



Synthesis and characterization of new germylferrocenyl, germylferrocenophane and polymeric germyleneferrocenylene systems

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Abstract

New germanium-bridged [1]ferrocenophanes $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeClR}$ (**1**), ($\text{R} = \text{Me}$ (**1a**), $t\text{-Bu}$ (**1b**), Ph (**1c**)) were prepared by the reaction of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\cdot\text{TMEDA}$ (TMEDA = tetramethylethylenediamine) with the corresponding chlorogermenes, RGeCl_3 ($\text{R} = \text{Me}$, $t\text{-Bu}$, Ph). Ring-opening addition of HCl to **1c** resulted in the formation of $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{GeCl}_2\text{Ph}$ (**2**) which was reacted with dilithioferrocene·TMEDA to form $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{FcPhGe}$ (**3**). All complexes were characterized by ^{13}C and ^1H NMR, and the structure of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeClPh}$ was determined by single-crystal X-ray diffraction analysis and exhibits a dihedral angle between the planes of the cyclopentadienyl rings of 18.4° . Cyclic voltammetric analysis of **1a**, **1b**, and **1c** in CH_2Cl_2 revealed that each ferrocenophane exhibits a reversible, one-electron oxidation, at a higher oxidation potential than that of ferrocene. The voltammogram of **3** shows two reversible redox processes, one for the ferrocenophane moiety and a second for the pendant ferrocene group. Thermal ring-opening of **3** produced good yields of the corresponding polymer $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{FcPhGe}]_n$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germylferrocenophane; Germyleneferrocenylene systems; [1]Ferrocenophanes

1. Introduction

The interest in developing ferrocene-containing materials is due to the thermal and photochemical stability, non-linear optical effects, and reversible redox properties of the ferrocene group (Fc) and the hope that some of these properties will result in novel materials [1–3]. The recent discovery that silicon-bridged [1]ferrocenophanes ($\text{R} = \text{R}' = \text{Me}$ or Ph) undergo thermally induced ring-opening polymerization (ROP) reactions to yield poly(ferrocenylenesilylenes) has prompted an interest in synthesizing a variety of [1]ferrocenophanes [4]. Today, a wide range of silicon-bridged [1]ferrocenophanes with either symmetrically or unsymmetrically substituted silicon atoms are known. In addition, substituents such as hydrogen, chlorine, trifluoropropyl, norbornyl, and ferrocenyl groups have also been introduced [5].

[1]Ferrocenophanes containing bridging germanium and tin groups are also known but are much less studied; however, their thermal ROP has been used for the synthesis of poly(ferrocenylene)germylenes/stannylenes [6,7]. We now report the synthesis, structural characterization, and electrochemical properties of new [1]germyl ferrocenophanes, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeClR}$ (**1**), $\text{R} = \text{Me}$ (**1a**), $t\text{-Bu}$ (**1b**), Ph (**1c**), $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeFcPh}$ (**3**) and the polymers resulting from thermal ring-opening of **3**.

2. Experimental

All manipulations were carried out under an Ar atmosphere. Solvents were dried prior to use by conventional methods. Tetramethylethylenediamine (TMEDA), ferrocene and 1.6 M $n\text{-butyllithium}$ in hexanes were purchased from Aldrich; MeGeCl_3 , PhGeCl_3 and $t\text{-BuGeCl}_3$ were purchased from Gelest, Inc.;

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TMEDA, PhGeCl_3 and MeGeCl_3 were distilled prior to use.

A Lambda 14 Perkin–Elmer spectrophotometer was employed to obtain the UV–vis spectra in CH_2Cl_2 solutions using a 1 cm quartz cell; NMR spectra were obtained using a Bruker 300 MHz spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

2.1. Synthesis of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeClPh}$ (*fcGePhCl*, **1c**)

To a solution of ferrocene (7.27 g, 0.04 mol) and TMEDA (13.60 ml, 0.09 mol) in hexane (120 ml) was

added *n*-BuLi (56 ml, 0.09 mol) and the mixture was stirred for 18 h. An orange precipitate formed, which was washed with hexane until the hexane was colorless. To the solid materials was added 80 ml of ether and the resulting slurry was stirred at -78°C . To this slurry was added PhGeCl_3 (10 g, 0.04 mol) over 10 min and the resulting mixture was permitted to warm to room temperature (r.t.) and stirred overnight. The solution was filtered and the solvent was removed in vacuo to form **1c** as a red solid, yield 9.01 g (0.024 mol, 62%). The solid was crystallized from hexane.

