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Bis(ferrocenylsilyl)thiophenes and ferrocenylene(silylene)thiophene oligomers

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Abstract

The reaction between 1,1'-dilithioferrocene and 2,5-bis(chlorodimethylsilyl)thiophene (**I**), leads to a series of cyclic oligomers of basic formulation [Fc-SiMe₂-TH-SiMe₂]_n (**II**); $Fc = (\eta^5 - C_5H_4)_2Fe$, $TH = C_4H_2S$. The material n = 2, **IIa**, has been completely characterized by spectroscopic and single crystal X-ray diffraction. Cyclic voltammetric analysis of **IIa** illustrates two reversible redox processes, indicating a significant interaction between the two ferrocenylene units despite the 5 atom bridge. By comparison, the monomeric analog Fc-SiMe₂-TH-SiMe₂-Fc (**III**), $Fc = (\eta^5 - C_5H_4)$, prepared from the reaction of mono-lithioferrocene with **I**, exhibits a single redox process, even though there is the same bridge between the two Fe centers. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Cyclic oligomers; Thiophenes; Ferrocenes

1. Introduction

The interesting properties of polythiophenes are well studied [1] and recently the synthesis and study of thiophenesubstituted derivatives of the Group 14 elements has also received attention due to their potential as electroactive materials [2–5]. We have an interest in similar ferrocenyl-substituted Group 14 materials [6–17], and now report studies aimed at the introduction of both the ferrocene and thiophene units into a silicon-containing molecular structure. We hope to produce monomers, oligomers and polymers with interesting structural and electrical properties. As a general procedure for the synthesis of such systems we have used the chemistry outlined in Eqs. (1) and (2) in which either monolithioferrocene or dilithioferrocene is reacted with a 2,5-(chlorosilyl) thiophene (Ia R = Me; Ib R = Ph).

Whereas the reaction of dilithioferrocene with I would, in theory, yield polymeric materials, the use of monolithioferrocene, $[Fc]^-Li^+$, was to provide monomers from which the basic optical and electrochemical properties of the system 2,5-bis(ferrocenylsilyl)thiophene could be obtained.

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2. Results and discussion

The reaction between 2,5-bis(chlorodimethylsilyl)thiophene, **Ia**, and dilithioferrocene, Eq. (1), resulted in the formation of a series of low molecular weight cyclic oligomers. We attempted to separate these materials by column chromatography and were able to obtain the first of this series, **IIa**, n = 2, as pure red crystals. The spectroscopic data for **IIa** are recorded in Table 1 and its structure is presented in Fig. 1, and selected bond angles and lengths in Table 2.

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Table 1	
NMR a, UV-Vis, and analytical properties of the new compound	s

