

Synthesis of ferrocene-based redox-active polymers via palladium-catalysed coupling reactions

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Abstract

1,1'-Difunctionalised ferrocenes $\text{Fe}(\text{C}_5\text{H}_4\text{Z})_2$ [$\text{Z} = 4\text{-BrC}_6\text{H}_4$ (**1**), $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{C(O)-}$ (**4a**), $4\text{-BrC}_6\text{H}_4\text{CH=CH-}$ (**6a**)] undergo cross-coupling reactions with the dizinc reagent $(\text{ClZnC}_6\text{H}_4)_2\text{C(O)CH}_2\text{CHC(Me)O}$ (**2**) to give a series of conjugated and non-conjugated aromatic poly(ferrocenes) with ferrocenediyl moieties as part of the polymer backbone. Similar products are obtained by Heck-arylation of 1,1'-divinylferrocene with diiodoarenes 1-R-I ($\text{R} = 1,4\text{-C}_6\text{H}_4$, $1,1'\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4$, $2,5\text{-C}_4\text{H}_2\text{S}$, $1,1'\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4$). The coupling products form orange to deep red solids, which are poorly soluble and oligomeric in most cases. Cyclic voltammetry measurements in dichloromethane solution give redox potentials close to the parent ferrocenes, with apparently very little interaction between the widely spaced iron centres.

Keywords: Ferrocene polymers; Cross-coupling; Palladium catalyst; Electrochemistry; Redox-active polymers; Zinc reagent

1. Introduction

Redox-active polymers containing ferrocene moieties have attracted considerable attention over many years [1]. The ferrocene substituents may be pendent, for example as in poly(vinylferrocene) [2], poly(ferrocenylacrylate) [3] and poly(ferrocenylphosphazines) [4], they may be present as ferrocene-containing side chains in liquid crystal polymers [5], or the polymer may contain 1,1'-disubstituted ferrocenes as backbone building blocks. Numerous synthetic strategies have been employed in an effort to obtain oligomers or polymers of the latter type. These include the reductive coupling of 1,1'-ferrocenedicarboxaldehyde with $\text{TiCl}_4/\text{LiAlH}_4$ [6], condensation of ferrocenedicarboxaldehyde with difunctional Wittig reagents [7], polycondensations of hydroxy- and amino-substituted ferrocenes with diacid chlorides [8], metathesis random copolymerisation of 1,1'-divinylferrocene with α,ω -dienes [9] and ring-opening polymerisation of ansa-ferrocenes $\text{Fe}\{\text{Y}(\text{C}_5\text{H}_4)_2\}$ under thermolysis conditions ($\text{Y} = \text{SiMe}_2$ [10],

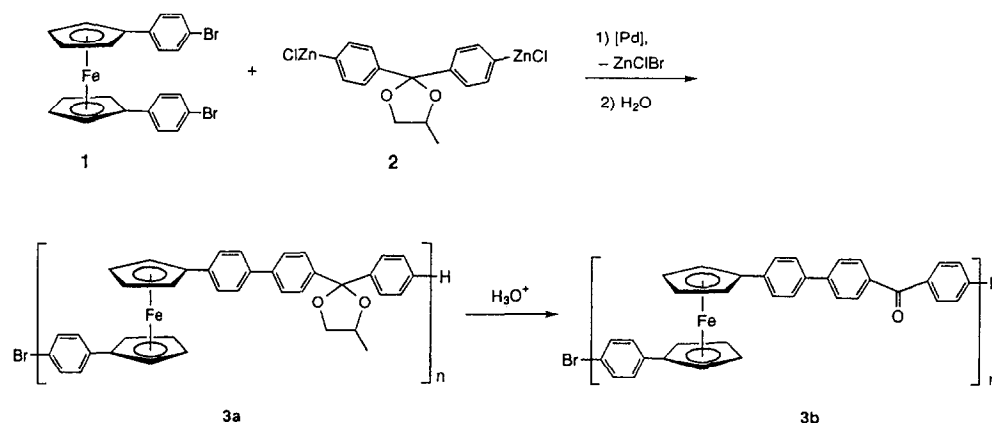
C_2H_4 [11], S [12], S_3 [13]). We have recently described the synthesis of aromatic polyethers and polyketones via palladium catalysed cross-coupling reactions of aryl tin and zinc reagents [14] and report here the application of related coupling reactions involving ferrocene derivatives to the preparation of redox-active polymers.