In a similar manner we obtained fcGeMeCl (**1a**, 54%) and $\text{fcGe-}t\text{-BuCl}$ (**1b**, 55%). Spectroscopic and elemental analysis data are presented in Table 1.

2.2. Synthesis of $1,1'\text{-FcPhGe}(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}$, (**3**)

To a solution of **1c** (3.40 g, 9.2 mmol) in 100 ml of hexane was added dropwise at r.t. 9.2 ml (9.2 mmol) of a 1 M HCl in ether solution. During the addition, the solution changed from red to yellow. The solution was stirred for 15 min and filtered. The solvent was removed in vacuo to yield the product FcGePhCl_2 (**2**) as a red viscous liquid 3.30 g (8.14 mmol, 89%). This product was characterized by NMR and used immediately.

To a slurry of dilithioferrocene (prepared from 1.89 g of ferrocene, 2.61 g of TMEDA, and 13.4 ml of 1.6 M *n*-BuLi), maintained at -78°C , was added 3.30 g (8.14 mmol) of **2** dissolved in ether. The solution was allowed to warm to r.t. and stirred overnight. The solvent was removed under vacuum to leave a red precipitate. The product was washed twice with 50 ml of hexane and then dissolved with a mixture of toluene and THF (3:1). The solution was filtered to remove the lithium salts and the solvent was removed under vacuum to produce the red powder fcGeFcPh (**3**) (2.88 g, 5.6 mmol, 69%). The ferrocenophane **3** could be further purified by recrystallization from THF.

2.3. Synthesis of poly-ferrocenylenephenylferrocenylgermylene (**4**)

(A) Ferrocenophane **3** (0.60 g, 1.16 mmol) was placed in a sealed, evacuated Pyrex tube and directly heated at ca. 170°C for 3 h. The powder gradually became more viscous and eventually immobile. Extraction with THF and precipitation into 200 ml of MeOH afforded the orange powder poly(phenylferrocenylgermaneferrocenylene) (0.48 g, 0.93 mmol, 80%), $M_w = 26\,000$ (using polystyrene standards), with a polydispersity range of 1.9–3.9 from different analyses.

(B) A solution of ferrocenophane **3** (0.60 g, 1.16 mmol) in toluene was refluxed for 50 h. The toluene was removed under vacuum, and the polymeric residue was dissolved in THF (5 ml), filtered, and precipitated

