2O$). A smaller portion of crude salt (200 mg), recrystallized from MeCN–EtOH (1:1), gave **3c** (140 mg) containing zwittersalt.

IR(cm^{-1}): 1700w(sh), 1590s. Analysis: Found: C, 38.11; H, 3.37; Cl, 26.78. Calc. for $C_{16.8}H_{19}Cl_4Fe_{2.2}O_{2.4}$ [**3c**+0.2 (**2c**−H)]: C, 38.51; H, 3.66; Cl, 27.06%.

(4) 2,2-Dicarboxyethylferricenium tetrachloroferrate(III) (3d)

(A) By oxidation of 2d with *p*-benzoquinone *p*-Benzoquinone (81 mg, 0.75 mmol), and aqueous 10 mol dm^{-3} HCl (0.3 cm^3, 3.0 mmol) were added with shaking to the solution of ferrocylmalonic acid (**2d**) (302 mg, 1.0 mmol) in a mixture of toluene (9 cm^3) and Et_2O (2 cm^3), and the dark green solution was stirred for 5 min. $FeCl_3$ (171 mg, 1.05 mmol) was added, and the mixture was sonicated for 4 h and stirred for 24 h at room temperature. It was then stored for 20 h at −20°C, after which a dark green solid had settled out. This was collected by filtration, washed with Et_2O and pentane and dried ultimately at 40°C. Yield 493 mg (98.6%; 88–96% in repeat runs). The crude salt dissolved completely in H_2O, MeCN and DMSO and melted at 140–145°C dec.; other samples had m.p. 130–135°C dec.

IR(cm^{-1}): 1710s(d). Analysis: Found: C, 33.59; H, 2.98; Cl, 27.91; Fe, 22.02. Calc. for $C_{14}H_{14}Cl_4Fe_2O_4$ (499.75) (**3d**): C, 33.64; H, 2.82; Cl, 28.37; Fe, 22.35.

A sample (450 mg) of crude **3d** was purified by dissolution in $MeNO_2$ (0.7 cm^3), filtration, and cooling to −20°C. A portion of bluish-black crystalline solid (30 mg) separated after 24 h; it was washed and dried as before. The salt possessed complete solubility in H_2O (blue) and MeCN (bluish-green), m.p. 142–146°C dec. (occasionally, m.p. 146–149°C dec. was observed).

IR(cm^{-1}): 1710s(d), 1625m. Analysis: Found: C, 33.79; H, 2.96; Cl, 28.62; Fe, 22.27%.

The combined upper phase and Et_2O–pentane washings were reduced in volume to 0.5 cm^3. After 15 h at −20°C a second, major fraction of **3d**, 370 mg, identical in composition, solubility and IR spectral behavior with the first portion, had deposited and was collected as above; m.p. 141–145°C dec.

(B) By oxidation of 2d with $FeCl_3$ Ferrocylmalonic acid (**2d**) (302 mg, 1.0 mmol) was dissolved in toluene (120 ml) with warming. To the filtered solution was added $FeCl_3$ (342 mg 2.1 mmol), with shaking. The mixture was treated and worked up as in Section 1A, to give greenish-black, crude **3d** contaminated with $FeCl_2$ (415 mg, 64.2%). The solid was completely soluble in H_2O, MeCN, and DMSO (rapid degradation).

IR(cm^{-1}): 1710wm(d), 1620s. Analysis: Found: C, 26.37: H, 2.99; Cl, 30.98; Fe, 23.86% Calc. for $C_{14}H_{17.6}Cl_{5.8}Fe_{2.9}O_{5.8}$ (**3d**+0.9 ($FeCl_2.2H_2O$)): C, 26.02; H, 2.75; Cl. 31.82; Fe, 25.06%.

While recrystallization from MeCN by excess Et_2O–pentane gave a product of very similar composition, major removal of admixed ferrous salt was brought about by washing with EtOH, followed by recrystallization from $MeNO_2$ (8–15% recovery) as described in Section 1A for **3a**. The solid so obtained showed the same solubility characteristics as did the crude product.

IR(cm^{-1}): 1710m(d), 1620s(d). Analysis: Found: C, 29.56; H, 2.66; Cl, 30.69; Fe, 23.25. Calc. for $C_{14}H_{15.6}Cl_{4.8}Fe_{2.4}O_{4.8}$ [**3d**+0.4 ($FeCl_2 . 2H_2O$)]: C, 29.77; H, 2.78; Cl, 30.12; Fe, 23.73%.

