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# A Synthetic Route to Borylene-Bridged Poly(ferrocenylene)s**

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*Dedicated to Professor Herbert W. Roesky*
*on the occasion of his 70th birthday*

The chemistry of metal-containing polymers is receiving increasing attention in the search for new materials that possess useful optical, electronic, and magnetic properties.[1–4] Among the compounds developed so far, organometallic macromolecules have become particularly attractive targets ever since the ring-opening polymerization (ROP) of strained

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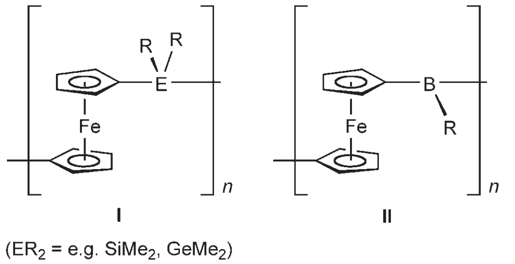
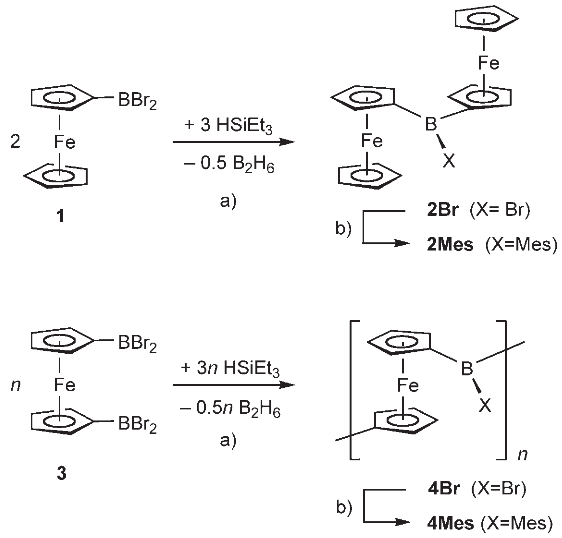
ring-tilted [1]ferrocenophanes[5] was used to synthesize the first high-molecular-weight poly(ferrocenylene)s (**I**, Scheme 1) with skeletal iron atoms. Within this particular class of compounds, boranediyl-bridged poly(ferrocenylene)s (**II**, Scheme 1) are of paramount interest because the three-coordinate boron spacer offers a vacant p orbital for conjugative interaction with the cyclopentadienyl π-systems. Boranediyl bridges should therefore be capable of mediating electronic interactions between the iron centers very efficiently.[6,7] The degree of electronic communication via the boron atom can be fine-tuned by modifying the π-donor ability of its substituent R, thereby offering a way for the rational design of novel materials with potentially useful electronic properties. Attempts to polymerize boron-bridged [1]ferrocenophanes using the ROP approach have so far been restricted to boron moieties bearing amino substituents. Moreover, the products obtained proved to be mainly insoluble in organic solvents and the minor soluble fraction was shown by NMR spectroscopy and mass spectrometry to consist primarily of small, cyclic oligomers ($n = 2, 3$).[8,9] The purpose of this paper is to present a new synthetic strategy that provides convenient access to the first soluble ferrocenylborane polymers containing electron-deficient, three-coordinate boron spacers in the polymer main chain. Our key discovery in this context is the facile and quantitative coupling reaction that occurs upon treatment of $FcBBr_2$ with $HSiEt_3$ to yield the diferrocenylborane $Fc_2BBr$ (Fc = $(C_5H_5)Fe(C_5H_4)$). We show here that the same synthetic protocol can successfully be applied to the preparation of the corresponding polymers $[\text{-fc-B(Br)-}]_n$ starting from the difunctional monomer $fc(BBr_2)_2$ (fc = $Fe(C_5H_4)_2$).



