

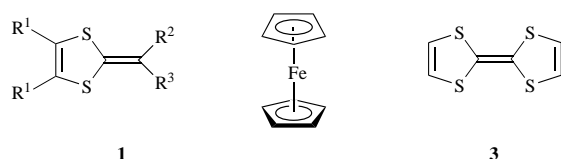
# 1,4-Dithiafulvene-substituted ferrocenes and their conversion into extended tetrathiafulvalene electron donors: synthetic, electrochemical and X-ray structural studies

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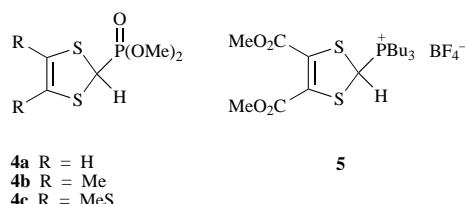
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The synthesis of 1,4-dithiafulvene-substituted ferrocene derivatives **7**, **11** and **12** by reaction of formyl-, diformyl- and diacetyl-ferrocene, respectively, with the carbanion generated from reagents **4a–c** and the ylide prepared from reagent **5** is reported. Upon reaction with HCl–diethyl ether, compounds **7a–c** undergo an oxidative dimerisation to yield extended tetrathiafulvalene (TTF) derivatives **8a–c**. The solution electrochemistry of compounds **7**, **8**, **11**, **12**, **14** and **16** has been studied by cyclic voltammetry. The X-ray crystal structures of compounds **8b** and **12a** are presented.

Derivatives of 1,4-dithiafulvene **1** and ferrocene **2** are well-established as building blocks of prime importance in the synthesis of organic and organometallic materials which possess unusual solid-state properties. In this context, the key feature of both systems **1** and **2** is their ability to act as electron donors and thereby to form stable charge-transfer complexes and radical ion salts with a wide range of organic and inorganic acceptor species. For example, 1,4-dithiafulvene derivatives, including tetrathiafulvalenes **3**,<sup>3</sup> are components of crystalline molecular conductors,<sup>4,5</sup> semiconducting Langmuir–Blodgett films,<sup>6,7</sup> electroactive polymers<sup>8</sup> including low bandgap materials,<sup>8c</sup> potential organic ferromagnets,<sup>8b,9</sup> cation sensors<sup>1</sup> and molecular switches.<sup>10</sup> Ferrocene derivatives are components of molecular wires<sup>11</sup> and anion sensors,<sup>12</sup> and decamethylferrocene–tetracyanoethylene (TCNE) complex is famous as a ferromagnet.<sup>13</sup>



**1**  
R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = a wide range of substituents, e.g. alkyl, alkylthio, aryl



It was of interest, therefore, to explore the synthesis and properties of compounds comprising covalently-linked 1,4-dithiafulvene **1** and ferrocene **2** moieties. The synthetic approach we have adopted stems from the work of Akiba *et al.* who established that benzo-1,4-dithiafulvenes could be obtained by reaction of benzo-1,3-dithiole Wittig reagents with aldehydes and ketones.<sup>14</sup> More recently, we,<sup>5c,15</sup> and others,<sup>5a,b,7b,8b,9</sup> have made extensive use of analogous 1,3-dithiole reagents to synthesise new 1,4-dithiafulvenes. In this paper we describe: (i) the application of this methodology to

the synthesis of ferrocene derivatives **7**, **11** and **12**;<sup>16</sup> (ii) the facile conversion of compounds **7a–c** into the extended TTF systems **8a–c**; (iii) electrochemical data for all the new compounds; and (iv) X-ray crystallographic studies on compounds **8b** and **12a**.

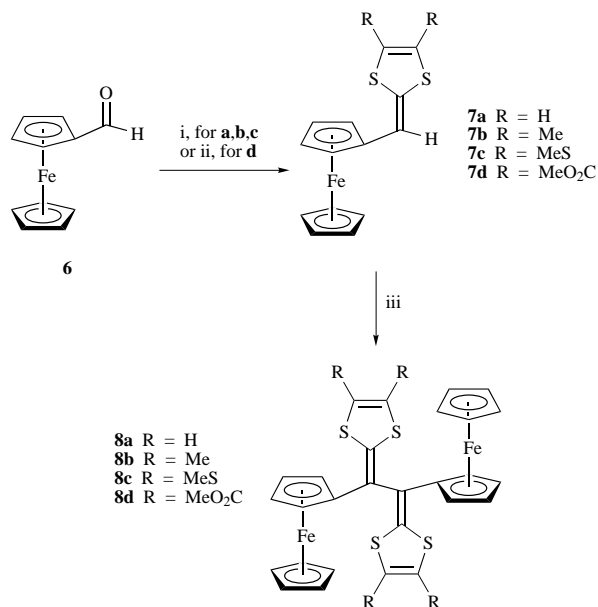
## Results and discussion

### Synthesis

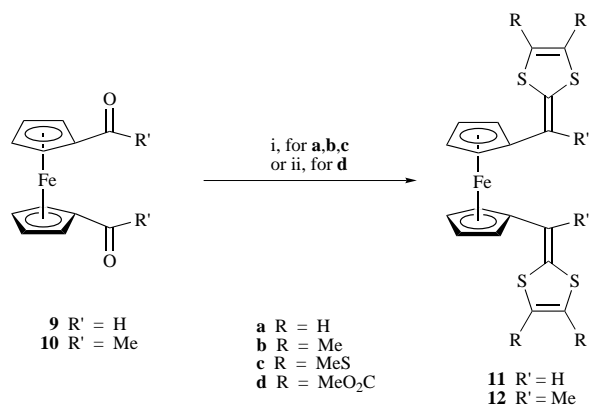
Deprotonation of phosphonate esters **4a**,<sup>15</sup> **4b**<sup>14,15</sup> or **4c**<sup>17</sup> (butyllithium at –78 °C in dry tetrahydrofuran) followed by the addition of formylferrocene **6**, 1,1'-diformylferrocene **9**<sup>18</sup> or 1,1'-diacetylferrocene **10** yielded products **7**, **11** or **12**, respectively, which were isolated, after purification, as air-stable crystalline solids (compound **12c** is an oil) in 58–81% yields (Schemes 1 and 2). The analogous compounds **7d** and **11d** bearing methoxycarbonyl substituents were prepared from phosphonium salt **5**<sup>19</sup> and either compound **6** or **9**, in the presence of triethylamine at 20 °C (69–88% yields). It is notable that reaction of compound **10** with phosphonium salt **5** under similar conditions lead only to the recovery of unchanged starting reagent **10**. The structure of **12a** was confirmed by X-ray crystallography (see below).<sup>16</sup>