Oxidation experiments performed as above but with Et_2O in place of toluene (20 cm^3 per 1 mmol of **2d**) gave higher yields (80–90%). However, the products, while of similar composition, precipitated as sticky solids, which were separated by decantation of the supernatant Et_2O phase and were washed with Et_2O–pentane and pentane until solidified. In other experiments, toluene–MeCN (1:1; 2.5 cm^3 per mmol of **2d**) was used as the medium. The reactions proceeded in homogeneous phase. Volume reduction to 1 cm^3 and cooling gave black microcrystals in 30–35% yield, soluble in H_2O and MeCN, which essentially conformed in composition to **3d**+0.3 ($FeCl_2 . 2H_2O$).

(5) *S*-(2-Carboxyethyl)mercaptomethylferricenium tetrachloroferrate(III) (3e)

(A) By oxidation of 2e with *p*-benzoquinone *S*-Ferrocyl-*β*-mercaptopropionic acid (**2e**) (304 mg, 1.0 mmol) in toluene (3 cm^3) was oxidized with *p*-benzoquinone (59 mg, 0.55 mmol), in the presence of aqueous 10 mol dm^{-3} HCl, 0.3 cm^3 (3.0 mmol), and $FeCl_3$ (171 mg, 1.05 mmol) as described in Section 1A, and the product, which settled out as the liquid bottom layer in a two-phase system, was worked up in the conventional fashion. The crude product, not quite dry (555 mg, 110%), predominantly soluble in H_2O and MeCN, was used for further purification (*vide infra*), and only a small sample was submitted for analysis.

IR(cm^{-1}): 1700s, 1620s. Analysis: Found: C, 32.66; H, 3.03. Calc. for $C_{14}H_{16}Cl_4Fe_2O_2S$ (501.8) (**3e**): C, 33.51; H, 3.21%.

The main portion (525 mg) was dissolved in $MeNO_2$ (1.5 cm^3), and to the filtered solution was added Et_2O–pentane (2:1; 5 cm^3). Two phases formed; after storage at −20°C overnight these were separated and worked up as in previous experiments. The lower phase yielded black, sticky material, which gradually solidified on drying at room temperature and, ultimately, at 40°C. The solid, impure **3e** (45 mg), was partially soluble in H_2O (blue) and predominantly soluble in MeCN (greenish), m.p. 120–125°C (sintering at 85°C).

IR(cm^{-1}): 1708s, 1615w. Analysis: Found: C, 33.84; H, 3.88; Cl, 25.59; Fe, 20.46. Calc. for **3e**: C, 33.51; H, 3.21; Cl, 28.26; Fe, 22.26%.

From the combined upper phase and washings, a second, even less pure portion of **3e** was isolated (105 mg), slightly soluble in H_2O and partially soluble in MeCN, m.p. 85–102°C (sintering at 78°C).

IR(cm^{-1}): as above. Analysis: Found: C, 34.37; H, 3.52; Cl, 24.77; Fe, 20.86%.

(B) By oxidation of 2e with $FeCl_3$ The mercaptopropionic acid derivative **2e** (152 mg, 0.5 mmol) in toluene (5 cm^3) was treated with $FeCl_3$ (179 mg, 1.1 mmol), as in Section 1B, except that the stirring period was reduced to 24 h. This afforded $FeCl_2$-contaminated **3e** as a greenish-black solid (280 mg, 86.4%; 78–90% in repeat experiments). The salt was only partially soluble in H_2O and MeCN (rapid degradation), but completely so (albeit with degradation) in DMSO.

IR(cm^{-1}): 1702ms, 1600s. Analysis: Found: C, 24.89; H, 3.30; Cl, 30.96; Fe, 24.90. Calc. for $C_{14}H_{20}Cl_6Fe_3O_4S$ [**3e**+($FeCl_2 . 2H_2O$)]: C, 25.30; H, 3.03; Cl, 32.00; Fe, 25.21%.

Washing of the crude salt with absolute EtOH, followed by repeated recrystallization from $MeNO_2$ as in Section 1B, gave impute **3e** only mildly contaminated with $FeCl_2$ (8–12% recovery). The salt was only partially soluble in H_2O and MeCN.

IR(cm^{-1}): 1710s, 1605s(br). Analysis: Found: C, 31.05; H, 3.37; Cl, 27.86; Fe, 21.69. Calc. for $C_{14}H_{16.4}Cl_{4.4}Fe_{2.2}O_{2.2}S$ [**3e**+0.2 ($FeCl_2 . H_2O$)]: C, 31.68; H, 3.11; Cl, 29.39; Fe, 23.15%.