2. Results and discussion

Whereas coupling reactions of aryl, benzyl and vinyl halides in the presence of suitable catalysts, typically palladium salts, with organometallic reagents are a highly efficient and versatile method for the formation of C–C bonds, preliminary attempts to couple $\text{Fe}(\text{C}_5\text{H}_4\text{Br})_2$ with zinc reagents or $\text{Fe}(\text{C}_5\text{H}_4\text{X})_2$ ($\text{X} = \text{B(OH)}_2$, SnBu_3) with aryl halides proved unsuccessful, probably for steric reasons. Coupling reactions are, however, observed if the reactive site is separated from the ferrocene unit by a suitable spacer group. Thus refluxing $\text{Fe}(\text{C}_5\text{H}_4\text{-C}_6\text{H}_4\text{Br-4})_2$ (**1**) with the zinc reagent **2** in the presence of 1 mol.% $\text{PdCl}_2(\text{PPh}_3)_2$ in *N,N*-dimethylacetamide (DMAc) leads to the coupling product **3a** which, on washing with acid, is hydrolysed to the ferrocenyl ketone polymer **3b** (Scheme 1). Although the presence of the methyl-substituted dioxolane

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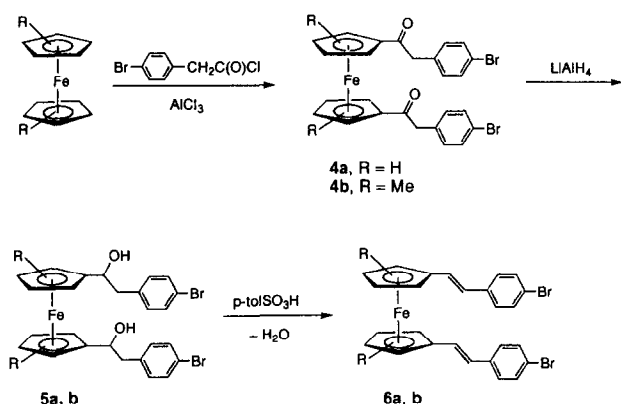
Scheme 1.

ring helps to increase the solubility of **3a**, the compound precipitates from DMAc solution after a few hours even at reaction temperatures of 160°C as a red-brown powder. The hydrolysed polymer **3b** is even insoluble in concentrated sulfuric acid at room temperature. The elemental analysis indicates a significant residual bromine content which indicates an oligomeric rather than a polymeric structure for **3**. A small fraction of **3a** was soluble in acetone; this fraction gave a low intrinsic viscosity value of 0.042 dl g⁻¹ (CHCl₃, 25 ± 0.1°C), again suggestive of a low molecular weight product. Low degrees of polymerisation $\overline{DP}$ are frequently en-

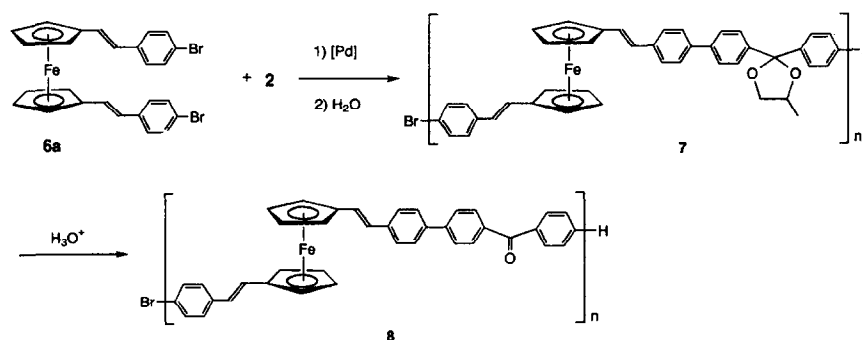
countered in coupling condensations and are a function of both polymer solubility and catalyst concentration [15].