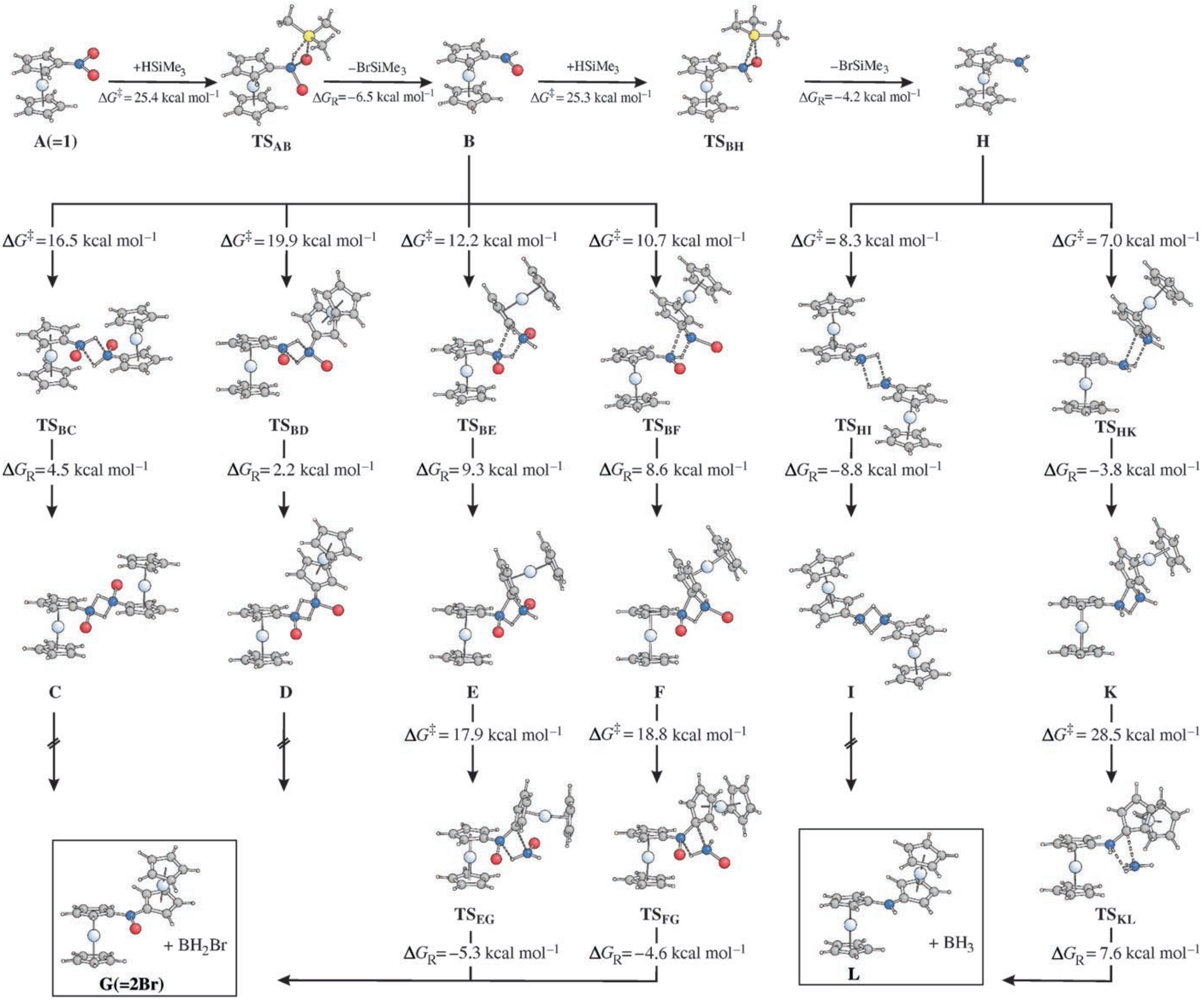
***Scheme 1.*** Poly(ferrocenylene)s **I** generated by ring-opening polymerization of [1]ferrocenophanes; the boron-bridged target polymer **II**.

