

Note

# Mono- and di-*t*-butyl substituted 2,2'-bis(1,3-dithia[3]ferrocenophane-2-ylidene) derivatives: TTF-like ferrocene analogs

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## Abstract

Mono- and di-*t*-butyl substituted 2,2'-bis(1,3-dithia[3]ferrocenophane-2-ylidene) derivatives were prepared. These derivatives showed the  $E_{1/2}(1)$  in lower potential region than that of differrocenyl-ethene and -ethyne. Also, the  $\Delta E_{1/2}$  value declined according to the increase of a *t*-butyl group.

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## 1. Introduction

Much recent interest has been focused in the creation of the substances bringing out a novel functionality. The chemistry of ferrocene is attracting a great deal of attention in succession because of the facility for organic functionalization and the chemical stability of both ferrocene and ferricenium species. These unique properties make complexes having ferrocenes good candidates for preparation of new materials with application to material science [1]. Tetrathiafulvalenes (TTFs) are highly promising  $\pi$ -electron donors for the exploration of new, molecular-based organic metals and super conductors [2] and for building blocks of supermolecular architectures [3], which was spawned by the progenitor complex TTF–TCNQ [4]. The electron-rich compounds such as TTF and its analogs are still searching at present and the combination of ferrocene with TTF seems to be a valid candidate. The ferrocene-substituted TTF derivatives were prepared [5,6]. Although no ferrocene-condensed TTF derivatives have been reported, a strikingly similar tetrathioethene derivative

was prepared [7]. However, the complex was sparingly soluble in organic polar solvent and little property was reported. So, we examined the preparation of more soluble mono- and di-*t*-butyl derivatives.

## 2. Results and discussion

### 2.1. Synthesis and structural assignment

1,2,3-Trithia-6,12-di-*t*-butyl[3]ferrocenophane (**1a**) [8] was converted with  $\text{LiAlH}_4$  to the corresponding dithiol which was treated with 1,1'-thiocarbonyldiimidazol in THF to give 1,3-dithia-6,12-di-*t*-butyl[3]ferrocenophane-2-thione (**2a**) as red crystals in 51% yield. In a similar manner, 1,3-dithia-6-(*t*-butyl)[3]ferrocenophane-2-thione (**2b**) was obtained from 1,2,3-trithia-6-*t*-butyl[3]ferrocenophane (**1b**) [8] in good yield. The  $^1\text{H}$  NMR spectrum of **2a** showed the *t*-butyl protons at  $\delta$  1.22 and the  $\eta$ - $\text{C}_5\text{H}_3$  ring protons at  $\delta$  4.10 (t,  $J = 1.4$  Hz), 4.45 (dd,  $J = 2.4$  and 1.4 Hz), and 4.49 (dd,  $J = 2.4$  and 1.4 Hz). The appearance of only the three  $\eta$ - $\text{C}_5\text{H}_3$  ring protons implied the presence of a process averaging the circumstance of the  $\eta$ - $\text{C}_5\text{H}_3$  ring protons in the molecule of **2a**. That is, the plane containing the two sulfur atoms and the thiocarbonyl group is quickly moving

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concerning the axis passing two sulfur atoms such as a butterfly flaps its wings. The signal pattern of the  $\eta\text{-C}_5\text{H}_3$  ring protons showed no change until  $-30\text{ }^\circ\text{C}$ . This flexibility is not due to the presence of two *t*-butyl groups, because in the unsubstituted 1,2,3-trithia[3]ferrocenophane-2-thione (**2c**) the Cp ring protons appeared as two triplets and no spectral change was also observed until  $-30\text{ }^\circ\text{C}$ . This behavior is contrary to that in the trisulfide-bridged complexes **1a–1c**, whose *anti* and *syn* isomers are interconverting very slowly and the bridge reversal barrier is quite high ( $80\text{ kJ mol}^{-1}$  in **1c**) [9]. The great flexibility of the trithio-carbonate moiety in **2a–2c** compared with that of trisulfide bridge in **1a–1c** is probably caused by the decreasing steric strain due to the shorter length of the S–C bond compared with the S–S bond.

