Some New and Recent Ferrocene- and Ruthenocene-centred Reagents for n-Type Silicon Surfaces in Photoelectrochemical Use†

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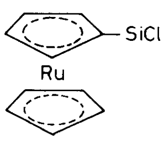
The synthesis and characterisation of trichlorosilylruthenocene (1) and seven ferrocene derivatives, namely bis(1,1′-ferrocenediyl)germane (3), 1,1′-dichloro-2,2′-ferrocenediyldiphenylsilane (4), bis(1,1′-dichloro-2,2′-ferrocenediyl)silane (5), 1,1′-dichloro-2-trichlorosilylferrocene (6), 1-dimethylaminomethyl-2-trichlorosilylferrocene (7), 1,1′-dichloro-2,2′-dicarboxyferrocene (8), and 1,1′-dichloro-2,2′-ferrocenediyldichlorosilane (9), are reported. The derivatisation of n-type silicon electrodes using these materials and 1,1′-dicarboxyruthenocene (2), 1,1′-ferrocenediylphenylphosphine (10), bis(1,1′-ferrocenediyl)silane (11), 1,1′-ferrocenediyldiphenylsilane (12), and 1,1′-dicarboxyferrocene (13) was investigated by cyclic voltammetry. The results showed wide variations in electrode behaviour; none of the systems showed a photoreponse which persisted beyond several hundred cycles.

The attachment of electroactive groups to the surface of electrodes has recently received much attention, and prominent among these investigations have been the studies of Wrighton and co-workers [1,2] on the attachment of ferrocene derivatives to several types of electrode for photovoltaic purposes. Variations of the materials originally used [3] appeared to offer prospects for development of this procedure: the prototype metallocenophane, 1,1′-ferrocenediyldichlorosilane, can be modified by variation of the central metal atom, the cyclopentadienyl ligands, and the linkage group, to effect changes in redox potential and in method of attachment to the electrode surface. If, on an absolute scale, the electrode potential of a solution or surface species falls in the band gap of the semiconductor, then it is capable of undergoing electron transfer to or from the semiconductor. The ferrocene-based surface species have this property. It was of interest to attempt a ruthenocene equivalent and two such compounds were therefore synthesised for derivatisation. Changes in the linkage group were effected by replacing silicon by germanium in ferrocene derivatives and replacing siloxy by carboxy in ferrocene and ruthenocene derivatives. While it might have been preferable to effect only minor structural changes within the group, the limitations of stability have dictated the accessibility of test compounds.

In this paper we report the synthesis of seven new derivatives of ferrocene and one new derivative of ruthenocene for such photovoltaic purposes. These eight compounds, together with five known ferrocene and ruthenocene derivatives, have been attached to n-type silicon semiconductor electrodes and their photoelectrochemical characteristics are reported.

The electrochemistry of the surface species on Pt electrodes could be examined as a separate exercise, but as a survey of the derivatising properties on silicon formed the main aim of the study, and because the stabilities of the materials were often low, it was decided to combine the electrochemical and photovoltaic studies following Wrighton and co-workers.[1–3] The Si electrodes were thus derivatised, and their dark and illuminated responses monitored by cyclic voltammetry. This technique, giving the potential of maximum response, also serves as electrical on-off testing, akin to testing under chopped light.



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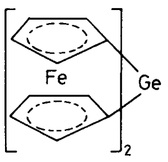

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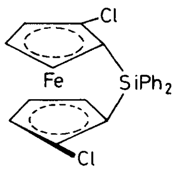

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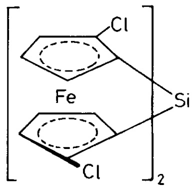

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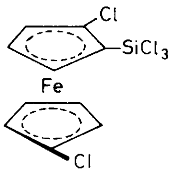

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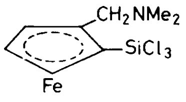

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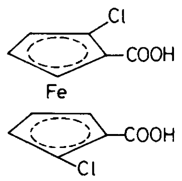

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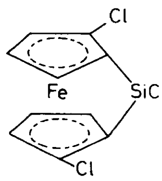