We began our study with a detailed investigation of the key coupling step. As mentioned above, $Fc_2BBr$ (**2Br**, Scheme 2) can be obtained by treating two equivalents of $FcBBr_2$ (**1**)[10] with three equivalents of $HSiEt_3$ in toluene;[11] in addition, half an equivalent of $B_2H_6$ and three equivalents of $BrSiEt_3$ are liberated in the course of the reaction. The NMR spectra of **2Br** agree with those of a structurally authenticated sample of $Fc_2BBr$ that was synthesized independently from $FcSnMe_3$ and $FcBBr_2$.[12] Since there is no indication of the presence of $Fc_2BH$[13] in the crude reaction mixture, ferrocenyl transfer obviously proceeds not only with practically quantitative yield but also with excellent selectivity towards the formation of BBr bridges. A series of NMR experiments showed that the reaction of $FcBBr_2$ with $HSiEt_3$ in a molar ratio of 2:1 leads to a mixture of $FcBBr_2$, $Fc_2BBr$, and $B_2H_6$. For quantitative conversion, a minimum of 1.5 equivalents of $HSiEt_3$ is required.



***Scheme 2.*** Synthesis of **2Br**, **4Br**, **2Mes**, and **4Mes**. a) toluene, −78 °C to RT; b) $[CuMes]_n$, toluene, 80 °C; Mes = mesityl.

Details of the reaction mechanism for the formation of **2Br** (**G** in Scheme 3) were elucidated by means of quantum chemical calculations employing the ONIOM extrapolation scheme (see Supporting Information[11] for details). These calculations were performed with the real molecular models, except for the use of $HSiMe_3$ instead of $HSiEt_3$ as the hydride source. In line with the experimental finding that $FcBBr_2$ does not dimerize under any experimental conditions, we were unable to locate a doubly bromide-bridged dimer of **1** (**A** in Scheme 3). Instead, the reaction commences with formation of FcBHBr (**B**) from $FcBBr_2$ (**A**) via $\mathbf{TS_{AB}}$, the transition structure of a concerted Br/H exchange by $HSiMe_3$ (Scheme 3). $\mathbf{TS_{AB}}$ is connected with an energy barrier of $\Delta G^{\neq} = 25.4\ \text{kcal mol}^{-1}$, and formation of **B** is exergonic by $\Delta G_R = -6.5\ \text{kcal mol}^{-1}$. **B** can dimerize to the doubly hydride-bridged *cis*/*trans* isomers **C** and **D**. We did not find reaction pathways leading from **C** or **D** to the experimentally characterized final product **G**. Instead, we identified alternative routes via the two isomeric (μ-H)(μ-C)-bridged dimers **E** and **F**. Both are higher in energy than their doubly hydride-bridged counterparts, but are formed with significantly lower barriers. Subsequent product formation from **E** and **F** is an exergonic process and occurs with elimination of $BH_2Br$. Assuming fast pre-equilibria between **B** and **E** and **B** and **F**, the effective activation barriers for the formation of **G** from **B** amount to $\Delta G^{\neq} = 27.2$ and $27.4\ \text{kcal mol}^{-1}$, respectively. Yet another reaction pathway opens up for **B** after consumption of a second equivalent of $HSiMe_3$ to yield $FcBH_2$ (**H**). With $\Delta G^{\neq} = 25.3$ and $\Delta G_R = -4.2\ \text{kcal mol}^{-1}$, the energetic characteristics of this process are very similar to those of the initial step **A**→**B**. Dimerization of **H** to **I** closely resembles the corresponding elementary steps **B**→**C** and **B**→**D** and is kinetically and thermodynamically feasible, but represents a



***Scheme 3.*** Computed reaction pathways leading to the formation of **G** (=**2 Br**); gray C, light blue Fe, blue B, red Br, yellow Si.

dead end for the reaction cascade as well. Thus, also in this region of the potential-energy surface, the productive pathway (now leading to diferrocenylborane **L** with $\Delta G^{\neq} = 28.5\,\text{kcal mol}^{-1}$) proceeds via a (μ-H)(μ-C)-bridged dimer (**K**).