In an effort to extend the conjugated linkages between ferrocene units, the 1,1'-bis(arylvinyl) complexes **6a** (R = H) and **6b** (R = Me) were prepared following the reaction sequence shown in Scheme 2. Acylation of ferrocene with p-BrC₆H₄CH₂C(O)Cl, freshly prepared from p-bromophenylacetic acid and thionyl chloride, in the presence of an excess of AlCl₃, affords **4a** together with unreacted and monoacylated ferrocene. The by-products are separated by column chromatography and eluted with light petroleum/ethyl acetate 9:1, while the less soluble **4a** is washed off with dichloromethane and obtained as a deep red microcrystalline solid ($\nu_{C=O}$ 1670 cm⁻¹). Reduction of **4a** with excess LiAlH₄ in THF gives **5a** as a pale red solid which was converted into **6a** without further purification by stirring a solution of **5a** in THF at room temperature with p-toluenesulfonic acid. Compound **6a** is isolated in good yield as a dark red solid.

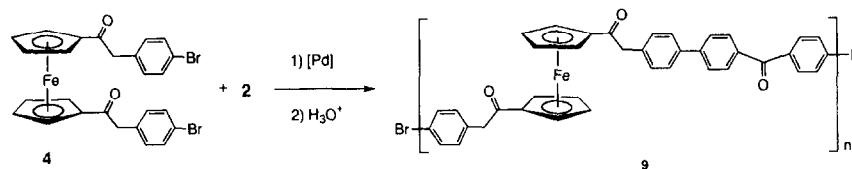
Since the solubility of aromatic polymers largely depends on the rigidity of the polymer backbone and the degree of crystallinity of the polymer, it was felt desirable to prepare similar ferrocene derivatives bearing substituents which might improve backbone flexibility. This could, for example, be achieved by introducing a



Scheme 2.



Scheme 3.



Scheme 4.

methyl substituent on the Cp ring, as in **6b**. Several substitutional isomers are possible, such as 1,1',2,2', 1,1',2,3', 1,1',3,3' which exist as *rac* and *meso* diastereomers, and the presence of such isomeric mixtures could be expected to further improve the solubility characteristics of the coupling products.

Compound **6b** was prepared in analogy to **6a**. It proved unnecessary to isolate the intermediates **4b** and **5b**, and hence the synthesis was carried out essentially as a one-pot procedure which after chromatography afforded **6b** as a deep red solid in modest yield.

Heating a mixture of compounds **6a** and **2** in the presence of 1 mol.% PdCl₂(PPh₃)₂ and triethylamine in DMAc to 120°C for several hours leads to the formation of the expected coupling product **7** as a red–brown solid (Scheme 3). In spite of the presence of triethylamine some hydrolysis of the dioxolane ring to the arylketone **8** is evident from the IR spectrum; the hydrolysis was completed by heating **7** with a 1:1 mixture of 6 M

HCl/isopropanol to give **8**. The product requires extensive washing with methanol and water to remove inorganic by-products; even so, the elemental analysis indicated a presence of both chloride and bromide which prevented a sensible estimate of the degree of polymerisation from the C:Br ratio. The coupling product **8** is insoluble in acetone and THF and partly soluble in dichloromethane.

The coupling of **4a** and **2** proceeds under similar conditions to give, after acid hydrolysis, compound **9** as a red–brown solid, the IR spectrum of which exhibits two broad $\nu_{C=O}$ bands at 1710 and 1660 cm⁻¹. The solubility properties of **9** are similar to those of **8**. Assuming the presence of, on average, one Br per chain, the C:Br ratio of **9** suggests a $\overline{DP}$ of about 2. Coupling reactions between **6b** and **2** remained inconclusive.

Analytical data for coupling reactions involving **2** are collected in Table 1.

Table 1

Analytical data for coupling products of halide-substituted ferrocenes with zinc reagent **2**

Ferrocene derivative	Product	Analysis (%) ^a			C: Br ratio	$\overline{DP}$
		C	H	Br		
Fe(C ₅ H ₄ –C ₆ H ₄ Br) ₂ (1)	3b	75.4 (76.8)	4.2 (4.4)	5.5 (5.6)	91.7	2.6
Fe(C ₅ H ₄ C(O)CH ₂ C ₆ H ₄ Br) ₂ (4)	5	69.8 (73.0)	4.3 (4.4)	6.1 (6.4)	76.3	2.0
Fe(C ₅ H ₄ CH=CHC ₆ H ₄ Br) ₂ (6a)	8	71.2	4.4	ca. 8.0 Cl ca. 3.0		

^a Calculated values based on the C: Br ratio indicated are given in parentheses.