(6) *S*-(1,2-Dicarboxyethyl)mercaptomethylferricenium tetrachloroferrate(III) (3f)

(A) By oxidation of 2f with *p*-benzoquinone *S*-Ferrocylthiomalic acid (**2f**) (348 mg, 1.0 mmol), suspended and partly dissolved in toluene–Et_2O (4:1; 25 cm^3), was treated with *p*-benzoquinone (59 mg, 0.55 mmol), aqueous 10 mol dm^{-3} HCl (0.2 cm^3, 2.0 mmol), and $FeCl_3$ (171 mg, 1.05 mmol), as described in Section 1A for the acetic acid derivative. The crude, dark green salt, collected in 98% yield (537 mg), was completely soluble in H_2O and MeCN and partially melted at 175–179°C.

IR(cm^{-1}): 1708s(d). Analysis: Found: C, 32.78; H, 3.10; Cl, 26.37; Fe, 19.87; S, 5.52. Calc. for $C_{15}H_{16}Cl_4Fe_2O_4S$ (545.8) (**3f**): C, 33.00; H, 2.95; Cl, 25.98; Fe, 20.46; S, 5.86%.

The crude greenish-black salt (500 mg) was recrystallized from $MeNO_2$ (2 cm^3). From the filtered solution, kept at −20°C, a fraction of greenish-black **3f** (245 mg) crystallized overnight. It was washed with Et_2O–pentane (2:1) and dried ultimately at 40–45°C, m.p. 182–184°C (partial).

Analysis: Found: C, 32.98; H, 3.01; Cl, 26.87; Fe, 20.19; S, 6.18%.

A second fraction of **3f** (95 mg) was collected after volume reduction of the filtrate and cooling it at −20°C as before; m.p. 174° (partial). Both fractions possessed complete solubility in H_2O (bluish), MeCN (green), and DMSO (yellow) (slightly reduced solubility in one out of seven samples from repeat experiments).

IR(cm^{-1}): 1702s(d), 1610w(sh).

(B) By oxidation of 2f with ferricenum tetrachloroferrate The thiomalic acid derivative **2f** (348 mg, 1.0 mmol) was dissolved in Et_2O–benzene (1:1; 20 cm^3) with warming, and the solution was filtered. Upon the addition of $FcFeCl_4$ (388 mg, 1.01 mmol), the mixture was shaken for 4 h and kept for 18 h at room temperature. The suspended greenish-black solid was filtered off, washed with Et_2O, then pentane, and was dried at ultimately 40–45°C. Yield 482 mg (73%; 65–76% in repeat runs). The product was almost completely soluble in H_2O, MeCN and DMSO.

IR(cm^{-1}): 1705s(d). Analysis: Found: C, 32.39; H, 2.87; Cl, 27.87; Fe, 22.23; O, 9.37. Calc. for $C_{18}H_{18.7}Cl_{5.2}Fe_{2.6}O_4S$ (**3f**+0.3 $FcFeCl_4$): C, 32.71; H, 2.90; Cl, 27.89; Fe, 21.97; O, 9.68%.

Removal of the majority of solvent from the combined filtrate and washings caused separation of a brownish-black solid (212 mg), mostly consisting of unreacted **2f** and $FcFeCl_4$. Use of an excess of $FcFeCl_4$ in the described electron exchange reaction resulted in larger fractions of this salt being incorporated into the crude product. Thus, with 1.2 mmol of $FcFeCl_4$ under otherwise unchanged conditions, the crude solid obtained (79%) conformed in elemental composition to **3f**+0.4 $FcFeCl_4$.

A different experiment was conducted as described above, with Et_2O–$MeNO_2$ (1:1; 15 cm^3) in lieu of Et_2O–benzene medium. The greyish-green solid salt collected (504 mg, 92.3%) showed the same solubility and IR spectral behavior as did the crude product of the preceding experiment.

Analysis: Found: C, 33.12; H, 3.21; Cl, 26.96; Fe, 20.99. Calc. for $C_{17}H_{18}Cl_{4.8}Fe_{2.4}O_4S$ (**3f**+0.2 $FcFeCl_4$): C, 32.79; H, 2.91; Cl, 27.33; Fe, 21.53%.