2,5-bis(hydrodimethylsilyl)thiopher	ie
¹ H	0.26 (d, SiMe ₂); 4.76 (sept. SiH); 7.30 (thiophene)
¹³ C	- 2.64 (SiMe ₂); 136.7 (thiophenyl C _{3,4}); 142.8 (thiophenyl C _{2,5})
²⁹ Si	- 23.3
$IR (CCl_4, cm^{-1})$	2128.7
2,5-bis(hydrodiphenylsilyl)thiopher	the
¹ H	5.66 (SiH $J_{SiH} = 206$ Hz); 7.40–7.68 (phenyl, thiophene)
¹³ C	128.1, 130.1, 132.9 (<i>ipso</i>), 135.5 (phenyl); 138.9 (thiophene $C_{3,4}$); 140.0 (thiophene $C_{2,5}$)
IR (hexane, cm ⁻¹)	2136
2,5-bis(chlorodimethylsilyl)thiophe	ne (Ia)
¹ H	0.76 (SiMe ₂); 7.52 (thiophene)
¹³ C	3.36 (SiMe ₂); 136.7 (thiophenyl C _{3,4}); 143.3 (thiophenyl C _{2,5})
²⁹ Si	15.2
2,5-bis(chlorodiphenylsilyl)thiophe 1 H 13 C	ne (Ib) 7.42–7.72 (phenyl, thiophene) 128.2, 131.1, 132.4 (<i>ipso</i>), 134.9 (phenyl); 139.4 (thiophene C _{3,4}); 141.5 (thiophene C _{2,5})
[(ferrocenylenedimethylsilyl)thioph	nenylene] ₂ (Ha)
Analysis	Calc.: C, 56.5; H, 5.80. Found: C, 55.9; H, 5.88
¹ H	0.27 (SiMe ₂); 3.93, 4.08 (ferrocenylene); 6.91 (thiophene)
¹³ C	0.43 (SiMe ₂); 70.3, 72.2, 74.2 (ferrocenylene); 136.1 (thiophene C _{3,4}); 144.4 (thiophene C _{2,5})
²⁹ Si	-9.7
UV–Vis (THF) (nm)	279, 449
[(ferrocenylenedimethylsilyl)thioph	nenylene] _n (IIn)
¹ H	0.27, 0.40, 0.54 (SiMe ₂); 4.08, 4.17 (ferrocenylene); 7.34 (thiophene)
¹³ C	-0.1, 2.1 (SiMe ₂); 68.7, 70.2, 72.1, 73.8 (ferrocenylene); 135.8 (thiophene C _{3,4}); 145.2 (thiophene C _{2,5})
²⁹ Si	-4.85, -9.7, -10.4, -10.6, -15.2
UV–Vis (THF) (nm)	279, 449
2,5-bis(ferrocenyldimethylsilyl)thio	phene (III)
Analysis	Calc.: C, 59.2; H, 5.67. Found: C, 58.4; H, 5.85
¹ H	0.57 (SiMe ₂); 4.01 (C ₅ H ₅), 4.13, 4.19 (C ₅ H ₄), 7.43 (thiophene)
¹³ C	-0.1 (SiMe ₂); 68.7 (C ₅ H ₅), 69.7 (<i>ipso</i>), 71.5, 73.6 (ferrocenyl); 136.0 (thiophene C _{3,4}); 145.3 (thiophene C _{2,5})
²⁹ Si	-10.6
UV–Vis (THF) (nm)	271, 448
2,5-bis(ferrocenyldiphenylsilyl)thio	phene (IV)
Analysis	Calc.: C, 70.6; H, 4.93. Found: C, 69.9; H, 5.50
¹ H	$3.95 (C_5H_5)$; 4.22, 4.41 (C_5H_4); 7.30–7.60 (phenyl, thiophene)
¹³ C	65.8, 68.8, 71.4, 74.9 (ferrocenyl); 127.7, 129.6, 135.6 (phenyl), 138.7 (thiophene $C_{3,4}$); 141.9 (thiophene $C_{2,5}$)
²⁹ Si	- 16.9

^a Spectra were recorded in C₆D₆ with the exception of **IV** which was recorded in CDCl₃.

The structure of **Ha** possesses normal bond lengths and angles and the cycle shows no structural sign of ring strain. The two ferrocene groups are completely eclipsed, as noted in Fig. 1(b), and the two thiophene groups are positioned in opposition to each other.

At the present time we have been unable to characterize completely the remainder of the product obtained from the reaction described in Eq. (1). Fast atom bombardment MS indicated the presence of trimeric (m/e = 1147) and tetrameric (m/e = 1529) analogs of **Ha** and the NMR data recorded in Table 1 are consistent with this observation. However, other materials are also present, witness for example the ²⁹Si NMR signals at -15.2 and -4.85 ppm. We continue to study this system.

The reaction outlined in Eq. (2) was satisfactory for the formation of monomeric 2,5-bis(ferrocenyldimethylsilyl)-thiophene, **III**, and the diphenylsilyl analog **IV**, in good yield.

The spectroscopic data for **III** and **IV** are in accord with their proposed structures and are recorded in Table 1. The single crystal structure of **III** is recorded in Fig. 2, and representative bond lengths and angles are presented in Table 2. This complex was synthesized to provide baseline data to facilitate the analysis of polymeric and oligomeric analogs.

The related bond lengths and angles of **Ha** can be compared to those of **HI** and it is immediately clear that there are no truly significant differences between the two sets. The single exception to this generality are the possibly shorter silicon– thiophene–carbon bond lengths in **Ha** (Si1–C1 = 1.861(3) and Si2–C4a = 1.864(2) Å) compared with those in **HI** (Si1–C1 = 1.874(3) and Si2–C1 = 1.872(5) Å). In both structures there are essentially no dihedral angles between the two cyclopentadienyl rings in the ferrocene units, and the thiophene rings are planar with normal bond lengths and angles. The key distinction between the two structures are the



Fig. 1. Crystal structure of **Ha**: (a) regular view, (b) view to show eclipsed ferrocenylene units.

