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The synthesis and polymerisation of some new 1,1′-substituted vinylferrocenes of the type $[Fe(\eta^5\text{-}C_5H_4X)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$ $(X = Cl, Br, CN \text{ or } CONH_2)$

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Abstract

Some substituted vinylferrocenes of the type $[Fe(\eta^5\text{-}C_5H_4X)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$ (X = Cl, Br, CN or $CONH_2$) have been prepared. Free radical polymerisation of substituted vinylferrocenes $[Fe(\eta^5\text{-}C_5H_4X)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$ (X = Cl, Br or CN) with AIBN (AIBN = 2,2′-azobis-2-methylpropionitrile) as initiator gave polymers with molecular weights ranging from 13,700 (X = Cl) to 44,300 (X = CN).

Introduction

There is considerable interest in developing electronic devices based on electroactive polymer films. Recently it has been shown [1–5] that micron-sized molecular-based devices can be fabricated that have electronic characteristics similar to those of diodes and transistors. They depend on the uni-directional flow of electrons across the interface between two different redox polymers, such as polyvinylferrocene and those based on polybipyridine groups. Wrighton and coworkers [2] have fabricated a working device based on a bilayer combination of polyvinylferrocene and poly-*N*,*N*′-dibenzyl-4,4′-bipyridinium $2+/3+$ materials. Another material studied in the laboratories of Murray and Wrighton [3–5] is the polymeric form of $[Ru(2,2'\text{-bipy})_2(4\text{-vinylpyridine})_2][ClO_4]$ and related materials. Electron transport in this material occurs through self-exchange of electrons between neighbouring polymeric-Ru^{II} and Ru^{III} species but electron transport results in a charge-compensating movement of $[ClO_4]^-$ counterions that limits the switching rates of these molecular diodes.

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We are currently studying the synthesis and electrochemical characterisation of some new redox-active polymers and describe below the preparation and polymerisation of a range of substituted vinylferrocenes of the type [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH=CH$_2$))] (X = Cl, Br, CN or CONH$_2$). The electrochemical characterisation of these vinylferrocene monomers and their polymers are described elsewhere [6].

Results and discussion

Substituted vinylferrocenes, [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH=CH$_2$))] were made by the route shown in Scheme 1. The substituted ferrocenes were prepared by an adaption of the method described by Sato and co-workers [7]. This method involves a halogen exchange reaction of iodoferrocene with a copper(I) salt (CuCl, CuBr or CuCN) in pyridine. The 1-substituted ferrocenes were obtained in fair yields by this route. Friedel–Crafts acylation of [Fe(η^5-C_5H_4X)(η^5-C_5H_5)] was carried out by the method described by Arimoto and Haven [8]. The alcohols [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH(OH)Me))] were dehydrated with alumina by a previously reported method [9] at 160–200°C to give the new substituted vinylferrocenes [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH=CH$_2$))]. Amido-1'-vinylferrocene, [Fe(η^5-C_5H_4 CONH$_2$)(η^5-C_5H_4(CH=CH$_2$))] was prepared by hydration of [Fe(η^5-C_5H_4CN)(η^5-C_5H_4(CH=CH$_2$))] with H_2O_2 and [N^{n}Bu$_4$][HSO$_4$] in dichloromethane [10].