Table 2

Analytical data for coupling products between 1,1'-divinylferrocene and organic dihalides

Dihalide	Product	Analysis (%) ^a			C: halide ratio	dp
		C	H	I		
I–C ₆ H ₄ –I	10	66.1 (66.9)	4.7 (4.5)	12.9 (13.0)	54.1	2.7
I–C ₆ H ₄ –C ₆ H ₄ –I	11	69.1 (69.6)	4.5 (4.5)	13.2 (13.5)	55.2	2.1
Br–C ₆ H ₄ –O–C ₆ H ₄ –Br	12a	79.1 (74.9)	5.7 (4.8)	Br 3.2 (3.0)	167	6.4
I–C ₆ H ₄ –O–C ₆ H ₄ –I	12b	68.6 (68.9)	4.5 (4.5)	10.7 (10.8)	67.9	2.6

^a Calculated values based on the C: halide ratio indicated are given in parentheses.

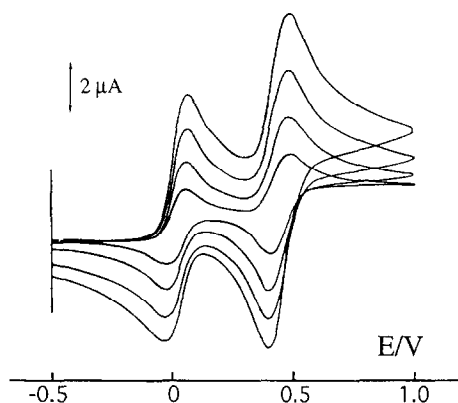


Fig. 1. Cyclic voltammograms of oligomer **11** (Scheme 5, R = –C₆H₄–C₆H₄–) in dichloromethane at 20 ± 0.1°C. Scan rates 200, 100, 50 and 20 mV s⁻¹, concentration 4.0 g dm⁻³, 0.5 M [NⁿBu₄]ClO₄, reference electrode Ag/AgCl. Left-hand wave is due to [Fe(C₅Me₅)₂]^{+/0} internal reference standard.

A versatile alternative to coupling reactions of the type described above is the Heck-arylation of ferrocenylalkenes. 1,1'-Divinylferrocene reacts with di-bromo- and diiodoarenes in the presence of catalytic amounts of PdCl₂(PPh₃)₂ and triethylamine to give the oligomeric coupling products **10–13** as orange to red-brown solids. The products are isolated by precipitation with methanol, followed by repeated washings with acidified methanol, water and methanol. In spite of this, the compounds retain significant amounts of halide, some of which may be of inorganic origin. The given $\overline{DP}$ values (Table 2) based on the C:halide ratios should therefore be regarded as lower limit estimates. Compounds **10** and **11** started to fuse at above 150°C and gave black melts at 240°C, **10** is soluble in concentrated sulfuric acid and gives a brown solution, whereas **11** is only sparingly soluble in all solvents tested. Compounds **12** and **13** are moderately soluble in dichloromethane, **13** showed no melt transition below 300°C.

Cyclic voltammetry measurements on **10–13** were carried out in dichloromethane at 20 ± 0.1°C using 0.5

Table 3
Cyclic voltammetry data for products **10–13**^a

Compound	R	$E^{1/2}$ ^b [mV]	ΔE ^c [mV]
10		-20	85
11		-30	70
12		-10	85
13		-30	120 ^d

^a In dichloromethane, 0.5 M [NⁿBu₄]ClO₄, 20°C.

^b Versus [FeCp₂]^{+/0}.