Compound **2a** was refluxed with triethylphosphite for 7 h under N to give the coupling product (**3a**) as yellow crystals in 58% yield. The  $^1\text{H}$  NMR spectrum of **3a** showed that the product consisted of two isomers with nearly equal ratio and only the three signals appeared for the  $\eta\text{-C}_5\text{H}_3$  ring protons. The latter observation means that there is fast motion around the axis passing two sulfur atoms in the 1,1'-position of the ferrocene moiety in solution, similarly as seen in **2a**. The fractional crystallization of **3a** from  $\text{CHCl}_3$ /hexane gave a single-crystal of one isomer, the X-ray diffraction of which was carried out. The crystallographical data are collected in Table 1 and the bond dis-

Table 2  
Selected bond distances and bond angles for **3a**

Bond distances ( $\text{\AA}$ )			
C(1)–S(3)	1.781(7)	C(1)–S(4)	1.773(7)
C(2)–S(1)	1.765(6)	C(2)–S(2)	1.784(6)
C(3)–S(1)	1.744(7)	C(8)–S(2)	1.752(7)
C(13)–S(3)	1.735(8)	C(18)–S(4)	1.744(8)
C(1)–C(2)	1.334(9)	Fe–C(Cp) av.	2.053
C(Cp)–C(Cp) av.	1.432		
Bond angles ( $^\circ$ )			
S(1)–C(2)–S(2)	119.7(4)	S(3)–C(1)–S(4)	118.8(4)
C(1)–C(2)–S(1)	119.2(5)	C(1)–C(2)–S(2)	119.5(5)
C(2)–C(1)–S(3)	120.0(5)	C(2)–C(1)–S(4)	120.0(5)
C(2)–S(1)–C(3(1))	104.6(3)	C(2)–S(2)–C(8)	106.8(3)
C(1)–S(3)–C(13)	102.8(3)	C(1)–S(4)–C(18)	106.3(3)

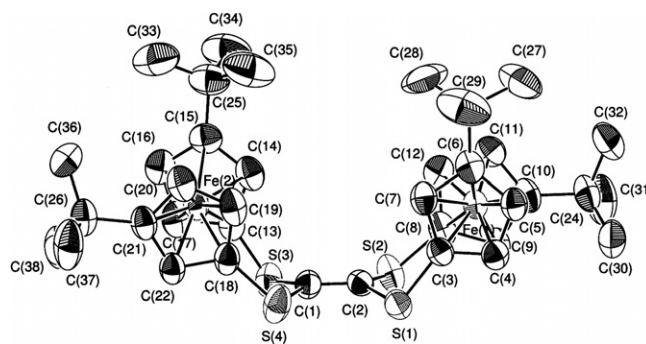


Fig. 1. ORTEP view of complex **3a**.

Table 1  
Crystallographic data for **3a**

<b>3a</b>	
Molecular formula	$\text{C}_{38}\text{H}_{48}\text{S}_4\text{Fe}_2$
Molecular weight	744.752
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> ( $\text{\AA}$ )	13.1540(3)
<i>b</i> ( $\text{\AA}$ )	17.9730(6)
<i>c</i> ( $\text{\AA}$ )	16.2470(4)
$\alpha$ ( $^\circ$ )	90.00
$\beta$ ( $^\circ$ )	104.725(2)
$\gamma$ ( $^\circ$ )	90.00
<i>V</i> ( $\text{\AA}^3$ )	3714.9(2)
<i>Z</i>	4
$D_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.332
Crystal dimension (mm)	$0.60 \times 0.40 \times 0.20$
Radiation ( $\lambda$ , $\text{\AA}$ )	Mo $\text{K}\alpha$ (0.71073)
Reflection ( <i>hkl</i> ) limits	$0 \leq h \leq 16; 0 \leq k \leq 22;$ $-19 \leq l \leq 19$
Total reflections measured	7664
Unique reflections	7482
Linear absorption coefficient ( $\text{mm}^{-1}$ )	1.03
Reflections used in L.S.	5018
L.S. parameters	397
<i>R</i>	0.050
$R_w$	0.157
<i>S</i>	2.619
Maximum peak in final Fourier map ( $\text{e}\text{\AA}^{-3}$ )	0.47
Minimum peak in final Fourier map ( $\text{e}\text{\AA}^{-3}$ )	-0.64