Formylation of compounds **7b** and **11b** using the methodology employed by Misaki *et al.*<sup>20</sup> for the Vilsmeier formylation of 1,4-dithiafulvenes (*viz.* reaction with Me<sub>2</sub>N<sup>+</sup>=CHCl Cl<sup>–</sup>, formed from the reaction of oxalyl chloride with *N,N*-dimethylformamide, followed by alkaline hydrolysis) gave cleanly compounds **13** and **15** (86 and 71% yields, respectively) (Schemes 3 and 4). Subsequent reaction of compounds **13** and **15** in a Wittig–Horner-type reaction with phosphonate ester **4b** in basic medium afforded compounds **14** and **16** (78 and 66% yields, respectively).

During routine NMR analysis of compounds **7a–c** it was found that the CDCl<sub>3</sub> solution darkened on standing and TLC and <sup>1</sup>H NMR spectral evidence showed that another compound was being formed in solution. In particular, the vinyl proton of **7a–c** at *ca.* 6.1 ppm disappeared, and for **7b** clear changes were seen in the methyl signals: the two singlets at 1.96 and 1.91 ppm were replaced by singlets at 2.02 and 1.94 ppm. The new products **8a–c** were isolated by preparative TLC and were identified initially from mass spectrometric data (which were consistent with a dimer of **7** less two hydrogen atoms) and their <sup>1</sup>H and <sup>13</sup>C NMR spectra. Subsequently, structure **8b** was confirmed by X-ray crystallography (see below). To demonstrate that this

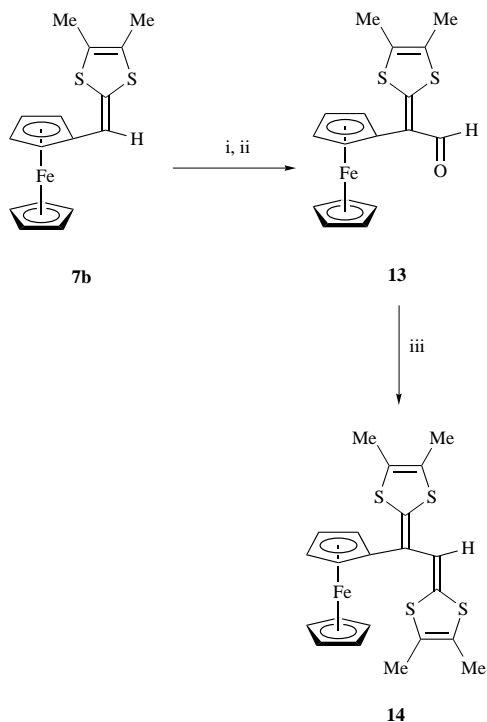


**Scheme 1** Reagents and conditions: i, **4**, Bu<sup>n</sup>Li, THF, -78 °C, 0.5 h; then **6**, -78 to 20 °C, 16 h; ii, **5**, THF, Et<sub>3</sub>N, 20 °C, 16 h; iii, HCl·Et<sub>2</sub>O, Et<sub>2</sub>O, 24 h (96 h for **7c**)

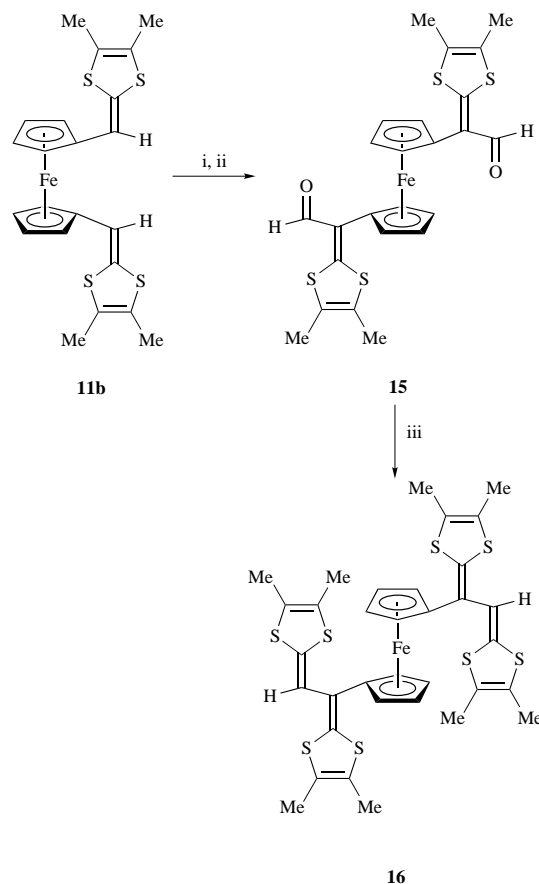


**Scheme 2** Reagents and conditions: i, **4**, Bu<sup>n</sup>Li, THF, -78 °C, 0.5 h; then either **9** or **10**, -78 to 20 °C, 16 h; ii, **5**, THF, Et<sub>3</sub>N, 20 °C, 16 h