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Results and Discussion

Six new derivatives of ferrocene, compounds (3), (4),* (5),* (6),* (7), and (9) * have been prepared by salt-elimination reactions between lithioferrocene derivatives and halogen compounds of silicon and germanium. Compound (8) * was synthesised by the classical reaction of the corresponding organodilithio-compound with solid carbon dioxide. The known compounds 1,1′-ferrocenediylphenylphosphine (10), bis(1,1′-ferrocenediyl)silane (11), 1,1′-ferrocenediyldiphenylsilane (12), and 1,1′-dicarboxyferrocene (13) were also synthesised and studied. For comparison purposes trichlorosilylruthenocene (1) and 1,1′-dicarboxyruthenocene (2) were synthesised and studied.

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† *Non-S.I. unit employed:* 1 Torr = 101 325/760 Pa.

* Structural isomerism is possible.

Table 1. Hydrogen-1 n.m.r. spectra of some ferrocene and ruthenocene derivatives

	Chemical shifts (multiplicity, relative intensity) [a]			
	Ferrocenyl signals			
Compound	C_5H_5	C_5H_4	C_5H_3	Other signals and assignments
(1)	4.64 (s, 5)	4.75 (t, 2), 4.87 (t, 2)		
(3)		4.68 (t, 4), 4.74 (t, 1)		
(4)			3.79 (m, 2), 4.74 (t, 1)	7.28—7.58 (m, 3; *m*- and *p*-C_6H_5), 8.11—8.21 (m, 2; *o*-C_6H_5)
(5)			4.01 (t, 1), 4.79 (t, 1), 4.87 (t, 1)	
(6)		4.12 (t, 2), 4.41 (t, 2)	4.25 (m, 1), 4.56 (m, 1), 4.78 (m, 1)	
(7)	4.17 (s, 5)		4.40 (m, 3)	[3.79, 3.66, 2.95, 2.82] (q, 2; CH_2), 2.07 [s, 6; $N(CH_3)_2$]
(8) [b]			4.43 (m, 1), 4.80 (m, 1), 5.10 (m, 1)	12.64 [c] (br, 1; COOH)
(9)			3.77 (m, 1), 4.83 (t, 2)	

[a] δ(p.p.m.), δ($SiMe_4$) = 0; $CDCl_3$ solutions unless otherwise indicated; s = singlet, t = unsymmetrical triplet, m = multiplet, br = broad, q = AB quartet. [b] C_5D_5N solution. [c] Disappears on addition of D_2O.

For tetrasubstituted ferrocenes carrying two different substituents on each ring, the possibility of structural isomerism arises. Thus isomerism is possible for all of the disubstituted derivatives of 1,1′-dichloroferrocene described here [(4), (5), (8), and (9)]. We have no evidence as to whether or not the compounds as prepared are isomeric mixtures. Assuming the free rotation of the cyclopentadienyl rings it is not expected that the structural isomerism would significantly alter the reactivity towards attachment to the electrode surface.

Most of the compounds described in this paper are, by design, extremely reactive, and moisture sensitive, particularly the compounds containing Si–Cl bonds. Because of this reactivity, difficulty was experienced in obtaining reliable microanalytical results for some compounds, and characterisation was therefore best achieved by means of mass spectral results and ^1H n.m.r. spectra related to less reactive analogous compounds.

The ^1H n.m.r. spectra of the eight new compounds are detailed in Table 1. The results are in agreement with the assigned structures and are similar to published examples of analogous compounds. In the mass spectra the compounds all show molecular ions, often as the most abundant species, and always with good agreement of the isotope pattern with theory, Figure 1.

After hydroxylation of the silicon surface the attachment of the organometallic species to the electrode was effected by one of three methods. For compounds containing Si–Cl bonds [(1), (6), (7), and (9)], a hydrolytic reaction was employed, involving the surface hydroxyl groups and the chlorosilane moieties with the concomitant formation of a siloxane-type link to the surface. The carboxylate derivatives (2), (8), and (13) were attached by an esterification reaction with the surface hydroxy groups in the presence of dicyclohexylcarbodiimide. For the [1]ferrocenophanes [(3)—(5) and (9)—(12)], the ring-opening process established by Wrighton [1] was employed for the surface bonding. Following derivatisation the electrodes were washed and monitored by cyclic voltammetry, in the dark and under tungsten lamp illumination.