With the scenario outlined in Scheme 3, key elementary steps leading to diferrocenylboranes **G** (=**2 Br**) and **L** have been unveiled. The experimentally observed exclusive formation of **G** can be explained by a H/Br exchange reaction according to $\mathbf{L}+\tfrac{1}{2}(BH_2Br)_2 \rightarrow \mathbf{G}+\tfrac{1}{2}B_2H_6$, for which we compute a thermodynamic driving force of $\Delta G_R = -7.9$ kcal mol$^{-1}$. In addition, we found a thermodynamically viable shunt pathway that competes for the formation of **L** via regeneration of **B** from **H** according to $\mathbf{H}+\tfrac{1}{2}(BH_2Br)_2 \rightarrow \mathbf{B}+\tfrac{1}{2}B_2H_6$ ($\Delta G_R = -7.7\,\text{kcal mol}^{-1}$). In conclusion, theory indicates that the overall reaction $2\,\mathbf{A}+3\,HSiMe_3 \rightarrow \mathbf{G}+\tfrac{1}{2}B_2H_6+3\,BrSiMe_3$ is highly exothermic (by $\Delta G_R = -26.2\,\text{kcal mol}^{-1}$) and that competing alternative reaction pathways converge to the sole product **G**, which is fully in line with the experimental observations. Hence, this condensation reaction meets all the requirements for an efficient polymerization process.

Accordingly, the bromo-substituted polymer **4 Br** was prepared from fc$(BBr_2)_2$ (**3**)[14] and three equivalents of $HSiEt_3$ in a very clean reaction. This polymer is highly sensitive to air and moisture and does not dissolve in common inert solvents. It was therefore transformed into the corresponding mesityl-substituted polymer **4 Mes** by treating a slurry of **4 Br** in toluene with $[CuMes]_n$ ($n = 4, 5$).[15–17] The mesityl substituent was chosen because it aids in the solubilization of the material and also provides steric protection to the boron sites (Scheme 2).[18] This new polymer is only moderately sensitive to air and has a high thermal stability, according to thermogravimetric analysis (TGA) under nitrogen. A single-step weight loss of 72 %, with an inflection point at 403 °C, gave a brown ceramic material in 28 % yield. Differential scanning calorimetry[11] revealed a glass-transition temperature, $T_g$, of 110 °C, which is similar to that reported for poly(ferrocenylphenylphosphane)

([-fcP(Ph)-]$_n$, 126 °C), which also contains tricoordinate bridging units.[19] The molecular weight and dispersity of **4Mes** were analyzed by gel permeation chromatography (GPC) on a chromatograph equipped with refractive index (RI) and multi-angle laser light scattering (MALLS) detectors, and further studied by MALDI TOF mass spectrometry.[11] The mesityl-stabilized polymer **4Mes** was found to be well compatible with GPC separation in THF. The GPC trace shows a monomodal distribution with an average molecular weight, $M_n$, of 5160 and a polydispersity index (PDI) of 1.45 based on in-line static light scattering detection. In order to investigate the structure of these low-molecular-weight polymers further, and to determine the nature of the end-groups, a MALDI TOF–TOF mass spectrum of **4Mes** was acquired in reflectron (+) mode with benzo[*a*]pyrene as the matrix.[20] The spectrum is characterized by three series of peaks (Figure 1), which, by comparison with the peak patterns of the respective calculated molecular ion peaks, can confidently be assigned to polymers bearing two -BMes$_2$ termini, one -BMes$_2$ and one -Fc end group, and two -Fc caps, respectively (see Figure 1b: *m*/*z* 2880, [Mes$_2$B{-fc-B(Mes)-}$_8$Mes]$^+$; *m*/*z* 2946, [H{-fc-B(Mes)-}$_9$Mes]$^+$; *m*/*z* 3012, [H{-fc-B(Mes)-}$_9$-Fc]$^+$). The series of peaks representing polymers with two ferrocenyl end groups possesses by far the lowest intensity, while Mes$_2$B[-fc-B(Mes)-]$_n$Mes molecules bearing two boryl end groups are clearly the most abundant ones. Within each series the difference between adjacent peaks, Δ(*m*/*z*), is always 314, which corresponds to one [-fc-B(Mes)-] repeat unit. The highest molecular weight peak that was unambiguously detectable appears at *m*/*z* 6962 and belongs to a polymer containing 21 ferrocenylene fragments (Mes$_2$B[-fc-B(Mes)-]$_{21}$Mes).