In a parallel experiment, **2f** was dissolved in Et_2O–$MeNO_2$ (1:1; 10 cm^3), and to this solution was added $FcFeCl_4$ (1.1 mmol) dissolved in $MeNO_2$ (5 cm^3). Under these conditions, all reactants remained in solution. This was kept for 30 min at 50°C and for 2 h at 25°C; it was then reduced in volume to 2–3 cm^3 and was mixed with Et_2O–pentane (2:1; 6 cm^3) and stored at −20°C overnight. Two layers formed; these were separated in the conventional fashion, ultimately giving a first crop of solid (306 mg, 52.4%), very similar in properties and composition (**3f**+0.2 $FcFeCl_4$) to that obtained in the preceding run, and a second crop (170 mg), mostly consisting of unreacted $FcFeCl_4$.

Recrystallization of any one of the crude salts isolated in these experiments from MeCN (Et_2O–pentane added to the filtrate) failed to reduce the content of admixed $FcFeCl_4$. Better results were obtained with $MeNO_2$ as the medium. Thus, a crude sample (150 mg) of composition **3f**+0.2 $FcFeCl_4$ was dissolved in $MeNO_2$ (5 cm^3) at 50–60°C and was clarified by centrifugation. The blue supernatant solution was decanted and the residue was treated with $MeNO_2$ (2 cm^3) and centrifuged. The combined supernatant solutions were reduced in volume to 2 cm^3 and left for 24 h at −20°C. The greenish-black solid that had crystallized (55 mg), collected by filtration, was completely soluble in H_2O, MeCN, and DMSO (with degradation), m.p. 180–181°C (partial).

IR(cm^{-1}): 1705s(d). Analysis: Found: C, 33.02; H, 2.98; Cl, 26.38; Fe, 20.41; O, 10.63. Calc. for $C_{16}H_{17}Cl_{4.4}Fe_{2.2}O_4S$ (**3f**+0.1 $FcFeCl_4$): C, 32.89; H, 2.93; Cl, 26.70; Fe, 21.03; O, 10.95%.

A final recrystallization as before gave reasonably pure **3f** showing the same solubility, melting and spectroscopic behavior as the precursor salt.

Analysis: Found: C, 33.21; H, 2.85; Cl, 25.79: Fe, 19.77%.

(C) By oxidation of 2f with $FeCl_3$ The mixture of **2f** (348 mg, 1.0 mmol), toluene (20 cm^3) and Et_2O (6 cm^3) was warmed with stirring until the majority of the salt had dissolved. To the suspension was added $FeCl_3$ (359 mg, 2.2 mmol). The mixture was sonicated for 6 h and stirred for 24 h at room temperature. The suspended greyish-black solid was collected by filtration, washed with toluene and Et_2O and was partially dried overnight at 20–25°C. The crude, greenish-black salt at this stage was fully soluble in H_2O and MeCN. After further drying for 24 h at 45–50°C it was still completely soluble in H_2O but only partially in MeCN. Yield 655 mg (94.6%; 82–100% in other runs).

Analysis: Found: C, 25.39; H, 2.95; Cl, 29.45; Fe, 22.83. Calc. for $C_{15}H_{19.6}Cl_{5.8}Fe_{2.9}O_{5.8}S$ (692.3) [**3f**$+0.9(FeCl_2.2H_2O)$]: C, 26.02; H, 2.85; Cl, 29.70; Fe, 23.39%.

A sample (400 mg) of the crude salt was washed with absolute EtOH and was recrystallized from $MeNO_2$ (4 cm^3) by storing the filtered solution overnight at −20°C. A small crop (23 mg) of solid settled out; this constituted impure **3f**. The filtrate was reduced in volume to *ca.* 1 cm^3, and a larger portion (105 mg) of product salt crystallized after 24 h at −20°C. A second recrystallization afforded a black, microcrystalline solid (37 mg), corresponding in composition to **3f**$+0.2(FeCl_2.H_2O)$; the salt was almost completely soluble in H_2O and MeCN.

IR(cm^{-1}): 1708s(d), 1610m.