The photoexcitation of silicon produces an excess of conduction band (cb) electrons, and holes (h) in the valence band (vb): $Si \xrightarrow{h\nu} e_{Si,cb} + h_{Si,vb}$. In a simplified view, the role of the derivatising agent is to obviate the oxidation, by the holes, of surface silicon, in the presence of trace amounts of water, and at a positive applied potential. The stoicheiometry is *e.g.* $Fe^{II} + h \longrightarrow Fe^{III}$. In the presence of redox electrolyte, Fe^{III} would be reduced, and in the cells employed, the reduction process $Fe^{III} + e \longrightarrow Fe^{II}$ was effected by the applied potential. (In a solar-cell operation, biassing to the operational potentials would be achieved by an appropriate counter electrode–electrolyte system, for steady photocurrent.) A major role of the inert electrolyte is to supply counter ions for surface electroneutrality, the currents being diffusion controlled.[3] In no experiments did the integrated current–time plot provide coulometric evidence of an even monolayer derivatising agent; observed traces implied 10% or less coverage.

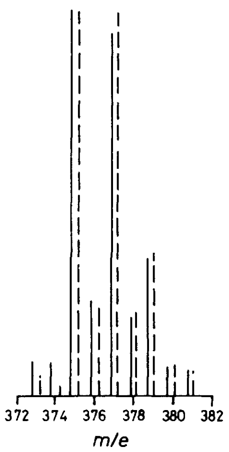

Figure 1. Theoretical (- - -) and observed (——) isotopic abundance of the molecular ion of (7)

However, that attachment had occurred was borne out by the observation of anodic and cathodic photocurrents, only the former being (feebly) observed on naked silicon due to the barrier to silicon oxide reduction.

Derivatised electrodes exhibited a wide range of responses in the dark and under illumination (Table 2 and Figures 2—4). Several gave no voltammetric response in either case [(3)—(5)] implying insulation of the surface; virtually identical traces for dark and light scans were observed for (1) (Figure 2) and (10); (6) and (12) showed only rather weak photocurrents which decayed rapidly in successive cycles. Several electrodes [(2), (8), and (9)] were tested under higher levels of illumination (0.4—1.0 W cm^{-2}) but here too, the photocurrents for (2) and (8) were relatively small and did not persist.

The compounds of principal interest are therefore: one which yielded a relatively large initial photocurrent but which decayed rapidly, (9) (Figure 3); those which gave small but

Table 2. Photoelectrochemical responses of silicon electrodes treated with various derivatising compounds [a]

Compound	Treatment time/h [b]	Dark scan [c]		Illuminated scan [c,d]		Comments
		E_P/V	i_P/μA	E_P/V	i_P/μA	
(1)	16 18 **70**	(−0.3)	(30)	No change		i_p decreases by 20% in 7 cycles
(2)	15		0	0.36 (−0.16)	3 (1)	Flat peaks; illuminated i_p decays by 90% in 7 cycles (scanned at 160 mV s^{-1}; ~0.6 W cm^{-2})
(6)	1				<1	i_p zero in 10 cycles. Flattened peak
(7)	0.5 **2**		0	0.38 (0.28)	6.4 (3.8)	Sharp peaks; i_p decays only 6% in 10 cycles
(8)	48	0.56	3.5	0.34 (−0.06)	4.5 (0.5)	Sharp peaks; illuminated i_p decays only 6% in 15 cycles (scanned at 160 mV s^{-1}; ~0.6 W cm^{-2})
(9)	3.5 **21** [e] 40	0.02 (0.02)	1 (2)	0.43 (0.05)	130 (14)	Smoothly incremental dark limb. Illuminated decays by 97% in 5 cycles (100 mV s^{-1} and ~0.6 W cm^{-2})
(10)	15		5	No change		Flattened peaks in dark decay to 10% in 3 cycles
(11)	120	0.93 (0.10)	40 (11)	0.9 (0.1)	70 (11)	Dark i_p decays by 30% in 7 cycles, illuminated i_p by 50% in 7 cycles
(12)	10		0		~1	Flat peak decays to 10% in 2 cycles
(13)	1.5 **2** [e] 170	As Figure 4		(0.19)	(35)	Incremental anodic limb. Illuminated i_p decays by 40% in 15 cycles (100 mV s^{-1})