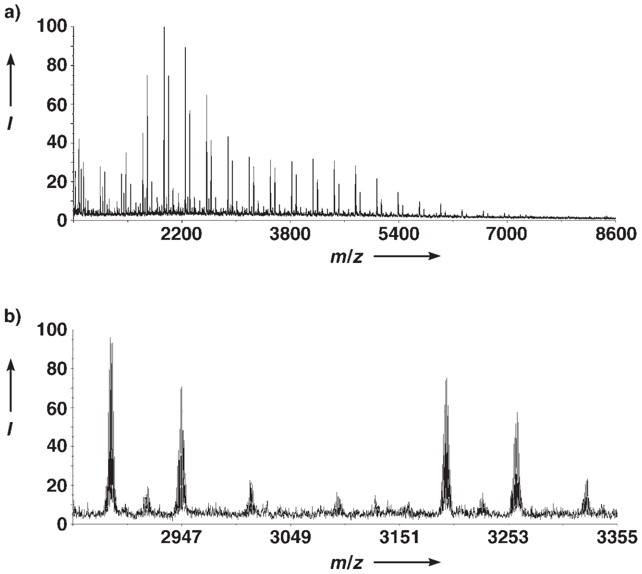


**Figure 1.** a) MALDI TOF-TOF MS of **4Mes** (reflectron (+) mode with benzo[*a*]pyrene as matrix); b) region between *m*/*z* 2845 and 3355 enlarged.

To facilitate the analysis of the NMR and UV/Vis spectra as well as the electrochemical data of **4Mes** we prepared two model systems representing different segments of the polymer chain, the dinuclear compound **2Mes** and the 1,1′-diborylated ferrocene fc(BMes$_2$)$_2$ (**5Mes**). While **2Mes** is readily available using the synthesis protocol developed for **4Mes** (Scheme 2), compound **5Mes** is best prepared from 1,1′-dilithioferrocene[21] and Mes$_2$BF.[11]

In the temperature range between 25 and 70 °C, the $^{11}$B NMR resonances of **2Mes**, **4Mes** and **5Mes** are broadened beyond detection. The proton NMR spectrum of **2Mes** shows a singlet at $\delta = 6.81$ ppm ($C_6H_2$), two virtual triplets at $\delta = 4.58$ and $\delta = 4.42$ ppm ($C_5H_4$), and resonances for the *para* and *ortho* methyl groups at $\delta = 2.31$ and 2.23 ppm, respectively. The $^1$H NMR spectrum of **5Mes** is characterized by the following resonances: $\delta = 6.75$ (s, $C_6H_2$), 4.73/4.41 (2 × vtr, $C_5H_4$), 2.27 ppm (*o*,*p*-$CH_3$). Correspondingly, five major NMR signals [$\delta(^1H) = 6.79$, 4.48/4.28, 2.30/2.14 ppm] are found in the spectrum of **4Mes** and assigned to internal [-($C_5H_4$)Fe($C_5H_4$)-B(Mes)-] fragments constituting the polymer chain. These major signals are accompanied by several smaller resonances attributable to the chain end groups [-(Mes)B-Fc] and [-BMes$_2$]. For an infinitely long polymer, the ratio between the cyclopentadienyl protons and aromatic mesityl protons would be 4:1. In the case of **4Mes**, the ratio between the integral values of all cyclopentadienyl signals on one hand and all aromatic mesityl resonances on the other is 4:1.14.