tances and the bond angles are shown in Table 2. The ORTEP view of **3a** is shown in Fig. 1. The *t*-Bu groups in the two ferrocenyl moieties are in *anti* relationship with each other. The two ferrocenyl moieties are folded in the same side of the plane of the tetrathioethene group. The plane consisting of C(3), C(8), S(1), and S(2) atoms is folded by  $47.07(3)^\circ$  from the plane of the tetrathioethene group. The plane consisting of C(13), C(18), S(3), and S(4) atoms is also folded by  $50.79(3)^\circ$  in the same direction. The C(1)–C(2) distance [1.334(9)  $\text{\AA}$ ] is normal as a double bond. The average distance [1.776 (7)  $\text{\AA}$ ] of the C(2)–S(1), C(2)–S(2), C(1)–S(3), and C(1)–S(4) bonds is typical as a single C–S bond. The tilt angles in the ferrocene moieties are small [ $8.58(3)^\circ$  and  $8.20(3)^\circ$ ]. Similarly, the reaction of **2b** with triphenylphosphine in refluxing benzene led to the coupling compound **3b** in 41% yield. Four isomers exist in **3b**. However, the isomer ratio could not be ascertained from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, because the methyl proton and carbon signals in **3b** were observed as a singlet, the  $\eta\text{-C}_5\text{H}_3$  ring protons appeared as eight multiplets in the  $^1\text{H}$  NMR spectrum, and many signals for the  $\eta\text{-C}_5\text{H}_3$  ring carbons were observed in the  $^{13}\text{C}$  NMR spectrum.

## 2.2. Cyclic voltammetry

The cyclic voltammograms of **3a–3c** were measured in a solution of 1 M (*n*-Bu) $_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$  at a glassy carbon electrode and a sweep rate of  $0.1\text{ V s}^{-1}$ . Their redox

Table 3  
Redox potentials of dinuclear ferrocenes (vs. FcH/FcH<sup>+</sup>, V) in CH<sub>2</sub>Cl<sub>2</sub>

Complexes	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}^a$
<b>3a</b> <sup>b</sup>	0.153	0.245	0.092
<b>3b</b> <sup>b</sup>	0.196	0.328	0.132
<b>3c</b> <sup>b</sup>	0.221	0.357	0.136
FcCCFc <sup>c</sup>	0.383	0.513	0.130
FcCH = CHFc <sup>d</sup>	0.395	0.948	0.553

<sup>a</sup>  $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$ .

<sup>b</sup> Supporting salt: *n*-Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M), Sweep rate: 0.1 V/s.

<sup>c</sup> Supporting salt: *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M), Sweep rate: 0.1 V/s. Converted from the value in Ref. [10].

<sup>d</sup> Supporting salt: *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.2 M), Sweep rate: 0.2 V/s. Converted from the value in Ref. [11].