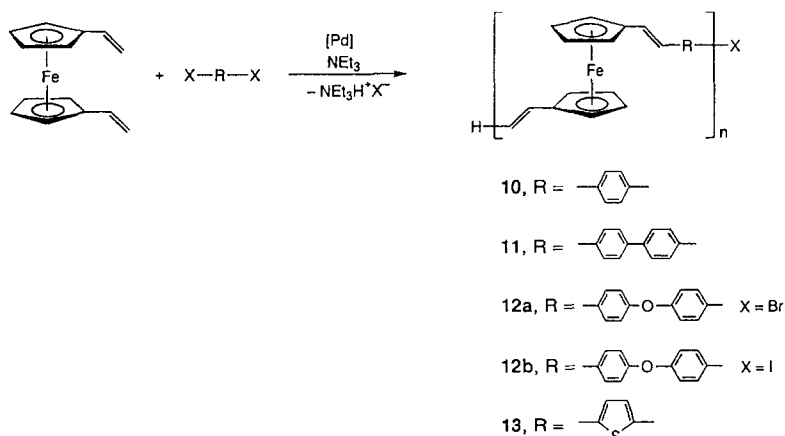
^c $\Delta E = E_{\text{anodic}} - E_{\text{cathodic}}$; scan rates 20–200 mV s⁻¹.

^d Scan rate 20 mV s⁻¹.

M tetrabutylammonium perchlorate as supporting electrolyte and the FeCp₂^{*/2}/FeCp₂^{+/2} couple as internal standard [$E^{1/2}(\text{FeCp}_2^*) = -0.535$ V vs. FeCp₂/FeCp₂⁺] at scan rates of 20, 50, 100 and 200 mV s⁻¹ (Cp^{*} = η⁵-C₅Me₅). Fig. 1 shows a voltammogram of **11** which is typical for this series of compounds. The $E^{1/2}$ values deviate surprisingly little from the values of unsubstituted ferrocene and 1,1'-divinylferrocene ($E^{1/2} = -30$ mV, $\Delta E = 190$ mV), and within experimental error there is no discernible dependence of E^0 on the nature of the linking group R (Table 3). Not surprisingly in view of the large linkage groups, there is no evidence for interaction between neighbouring redox centres.

3. Experimental

All reactions were carried out under nitrogen using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium-benzophenone [di-



Scheme 5.

ethyl ether, THF, light petroleum (b.p. 40–60°C), sodium (toluene) or calcium hydride (dichloromethane). The NMR solvents were stored over 4A molecular sieves under nitrogen. The compounds $\text{Fe}(\text{C}_5\text{H}_4\text{Br}-4)_2$ [16], $[\text{Fe}(\text{C}_5\text{H}_4\text{CH}=\text{CH}_2)_2]$ [17] and FeCp'_2 ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$) [18] were prepared as described; $\text{BrC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Cl}$ was made by refluxing the carboxylic acid with SOCl_2 and used without further purification. 4,4'-Diiodobiphenyl was recrystallised from toluene, other reagents were used as purchased. Mattson Polaris (FT-IR) and JEOL EX270 (^1H , ^{13}C NMR) instruments were used. Cyclic voltammetry was performed with a Princeton Applied Research Model 174A polarographic analyser with a Model 175 Universal Programmer and X-Y recorder. A bright platinum disk (0.8 mm diameter) was used as the working electrode. The reference electrode was Ag/AgCl in tetrabutylammonium perchlorate (TBAP) in water, separated from the reaction compartment by a salt bridge of TBAP in dichloromethane and a fine glass frit as close as possible (0.5 cm) to the working electrode. All electrochemical measurements were performed under N_2 at $20 \pm 0.1^\circ\text{C}$ in dry dichloromethane using TBAP as supporting electrolyte. Potentials are given relative to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple with $\text{Cp}^*_2\text{Fe}/\text{Cp}^*_2\text{Fe}^+$ as internal standard ($E^{1/2} = -535 \text{ mV}$).