One of the key questions with regard to the electronic properties of **4Mes** is whether a conformation is possible that allows for efficient π-conjugation of the ferrocenes via the empty p orbital of the boron bridge. To this end, the model compound **2Mes** was investigated by X-ray crystallography (Figure 2).[11] An inspection of the dihedral angles between the cyclopentadienyl rings and the B1 C1 C11 C31 plane

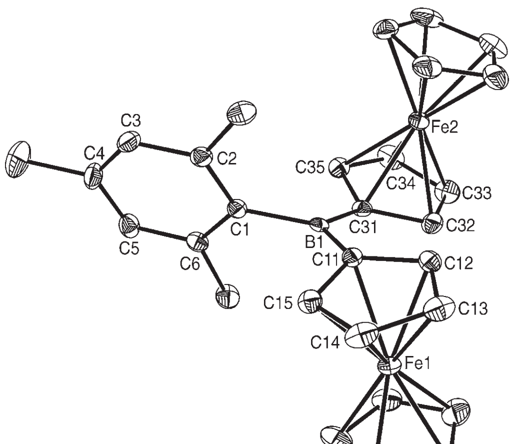


**Figure 2.** Molecular structure and numbering scheme of compound **2Mes**; thermal ellipsoids shown at the 50% probability level; hydrogen atoms omitted for clarity. Selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B1–C1 1.590(4), B1–C11 1.554(4), B1–C31 1.555(4); C1-B1-C11 119.3(2), C1-B1-C31 117.3(2), C11-B1-C31 123.4(2); C1-B1-C11-C12 −163.2(2), C1-B1-C31-C32 −173.2(2), C11-B1-C31-C32 7.0(4), C31-B1-C11-C12 16.7(4), C11-B1-C1-C6 −119.8(3), C31-B1-C1-C6 60.4(3); C1 to C6 ring//C1 B1 C11 C31 plane 61.2, C11 to C15 ring//C31 to C35 ring 23.4.

revealed values of 21.8° [C11 to C15] and 14.1° [C31 to C35] in line with a substantial overlap of the corresponding π-electron clouds.

π-Overlap between the p orbital on boron and the ferrocene units is expected to influence the UV/Visible spectra, and the ensuing electronic communication between the ferrocene moieties should be reflected in the redox properties of **4Mes**. Parent ferrocene has its longest wavelength absorption maximum at $\lambda = 440$ nm in the UV/Vis spectrum. This band is pronouncedly shifted to the red upon going to diferrocenylborane **2Mes** ($\lambda = 490$ nm) and experiences a further bathochromic shift in polymeric **4Mes** ($\lambda = 505$ nm), in agreement with an increasing degree of π-delocalization within this series of compounds. Cyclic voltammograms were recorded in $CH_2Cl_2$ with $[NBu_4][B(C_6F_5)_4]$ (0.1 M) as supporting electrolyte and are referenced against the FcH/FcH$^+$ couple.[11] The mononuclear model system **5Mes** is reversibly oxidized at a potential of $E^{\circ\prime} = 196$ mV. This anodic shift with respect to parent ferrocene may be explained by the π-electron withdrawing nature of the $BMes_2$ substituents. In the case of the dinuclear compound **2Mes**, two well resolved redox waves of equal intensity and features of chemical reversibility appear at $E^{\circ\prime} = 45$ mV and 467 mV. These transitions are assigned to the successive one-electron oxidations of the two iron centers. The large separation of $\Delta(E^{\circ\prime}) = 422$ mV between the two redox waves indicates pronounced electronic communication between the two ferrocenyl moieties in **2Mes**.[22] The first oxidation event of polymer **4Mes** (one ferrocenylene donor per BMes acceptor) is reversible on the CV timescale and occurs at 140 mV (Figure 3). This value lies between the first redox potential of **2Mes** possessing two donors/one acceptor (45 mV) and the redox potential of **5Mes** with one donor/two acceptors (196 mV). A second redox wave with features of chemical reversibility is recorded for **4Mes** at $E^{\circ\prime} = 845$ mV. This transition is absent in the cyclic voltammograms of the model systems and tentatively assigned to a second Fe$^{II}$/Fe$^{III}$ oxidation. This second redox event is observed at a much higher potential than that of the diferrocene **2Mes** (467 mV), which is probably due to the presence of two neighboring ferrocenium moieties adjacent to each neutral ferrocene in the polymer chain -fc$^+$-B(Mes)-fc-B(Mes)-fc$^+$-B(Mes)- following oxidation of alternating ferrocenylene moieties ([Fc-B(Mes)-Fc$^+$] in the case of the dimer).[23] The large splitting $\Delta(E^{\circ\prime}) = 705$ mV for **4Mes** further suggests very pronounced electronic interactions in this polymer.