reaction was linked to the acidity of the solvent medium, we prepared 0.1 mmol solutions of compound **7b** in: (i) commercial chloroform (Prolabo, technical grade, weakly acidic); (ii) anhydrous diethyl ether with addition of HCl (1 M solution in anhydrous diethyl ether, acidic); (iii) anhydrous diethyl ether (neutral); and (iv) chloroform, filtered through basic alumina followed by the addition of two drops of pyridine (weakly basic). In cases (iii) and (iv) we observed no formation of compound **8b** on standing for 7 days (TLC evidence), whereas in cases (i) and (ii), the conversion of compounds **7a-c** to **8a-c** was essentially complete after 24 h (96 h for **7c**). A preparative scale synthesis of compounds **8a-c** was achieved by reaction of an anhydrous ethereal solution of compounds **7a-c** with 1 M HCl (solution in anhydrous diethyl ether) at room temperature leading to the formation of a dark solution from which compounds **8a-c** were readily isolated in 75–84% yields (Scheme 1). Compound **7d** showed no indication of undergoing reaction to afford compound **8d** under these conditions, even on standing for 8 weeks at room temperature. Unlike other reactions involving the interaction of 1,4-dithiafulvene derivatives with acid, which lead to isomerisation of the protonated derivative,<sup>21</sup> in the present system we propose an oxidative role for the acid<sup>22</sup> facilitated by the low oxidation potential of compounds **7a-c** (see below). Semi-empirical ZYMD01 calculations on compound **7b** show that the ferrocenyl and dithiafulvenyl groups both have large atomic orbital coefficients in the HOMO



**Scheme 3** Reagents and conditions: i, ClC(O)C(O)Cl, DMF, 20 °C, 0.25 h, then **7b**, 16 h; ii, 2 M NaOH; iii, **4b**, Bu<sup>n</sup>Li, THF, -78 °C, 0.5 h, then **13**, -78 to 20 °C, 16 h

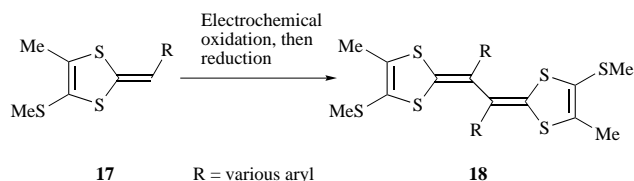


**Scheme 4** Reagents and conditions: i, ClC(O)C(O)Cl, DMF, 20 °C, 0.25 h, then **11b**, 16 h; ii, 2 M NaOH; iii, **4b**, Bu<sup>n</sup>Li, THF, -78 °C, 0.5 h, then **15**, -78 to 20 °C, 16 h

indicative of a highly delocalised system involving significant interaction between the 1,4-dithiafulvene rings and ferrocene.<sup>23</sup>

The intermolecular oxidative dimerisation of 1,4-dithiafulvenes to yield the dication of the corresponding extended

TTF system has been reported previously for a few derivatives,<sup>24</sup> and a similar process is thought to occur in the electrochemical polymerisation of a tris(1,4-dithiafulvene) derivative.<sup>8b</sup> Whilst the present work was in progress, Lorcy and co-workers, reported the isolation of neutral species **18** from monomer units **17**, by a two-step electrochemical synthesis (an oxidation followed by a reduction) and concluded that the reaction involved dimerisation of the cation radical of **17** (Scheme 5).<sup>25</sup> In our hands, such an electrochemical protocol undertaken