3.1. Preparation of $[\text{Fe}(\text{C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{Br}-4)_2]$ (**4a**)

This compound was prepared following the method given for the C_6H_5 derivative [19]. To a suspension of 15.6 g AlCl_3 (0.117 mol) in 50 ml CH_2Cl_2 was added dropwise a solution of 14 g $\text{p-BrC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Cl}$ (0.078 mol) in 50 ml CH_2Cl_2 . The reddish suspension was cooled to -20°C and 5.6 g ferrocene (0.03 mol) in 60 ml CH_2Cl_2 was added dropwise over a period of 2 h. The reaction mixture was allowed to warm to 0°C and stirred for another 4 h. The deep red mixture was poured onto 500 g ice. The organic layer was separated, washed with water and dried over K_2CO_3 . The solvent was removed *in vacuo* and the residue washed with acetone. The solid was mixed with 10 g silica gel and loaded on a silica gel column. Two bands were eluted with petroleum/ethylacetate 9:1 (mainly ferrocene and monoacetylated ferrocene), the third component was washed off with dichloromethane. Yield of **4a** 5.85 g (10.1 mmol, 33.6%). IR (Nujol mull, cm^{-1}): 3105w, 3095w, 1670s [$\nu(\text{C}=\text{O})$], 1490s, 1450s, 1410m, 1400m, 1380m, 1350w, 1330m, 1245s, 1200m, 1105s, 1070s, 1030m, 1010m, 920w, 890m, 830s, 800s, 760s. ^1H NMR (CDCl_3 , 270 MHz): δ 3.84 (s, 2H, CH_2), 4.45 (s, br, 2H, Cp), 4.74 (s, br, 2H, Cp), 7.15 (s, br, 2H, C_6H_4), 7.44 (s, br, 2H, C_6H_4). ^{13}C NMR (CDCl_3): δ 46.08 (CH_2), 71.03 (Cp), 73.62 (Cp), 79.79 (*ipso*-C of Cp), 120.95 (*ipso*-C of C_6), 131.31, 131.60 (C_6), 133.38 (*ipso*-C of C_6), 200.24 ($\text{C}=\text{O}$).

3.2. Preparation of $[\text{Fe}(\text{C}_5\text{H}_4\text{CH}(\text{OH})\text{CH}_2\text{C}_6\text{H}_4\text{Br}-4)_2]$ (**5a**)

To a vigorously stirred solution of 5.85 g (10.08 mmol) **4a** in 150 ml THF was added 1.0 g (26.4 mmol) LiAlH_4 in small portions. After stirring for 40 min a yellow–grey mixture was obtained to which 50 ml of a saturated aqueous solution of NH_4Cl was added dropwise to destroy excess LiAlH_4 . The organic layer was separated, washed with water and taken to dryness to leave 4.5 g of a pale red solid (7.7 mmol, 76%). IR Nujol mull, cm^{-1} : 3600–3100 (vs, br), 3090w, 3010w, 1650vw, 1490s, 1400m, 1100m, 1070s, 1040s, 1010s, 835m, 800s, 770w. The compound was converted to **6a** without further purification.

3.3. Synthesis of $[\text{Fe}(\text{C}_5\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{Br}-4)_2]$ (**6a**)

To a solution of 4.5 g of **5a** (7.7 mmol) in 150 ml THF was added 2.0 g *p*-toluenesulfonic acid. The mixture was stirred at room temperature for 10 h. Removal of the solvent left a dark red residue which was purified by column chromatography, yielding 3.2 g dark red **6a** (5.8 mmol, 75.8%). The compound is poorly soluble in acetone but may be recrystallised from dichloromethane/light petroleum (1:1), m.p. 180–186°C. Anal. Found: C, 56.47; H, 3.63; Br, 28.50. Calc.: C, 56.97; H, 3.68; Br, 29.16%. ^1H NMR (CDCl_3 , 270 MHz): δ 4.54 (s, br, 2H, Cp), 4.73 (s, br, 2H, Cp), 6.23 (d, 1H, $J = 7.8 \text{ Hz}$, $\text{CH}=\text{CH}$), 6.63 (d, 1H, $J = 7.8 \text{ Hz}$, $\text{CH}=\text{CH}$), 6.97 (d, 2H, $J = 4.1 \text{ Hz}$, C_6), 7.32 (d, 2H, $J = 4.1 \text{ Hz}$, C_6). ^{13}C NMR (CDCl_3): δ 68.20 (Cp), 70.82 (Cp), 120.58 ($\text{C}=\text{C}$), 126.20 ($\text{C}=\text{C}$ and *ipso*-C of C_6), 127.33 (C_6), 131.41 (C_6), 136.10 (*ipso*-C of C_6).