Table 2

Selected bond lengths (Å) and angles (°) for IIa and III

IIa		ш	
C9–Si1	1.857(3)	C5–Si1	1.843(5)
C11–Si2	1.856(3)	C15-Si2	1.856(4)
Si1-C1	1.861(3)	Si1-C4	1.874(5)
Si2–C4a	1.864(2)	Si2-C1	1.872(5)
C9-Si1-C1	109.3(1)	C4-Si1-C5	107.7(2)
C11–Si2–C4a	109.1(1)	C1-Si2-C15	111.4(2)
C16-Si1-C15	109.5(1)	C25-Si1-C26	112.0(2)
C18-Si2-C17	111.5(1)	C27-Si2-C28	110.3(2)

two intramolecular Fe···Fe distances. For **IIa** this distance is 7.57 Å, whereas for **III** it is significantly longer at 11.28 Å, and this will impact many properties, vide infra.

One of the diagnostic features of polyferrocenyl and ferrocenylene complexes and materials is their capacity to



Fig. 2. Crystal structure of III.

exhibit more than a single redox process even though the iron containing groups are nominally identical. We have previously noted that in the α , ω diferrocenyl oligosilanes, $Fc(SiMe_2)_{n}Fc$, when the bridging chain is equal or greater than 4, the two ferrocenyl groups do not interact and only a single redox process is observed via cyclic voltammetry [11]. Shorter chains result in two distinct processes: an initial step involving oxidation of alternate Fc groups, and a second step where the presence of a neighboring ferrocenium ion raises the oxidation potential of the remaining ferrocenylene groups. The transmission of the electronic effects from a ferrocenium ion to a neighboring unoxidized Fe center can be a through bond inductive effect, or through space. Silicon atom bridges and acetylenic bridges effectively facilitate such through bond interactions [11,18]. The degree to which the ferrocene groups in IIa and III can interact in this manner was investigated by cyclic voltammetry. Complex IIa exhibited two discrete redox processes when the experiment was performed in CH₂Cl₂; $E_{ox} = 0.51$ V and $\dot{E}_{ox} = 0.56$ V, $E_{red} = 0.48$ V and $E_{red} = 0.41$ V (relative to Ag/Ag⁺). In acetonitrile, a superior coordinating solvent in which the positive charge is better delocalized, only a single process was observed, $E_{\rm ox} = 0.56$ V, $E_{\rm red} = 0.48$ V. By contrast, regardless of the solvent, only a single process was observable when complex III was examined, $E_{ox} = 0.56$ V, $E_{red} = 0.46$ V. These results clearly show that the capacity for interaction between the ferrocenium ion and the unoxidized ferrocenylene group can occur through space as well as via an atomic backbone. It is not surprising that in III, where the two Fe atoms are separated by > 11 Å, the two redox processes are equivalent.

3. Experimental

All reactions were performed with dry oxygen free solvents in N_2 or Ar atmospheres. Analyses were perfromed by Galbraith Laboratories Inc.; NMR were recorded on a Bruker 250 MHz instrument. LRMS was obtained from the Nebraska Center for Mass Spectrometry. Electrochemical analysis was performed as previously reported, with tetraethylammonium tetrafluoroborate as supporting electrolyte [11].

3.1. Synthesis of 2,5-bis(hydridodimethylsilyl)thiophene [2]

In a 250 ml flask, equipped with a reflux condenser, rubber septum and dropping funnel was added 13.3 g (55 mmol) of

2,5-dibromothiophene in 20 ml of THF to 2.90 g (119 mol) of Mg and 0.4 g I_2 in 100 ml of dry THF. The formation of the Grignard was initiated by mild external heating with a hair dryer and then an exothermic reaction occurred. After complete addition, 3 h, the flask was cooled on an ice bath and 10.4 g (110 mmol) of Me₂SiHCl in 20 ml of THF was added over 20 min. The reaction mixture was stirred overnight and then the solvent removed in vacuo. The crude product was extracted into hexane and filtered. Distillation of the liquid residue after removal of the hexane yielded 6.1 g (30 mmol, 55%) of the title compound, b.p. 90°C/8 mm Hg.

3.2. Chlorination of 2,5-bis(hydridodimethylsilyl)thiophene [2]

In a 100 ml side-arm flask, 3 g (15 mmol) of 2,5bis(hydridodimethylsilyl)thiophene was added slowly to a catalytic amount of PdCl₂ (0.2 g) in 40 ml of carbon tetrachloride. The reaction was monitored by IR spectroscopy and after 30 min the Si–H stretching frequency at ~ 2128 cm⁻¹ had disappeared. The solvent was removed in vacuo and the liquid product was distilled to yield 2,5-bis(chlorodimethylsilyl)thiophene, (b.p. 125–130°C/14 mm Hg, 2.12 g, 7.8 mmol, 52%).