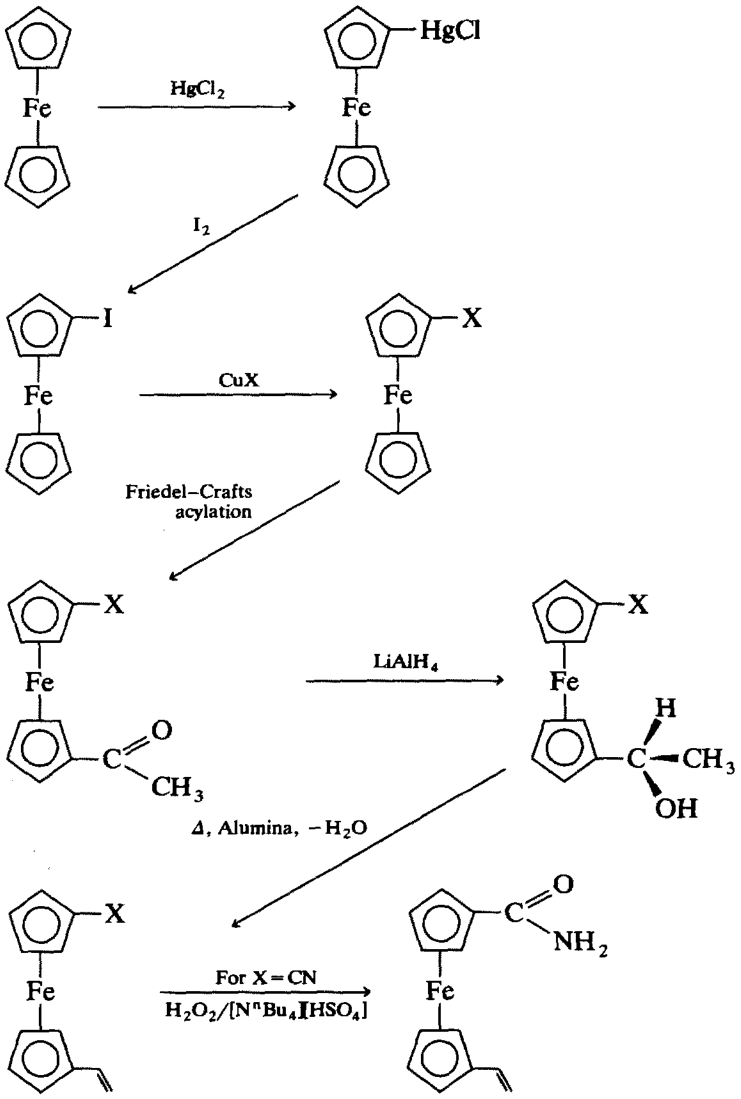
Precursors and substituted vinylferrocenes [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH=CH$_2$))] (X = Cl, Br, CN or CONH$_2$) (**1–4**) were characterized by ^{1}H NMR spectroscopy, mass spectometry and in selected cases, elemental analyses (C, H and N) and IR spectroscopy (see Experimental section). The substituted vinylferrocenes **1–4** are all low melting, air stable orange or yellow crystalline solids. The ^{1}H NMR spectra of compounds **1–4** show the expected features for substituted vinylferrocenes shown in Scheme 1.

The monomeric substituted vinylferrocenes [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH=CH$_2$))] (X = Cl, Br or CN) (**1–3**) were bulk-polymerised by thermally initiated radical polymerisation reaction with AIBN (2,2'-azobis-2-methylpropionitrile) as the radical initiator. Bulk polymerisation of the amido complex was not possible owing to its high melting point, and attempts to polymerise the material in benzene and 1,2-difluorobenzene solution were unsuccessful because of the insolubility of the compound in these solvents. The molecular weights of polymers were determined by gel permeation chromatography and are given in Table 1, and will be seen to range from 13,700–44,300.

We have made a detailed study of the electrochemical properties of both the monomers [Fe(η^5-C_5H_4X)(η^5-C_5H_4(CH=CH$_2$))] (X = Cl, Br or CN) and their respective polymers [6], and are currently attempting to fabricate diode devices containing two of these different redox polymers.

Experimental

All reagents and solvents used in this research were obtained from commercial sources. The complexes [Fe(η^5-C_5H_5)(η^5-C_5H_4I)] [11], [Fe(η^5-C_5H_5)(η^5-C_5H_4X)] (X = Cl, Br, CN) [7] and [Fe(η^5-C_5H_4X)(η^5-C_5H_4(COMe))] [8] were prepared by published methods and all complexes had physical properties (melting points, *etc.*)



Scheme 1.