3.4. Preparation of $[\text{Fe}(\text{C}_5\text{H}_3(\text{Me})\text{CH}=\text{CHC}_6\text{H}_4\text{Br}-4)_2]$ (**6b**)

This compound was prepared using a similar procedure as for **6a**, but without the isolation of the intermediates **4b** and **5b**. To a suspension of 18 g (0.135 mol) AlCl_3 in 100 ml dichloromethane was added 21 g (0.09 mol) freshly prepared $\text{BrC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Cl}$. The reddish suspension was cooled to -20°C , and a solution of 6.42 g (0.03 mol) FeCp'_2 in 100 ml dichloromethane was added over a period of 2 h. Stirring was continued for another 30 min before the mixture was poured onto ice. The deep red organic layer was separated. Evaporation of the solvent left a deep red oil (**4b**), the IR spectrum of which showed a strong band at 1670 cm^{-1} ($\nu_{\text{C}=\text{O}}$). The product was dissolved in 300 ml THF, and 3.8 g (0.1 mol) LiAlH_4 was added in small portions. The colour changed from deep red to yellow. The mixture was stirred at room temperature for 1 h. Excess LiAlH_4 was destroyed by the careful addition of 150 ml saturated ammonium chloride solution. After adding 50 ml

THF and 100 ml light petroleum the organic layer was separated and the solvent evaporated to leave an oily residue (**5b**), IR 3500–3200 cm^{-1} (s, $\nu_{\text{O-H}}$), no band in the 1800–1600 cm^{-1} region. The product was dissolved in 250 ml THF and 0.5 g p-toluenesulfonic acid was added. After stirring the mixture for 1 h at room temperature a TLC spot check showed the complete conversion of **5b** to a new compound (**6b**) which was obtained as a thick deep red oil and purified by column chromatography (light petroleum/ethyl acetate 10:1). The oil solidified on drying in vacuo. Yield 3.5 g (6.1 mmol, 20%). Anal. Found: C, 59.2; H, 4.2; Br, 26.8. Calc.: C, 58.4; H, 4.2; Br, 27.7%. IR (KBr disk, cm^{-1}): 3080w, 3020w, 1630s, 1585s, 1440m, 1400m, 1250w, 1200w, 1180w, 1100m, 1070s, 1035m, 1005s, 955s, 855m, 800s. ^1H NMR (CDCl_3): δ 1.93–2.08 (m, 3H, CH_3), 4.07–4.45 (m, 3H, Cp), 6.41–6.82 (m, 2H, $\text{CH}=\text{CH}$), 7.09–7.18 (m, 2H, C_6), 7.30–7.41 (m, 2H, C_6).

3.5. Coupling reaction of $\text{Fe}(\text{C}_5\text{H}_4-\text{C}_6\text{H}_4\text{Br})_2$ (**1**) with **2**

A mixture of 1.24 g (2.5 mmol) **1**, 2.5 mmol **2**, 17.5 mg (0.025 mmol) $\text{PdCl}_2(\text{PPh}_3)_2$ and 13.2 mg (0.05 mmol) PPh_3 in 10 ml DMAc was heated to 165°C for 8 h. A nearly black heterogeneous mixture was obtained which was poured into 200 ml water. The solid precipitate was filtered off, washed several times with water and methanol (3×50 ml) and dried to give **3a** as a fine yellow–brown powder (1.2 g). A small proportion of this was soluble in acetone; this fraction gave an intrinsic viscosity value of 0.042 dl g^{-1} , indicative of a low molecular weight oligomer. The remainder was hydrolysed by stirring with 6 M HCl/isopropanol (1:1) for 2 h, washed with water and methanol and dried to give **3b** (0.9 g). The compound is essentially insoluble in dichloromethane or concentrated sulfuric acid at room temperature. IR (Nujol mull, cm^{-1}): 3080w, 3020w, 1650s ($\nu_{\text{C}=\text{O}}$), 1595s, 1315m, 1270m, 1005m, 933s, 890m, 825vs, 775m.