Table 3 Crystal and refinement data

3.3. Reaction of 2,5-bis(chlorodimethylsilyl)thiophene with dilithioferrocene

To a 40 ml hexane slurry of 1,1'-dilithioferrocene \cdot tmeda (prepared from ferrocene (3.0 g, 16 mmol), *n*-butyllithium (24.4 ml of a 1.6 M solution) and 5.8 ml of freshly distilled TMEDA in 150 ml of hexane) [19] was added dropwise 2.7 g (10 mmol) of bis-2,5(chlorodimethylsilyl)thiophene at -78° C. The mixture was stirred for 1 h at this temperature and then permitted to warm to room temperature and stirred overnight. After filtration the solvent was removed in vacuo to produce a brown oily material which was dissolved in the minimum of hexane and placed upon a 2×25 cm silica gel column (60-200 mesh). Development with hexane produced two distinct bands. The initial yellow band was collected and after removal of solvents produced 50 mg (0.07 mmol, 14%) of **IIa** as a red powder which was further purified by recrystallization from hexane, m.p. 230-234°C. A second band eluted with hexane yielded an orange-red oil, IIn.

3.4. Synthesis of 2,5-bis(ferrocenyldimethylsilyl)thiophene (III)

A solution of ferrocenyllithium (prepared from the reaction of 9.28 ml of 1.6 M n-butyllithium with 1.0 g (2.4 mmol)

	Ша	Ш
Empirical formula	C ₁₈ H ₂₂ Si ₂ SFe	$C_{28}H_{32}$ · Si ₂ SFe
Color, habit	orange prism	orange-yellow fragment
Crystal size (mm)	$0.32 \times 0.44 \times 0.80$	$0.60 \times 0.60 \times 0.40$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	11.734(2)	21.429(5)
b (Å)	11.999(2)	8.775(2)
<i>c</i> (Å)	13.444(2)	14.824(4)
α (°)	90.00	90.00
β (°)	99.14(1)	106.95(2)
γ (°)	90.00	90.00
Volume $(Å^3)$	1868.8(5)	2666.4(11)
Ζ	4	4
2θ range (°)	3.5-45	4.0-45
Scan type	ω	ω
Scan speed (° min ^{-1})	3–20	3–15
Scan range w (°)	1.40	1.20
Standard reflections	3 measured every 97 reflections	3 measured every 97 reflections
Index ranges		
h	0 to 12	-23 to 22
k	-2 to 12	-9 to 2
l	- 14 to 14	-3 to 15
Reflections collected	3189	3794
Independent reflections	2462	3476
Observed reflections	2286 $(F > 3.0\sigma(F))$	3195 $(F > 3.0\sigma(F))$
Absorption correction	Semi-empirical	N/A
Min./max. transmission	0.221/0.254	N/A
Final <i>R</i> indices (observed data)	R = 3.07%, wR = 5.07%	R = 4.75%, wR = 7.32%

of FcHgCl) was added dropwise to 1.0 g (3.7 mmol) of 2,5bis(chlorodimethylsilyl)thiophene in 30 ml of THF at -78° C. The mixture was stirred overnight and then the solvent was removed in vacuo. The product was extracted with hexane, and the solution filtered. After removal of the solvent di-*n*-butylmercury was distilled to leave a gummy residue. This was dissolved in the minimum of hexane and placed upon a 10×2 cm silica gel column (60–200 mesh) and eluted with hexane. An orange band developed and was collected, the solvent removed and the final residue recrystallized from hexane to yield **III**, 1.2 g (2.1 mmol, 57%), m.p. 77°C.

Also prepared by the same general route, in 65% yield, was 2,5-bis(ferrocenyldiphenylsilyl)thiophene (**IV**) from the reaction of ferrocenyllithium and 2,5-bis(chlorodiphenylsilyl)thiophene.