[a] Compounds (3), (4), and (5) showed no voltammetric response in dark or light. [b] Times in bold type are for best electrode, to which i_p and E_p data refer. [c] Parenthesised value is for reverse, cathodic direction *vs.* s.c.e. (saturated calomel electrode); subscripts p indicate peak. [d] Illuminated at 12.5 mW cm^{-2} unless otherwise stated. [e] Increased derivatisation times give larger but less well defined peaks.

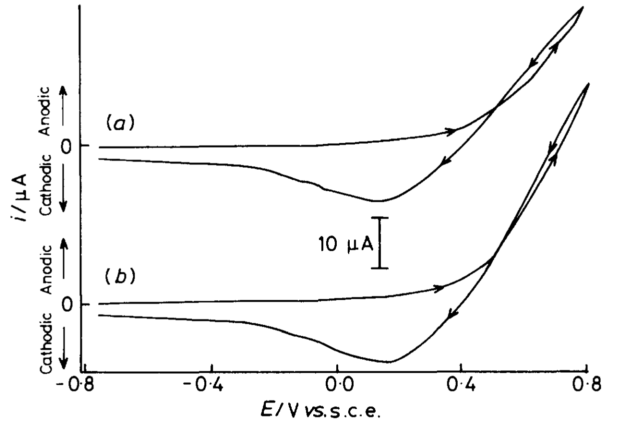

Figure 2. Cyclic voltammograms of n-type Si derivatised with (1); (*a*) in the dark and (*b*) with illumination of 12.5 mW cm^{-2}

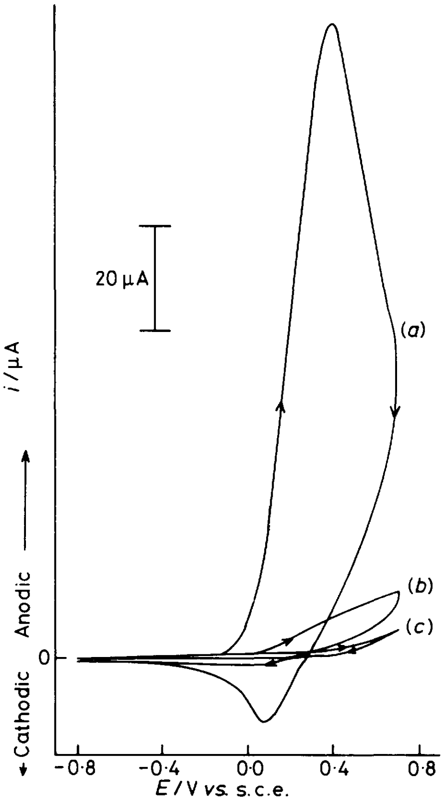

Figure 3. Cyclic voltammograms of n-type Si derivatised with (9); (*c*) in the dark and with illumination of 1 W cm^{-2} where (*a*) is the first such cycle and (*b*) is the fifth

fairly stable traces, (7) and (13) (Figure 4); and one which showed relatively high photocurrents and stability, (11). For these four compounds the positions of the reduction peak varied from +0.05 to +0.28 V, whilst those of their oxidation peaks varied more widely, +0.22 to +0.90 V. This variation possibly reflects different coverages by SiO_2 resulting from photodecomposition at unprotected sites on the surface. This is borne out by the observation that on the return (cathodic) scan of several voltammograms (*e.g.* as in Figure 2) the current trace crosses over the anodic trace, an unlikely phenomenon unless the intrinsic nature of the electrode surface is undergoing transformation during the voltammetric scan.