3.6. Coupling reaction of **6a** with **2**

To a solution of 0.685 g **6a** (1.25 mmol), 7.6 mg $\text{PdCl}_2(\text{PPh}_3)_2$ (0.0125 mmol) and 6.6 mg triphenylphosphine (0.025 mmol) in 10 ml DMAc was added a freshly prepared solution of **2** (1.25 mmol) in 10 ml DMAc. The mixture was heated at 120°C for 20 h, when it became heterogeneous. At this stage a TLC check still showed the presence of residual **6a**. Triethylamine (4 ml) was added and heating was continued for a further 10 h. The mixture was cooled to room temperature and poured into methanol, washed extensively with water and methanol and dried to give **7** as a red–brown powder (0.35 g). The compound blackened

on heating to 220°C but did not melt; it is soluble in concentrated sulfuric acid, partly soluble in dichloromethane and insoluble in methanol or acetone. IR (KBr pellet, cm^{-1}): 3080w, 3020w, 2960w, 2925w, 1630s, 1588s, 1490s, 1400s, 1260m, 1210m, 1185m, 1105m, 1070s, 1010s, 955s, 805vs. The as-prepared polymer was hydrolysed by treatment with HCl/isopropanol to give dark red–brown **8** which exhibits physical properties similar to **7**. The compound could not be freed completely of inorganic halide and contained ca. 8% Br together with 3% Cl. IR (KBr pellet, cm^{-1}): 3080w, 3025w, 1668m, 1630m, 1600s, 1490s, 1400m, 1315m, 1280s, 1185m, 1105m, 1070m, 1010m, 955s, 930m, 810vs.

3.7. Coupling reaction of **4** and **2**

A solution of 1.45 g (2.5 mmol) **4**, 2.5 mmol **2** in DMAc, 17.5 mg (0.025 mmol) $\text{PdCl}_2(\text{PPh}_3)_2$ and 13.2 mg (0.05 mmol) PPh_3 in 10 ml DMAc were heated to 165°C for 4 h. A heterogeneous dark red mixture was obtained which was poured into 200 ml acetone. The precipitate was filtered off, washed several times with acetone, water and methanol and dried to give a dark red solid (1.25 g). The compound was hydrolysed by refluxing with 20 ml HCl/isopropanol (1:1) for 2 h to give **5** as a poorly soluble deep red–brown solid. IR (Nujol mull, cm^{-1}): 3080w, 3020w, 1710 (br,sh), 1670s, 1600m, 1280w, 1260w, 1180m, 1110m, 1070m, 1015w, 840m, 820m.

3.8. Coupling reactions of 1,1'-divinylferrocene with organic dihalides

The preparative method is exemplified below for 1,4-diiodobenzene. A mixture of 0.48 g divinylferrocene (2.0 mmol), 0.66 g (2.0 mmol) 1,4-diiodobenzene, 4.5 mg $\text{Pd}(\text{OAc})_2$ (0.002 mmol), 32 mg PPh_3 (0.012 mmol) and 0.7 ml (5.0 mmol) triethylamine in 5 ml DMAc was heated to 120°C for 40 h. A dark red heterogeneous mixture was obtained which was poured into 100 ml methanol. The red precipitate was filtered off, washed extensively with 3 M hydrochloric acid, water and methanol and dried in vacuo to give **10** as a red–orange solid (0.50 g). On heating the compound started to fuse at 170°C and gave a dark brown melt at 240°C. IR (Nujol mull, cm^{-1}): 3080w, 3020w, 1627m, 1588m, 1300w, 1245w, 1110m, 1045m, 1030m, 957s, 810s.

Coupling products with other p-dihalides were prepared similarly.

11: red solid, 0.66 g. IR (Nujol mull, cm^{-1}): 3080m, 3020w, 1630m, 1595m, 1248w, 1385w, 1315w, 1045m, 1030m, 1003m, 960s, 810vs.

12a, beige–orange solid, 0.60 g. IR (Nujol mull, cm^{-1}): 3085w, 3020w, 1630w, 1585s, 1500s, 1240vs,

1200w, 1170m, 1110m, 1045w, 1030w, 1005w, 960m, 875m, 820s.

12b, orange solid, 0.40 g. The physical and spectroscopic properties were essentially identical to **12a**.

13, dark red–brown solid, 0.5 g. IR (Nujol mull, cm^{-1}): 3080m, 1620m, 1580m, 1240m, 1045m, 1025m, 960w, 825s, 795s.

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