3.5. Structural analysis of IIa and III

crystal of approximate An orange dimensions $0.32 \times 0.44 \times 0.80$ mm (IIa) and an orange-yellow crystal approximately $0.60 \times 0.60 \times 0.40$ mm in size (III) were mounted on glass fibers in a random orientation. Intensity data were collected at room temperature for **IIa** and -100° C for III, which decayed under the X-ray beam at room temperature, using a Siemens/Bruker four circle diffractometer with graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å. Unit cell parameters and standard deviations were obtained by least-squares fit of 25 reflections randomly distributed in reciprocal space in the 2θ range of 15–30°. The ω -scan technique was used for intensity measurements in both cases. A range of 1.4° in ω and variable speed of 3.00 to 20.00° min⁻¹ was used for IIa and a 1.2° ω -range and a 3.00 to 15.00° \min^{-1} speed for III. Background counts were taken with stationary crystal and total background time to scan time ratio of 0.5. Three standard reflections were monitored in both cases every 97 reflections and showed no significant decay for IIa and an average intensity decay of 8.2% for III even at -100° C. The data were corrected for Lorentz and polarization effects but only IIa was corrected semi-empirically for absorption giving a min./max. transmission ratio of 0.221/ 0.254.

Both structures were solved by direct methods and refined using the PC-version of the SHELXTL PLUS crystallographic software by Siemens. Full-matrix least-squares refinement minimizing $\Sigma w (F_o - F_c)^2$ was carried out with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were placed at calculated positions (C–H 0.96 Å; $U_{\rm H}$ =0.08) during refinements. The weighing scheme has the form $w^{-1} = \sigma^2(F) + gF^2$ and the final *R* factors the form $R = \Sigma |F_o - F_c| / \Sigma F_o$ and $R_{\rm w} = [w|F_o - F_c|^2 / \Sigma w F_o^2]^{1/2}$. Relevant crystal and refinement data are provided

4. Supplementary data

Crystallographic data for structures **IIa** and **III** are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk), quoting the deposition numbers CCDC 140477 (**IIa**) and CCDC 140478 (**III**).

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References

- [1] J. Roncali, Chem. Rev. 92 (1992) 711.
- [2] J. Oshita, D. Kanaya, M. Ishikawa, T. Koike, T. Yamanaka, Macromolecules 24 (1991) 2106.
- [3] P. Chicart, R.J.P. Corriu, J.J.E. Moreau, F. Garnier, A. Yassar, Chem. Mater. 3 (1991) 8.
- [4] P. Chicart, R.J.P. Corriu, J.J.E. Moreau, F. Garnier, A. Yassar, in: R.M. Laine (Ed.), Inorganic and Organometallic Polymers with Special Properties, Kluwer, 1992, p. 179.
- [5] S.K. Riter, R.E. Noftle, Chem. Mater. 4 (1992) 872.
- [6] D.A. Foucher, B.-Z. Tang, I. Manners, J. Am. Chem. Soc. 114 (1992) 6246.
- [7] D.A. Foucher, R. Ziembinski, B.-Z. Tang, P.M. Macdonald, J. Massey, C.R. Jaeger, G.J. Vancso, I. Manners, Macromolecules 26 (1993) 2878.
- [8] I. Manners, Adv. Organomet. Chem. 37 (1995) 131.
- [9] M.T. Nguyen, A.F. Diaz, V.V. Dementiev, H.K. Sharma, K.H. Pannell, SPIE Proc. 1910 (1993) 230.
- [10] M.T. Nguyen, A.F. Diaz, V.V. Dementiev, K.H. Pannell, Chem. Mater. 5 (1993) 1389.
- [11] V.V. Dementiev, F. Cervantes-Lee, L. Párkányi, H.K. Sharma, K.H. Pannell, M.-T. Nguyen, A.F. Diaz, Organometallics 12 (1993) 1983.
- [12] M.T. Nguyen, A.F. Diaz, V.V. Dementiev, K.H. Pannell, Chem. Mater. 6 (1994) 952.
- [13] K.H. Pannell, V.V. Dementiev, H. Li, F. Cervantes-Lee, M.T. Nguyen, A.F. Diaz, Organometallics 13 (1994) 3644.
- [14] M. Tanaka, T. Hayashi, Bull. Chem. Soc. Jpn. 66 (1993) 334.
- [15] N.P. Reddy, H. Yamashita, M.J. Tanaka, Chem. Soc., Chem. Commun. (1995) 2263.
- [16] M. Hmyene, A. Yasser, M. Escorne, A. Percheron-Guegan, F. Garnier, Adv. Mater. 6 (1994) 564.
- [17] K. Mochida, N. Shibayama, M. Goto, Chem. Lett. (1998) 339.
- [18] C. Le Vanda, K. Berchgaard, D.O. Cowan, J. Org. Chem. 41 (1976) 2700.
- [19] J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenberg, R.E. Merrill, J.C. Smart, J. Organomet. Chem. 27 (1971) 241.