potentials and those of the related complexes were summarized in Table 3. The  $E_{1/2}(1)$  of **3c** is considerably lower than that of diferrocenylethyne [10] or ethene [11] ( $\Delta E$  0.16–0.17 V). This is in disagreement with the fact that a sulfur substituent works as an electron-attracting substituent in ferrocene derivatives, nevertheless it behaves as an electron-releasing substituent in benzenoid derivatives [12]. However, the conformation of the sulfur atom in **3** is restricted owing to the bridging and the orbital of a lone pair in the S atom can be almost parallel to the  $\pi$ -orbital of the  $\eta$ -C<sub>5</sub>H<sub>4</sub> ring. So, electron-donation may be possible from the lone pair orbital in the S atom to the  $\pi^*$ -orbital of the  $\eta$ -C<sub>5</sub>H<sub>4</sub> ring. The shift of the  $E_{1/2}(1)$  of **3a** and **3b** to a low potential region is probably due to the electron-releasing effect of the *t*-butyl substituent. The  $\Delta E_{1/2}$  value of **3c** is considerably smaller than that of diferrocenyl ethene [11], but similar to that of diferrocenylethyne [10]. This implies that there is some interaction between two metal sites in **3c** through the tetrathioethylene-bridge. The tetrathioethylene linker may possess an electron-transfer capability in a similar extent to that of an ethyne group, although the plane of the tetrathioethylene-bridge is almost perpendicular with the  $\eta$ -C<sub>5</sub>H<sub>4</sub> ring of the ferrocene moiety in **3c**. The electron-transfer by the tetrathioethylene linker may be caused by some possibilities: there is an electrostatic effect and an inductive effect through the sulfur atoms and the ethene group. A certain interaction seems also to exist between the non-bonding  $d_{x^2-y^2}$  orbital of the Fe atom and the  $\pi^*$ -orbital of the ethene bridge through or not through the d-orbital of the sulfur atoms, because the plane of the tetrathioethylene bridge is nearly perpendicular to the axis of the ferrocene nucleus, as seen in Fig. 1. The effect of the *t*-butyl substituent to the  $\Delta E_{1/2}$  value is interesting: 0.136 V (**3c**) > 0.132 V (**3b**) > 0.092 V (**3a**). Such decline according to the increase of the *t*-butyl group may be explained by the stabilization effect by the *t*-butyl group toward the two-electron oxidized species, because the  $E_{1/2}(2)$  descends more than  $E_{1/2}(1)$  with the increase of the butyl group. A similar order due to an alkyl group was also reported in biferrocene [13] and biferrocenylethyne derivatives [11,14], but the reason is likely to be different in each case.

### 3. Experimental

All reactions were carried out under an atmosphere of N<sub>2</sub> and/or Ar and workups were performed without precaution to exclude air. NMR spectra were recorded on Bruker AC300P, AM400 or ARX400 spectrometer. IR (KBr disc) spectra were recorded on Perkin–Elmer System 2000 spectrometer. Cyclic voltammetry was carried out by using BAS ALS600 in 10<sup>-1</sup> M solution of *n*-Bu<sub>4</sub>NClO<sub>4</sub> (polarography grade, Nacalai tesque) in CH<sub>2</sub>Cl<sub>2</sub>. CV's cells were fitted with glassy carbon (GC) working electrode, Pt wire counter electrode and Ag/Ag<sup>+</sup> pseudo reference electrode. The cyclic voltammograms were obtained at the scan rate of 0.1 V s<sup>-1</sup> in the 5 × 10<sup>-4</sup> M or saturated solution of complexes. All potentials were represented vs. FcH<sup>0/+</sup>, which were obtained by the preceding measurement of ferrocene at the same conditions. Dry solvents were prepared by distillation from the drying agent prior to use as follows: hexane (CaCl<sub>2</sub>); CH<sub>2</sub>Cl<sub>2</sub> (CaCl<sub>2</sub>); benzene (Na); THF (Na-benzophenone). 1,2,3-Trithia-6,12-bis(*t*-butyl)[3]ferrocenophane (**1a**) [8], 1,2,3-trithia-6-(*t*-butyl)[3]ferrocenophane (**1b**) [8], 1,2,3-trithia[3]ferrocenophane (**1c**) [15], 3,4'-di(*t*-butyl)ferrocene-1,1'-dithiol [16], and 3-(*t*-butyl)ferrocene-1,1'-dithiol [16] were prepared according to the literatures. Other reagents were used as received from commercial suppliers.