The stability conferred by these derivatisation materials on the silicon electrodes was impermanent; the most stable of the electrodes gave photocurrents decaying to about 10% of the initial within several hundred scans. The mechanisms of decomposition are at present speculative: (*i*) decomposition by loss of metal atom on photoexcitation, (*ii*) failure kinetically of the derivatising agent to compete for the holes with silicon and water, thus leading to SiO_2 formation, and (*iii*) rupturing

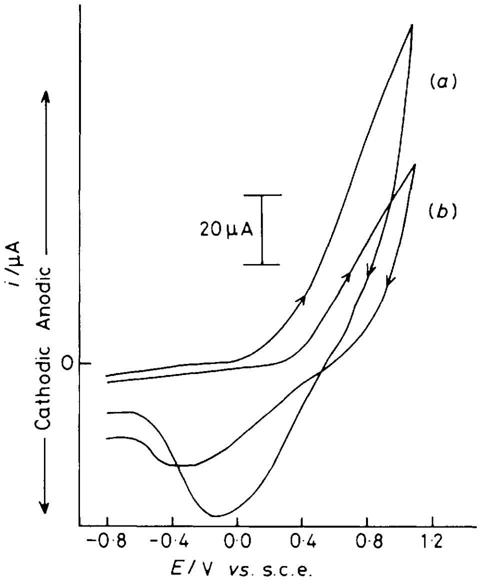

Figure 4. Cyclic voltammograms of n-type Si derivatised with (13) with illumination of 12.5 mW cm^{-2}; the (*a*) and (*b*) traces represent cycles 20 and 35 respectively

of the linkage to the surface by photochemical hole reaction; such possibilities could be investigated by ESCA, SIMS, and kindred surface probes. Thus it has not hitherto proved possible to improve on the performance of electrodes derivatised with 1,1′-ferrocenediyldichlorosilane, the prototype derivatising material. Although n-type silicon electrodes derivatised with (7), (9), (11), or (13) gave significantly more stable waves than naked silicon under the same experimental conditions, the protection afforded is transient, as indicated by the eventual decay of the photocurrents in every case.

Experimental

Hydrogen-1 n.m.r. spectra were recorded at 100 MHz and 60 MHz using JEOL MH100 and Perkin-Elmer R600 spectrometers respectively. Mass spectra were recorded on a V.G. Micromass 16F instrument and *m*/*e* values quoted are for the most intense peak in the molecular ion pattern. Melting points were measured using an Electrothermal apparatus and are corrected. Analyses were performed by the Exeter University departmental service or by Butterworth Laboratories, Teddington, Middlesex. All solvents were dried and degassed before use and all reactions were carried out under purified nitrogen.

The *NNN′N′*-tetramethylethylenediamine bis adduct of 1,1′-dilithioferrocene,[4,5] dimethylaminomethylferrocene,[6] 1,1′-dicarboxyruthenocene (2),[7] 1,1′-ferrocenediylphenylphosphine (10),[5] bis(1,1′-ferrocenediyl)silane (11),[5] 1,1′-ferrocenediyldiphenylsilane (12),[5] and 1,1′-dicarboxyferrocene (13) [7] were prepared by literature methods.

Preparations.—Trichlorosilylruthenocene (1). *NNN′N′*-Tetramethylethylenediamine (tmen) (0.58 g, 5 mmol) and n-butyl-lithium (5 mmol) were added to a stirred solution of ruthenocene (0.46 g, 2 mmol) in n-hexane (10 cm^3). After stirring for 18 h, cooling to −10 °C, removal of supernatant liquid, and washing by decantation with hexane (10 cm^3), hexane (10 cm^3) and tetrachlorosilane (2.0 g, 8 mmol) were added and the mixture stirred for a further 16 h. The residue, after solvent removal under vacuum, gave on fractional sublimation, first ruthenocene (65 °C, 0.05 Torr) then trichlorosilylruthenocene (130 °C, 0.05 Torr) as pale yellow crystals (Found: C, 33.60; H, 3.05. $C_{10}H_9Cl_3RuSi$ requires C, 32.95; H, 2.50%. Mass spectrum, found: M^+, 366; calc. 366).