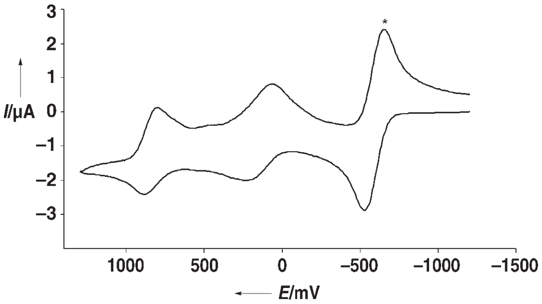


*Figure 3.* Cyclic voltammogram of **4Mes** ($CH_2Cl_2$, 0.1 M $[NBu_4][B(C_6F_5)_4]$, $\nu = 0.2$ V s$^{-1}$, vs. FcH/FcH$^+$; starred wave: $(C_5Me_5)_2Fe/(C_5Me_5)_2Fe^+$).

In summary, borylene-bridged poly(ferrocenylene)s $[\text{-fc-B(Br)-}]_n$ are readily prepared from $fc(BBr_2)_2$ and $HSiEt_3$ via a novel polycondensation reaction. Treatment with $[CuMes]_n$ gives a highly soluble polymer $[\text{-fc-B(Mes)-}]_n$ with three-coordinate boron centers, which, due to their empty p orbital, are well-suited for the promotion of electron delocalization along the polymer chain.

## Experimental Section

Synthesis of **4Br**: To **3** (3.990 g, 7.60 mmol) in toluene (20 mL) was added neat $HSiEt_3$ (3.888 g, 33.44 mmol) at −78 °C with stirring (note: even though 3 equiv of $HSiEt_3$ are sufficient for full conversion, we found it convenient to use the hydride transfer reagent in some excess when working on a preparative scale). The resulting red solution was allowed to warm to room temperature and stirred overnight, whereupon a red precipitate gradually formed. The microcrystalline solid was collected on a frit, triturated with toluene (10 mL) and dried in vacuo. Yield: 1.914 g (92 % repeat units).

Synthesis of **4Mes**: A solution of $[CuMes]_n$ (0.162 g, 0.89 mmol) in toluene (10 mL) was added slowly at room temperature to a slurry of **4Br** (0.255 g, 0.93 mmol repeat units) in toluene (20 mL). The resulting mixture was stirred overnight and then heated to 80 °C for 8 h, whereupon its color changed from red to purple accompanied by the formation of a greyish precipitate. After filtration and evaporation of solvent under reduced pressure, a purple microcrystalline solid was obtained. The crude product was dissolved in toluene and repeatedly precipitated from toluene into hexanes. Yield: 0.404 g (81 % repeat units).

$^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = **6.79** (2H, $C_6H_2$), 6.76, 4.63, 4.57, **4.48** (4H, $C_5H_4$), 4.42, **4.28** (4H, $C_5H_4$), 4.23, 4.08, 2.36, 2.34, **2.30** (6H, o-$CH_3$), 2.26, 2.24, 2.18, **2.14** (3H, p-$CH_3$), 2.09 ppm. Note: The five major peaks are printed boldface. UV/Vis (0.1 mM, $CH_2Cl_2$): $\lambda_{max} = 300$, 380, 505 nm. GPC-RI (THF, PS Standards): $M_w = 3880$, $M_n = 2890$, PDI = 1.34; GPC-MALLS (THF; dn/dc = 0.167): $M_w = 7480$, $M_n = 5160$; PDI = 1.45.

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[11] The Supporting Information contains the syntheses and spectroscopic data of **2Br**, **2Mes**, and **5Mes**, together with details of the theoretical calculations as well as of the DSC- and GPC measurements, the MALDI mass spectrometry, the electrochemical measurements, and the X-ray crystal structure analysis of **2Mes**. CCDC 284797 (**2Mes**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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