#### 3.1. 1,3-Dithia-6,12-di-*t*-butyl[3]ferrocenophan-2-thione (**2a**)

To a solution of 3,4'-di(*t*-butyl)ferrocene-1,1'-dithiol (210 mg, 0.58 mmol) in THF (13 ml) was added 1,1'-thiocarbonyldiimidazol (150 mg, 0.84 mmol). After the solution had been stirred for 15 min, the solution was filtered. The filtrate was evaporated and then the residue was chromatographed on SiO<sub>2</sub> with elution of hexane/benzene. The product was recrystallized from hexane. Red crystal (120 mg, 51%), m.p. 140–144 °C. Anal. Calc. for C<sub>19</sub>H<sub>24</sub>S<sub>3</sub>Fe: C, 56.43; H, 5.98. Found: C, 56.55, H, 5.97%. IR (ATR): 984 cm<sup>-1</sup> ( $\nu$  C=S). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  1.22 (s, 18H, Me), 4.10 (m, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.45 (m, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), and 4.49 (m, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  30.49C, *t*-Bu}, 31.50 (CH<sub>3</sub>, *t*-Bu), 71.04 ( $\eta$ -C<sub>5</sub>H<sub>3</sub>), 71.15 ( $\eta$ -C<sub>5</sub>H<sub>3</sub>), 74.70 ( $\eta$ -C<sub>5</sub>H<sub>3</sub>), 87.92 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>4</sub>S), 106.87 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>Bu-*t*), 218.25 (C=S).

#### 3.2. 1,3-Dithia-6-*t*-butyl[3]ferrocenophan-2-thione (**2b**)

This compound was prepared according to the procedure described in Section 3.1. Red orange crystals (51%), m.p. 133–134 °C. Anal. Calc. for C<sub>15</sub>H<sub>16</sub>S<sub>3</sub>Fe: C, 51.72; H, 4.63. Found: C, 51.83; H, 4.55%. IR (ATR): 984 cm<sup>-1</sup> ( $\nu$  C=S). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.23 (s, 9H, Me), 4.24 (t,  $J$  = 1.3 Hz, 1H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.28 (dd,  $J$  = 2.6 and 1.5 Hz, 1H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.31 dt,  $J$  = 2.6 and 1.1 Hz,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.38 (dt,  $J$  = 2.6 and 1.1 Hz,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.44 (dd,  $J$  = 2.6 and 1.5 Hz, 1H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), and 4.52 td (dt,  $J$  = 2.6

and 1.1 Hz,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.55 (dt,  $J$  = 2.6 and 1.1 Hz,  $\eta$ -C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  30.40 (*t*-Bu), 31.24 (CH<sub>3</sub>, *t*-Bu), 70.06, 72.52, 72.87, 74.49, 74.58, 74.70, 75.52 ( $\eta$ -C<sub>5</sub>H<sub>4</sub> or  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 88.05 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>S), 88.47, (*ipso*- $\eta$ -C<sub>5</sub>H<sub>4</sub>S), 107.30 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>Bu-*t*), 240.64 (C=S).

### 3.3. 2,2'-Bis(1,3-dithia-6,12-di-*t*-butyl[3]ferrocenophan-2-ylidene) (**3a**)

The solution of **2a** (100 mg, 0.25 mmol) and triethylphosphite (0.7 ml, 4.4 mmol) in benzene was refluxed for 7 h. After evaporation, the residue was chromatographed on SiO<sub>2</sub> to give the title complex (53 mg, 58%) as yellow crystals, which was a 1:1 mixture of two isomers by the <sup>1</sup>H NMR spectrum. M.p. 200 °C (dec). Anal. Calc. for C<sub>38</sub>H<sub>48</sub>S<sub>4</sub>Fe<sub>2</sub>: C, 61.29, H, 6.50. Found: C, 61.51; H, 6.42%. Anti-form: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.17 (s, 36H, Me), 4.10 (dd,  $J$  = 2.4 and 1.4 Hz, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.15 (t,  $J$  = 1.4 Hz, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), and 4.36 (dd,  $J$  = 2.4 and 1.4 Hz, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100MHz):  $\delta$  30.02 (C, *t*-Bu), 31.11 (CH<sub>3</sub>, *t*-Bu), 69.48 (double intensity,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 72.83 ( $\eta$ -C<sub>5</sub>H<sub>3</sub>), 80.96 ( $\eta$ -C<sub>5</sub>H<sub>3</sub>), 87.92 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>S), 104.40 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>Bu-*t*), 218.25 (C=S). Syn-form: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.18 (s, 72H, Me), 4.11 (bq, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.17 (bt, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), and 4.35 (bq, 2H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>) (see Scheme 1).