Table 1

The molecular weights of $[Fe(\eta^5\text{-}C_5H_4X)\{\eta^5\text{-}C_5H_4(CH\text{–}CH_2)\}]_n$ (X = Cl, Br or CN)

X	*MW*
Cl	13,700
Br	12,600
CN	44,300

in agreement with those previously reported. ^1H NMR spectra were recorded on a Bruker AC 250/CP MAS NMR spectrometer and were calibrated against tetramethylsilane. Mass spectra were recorded on a Finnigan 1020 GC mass spectrometer. Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106, using helium as the carrier gas. IR spectra were recorded on a Perkin–Elmer 1430 ratio recording infrared spectrometer. The molecular weights of the polymers were determined for us by RAPRA Technology Ltd using gel permeation chromatography, a combined viscosity/refractive index detection system and thf as the eluant. The combined detector system uses the Universal Calibration Procedure with internally derived Mark Houwink Parameters. The molecular weights determined by this procedure are much more likely to be closer to the actual molecular masses of the polymers because they are corrected for any interaction effects due to substituents. The molecular masses calculated by this method are similar to those obtained by conventional gel permeation chromatography where the molecular masses are expressed as "polystyrene equivalents", so facilitating comparisons with earlier work [12].

1,1'-Chloro(α-hydroxyethyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_4Cl)\{\eta^5\text{-}C_5H_4\{CH(OH)CH_3\}\}]$

Lithium aluminium hydride (0.75 g, 0.019 mol) was added to a stirred solution of 1-acetyl-1'-chloroferrocene (4.33 g, 0.016 mol) in dry Et_2O (200 cm^3). After 15 min a solution of saturated ammonium chloride was added dropwise. The organic layer was separated, and the aqueous layer extracted with Et_2O. The combined organic layers were dried (Na_2SO_4) and filtered and the solvent removed *in vacuo* to leave a yellow oil which was chromatographed on silica gel, with hexane/ethylacetate (1/1) as eluent, to give the title complex as a yellow oil. Yield 3.52 g, 80%. Analysis: Found: C, 54.8; H, 5.0; $C_{12}H_{13}ClFeO$ calc.: C, 54.5; H, 4.9%. Found, $M^+ = 264$; $C_{12}H_{13}ClFeO$ calc.: M, 264. ^1H NMR (δ, 25°C) 1.48 (d, 3H, $CH(OH)CH_3$); 2.47 (s, 1H, OH); 4.06 (t, 2H, $2 \times CCH(OH)CH_3CHCH$); 4.22 (m, 4H, $2 \times CClCH$ and $2 \times CH(OH)CH_3CH$); 4.5 (t, 2H, $CClCH$); 4.62 (q, 1H, $CH(OH)CH_3$).

1,1'-Bromo(α-hydroxyethyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_4Br)\{\eta^5\text{-}C_5H_4\{CH(OH)CH_3\}\}]$

Lithium aluminium hydride (0.5 g, 0.013 mol) was added to a stirred solution of 1-acetyl-1'-bromoferrocene (1.7 g, 0.005 mol) in dry Et_2O (150 cm^3). After 15 min saturated ammonium chloride solution was added dropwise. The organic layer was separated off and the aqueous layer extracted with Et_2O. The combined organic fractions were dried (Na_2SO_4) and filtered and the solid removed *in vacuo* to leave an orange oil, which was chromatographed on silica with hexane Et_2O (1/1) as eluent to give the title compound as a red-orange oil. Yield 1.42 g, 84%. Found, $M^+ - H_2O$ 290, $C_{12}H_{13}BrFeO$ calc.: $M - H_2O = 290$. IR ($CHCl_3$) $\nu(OH)$ 3460 cm^{-1}. ^1H NMR (δ, 25°C) 1.42 (d, 3H, $CH(OH)CH_3$); 2.0 (s, 1H, OH); 4.11; 4.22 and 4.4 (m, 8H, Cp-H's); 4.63 (q, 1H, $CH(OH)CH_3$).