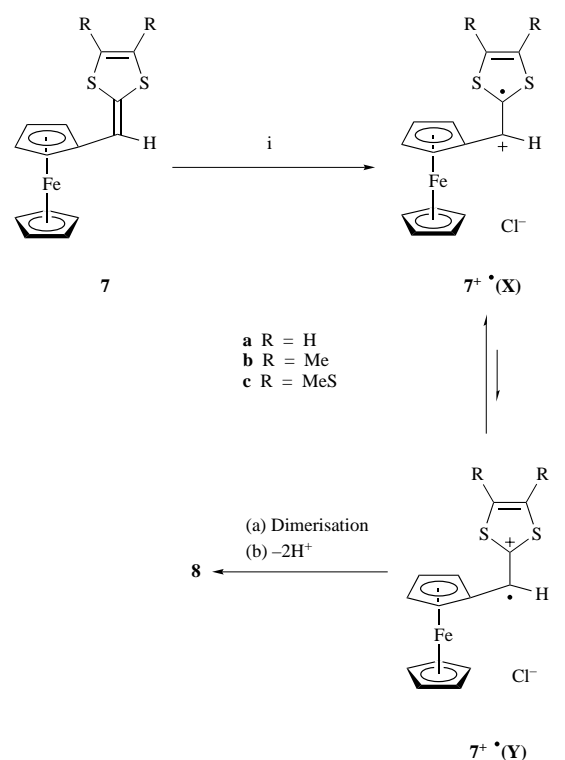


**Scheme 5** Electrochemical oxidative dimerisation of **17**

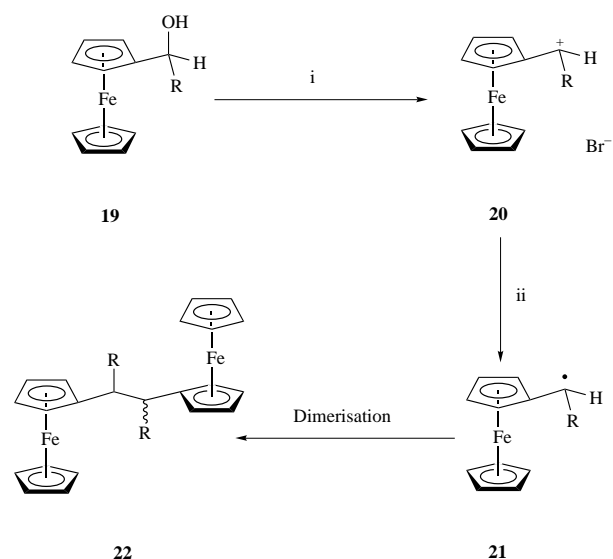
for compound **7b** after either the first, or the second, oxidation potential, did afford compound **8b**; however, yields were low (typically 15–25%) and many other uncharacterised by-products were formed rendering isolation of the product a time-consuming task. Furthermore, standard literature chemical oxidations [e.g. tris(4-bromophenyl)ammonium hexachloroantimonate<sup>24d,e</sup> and 2,3-dichloro-4,5-dicyano-1,4-benzoquinone<sup>24a,f</sup>] lead to decomposition of the starting reagent. It is notable that in contrast to the derivatives studied by, for example, Schöberl *et al.*<sup>24d</sup> and Lorcy and co-workers,<sup>25</sup> the oxidative dimerisation of ferrocene systems **7a–c** was not observed during cyclic voltammetry: on repeated cycling of the voltammogram of compounds **7a–c** there was no marked change in the trace (even at 20 mV s<sup>-1</sup> scan rates) and no evidence was obtained for the formation of compounds **8a–c** (compounds **7a–c** exhibit a two-step redox system, whereas compounds **8a–c** have a distinctive four-step redox system, see below). These observations are consistent with a slow chemical reaction following the initial electrochemical oxidation. We suggest that this is due to the ferrocenyl substituent of compounds **7a–c** increasing the stability of the derived cation radicals [two possibilities are **7<sup>+</sup>(X)** and **7<sup>+</sup>(Y)** (Scheme 6)] to the extent that they are significantly more stable than anticipated. It is known<sup>26</sup> that  $\alpha$ -ferrocenylcarbonium cations **20** are unusually stable (many stable salts of these cations have been isolated) and it is plausible that on oxidation, cation radical **7<sup>+</sup>(X)** predominates over cation radical **7<sup>+</sup>(Y)** thereby precluding rapid dimerisation (Scheme 6). It is to be expected that **7<sup>+</sup>(X)** will not react under the above conditions based on a wealth of TTF and 1,3-dithiole literature<sup>3</sup> in which there is no evidence for intermolecular dimerisation of radicals or radical cations of type **7<sup>+</sup>(X)** (ferrocenyl = any substituent). Analogous reactions of compounds **11a–c** in the presence of HCl lead to a complex mixture in which neither inter- nor intra-molecular dimerisation products were detected. It is noteworthy that Cais and Eisenstadt<sup>27</sup> have demonstrated that under suitable conditions, reductive dimerisation of ferrocenylcarbonium cations **20** (prepared *in situ* from the respective alcohol **19**) proceeding *via* a ferrocenylmethyl radical **21** is a general reaction leading to compounds of the type **22** (Scheme 7).

#### Electrochemical studies

The redox chemistry of compounds **7**, **8**, **11**, **12**, **14** and **16** has been studied by cyclic voltammetry and the data are collated in Table 1. Compounds **7** exhibit two reversible one-electron oxidations and compounds **8** exhibit four reversible one-electron oxidations (Figs. 1 and 2, respectively, for compounds **7b** and **8b**). Compounds **11** and **12** exhibit two reversible one-electron oxidations if the potential is limited to 1.0 V (1.2 V for **11d**); oxidation to the trication occurs between 1.1 and 1.2 V (1.5 V for **11d**) and is scan rate dependant and irreversible (even at



**Scheme 6** Reagents and conditions: i, HCl·Et<sub>2</sub>O, Et<sub>2</sub>O, 24 h (96 h for **7c**), 20 °C



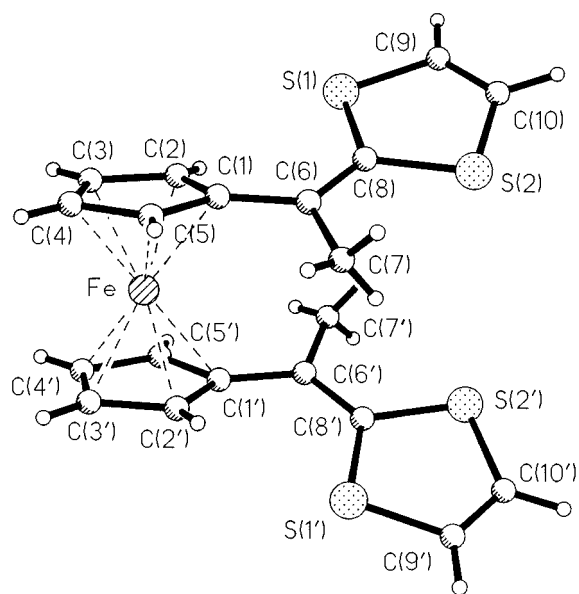
**Scheme 7** Reagents and conditions: i, HBr, HOAc, 5 min; ii, Zn, 12 h

0 °C and in the presence of active Al<sub>2</sub>O<sub>3</sub>) and it appears that a chemical reaction occurs, with a large number of unassignable peaks appearing in the reductive cycle. Compound **14** exhibits three reversible one-electron oxidations (Fig. 3) and compound **16** shows three reversible one-electron oxidation waves and a broad oxidation wave corresponding to the transfer of two electrons. In all cases, the first oxidation is observed at low potential which is consistent with a highly delocalised  $\pi$ -electron system, as observed previously when  $\pi$ -conjugation of 1,3-dithiol-2-ylidene derivatives is extended.<sup>1,17,25</sup> A non-conjugated 1,3-dithiol-2-ylidene is typically oxidised to the cation radical at between  $E^{\text{ox}} + 0.9$  and + 1.4 V, depending on the substituents present.

#### X-Ray crystal structures of compounds **8b** and **12a**

The asymmetric unit of **8b** comprises a half of the title molecule (Fig. 4) situated on a crystallographic two-fold axis [pass-





**Fig. 5** Molecular structure of **12a**, primed atoms are symmetrically dependent *via* two-fold axis. Bond distances (Å): Fe–C(1) 2.073(5), Fe–C(2) 2.049(7), Fe–C(3) 2.042(8), Fe–C(4) 2.049(5), Fe–C(5) 2.046(4), Fe–Cp(plane) 1.653, C(1)–C(6) 1.463(6), C(6)–C(8) 1.356(7), C(8)–S(1) 1.760(6), C(8)–S(2) 1.770(4), S(1)–C(9) 1.744(7), S(2)–C(10) 1.723(10), C(9)–C(10) 1.307(12).

reported analogues, the oxidative dimerisation was not observed during cyclic voltammetry, which suggests that the mechanism of the dimerisation is strongly influenced by the ferrocenyl substituents stabilising an intermediate radical cation. These severely-distorted extended TTFs are easily oxidised to multi-cationic species.