Bis(1,1′-*ferrocenediyl*)*germane* (3). To a cooled (−78 °C) slurry of the *NNN′N′*-tetramethylethylenediamine bis adduct of 1,1′-dilithioferrocene in hexane (100 cm^3) [prepared from ferrocene (4.65 g, 25 mmol), n-butyl-lithium (62.5 mmol), and tmen (7.25 g, 62.5 mmol)], tetrachlorogermane (1.87 g, 8.7 mmol) in hexane (50 cm^3) was added dropwise with stirring. The resulting red solution was stirred at room temperature for a further 2 h and filtered before solvent removal under reduced pressure. The residue was dissolved in the minimum of benzene, an equal volume of hexane was added, and after 15 h at −20 °C, deep red crystals formed. These were filtered off and washed with hexane (3 × 10 cm^3). Further purification was frustrated by decomposition of the compound in solution. [M.p. >205 °C (decomp.). Found: C, 53.25; H, 3.90. $C_{20}H_{16}Fe_2Ge$ requires C, 54.55; H, 3.65%. Mass spectrum, found: M^+, 442; calc. 442].

1,1′-*Dichloro*-2,2′-*ferrocenediyldiphenylsilane* (4). A solution of 1,1′-dichloroferrocene (1.02 g, 4 mmol) in hexane (20 cm^3) was treated with n-butyl-lithium (10 mmol) and tmen (1.16 g, 10 mmol) and stirred for 90 min. Dichlorodiphenylsilane (2.53 g, 10 mmol) was added to the stirred suspension and cooled to −78 °C; the mixture was stirred at 20 °C for a further 2 h. The crude product from filtration and vacuum drying was subjected to dry-column chromatography on Grade 2 alumina. Elution with hexane yielded a little 1,1′-dichloroferrocene, followed by a separate red band containing the product, which was recrystallised from hexane as orange-red needles. [M.p. 217—218 °C. Found C, 60.25; H, 3.75. $C_{22}H_{16}Cl_2FeSi$ requires C, 60.70; H, 3.70%. Mass spectrum, found: M^+, 434; calc. 434.]

Bis(1,1′-*dichloro*-2,2′-*ferrocenediyl*)*silane* (5). 1,1′-Dichloroferrocene (1.02 g, 4 mmol) was treated with n-butyllithium and tmen as in the synthesis of (4), then tetrachlorosilane (0.34 g, 2 mmol) in hexane (10 cm^3) was added slowly with stirring. The mixture was filtered, the residue extracted with cold hexane (4 × 20 cm^3), and the crude product from solvent removal from the combined extracts was subjected to dry-column chromatography on Grade 2 alumina. Elution with hexane yielded a little 1,1′-dichloroferrocene, followed by an orange-red band containing the product, which was recrystallised from benzene as orange-red plates. [M.p. 150—160 °C (decomp.). Found: C, 44.65; H, 2.90. $C_{20}H_{14}Cl_4Fe_2Si$ requires C, 44.50; H, 2.25%. Mass spectrum, found: M^+, 534; calc. 534.]

1,1′-*Dichloro*-2-*trichlorosilylferrocene* (6).—1,1′-Dichloroferrocene (1.02 g, 4 mmol) and n-butyl-lithium (4.9 mmol) in tetrahydrofuran (15 cm^3) were stirred for 1 h, then added over several hours to an excess of tetrachlorosilane (2.0 g, 8 mmol) and stirred for a further 3 h. Fractional sublimation of the residue from vacuum treatment yielded 1,1′-dichloroferrocene (30 °C, 0.05 Torr) and then the product (100 °C, 0.05 Torr), as a yellow microcrystalline solid. The high reactivity of the solid impaired microanalytical results, and the compound was characterised by its ^{1}H n.m.r. spectrum and mass spectrum (found: M^+, 388; calc. 388.)