1,1'-Cyano(α-hydroxyethyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_4CN)\{\eta^5\text{-}C_5H_4\{CH(OH)CH_3\}\}]$

Lithium aluminium hydride (0.3 g, 0.0079 mol) was added to a stirred solution of 1-acetyl-1'-cyanoferrocene (2 g, 0.0079 mol) in Et_2O (250 cm^3). A saturated solution of ammonium chloride was added dropwise and the organic layer separated, dried (Na_2SO_4) and filtered and the solvent removed *in vacuo*. The product was chromatographed on alumina with hexane/ethylacetate (3/2) as eluent and the fast-moving yellow band (title complex) was collected. Yield 0.7 g, 34%. Analysis: Found: C, 61.5; H, 5.3; N, 5.4. $C_{13}H_{13}FeNO$ calc.: C, 61.2; H, 5.1; N, 5.5%. Found, M^+, 255. $C_{13}C_{13}FeNO$ calc.: M, 255. IR ($CHCl_3$); $\nu(C{\equiv}N)$, 222.5 $cm^{-1} = \nu(OH) = 3454\ cm^{-1}$. ^1H NMR (δ, 25°C). 1.49 (d, 3H, $CH(OH)CH_3$); 2.0 (s, 1H, O*H*); 4.05 (q, 1H, C*H*CH_3); 4.3; 4.41 and 4.62 (m, 8H, Cp-*H*'s).

1-Vinyl-1'-chloroferrocene, $[Fe(\eta^5\text{-}C_5H_4Cl)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$

1,1'-Chloro(α-hydroxyethyl)ferrocene (2 g, 0.0075 mol) and activated alumina (6.5 g) were mixed and kept at 160°C for 5 h under a vacuum of 0.1 mmHg in a Kugelrohr distillation apparatus. The title compound sublimed out as an orange crystalline solid. Yield 1.4 g, 75%. Found: M^+, 246; $C_{12}H_{11}ClFe$ calc.: 246. ^1H NMR (δ, 25°C) 3.8–4.55 (m, 8H, Cp-*H*s); 5.1 (d, *J* 10 Hz, 1H, vinylic, C*H*, *H-trans* to ferrocene); 5.4 (d, *J* 22 Hz, 1H, vinylic C*H*, *H-cis* to ferrocene); 6.45 (q, 1H, vinylic C*H*).

1-Vinyl-1'-bromoferrocene, $[Fe(\eta^5\text{-}C_5H_4Br)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$

1,1'-Bromo(α-hydroxyethyl)ferrocene (1 g, 0.0032 mol) and activated alumina (2.26 g) were mixed and kept at 180°C under a vacuum of 0.1 mmHg for 5 h in a Kugelrohr distillation apparatus. The title compound sublimed out as an orange crystalline solid. Yield 0.52 g, 55%. Found: M^+, 290: $C_{12}H_{11}BrFe$ calc.: M, 290. ^1H NMR (δ, 25°C) 3.8–4.4 (m, 8H, Cp-Hs); 5.12 (d, *J* 10 Hz, 1H, vinylic C*H*, *H-trans*-to ferrocene); 5.4 (d, *J* 22 Hz, 1H, vinylic C*H*, *H-cis* to ferrocene); 6.45 (q, 1H, vinylic C*H*).

1-Vinyl-1'-cyanoferrocene, $[Fe(\eta^5\text{-}C_5H_4CN)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$

An intimate mixture of 1,1'-cyano(α-hydroxyethyl)ferrocene (0.7 g, 0.0028 mol) and activated alumina (Beckman grade 1) (2.74 g) was kept in a vacuum sublimation apparatus at 200°C for 5–6 h. The title compound was collected as an orange solid. Yield 0.5 g, 76%. Melting point 34–36°C. Analysis: Found: C, 66.1; H, 5.3; N, 4.8. $C_{13}H_{12}FeN$ calc.: C, 65.8; H, 5.9; N, 4.6%. Found: M^+ 237; $C_{13}H_{11}FeN$ calc.: 237. IR ($CHCl_3$) $\nu(C{\equiv}N)$ 2225 cm^{-1}. ^1H NMR (δ, 25°C) 4.2–4.6 (m, 8H, Cp-*H*'s); 5.1 (d, *J* 10 Hz, 1H, vinylic-C*H*, *H-trans* to ferrocene); 6.42 (q, 1H, vinylic C*H*).