## Experimental

### General methods

$^1\text{H}$  NMR spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz.  $^{13}\text{C}$  NMR spectra were obtained on a Varian VXR400S spectrometer operating at 100.581 MHz.  $J$  Values are given in Hz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. Infrared spectra were recorded on a Perkin-Elmer 1615 FTIR operated from a Grams Analyst 1600. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures. All column chromatography was performed using silica gel (70–230 mesh) and distilled solvents.

Cyclic voltammetric data were measured with iR compensation using an EG and G PARC 273 potentiostat and recorded on an Advanced Byrens XY recorder. The experiments were carried out under a nitrogen atmosphere at 20 °C at a platinum disc electrode (1.6 mm diameter) with a platinum gauze counter electrode in 5 cm<sup>3</sup> of a *ca.* 10<sup>−4</sup> M solution of the compound containing 0.2 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte. The solvent, dichloromethane, was dried and freshly distilled prior to use. The potentials were measured *versus* silver wire quasi-reference electrode and corrected *versus* ferrocene/ferrocene<sup>+</sup> as  $E^{\text{f}} = +0.36$  V by adding ferrocene to the studied solution after the experiment and referenced *versus* Ag/AgCl.

Phosphonate esters **4a**,<sup>15</sup> **4b**<sup>14,15</sup> and **4c**<sup>17</sup> and phosphonium salt **5**<sup>19</sup> were prepared by literature procedures.

**General procedure for compounds 7a–c, 11a–c, 12a–c, 14 and 16.** To a stirred solution of the Horner–Wittig reagent **4** (**a**, **b** or **c**) in dry THF (100 cm<sup>3</sup>) under argon at −78 °C was added *n*-

butyllithium (1.6 M in hexane) and the reaction allowed to stir at −78 °C for 0.5 h. The ferrocenyl aldehyde or ketone was then added and the reaction allowed to warm to 20 °C overnight. After evaporation of the solvent, water was added and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub>; the organic phase was separated, washed with water, dried (MgSO<sub>4</sub>) and evaporated. Column chromatography using CH<sub>2</sub>Cl<sub>2</sub>–hexane (1 : 1 v/v) as the eluting solvent afforded the desired products. The following compounds were thus obtained.

**1-[(1,3-Dithiol-2-ylidene)methyl]ferrocene 7a.** From compound **4a** (1.00 g, 4.75 mmol), *n*-butyllithium (3.25 cm<sup>3</sup>, 1.6 M in hexane, 5.20 mmol) and compound **6** (1.00 g, 4.67 mmol) and isolated as an orange solid (1.15 g, 81%), mp 81–82 °C (Found: C, 55.7; H, 4.1; S, 21.0. C<sub>14</sub>H<sub>12</sub>FeS<sub>2</sub> requires C, 56.0; H, 4.0; S, 21.4%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.25 (2 H, s), 6.16 (1 H, s), 4.39 (2 H, m), 4.22 (2 H, m), 4.18 (5 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  131.56, 117.63, 117.16, 109.81, 83.44 (Cp × 1), 68.93 (Cp × 5), 68.02 (Cp × 2), 66.83 (Cp × 2);  $m/z$  (DCI) 301 (M<sup>+</sup> + 1).

**1-[(4,5-Dimethyl-1,3-dithiol-2-ylidene)methyl]ferrocene 7b.** From compound **4b** (1.00 g, 4.17 mmol), *n*-butyllithium (2.87 cm<sup>3</sup>, 1.6 M in hexane, 4.59 mmol) and compound **6** (0.89 g, 4.16 mmol) and isolated as an orange solid (1.07 g, 78%), mp 109–111 °C (Found: C, 58.7; H, 5.0; S, 19.8. C<sub>16</sub>H<sub>16</sub>FeS<sub>2</sub> requires C, 58.5; H, 4.9; S, 19.5%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.01 (1 H, s), 4.35 (2 H, m), 4.18 (2 H, m), 4.15 (5 H, s), 1.96 (3 H, s), 1.91 (3 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.26, 121.25, 120.53, 108.51, 83.65 (Cp × 1), 68.90 (Cp × 5), 67.90 (Cp × 2), 66.79 (Cp × 2), 13.70, 13.05;  $m/z$  (DCI) 329 (M<sup>+</sup> + 1).

**1,1'-Bis[(methylsulfanyl)-1,3-dithiol-2-ylidene]methylferrocene 7c.** From compound **4c** (1.00 g, 3.29 mmol), *n*-butyllithium (2.26 cm<sup>3</sup>, 1.6 M in hexane, 3.62 mmol) and compound **6** (0.70 g, 3.28 mmol) and isolated as an orange solid (0.84 g, 65%), mp 56 °C (Found: C, 49.5; H, 4.4; S, 33.0. C<sub>16</sub>H<sub>16</sub>FeS<sub>4</sub> requires C, 49.0; H, 4.1; S, 32.7%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.10 (1 H, s), 4.34 (2 H, m), 4.22 (2 H, m), 4.16 (5 H, s), 2.44 (3 H, s), 2.42 (3 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  126.82, 126.57, 124.64, 112.34, 82.42 (Cp × 1), 69.01 (Cp × 5), 68.32 (Cp × 2), 67.15 (Cp × 2), 18.99, 18.83;  $m/z$  (DCI) 393 (M<sup>+</sup> + 1).

**1,1'-Bis[(1,3-dithiol-2-ylidene)methyl]ferrocene 11a.** From compound **4a** (1.00 g, 4.75 mmol), *n*-butyllithium (3.25 cm<sup>3</sup>, 1.6 M in hexane, 4.67 mmol) and compound **9**<sup>18</sup> (500 mg, 2.06 mmol) and isolated as an orange solid (580 mg, 68%), mp 99–101 °C (Found: C, 52.3; H, 3.5; S, 31.3. C<sub>18</sub>H<sub>14</sub>FeS<sub>4</sub> requires C, 52.2; H, 3.4; S, 31.0%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.20 (4 H, s), 6.02 (2 H, s), 4.32 (4 H, m), 4.17 (4 H, m);  $m/z$  (DCI) 415 (M<sup>+</sup> + 1).