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REFERENCES AND NOTES

1. Köpf-Maier, P, Köpf, H and Neuse, E W *Angew. Chem.* 1984, 96: 446; *idem J. Cancer Res. Clin. Oncol.*, 1984, 108: 336
2. (a) Hennig, H and Gürtler, O *J. Organomet. Chem.*, 1968, 11: 307; (b) Holloway, J D L and Geiger, W E *J. Am. Chem. Soc.*, 1979, 101: 2038; (c) Sahami, S and Weaver, M J *J. Solution Chem.*, 1981, 10: 199
3. Blom, N F, Neuse, E W and Thomas, H G *Transition Metal Chem.* (in press)
4. (a) Kuwana, T, Bublitz, D E and Hoh, G *J. Am. Chem. Soc.* 1960, 82: 5811; (b) Little, W F, Reilley, C N, Johnson, J D and Sanders, A P *J. Am. Chem. Soc.* 1964, 86: 1382. Quarter-wave potentials were used in these studies
5. Schumann, H *Chemiker Z.* 1984, 108: 289; J. *Organomet. Chem.* 1985, 290: C34
6. Neuse, E W, Khan, F B D, Berhalter, K and Thewalt, U *J. Cryst. Spectr. Res.*, 1986, 16: 483
7. Meirim, M G and Neuse, E W *Transition Metal Chem.*, 1984, 9: 337
8. (a) Nesmeyanov, A N, Perevalova, E G and Yureva, L P *Chem. Ber.*, 1960, 93: 2729; (b) Spilners, I J *J. Organomet. Chem.*, 1968, 11: 381; (c) Neuse, E W, Mojapelo, B S and Ensling, J *Transition Metal Chem.*, 1985, 10: 135
9. Neuse, E W and Khan, F B D *Macromolecules*, 1986, 10: 269
10. The standard free energy for the process of Eqn [1] can be expressed by $\Delta G^\circ = -nF(E^\circ_{Fc^+/Fc} - E^\circ_{Fc-R^+/Fc-R})$, where $E^\circ_{Fc^+/Fc}$ and $E^\circ_{Fc-R^+/Fc-R}$ are, respectively, the standard reduction potentials of the ferricenium/ferrocene and substituted ferricenium/substituted ferrocene couples, and n and F have the usual meanings. It is thus clear from the data of Table 1 that spontaneous reaction ($\Delta E^\circ > 0$) can be expected only for Eqn [1] with $R=(CH_2)_3COOH$ (formation of **3c**), for which $\Delta G \simeq -1.93$ kJ.
11. Bard, A J, Parsons, R and Jordan, J (eds) *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, 1985
12. Rinehart, K L Jr *Oxidation and Reduction of Organic Compounds*, Prentice Hall, Englewood Cliffs, NJ, 1973
13. (a) Wilkinson, G, Rosenblum, M, Whiting, M C and Woodward, R B *J. Am. Chem. Soc.*, 1952, 74: 2125; (b) Nesmeyanov, A N, Perevalova, E G, Yureva, L P and Grandberg, K I *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1962, 1772; (c) Hendrickson, D N, Sohn, Y S and Gray, H B *Inorg. Chem.*, 1971, 10: 1559; (d) Hillman, M and Kvick, A *Organometallics*, 1983, 2: 1780
14. Use of equimolar quantities of benzoquinone and substrate gave somewhat higher yields in several experiments, although the products tended to be less pure
15. The zwitterion contents are retained, or even increased, when polar, protic recrystallization solvents are used, such as MeOH or EtOH. Inner salts of the type Fc^+ ∿∿∿ COO^- were previously obtained in solution by γ-irradiation of ω-ferrocenylalkanoates in the presence of N_2O: Salmon, G A and Logan, S R *J. Chem. Soc., Faraday Trans. 1*, 1986, 82: 161, and Refs cited therein
16. Susceptibility of ferricenium compounds to reduction in dipolar aprotic solvents has been observed: (a) Schmid, R and Gutmann, V *Monatsh. Chem.*, 1973, 104: 864; (b) Prins, R, Korswagen, A R and Kortbeek, A G T G *J. Organomet. Chem.*, 1972, 39: 335
17. Neuse, E W In: *Metal-Containing Polymeric Systems*, Sheats, J E, Carraher, C E, Jr and Pittman, C U, Jr (eds), Plenum, NY, 1985, p 99
18. Boeyens, J C A, Lalloo, P C, Neuse, E W and Wei, H-H *S. Afr. J. Chem.*, 1984, 37: 32
19. Recrystallization from MeCN tends to introduce ferric carboxylate salt contamination. For a representative sample so recrystallized we found C, 30.88; H, 2.87; Cl, 28.06; O, 8.77%, in reasonable agreement with a composition $Fc^+(CH_2)_2COO^-.FeCl_4^-.0.5(FeOH^{2+})$. The IR spectrum in this case displayed the 1709 cm^{-1} band at very low intensity and, instead, showed strong carboxylate absorption at 1600 cm^{-1}