Table 1
Spectroscopic and analytical data for new complexes ^a

fcGeMeCl (1a) M.p. $88\text{--}90^\circ\text{C}$ ^1H NMR: $\delta = 0.75(\text{s}, 3\text{H}, \text{Me}), 3.82\text{--}4.48(\text{m}, 8\text{H}, \text{Cp})$ ^{13}C NMR: $\delta = 2.76(\text{Me}), 31.5(\text{ipso-C}), 73.6, 76.6, 77.7, 78.1(\text{Cp})$ UV–vis: λ (nm) (ϵ , $1\text{ mol}^{-1}\text{ cm}^{-1}$) (CH_2Cl_2): 482 (201)
fcGe-<i>t</i>-BuCl (1b) M.p. $104\text{--}106^\circ\text{C}$ ^1H NMR: $\delta = 1.26(\text{s}, 9\text{H}, t\text{-Bu}), 3.94\text{--}4.54(\text{m}, 8\text{H}, \text{Cp})$ ^{13}C NMR: $\delta = 26.9(\text{C}(\text{CH}_3)_3), 31.5(\text{ipso-C}), 31.8(\text{C}(\text{CH}_3)_3), 74.9, 77.8, 77.9, 78.1(\text{Cp})$ UV–vis: λ (nm) (ϵ , $1\text{ mol}^{-1}\text{ cm}^{-1}$) (CH_2Cl_2): 479 (225) Anal. Found: C, 47.48; H, 4.61. Calc. C, 48.15; H, 4.91%.
fcGePhCl (1c) M.p. $98\text{--}100^\circ\text{C}$ ^1H NMR: $\delta = 3.85, 4.25, 4.38, 4.49(\text{s}, \text{s}, \text{s}, \text{s}, 8\text{H}, \text{Cp}), 7.15\text{--}7.73(\text{m}, 5\text{H}, \text{Ph})$ ^{13}C NMR: $\delta = 30.8(\text{ipso-C}), 74.7, 77.1, 78.0, 78.5(\text{Cp}), 129.5, 131.8, 133.7, 135.3(\text{Ph})$ UV–vis: λ (nm) (ϵ , $1\text{ mol}^{-1}\text{ cm}^{-1}$) (CH_2Cl_2): 479 (234) Anal. Found: C, 51.92; H, 3.43. Calc. C, 52.05; H, 3.55%.
FcGePhCl₂ (2) ^1H NMR: $\delta = 4.04(\text{s}, 5\text{H}, \text{Cp}), 4.12, 4.25(\text{m}, \text{m}, 4\text{H}, \text{Cp}), 7.07\text{--}7.09(\text{m}, 3\text{H}, \text{Ph}), 7.71\text{--}7.73(\text{m}, 2\text{H}, \text{Ph})$ ^{13}C NMR: $\delta = 69.9, 71.1(\text{ipso-C}), 71.9, 72.5(\text{Cp}), 129.1, 131.6, 132.5, 136.7(\text{Ph})$ Anal. Found: C, 47.80; H, 3.56. Calc. C, 47.37; H, 3.48%.
fcGeFcPh (3) M.p. 145°C ^1H NMR: $\delta = 4.00\text{--}4.45(\text{m}, 17\text{H}, \text{Cp}), 7.26\text{--}7.28(\text{m}, 3\text{H}, \text{Ph}), 7.88\text{--}7.91(\text{m}, 2\text{H}, \text{Ph})$ ^{13}C NMR: $\delta = 30.4(\text{ipso-C of fc}), 69.0(\text{C}_5\text{H}_5), 69.4(\text{ipso-C of Fc}), 71.0, 73.6, 76.78, 76.81, 77.0, 77.4(\text{C}_5\text{H}_4), 128.9, 130.0, 134.7, 135.9(\text{Ph})$ UV–vis: λ (nm) (ϵ , $1\text{ mol}^{-1}\text{ cm}^{-1}$) (CH_2Cl_2): 465 (202) Anal. Found: C, 58.28; H, 4.76. Calc. C, 60.20; H, 4.27%.
(fcGeFcPh)_n (4) ^1H NMR: $\delta = 3.99, 4.26(\text{s}, \text{s}, 17\text{H}, \text{Cp}), 7.33(\text{s}, 3\text{H}, \text{Ph}), 8.12(\text{s}, 2\text{H}, \text{Ph})$ ^{13}C NMR: $\delta = 69.2(\text{C}_5\text{H}_5), 70.7, 71.9, 72.5(\text{ipso-C}), 73.08(\text{ipso-C}), 73.8, 74.1(\text{Cp}), 128.3, 129.2, 135.2, 139.3(\text{Ph})$ Anal. Found: C, 59.92; H, 4.40. Calc. C, 60.20; H, 4.27%.

^a NMR solvent C_6D_6 .

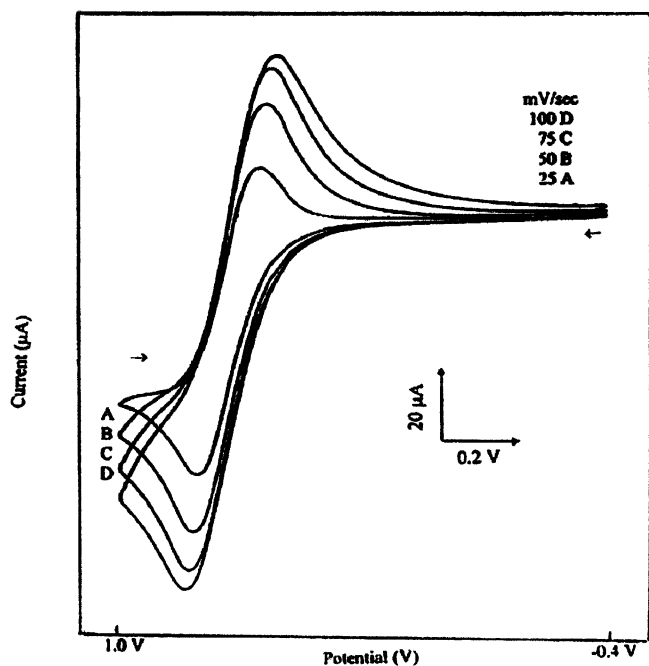


Fig. 1. Cyclic voltammogram for **1b** at variable scan rates.