**1,1'-Bis[(4,5-dimethyl-1,3-dithiol-2-ylidene)methyl]ferrocene 11b.** From compound **4b** (1.00 g, 4.17 mmol), *n*-butyllithium (2.87 cm<sup>3</sup>, 1.6 M in hexane, 4.59 mmol) and compound **9**<sup>18</sup> (485 mg, 2.00 mmol) and isolated as an orange solid (622 mg, 61%), mp 161–162 °C (Found: C, 56.4; H, 4.8; S, 27.2. C<sub>22</sub>H<sub>22</sub>FeS<sub>4</sub> requires C, 56.2; H, 4.7; S, 27.3%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.91 (2 H, s), 4.30 (4 H, m), 4.16 (4 H, m), 1.95 (6 H, s), 1.90 (6 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.14, 121.12, 120.36, 107.90, 84.53 (Cp), 68.64 (Cp × 4), 67.64 (Cp × 4), 13.36, 12.95 (all resonances correspond to two carbons except where indicated);  $m/z$  (DCI) 471 (M<sup>+</sup> + 1).

**1,1'-Bis[(4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene)methyl]ferrocene 11c.** From compound **4c** (1.0 g, 3.29 mmol), *n*-butyllithium (2.26 cm<sup>3</sup>, 1.6 M in hexane, 3.62 mmol) and compound **9**<sup>18</sup> (350 mg, 1.45 mmol) and isolated as an orange solid (640 mg, 74%), mp 41 °C (Found: C, 44.0; H, 4.0; S, 43.0. C<sub>22</sub>H<sub>22</sub>FeS<sub>8</sub> requires C, 44.1; H, 3.7; S, 42.8%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.93 (2 H, s), 4.30 (4 H, m), 4.19 (4 H, m), 2.43 (6 H, s), 2.42 (6 H, s);  $m/z$  (DCI) 599 (M<sup>+</sup> + 1).

**1,1'-Bis[1-(1,3-dithiol-2-ylidene)ethyl]ferrocene 12a.** From compound **4a** (1.00 g, 4.72 mmol), *n*-butyllithium (3.25 cm<sup>3</sup>, 1.6 M in hexane, 5.20 mmol) and compound **10** (590 mg, 2.19 mmol) and isolated as an orange solid (675 mg, 70%), mp 109 °C (Found: C, 54.3; H, 4.1; S, 28.9. C<sub>20</sub>H<sub>18</sub>FeS<sub>4</sub> requires C,

54.3; H, 4.1; S, 29.0%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.27 (4 H, s), 4.43 (4 H, m), 4.22 (4 H, m), 2.01 (6 H, s);  $m/z$  (DCI) 443 ( $\text{M}^+ + 1$ ).

**1,1'-Bis[1-(4,5-dimethyl-1,3-dithiol-2-ylidene)ethyl]ferrocene 12b.** From compound **4b** (1.00 g, 4.17 mmol), *n*-butyllithium (2.87 cm<sup>3</sup>, 1.6 M in hexane, 4.59 mmol) and compound **10** (540 mg, 2.00 mmol) and isolated as an orange solid (707 mg, 71%), mp 160–161 °C (Found: C, 57.7; H, 5.4; S, 25.8.  $\text{C}_{24}\text{H}_{26}\text{FeS}_4$  requires C, 57.8; H, 5.3; S, 25.7%);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.33 (4 H, m), 4.21 (4 H, m), 1.99 (6 H, s), 1.94 (12 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  124.58, 121.88, 120.43, 113.60, 88.56 (Cp), 68.66 (Cp  $\times$  4), 67.31 (Cp  $\times$  4), 22.01, 13.51, 13.15 (all resonances correspond to two carbons except where indicated);  $m/z$  (DCI) 499 ( $\text{M}^+ + 1$ ).

**1,1'-Bis[1-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]ethyl]ferrocene 12c.** From compound **4c** (1.00 g, 3.29 mmol), *n*-butyllithium (2.26 cm<sup>3</sup>, 1.6 M in hexane, 3.62 mmol) and compound **10** (405 mg, 1.50 mmol) and isolated as an orange-red oil (545 mg, 58%) (Found: C, 45.5; H, 4.6; S, 41.1.  $\text{C}_{24}\text{H}_{26}\text{FeS}_8$  requires C, 46.0; H, 4.2; S, 40.9%);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.37 (4 H, m), 4.20 (4 H, m), 2.38 (12 H, s), 1.95 (6 H, s);  $m/z$  (DCI) 627 ( $\text{M}^+ + 1$ ).

**1-[1,2-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)ethyl]ferrocene 14.** From compound **4b** (300 mg, 1.25 mmol), *n*-butyllithium (0.87 cm<sup>3</sup>, 1.6 M in hexane, 1.4 mmol) and compound **13** (400 mg, 1.12 mmol) and isolated as an orange solid (406 mg, 78%), mp 163–164 °C (Found: C, 56.0; H, 4.4; S, 27.5.  $\text{C}_{22}\text{H}_{22}\text{FeS}_4$  requires C, 56.2; H, 4.7; S, 27.3%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.97 (1 H, s), 4.49 (2 H, m), 4.19 (2 H, m), 4.16 (5 H, s), 1.99 (3 H, s), 1.96 (3 H, s), 1.90 (3 H, s), 1.88 (3 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  136.57, 128.94, 122.27, 122.21, 122.06, 120.14, 116.80, 111.85, 84.67 (Cp  $\times$  1), 68.99 (Cp  $\times$  5), 67.78 (Cp  $\times$  2), 66.94 (Cp  $\times$  2), 13.77, 13.68, 13.37, 13.22;  $m/z$  (DCI) 471 ( $\text{M}^+ + 1$ ).