1-Vinyl-1'-amidoferrocene $[Fe(\eta^5\text{-}C_5H_4CONH_2)\{\eta^5\text{-}C_5H_4(CH{=}CH_2)\}]$

To a solution of 1-vinyl-1'-cyanoferrocene (1.3 g, 5.48 mmol) in CH_2Cl_2 (2 cm^3) cooled in an ice bath was added a 30% solution of hydrogen peroxide (12.6 cm^3). Tetrabutylammonium sulphate (0.37 g) and a 20% solution of sodium hydroxide (2.1 cm^3) were then added and the vigorously stirred mixture was allowed to warm to room temperature. After 8 h another 10 cm^3 of 20% solution of hydrogen peroxide were added. After 30 h CH_2Cl_2 (50 cm^3) was added and the organic layer washed with a saturated solution of sodium chloride, dried (Na_2SO_4) and filtered, and the solvent was removed *in vacuo*. The yellow residue was chromatographed on alumina; elution with Et_2O removed unchanged starting material and then elution with ethyl acetate gave the title compound as a yellow solid. Yield 0.8 g, 57.2%. M.p. 125–127°C. Analysis: Found: C, 60.9; H, 5.3; N, 5.1. $C_{13}H_{13}FeNO$ calc.: C, 61.2; H, 5.1; N, 5.5%. Found: M^+, 255. $C_{13}H_{13}FeNO$ calc.: M, 255. IR ($CHCl_3$) $\nu(C{=}O)$ 1654, $\nu(NH)$ 3178 and 3354 cm^{-1}. ^1H NMR (δ, 25°C) 4.3, 4.34

and 4.37 (t, 6H, 2 × C(CH=CH$_2$) *CH* *CH*, 2 × C(CH=CH$_2$) *CH* and 2 × CCONH$_2$CHC*H*); 4.57 (t, 2H, 2 × CCONH$_2$C*H*); 5.15 (d, *J* 12 Hz, 1*H*, vinylic CH, H-*trans* to ferrocene); 5.38 (t, *J* 20 Hz, 1H, vinylic C*H*, *H-cis* to ferrocene); 5.6 (s, 2H, CON*H*$_2$); 6.4 (q, 1H, vinylic C*H*).

Poly(1-vinyl-1'-chloroferrocene), $[Fe(\eta^5\text{-}C_5H_4Cl)\{\eta^5\text{-}C_5H_4(CH\text{-}CH_2)\}]_n$

A mixture of 1-vinyl-1'-chloroferrocene (2.27 g, 9.22 mmol) and AIBN (0.0155 g, 0.094 mmol) was heated in a sealed evacuated glass tube at 70°C in water bath for 20 h. The mixture was dissolved in benzene and the yellow polymeric product was precipitated by dropwise additioning methanol. It was reprecipitated three times, and after the third precipitation the product was filtered off, and dried in a vacuum desiccator. Yield 0.37 g.

Poly(1-vinyl-1'-bromoferrocene), $[Fe(\eta^5\text{-}C_5H_4Br)\{\eta^5\text{-}C_5H_4(CH\text{-}CH_2)\}]_n$

A mixture of 1-vinyl-1-bromoferrocene (1.61 g, 5.54 mmol) and AIBN (0.0093 g, 0.057 mmol) was heated in an evacuated sealed tube at 70°C for 20 h in a water bath. The mixture was dissolved in benzene and the product precipitated by dropwise addition of methanol. The polymer was reprecipitated twice, and after the second precipitation, the product was filtered off, and dried in a vacuum desiccator. Yield 0.37 g.

Poly(1-vinyl-1'-cyanoferrocene), $[Fe(\eta^5\text{-}C_5H_4CN)\{\eta^5\text{-}C_5H_4(CH\text{-}CH_2)\}]_n$

A mixture of 1-vinyl-1'-cyanoferrocene (0.73 g, 3.1 mmol) and AIBN (0.0051 g, 0.031 mmol) was heated in an evacuated sealed tube at 60°C for 46 h in a water bath. The mixture was dissolved in benzene and the product precipitated by dropwise addition of methanol. The polymer was reprecipitated twice, and after the second precipitation, the product was filtered off and dried in a vacuum desiccator. Yield 0.374 g.

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