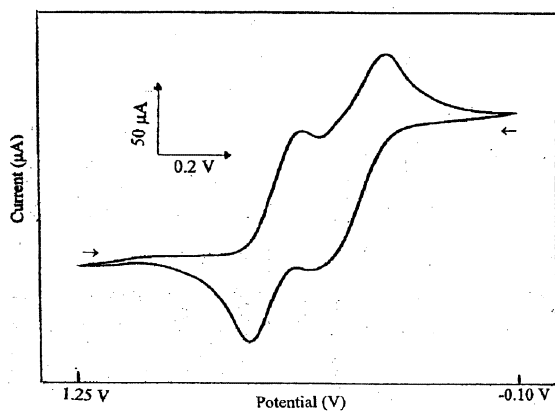


Fig. 2. Cyclic voltammogram for **3** at a 50 mV s⁻¹ scan rate.

Table 2
Cyclic voltammetry data (V) at scan rate 50 mV s⁻¹

Compound	R	R'	E_{pa}	E_{pc}		
Ferrocene			0.71	0.35		
1a	Me	Cl	0.88	0.53		
1b	<i>t</i> -Bu	Cl	0.84	0.55		
1c	Ph	Cl	0.83	0.45		
3	Ph	Fc	E_{pa1}	E_{pc1}	E_{pa2}	E_{pc2}
			0.50	0.28	0.77	0.56

by addition of MeOH (200 ml) to produce the poly(phenylferrocenylgermylene)ferrocenylene, as a pale yellow solid (0.31 g, 0.60 mmol, 52%) $M_w = 11\,000$, $M_n = 2500$, polydispersity = 4.3.

2.4. Electrochemistry

A fully equipped 10 ml voltammetric cell (Bioanalytical Systems, model C-3) was used. The cell contained either a glassy carbon or platinum electrode (3 mm diameter) as a working electrode, a reference electrode (Ag | AgCl, Model R E-1), and a platinum wire auxiliary. The glassy carbon and platinum electrode surfaces were polished daily with 0.05 μ m alumina slurry, rinsed with copious amounts of deionized water, and allowed to air-dry. Cyclic voltammograms were recorded with CV-27 cyclic voltammograph using a Model RXY recorder.

A 0.1 M *t*-butyl ammonium hexafluorophosphate (*t*-BAHP) buffer was prepared by dissolving 0.39 g in 10 ml of methylene chloride. Compounds **1a**, **1b**, **1c**, **3** and ferrocene were dissolved in methylene chloride and further diluted with the buffer solution. Nitrogen gas was purged for 15 min before each experiment. Cyclic voltammetry was performed over the potential range of -0.04 to 1.0 V. Fig. 1 shows the cyclic voltammograms obtained for **1b** at variable scan rates as a typical example, and Fig. 2 illustrates the cyclic voltammogram obtained from **3**; the various E_{pa} and E_{pc} values obtained for each compound are presented in Table 2.

2.5. X-ray structure of **1c**

Crystals suitable for single-crystal X-ray analysis were obtained for **1c**, and were sealed in epoxy glue for data collection, causing some difficulty with perfect alignment. Hydrogen atoms were included as riding atoms in the final refinement and the resulting structure is illustrated in Fig. 3. Crystal data are represented in Table 3 and selected bond lengths and angles in Table 4.

3. Results and discussion

Using the standard salt-elimination reaction outlined in Eq. (1) the [1]germyl ferrocenophanes **1** were readily prepared in good to moderate yields.