**1,1'-Bis[1,2-bis(4,5-dimethyl-1,3-dithiol-2-ylidene)ethyl]ferrocene 16.** From compound **4b** (340 mg, 1.4 mmol), *n*-butyllithium (0.94 cm<sup>3</sup>, 1.6 M in hexane, 1.5 mmol) and compound **15** (300 mg, 0.57 mmol) and isolated as an orange solid (284 mg, 66%), mp 100–101 °C (Found: C, 53.9; H, 4.7; S, 34.2.  $\text{C}_{34}\text{H}_{34}\text{FeS}_8$  requires C, 54.1; H, 4.5; S, 34.0%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.95 (2 H, s), 4.50 (4 H, m), 4.25 (4 H, m), 1.99 (6 H, s), 1.96 (6 H, s), 1.89 (6 H, s), 1.86 (6 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  136.18, 129.23, 128.30, 122.39, 122.80, 120.10, 116.30, 112.24, 85.20 (Cp), 69.16 (Cp  $\times$  4), 67.88 (Cp  $\times$  4), 13.73, 13.68, 13.36, 13.21 (all resonances correspond to two carbons except where indicated);  $m/z$  (DCI) 755 ( $\text{M}^+ + 1$ ).

**1-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]methylferrocene 7d.** To a stirred solution of compound **5** (1.00 g, 1.97 mmol) and compound **6** (0.42 g, 1.97 mmol) in dry THF (100 cm<sup>3</sup>) at 20 °C was added dropwise triethylamine (1 cm<sup>3</sup>, excess) and the reaction stirred for 16 h. After evaporation of the solvent, water (100 cm<sup>3</sup>) was added and the residue extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  50 cm<sup>3</sup>); the combined organic phase was washed with water (2  $\times$  50 cm<sup>3</sup>), dried ( $\text{MgSO}_4$ ) and evaporated. Column chromatography using  $\text{CH}_2\text{Cl}_2$  as the eluent afforded compound **7d** as an orange solid (0.72 g, 88%), mp 94–96 °C (Found: C, 52.0; H, 4.0; S, 15.2.  $\text{C}_{18}\text{H}_{16}\text{FeO}_4\text{S}_2$  requires C, 51.9; H, 3.9; S, 15.4%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1733, 1721 [C(=O)O];  $\delta_{\text{H}}(\text{CDCl}_3)$  6.09 (1 H, s), 4.34 (2 H, m), 4.24 (2 H, m), 4.18 (5 H, s), 3.86 (6 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  160.36, 160.00, 131.37, 129.61, 124.94, 113.22, 81.66 (Cp  $\times$  1), 69.05 (Cp  $\times$  5), 68.58 (Cp  $\times$  2), 67.22 (Cp  $\times$  2), 53.30, 53.19;  $m/z$  (DCI) 417 ( $\text{M}^+ + 1$ ).

**1,1'-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]methylferrocene 11d.** This was prepared analogously to compound **7d** from compound **5** (1.0 g, 1.97 mmol) and compound **9**<sup>18</sup> (240 mg, 0.99 mmol) and isolated as an orange solid (442 mg, 69%), mp 177–179 °C (Found: C, 48.5; H, 3.4; S, 20.0.  $\text{C}_{26}\text{H}_{22}\text{FeO}_8\text{S}_4$  requires C, 48.3; H, 3.4; S, 19.8%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1735, 1707 [C(=O)O];  $\delta_{\text{H}}(\text{CDCl}_3)$  5.92 (2 H, s), 4.32 (4 H, m), 4.23 (4 H, m), 3.84 (6 H, s), 3.83 (6 H, s);  $m/z$  (DCI) 647 ( $\text{M}^+ + 1$ ).

**1-[2-Oxo-1-(4,5-dimethyl-1,3-dithiol-2-ylidene)ethyl]ferrocene 13.** To anhydrous DMF (15 cm<sup>3</sup>, excess) under argon at 0 °C was added dropwise oxalyl chloride (0.2 cm<sup>3</sup>, 2.3 mmol) and the mixture stirred for 15 min. After this time, compound **7b** (500 mg, 1.52 mmol) was added and the mixture warmed to 20 °C and stirred for a further 16 h. The reaction was quenched with aqueous sodium hydroxide (50 cm<sup>3</sup>, 1.0 M), precipitating a deep red solid; this was collected by filtration and washed with water (25 cm<sup>3</sup>). The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 cm<sup>3</sup>), washed with water (25 cm<sup>3</sup>), the organic phase was separated, dried ( $\text{MgSO}_4$ ) and evaporated. Column chromatography of the residue using  $\text{CH}_2\text{Cl}_2$  as eluent afforded compound **13** as a deep red solid (466 mg, 86%), mp 161–162 °C (Found: C, 57.3; H, 4.4; S, 18.0.  $\text{C}_{17}\text{H}_{16}\text{FeOS}_2$  requires C, 57.3; H, 4.5; S, 18.0%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1618 [CH(=O)];  $\delta_{\text{H}}(\text{CDCl}_3)$  9.78 (1 H, s) 4.50 (2 H, m), 4.32 (2 H, m), 4.18 (5 H, s), 2.16 (3 H, s), 2.15 (3 H, s);  $m/z$  (DCI) 357 ( $\text{M}^+ + 1$ ).

**1,1'-Bis[2-oxo-1-(4,5-dimethyl-1,3-dithiol-2-ylidene)ethyl]ferrocene 15.** This was prepared analogously to compound **13** from oxalyl chloride (0.35 cm<sup>3</sup>, 4.0 mmol) and compound **11b** (500 mg, 1.06 mmol) and isolated as a deep red solid (397 mg, 71%), mp 215–216 °C (Found: C, 54.5; H, 4.2; S, 24.7.  $\text{C}_{24}\text{H}_{22}\text{FeO}_2\text{S}_4$  requires C, 54.7; H, 4.2; S, 24.4%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1621, 1615 [CH(=O)];  $\delta_{\text{H}}(\text{CDCl}_3)$  9.62 (2 H, s) 4.55 (4 H, m), 4.34 (4 H, m), 2.15 (12 H, s);  $m/z$  (DCI) 527 ( $\text{M}^+ + 1$ ).