1-*Dimethylaminomethyl*-2-*trichlorosilylferrocene* (7). 1-Dimethylaminomethyl-2-lithio-ferrocene was prepared [8] from n-butyl-lithium (5.5 mmol) and dimethylaminomethylferrocene (1.22 g, 5 mmol) in diethyl ether (10 cm^3) by stirring for 3 h. Excess tetrachlorosilane (3.4 g, 20 mmol) was added to the cooled (−78 °C) solution, which was then stirred for 16 h at 20 °C before exposure to vacuum. The resulting dark red liquid was distilled (120 °C, 0.05 Torr) but we could not completely separate the product and starting material. The product was identified from its ^{1}H n.m.r. spectrum and mass spectrum (found: M^+, 375; calc. 375).

1,1′-*Dichloro*-2,2′-*dicarboxyferrocene* (8). 1,1′-Dichloroferrocene (1.02 g, 4 mmol) was treated with n-butyl-lithium and tmen as in the synthesis of (4). The resulting suspension was added to crushed solid carbon dioxide and allowed to reach 20 °C. The solution in water (150 cm^3) was extracted with hexane (3×50 cm^3) to remove unreacted 1,1′-dichloroferrocene. The product was precipitated with dilute hydrochloric acid and filtered off, washed with dilute hydrochloric acid and acetone, and dried (60 °C, 3 h). [M.p. >230 °C (decomp.). Found: C, 42.05; H, 2.25. $C_{12}H_8Cl_2FeO_4$ requires C, 42.05; H, 2.35%. Mass spectrum, found: M^+, 342; calc. 342.]

1,1′-*Dichloro*-2,2′-*ferrocenediyldichlorosilane* (9). 1,1′-Dichloroferrocene (1.02 g, 4 mmol) was treated with n-butyl-lithium and tmen as in the synthesis of (4). The resulting suspension was added slowly (1 h) with stirring to tetrachlorosilane (6.8 g, 40 mmol) and left for a further hour. The dark red residue remaining after removal of the solvent *in vacuo* was fractionally sublimed to yield 1,1′-dichloroferrocene (35 °C, 0.05 Torr) and the product (150 °C, 0.05 Torr) as deep red block crystals. High reactivity impaired mircroanalysis and the material was characterised by its ^{1}H n.m.r. spectrum and mass spectrum (found: M^+, 352; calc. 352).

Derivatisation of Electrodes and Electrochemical Studies.— Monsanto single-crystal silicon wafer [(100) face, 0.36 mm thick, in 0.4 cm^2 pieces] was used as an electrode, with copper wire leads attached to the back face by means of Ga–In eutectic and silver paint. The sliver of silicon was mounted on glass tubing using epoxy resin. Pretreatment consisted of etching in HF for 10 s, immersion in 10 mol dm^{-3} sodium hydroxide solution for 1 min, washing with water for 1 min, washing with acetone for 10 s, and air-drying for 15 min. Surface coating was effected by immersion for 1 h to 14 d in 10^{-2} mol dm^{-3} solutions of derivatising agent, usually in hexane. The times in bold type in Table 2 for the derivatisation procedures are those which were found to give the most marked effects as noted in the series of experiments performed. Other, for example, greatly prolonged, times might result in better response, as might changes in other derivatisation conditions, *e.g.* solvent, temperature, *etc.* For the dicarboxylic acids, dry acetonitrile with 10^{-2} mol dm^{-3} dicyclohexylcarbodiimide added was used. The derivatised electrodes were washed with the solvent and air-dried. All derivatising agents were shown to be sufficiently stable in the n.m.r. measurements to persist throughout the derivatisation procedure.

Cyclic voltammetry was conducted under N_2 at 298 K using acetonitrile containing 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$ as supporting electrolyte, with illumination from a tungsten-halogen lamp giving 12.5 mW cm^{-2} at the electrode surface. In a few cases a higher power density (0.4—1.0 W cm^{-2}) was used. Voltammograms were obtained using Bruker E310 or E44S Polarographs at a scan rate of 50 mV s^{-1}, unless stated otherwise.

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