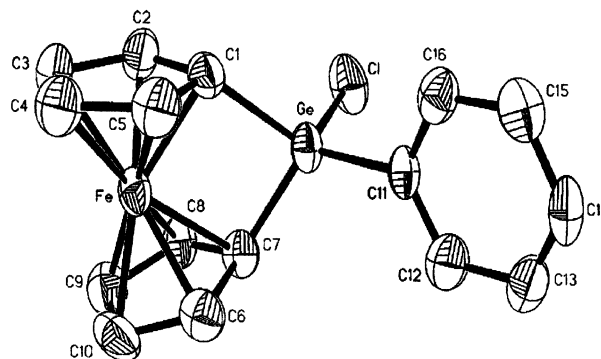


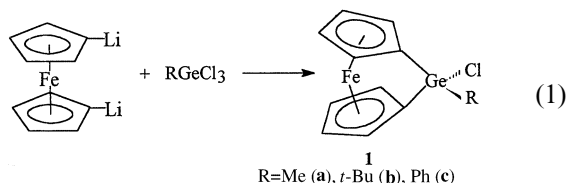
Fig. 3. Structure of **1c**.

Table 3
Summary of crystal data and intensity collection parameters for FcGePhCl

Empirical formula	$\text{C}_{16}\text{H}_{13}\text{ClFeGe}$
Crystal system	Triclinic
Space group	$P\bar{1}$
Wavelength ($\text{\AA}$)	Mo- K_{α} radiation (0.71073)
μ (mm^{-1})	3.311
Unit cell dimensions	
a ($\text{\AA}$)	7.440(3)
b ($\text{\AA}$)	9.467(4)
c ($\text{\AA}$)	10.621(5)
α ($^{\circ}$)	74.82(3)
β ($^{\circ}$)	79.49(4)
γ ($^{\circ}$)	89.79(3)
V ($\text{\AA}^3$)	709.1(5)
Z	2
D_{calc} (mg m^{-3})	1.729
$F(000)$	368
Theta range for data collection ($^{\circ}$)	2.02–22.55
Total no. of reflections	2017
No. of unique reflections	1841
Absorption correction	Semi-empirical SHELEXTL-PLUS 1988
Max/min transmission	0.31 and 0.11
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.933
Final R indices [$I > 2\sigma(I)$]	$R = 0.0669$, $R_w = 0.1655$
R indices (all data)	$R = 0.0740$, $R_w = 0.1756$
Largest differential peak and hole ($\text{e \AA}^{-3}$)	1.436 and -1.542

Table 4
Selected bond lengths ($\text{\AA}$) and bond angles ($^{\circ}$)

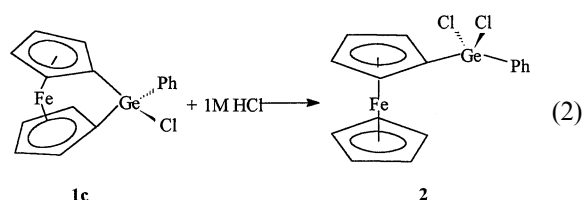
Fe–Ge	2.7162(16)	C(11)–Ge–C(1)	116.2(3)
Ge–C(1)	1.948(7)	C(11)–Ge–C(7)	115.0(3)
Ge–C(7)	1.951(8)	C(1)–Ge–C(7)	95.2(3)
Ge–C(11)	1.917(7)	C(11)–Ge–Cl	111.5(2)
Ge–Cl	2.173(2)	C(1)–Ge–Cl	108.4(2)



The complexes were isolated as red–orange, moisture-sensitive, materials that required storage in inert atmospheres at low temperatures to avoid decomposition. The spectroscopic data from the new materials are in accord with their structural assignments. Thus the ^{13}C NMR spectra for **1a**, **1b**, and **1c** exhibited chemical shifts for the *ipso* carbon atom resonances at 31.5, 31.5, and 30.8 ppm, respectively. This high-field value is characteristic for strained [1]ferrocenophanes which contain a single Group 14 atom in the bridge [4].

The synthesis of the ferrocenylgermylferrocenophane **3** involved the initial HCl induced ring-opening of **1c** to

form $\text{FcGePh}(\text{Cl})_2$ (**2**), Eq. (2) [8]. The ^{13}C NMR spectrum of **2**, is consistent with its structure. The resonance assigned to the *ipso* carbon atoms has shifted from 30.8 ppm in **1c** to 71.3 ppm in **2**.