**1,1'-[1,2-Bis(1,3-dithiol-2-ylidene)ethane-1,2-diyl]di(ferrocene) 8a.** To a stirred solution of compound **7a** (100 mg, 0.30 mmol) in dry diethyl ether (50 cm<sup>3</sup>) under argon at 20 °C was added anhydrous HCl (0.3 cm<sup>3</sup>, 0.30 mmol, of a 1 M solution in dry diethyl ether) and the reaction stirred for 24 h. The solvent was evaporated and the residue chromatographed eluting with hexane–dichloromethane (2:1 v/v) affording compound **8a** as an orange solid (80 mg, 80%), mp > 250 °C (Found: C, 56.1; H, 3.8; S, 21.3.  $\text{C}_{28}\text{H}_{22}\text{Fe}_2\text{S}_4$  requires C, 56.2; H, 3.7; S, 21.4%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.41 and 6.39 (4 H, 2AB, *J* 2), 4.48 (2 H, m), 4.38 (2 H, m), 4.23 (10 H, s), 4.17 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  134.40, 122.38, 118.92, 118.66, 84.43 (Cp), 69.09 (Cp  $\times$  10), 67.65 (Cp), 67.40 (Cp), 67.37 (Cp), 65.11 (Cp) (all resonances correspond to two carbons except where indicated);  $m/z$  (DCI) 599 ( $\text{M}^+ + 1$ ).

**1,1'-[1,2-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)ethane-1,2-diyl]di(ferrocene) 8b.** This was prepared analogously to compound **8a** from compound **7b** (100 mg, 0.33 mmol) and isolated as an orange solid (84 mg, 84%), mp > 250 °C (Found: C, 58.8; H, 4.7; S, 14.8.  $\text{C}_{32}\text{H}_{30}\text{Fe}_2\text{S}_4$  requires C, 58.7; H, 4.6; S, 14.6%);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.47 (2 H, m), 4.38 (2 H, m), 4.23 (10 H, s), 4.14 (4 H, m), 2.02 (6 H, s), 1.94 (6 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  131.77, 122.47, 122.34, 120.67, 84.98 (Cp), 69.12 (Cp  $\times$  10), 67.48 (Cp), 67.36 (Cp), 67.24 (Cp), 65.26 (Cp), 13.95, 13.26 (all resonances correspond to two carbons except where indicated);  $m/z$  (DCI) 655 ( $\text{M}^+ + 1$ ).

**1,1'-[1,2-Bis(4,5-dimethylsulfanyl-1,3-dithiol-2-ylidene)ethane-1,2-diyl]di(ferrocene) 8c.** This was prepared analogously to compound **8a** from compound **7c** (100 mg, 0.26 mmol) using a reaction time of 96 h and isolated as an orange solid (75 mg, 75%), mp 67 °C (Found: C, 49.2; H, 4.0; S, 33.0.  $\text{C}_{32}\text{H}_{30}\text{Fe}_2\text{S}_8$  requires C, 49.1; H, 3.9; S, 32.8%);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.45 (2 H, m), 4.28 (2 H, m), 4.24 (10 H, s), 4.16 (4 H, m), 2.52 (6 H, s), 2.45 (6 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.9, 128.6, 124.8, 122.8, 83.4 (Cp), 69.2 (Cp  $\times$  10), 68.0 (Cp), 67.9 (Cp), 67.6 (Cp), 65.1 (Cp), 19.1, 18.8 (all resonances correspond to two carbons except where indicated);  $m/z$  (DCI) 783 ( $\text{M}^+ + 1$ ).

#### X-Ray crystallography

The single crystal X-ray diffraction experiment for **8b** was carried out at room temperature on a Huber *Fddd* 4-circle diffractometer<sup>31</sup> (Siemens rotating-anode target, graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). *Crystal data:*  $\text{C}_{32}\text{H}_{30}\text{Fe}_2\text{S}_4 \cdot \text{CDCl}_3$ ,  $M = 774.9$ , monoclinic,  $a =$

21.977(1),  $b = 8.6364(3)$ ,  $c = 18.465(1)$  Å,  $\beta = 109.459(1)^\circ$ ,  $U = 3304.3(1)$  Å<sup>3</sup> (from 24 reflections with  $12 < \theta < 15^\circ$ ), space group  $C2/c$  (No. 15),  $Z = 4$ ,  $D_c = 1.56$  g cm<sup>-3</sup>,  $\mu = 14.0$  cm<sup>-1</sup>,  $F(000) = 1584$ , crystal size  $0.1 \times 0.15 \times 0.2$  mm,  $\theta/2\theta$  scan mode,  $2\theta \leq 60^\circ$ , 5216 reflections, of which 3862 unique ( $R_{\text{int}} = 0.048$ ). The structure was solved by direct methods and refined by full-matrix least-squares [non-H atoms anisotropic, methyl groups as rigid bodies, other H atoms 'riding'; 243 variables; weighting scheme  $w^{-1} = \sigma^2(F) + 0.0001F^2$ ] against  $F$  of 2368 data with  $I \geq 2\sigma(I)$ , converging at  $R = 0.059$ ,  $wR = 0.060$ , goodness-of-fit = 1.29; residual electron density  $\Delta\rho_{\text{max}} = 0.45$ ,  $\Delta\rho_{\text{min}} = -0.44$  e Å<sup>-3</sup>. The CDCl<sub>3</sub> molecule of crystallization is disordered. Its carbon atom occupies two positions, related via a two-fold axis. The chlorine atoms appear in a difference Fourier map as a nearly-uniform planar toroid of electron density, rationalised in the refinement as two (for each carbon position) molecular orientations, A and B, differing by a ca. 30° rotation around the molecular three-fold axis. With the symmetrical equivalents, this gives a total of 12 (almost coplanar) chlorine positions with occupancies of 25% each. SHELXTL-Plus software<sup>32</sup> was used. Atomic coordinates, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/153.

The structural study of **12a** has been described elsewhere;<sup>16a</sup> the structure has been deposited at the Cambridge Crystallographic Data Centre, reference code LADREN.

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