### 3.4. 2,2'-Bis(1,3-dithia-6-*t*-butyl[3]ferrocenophan-2-ylidene) (**3b**)

The solution of **3a** (0.11 g, 0.25 mmol) and triphenylphosphine (0.19 g, 0.72 mmol) in benzene (12 ml) was refluxed for 72 h. After evaporation, the chromatography of the residue on SiO<sub>2</sub> afforded yellow crystals

(41 mg), which was recrystallized from hexane to give pure product (33 mg, 41%). M.p. 208–209 °C. Anal. Calc. for C<sub>30</sub>H<sub>32</sub>S<sub>4</sub>Fe<sub>2</sub>: C, 56.97, H, 5.10. Found: C, 57.05; H, 5.15%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.20 (s, 18H, Me), 4.08 (m, 2.0 H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.11 (m, 2.3 H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.15 (m, 1.7 H,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.20 (m, 1.5 H,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.23 (m, 0.6 H), 4.25 (m, 1.9 H,  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 4.33 (m, 1.9 H,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), and 4.36 (m, 2.1 H,  $\eta$ -C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100MHz): Main component,  $\delta$  30.43 (C, *t*-Bu), 31.30 (CH<sub>3</sub>, *t*-Bu), 68.37, 70.84, 71.18, 72.84, 73.06, 73.22, 73.84 ( $\eta$ -C<sub>5</sub>H<sub>4</sub> or  $\eta$ -C<sub>5</sub>H<sub>3</sub>), 80.12 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>S), 80.88 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>4</sub>S), 105.60 (*ipso*- $\eta$ -C<sub>5</sub>H<sub>3</sub>Bu-*t*), 147.19 (C=C).

### 3.5. Structure determination

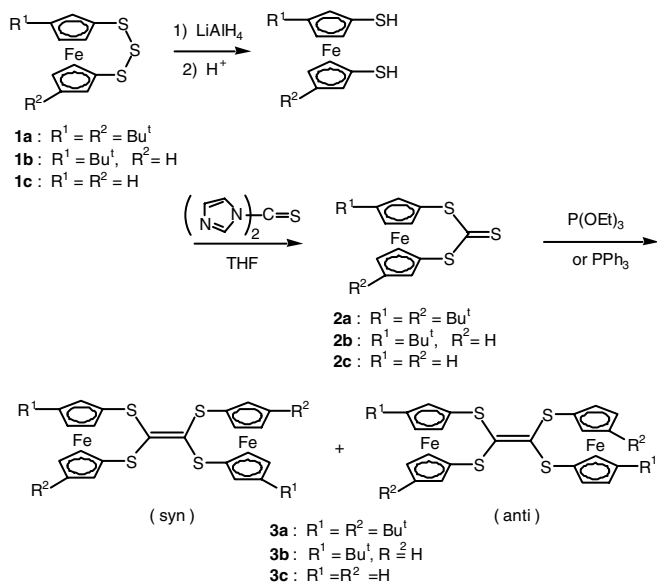
The crystallographic data are listed in Table 1 for **3a**. Data collection of their crystal data was performed at room temperature on Mac Science DIP3000 image processor with graphite monochromated Mo K $\alpha$  radiation and an 18-kW rotating anode generator. The structures were solved with the SIR97 method in MAXUS (software-package for structure determination) and refined finally by full-matrix least-squares procedure. Absorption correction was carried out by the Sortav method and anisotropic refinement for non-hydrogen atom was carried out. The hydrogen atoms, located from calculation, were isotropically refined.

## 4. Supplementary material

CCDC 627420 contains the supplementary crystallographic data for **3a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Scheme 1.

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