Compound **3** was then synthesized by the salt-elimination reaction between $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})_2\cdot\text{TMEDA}$ and **2**. The spectroscopic data for **3** are in accord with the structure, e.g. the ^{13}C resonance for the ferrocenophane *ipso* carbon atoms appears at 30.6 ppm. The UV–vis spectra for **1a**, **1b**, **1c**, and **3** show a band in the region of 465–481 nm that represents a bathochromic shift relative to the band of ferrocene at 440 nm in accord with data reported for other Group 14 [1]ferrocenophanes [4].

3.1. Crystal Structure for **1c**

The X-ray crystal structure of **1c** revealed a tilt-angle between the planes of the cyclopentadienyl ligands of 18.4° , changed from the parallel planes observed for ferrocene due to the single atom bridge. This value compares with $16.6(1.5)^{\circ}$ for $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GePh}_2$ [9] and $19.0(0.9)^{\circ}$ for $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeMe}_2$ [10]. At the Ge atom, a small bond angle of $95.2(3)^{\circ}$ was found for $\text{C}_{ipso}\text{--Ge--C}_{ipso}$, and a correspondingly larger angle of $111.5(2)^{\circ}$ was found for the $\text{C}_{phenyl}\text{--Ge--C}_{methyl}$. Both reflect a considerable distortion from tetrahedral geometry; a similar effect was observed for $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{GeMe}_2$ [10].

3.2. Electrochemistry discussion

Cyclic voltammetry studies of compounds **1a**, **1b**, **1c**, and **3** were performed on CH_2Cl_2 solutions at a variable scan rates under an inert atmosphere. Ferrocene was used as a reference compound. The voltammograms obtained from investigation of **1a**, **1b**, **1c** indicated that a completely reversible one-electron redox processes occurred. Despite the stretching of the inter-cyclopentadienyl ring distance upon oxidation of ferrocene to ferrocenium, the germylene bridge permits this expansion to occur without loss of reversibility. The oxidation potentials of the chloro-substituted materials are all significantly higher than ferrocene due to the electron-withdrawing nature of the halogen.

Compound **3** could in theory exhibit two distinct redox processes due to the presence of the ferrocenyl substituent on germanium. Indeed, as seen in Fig. 2,

two reversible redox processes are observed, $E_{\text{pa1}} = 0.50$ V, $E_{\text{pa2}} = 0.77$ V, $E_{\text{pc1}} = 0.28$ V, and $E_{\text{pc2}} = 0.56$ V, similar to the data obtained from a silicon analog $\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMeFc}$ ($\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)((\eta^5\text{-C}_5\text{H}_5))$) complex [5c]. We attribute the first redox process to the pendant ferrocene group and the second to the ferrocenophane moiety. The oxidation potentials for the pendant ferrocene groups in the bis(ferrocenyl) complex $\text{Fc}(\text{SiMe}_2)_2\text{Fc}$ are 0.56 and 0.67 V [11]. These values are close to the first oxidation potential observed in **3**. The second oxidation potential value observed at 0.77 V for **3** is closer to oxidation potentials found for the ferrocenophanes **1a**, **1b**, and **1c**.

3.3. Ring-opening polymerization of **3**

The thermal ring-opening of **3** produced good yields of the corresponding poly-ferrocenylenegermylene material. We performed this polymerization both in the melt and in toluene solution. The yield was superior in the melt reaction and the molecular weights also showed a distinct difference, $M_w(\text{melt}) = 26\,000$, $M_w(\text{solution}) = 11\,000$. Both samples are low molecular weight materials compared to other samples of the silylene(germylene)ferrocenylenes family; however, we made no attempt to optimize this aspect of the study. Both samples were completely amorphous as determined by powder X-ray diffraction, and this is in keeping with other systems with two different groups attached to the Si(Ge) backbone atom. Upon ring-opening the electrochemical properties of the polymer exhibit a more complex pattern. Not only are the adjacent Fe centers in the polymer backbone distinctive, as has been well documented, but the extra redox processes of the pendant ferrocenyl groups are also observed. Detailed studies on this and related polymers will be the subject of future publications.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157699 for compound **1c**. Copies of this information may be obtained free of charge from The Director, CCDC, 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>).

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