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# Synthesis and Characterization of Water-Soluble Cationic and Anionic Polyferrocenylsilane Polyelectrolytes

**Zhuo Wang, Alan Lough, and Ian Manners***

*Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada*

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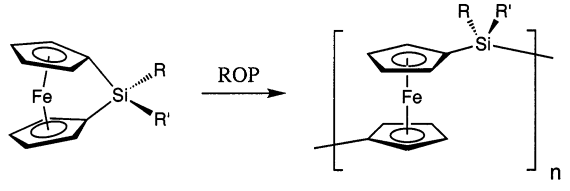
ABSTRACT: Convenient routes to a range of water-soluble polyferrocenylsilane polyelectrolytes are reported. Direct reaction of the protected aminopropynyl reagent $LiC\equiv CCH_2N(SiMe_2CH_2)_2$ (**8**) with the substitutionally labile ring-opened polymer $[fcSiMeCl]_n$ (**3**) ($fc = Fe(\eta-C_5H_4)_2$), which is generated via Pt-catalyzed ring-opening polymerization of the silicon-bridged [1]ferrocenophane fcSiMeCl (**6**), afforded the polymer $[fcSiMe\{C\equiv CCH_2N(SiMe_2CH_2)_2\}]_n$ (**10**). Polymer **10** was also obtained via ring-opening polymerization of the [1]ferrocenophane $fcSiMe\{C\equiv CCH_2N(SiMe_2CH_2)_2\}$ (**9**) prepared from the reaction of the lithium salt **8** and the substitutionally labile [1]ferrocenophane **6**, which is readily accessible via the reaction of $fcLi_2\cdot TMEDA$ with $MeSiCl_3$. Deprotection of **10** was readily achieved using THF/MeOH to yield $[fcSiMe(C\equiv CCH_2NH_2)]_n$ (**11**), which was conveniently reduced with hydrazine to the analogous aminopropyl polymer $[fcSiMe(CH_2CH_2CH_2NH_2)]_n$ (**12**). Treatment of polyferrocenylsilanes **11** and **12** with HCl generated the water-soluble cationic polyelectrolytes $[fcSiMe(C\equiv CCH_2NH_3Cl)]_n$ (**13**) and $[fcSiMe(CH_2CH_2CH_2NH_3Cl)]_n$ (**14**), respectively. Cationic polyferrocenylsilanes **13** and **14** were obtained in three steps from polymer **3** with an overall yield of 40−50%. An unexpected rearrangement process took place during the lithiation of the protected aminopropyl bromide $Br(CH_2)_3N(SiMe_2CH_2)_2$ (**15**) and a reaction of the resulting lithium salt with **6** yielded the novel [1]ferrocenophane $fcSiMe\{N(CH_2)_3SiMe_2(CH_2)_2SiMe_2\}$ (**17**) with a rearranged, and ring-expanded, cyclic silylamino substituent. Species **17** underwent thermal ring-opening polymerization to afford $[fcSiMe\{N(CH_2)_3SiMe_2(CH_2)_2SiMe_2\}]_n$ (**18**). Treatment of polymer **10** with 1,3-propane sultone afforded the anionic polyelectrolyte $[fcSiMe\{C\equiv CCH_2N(CH_2CH_2CH_2SO_3Na)_2\}]_n$ (**19**). Polymer **19** was readily reduced with hydrazine to give $[fcSiMe\{CH_2CH_2CH_2NH(CH_2CH_2CH_2SO_3)(CH_2CH_2CH_2SO_3Na)\}]_n$ (**20**) bearing saturated side chains; subsequent deprotonation yielded the anionic polyelectrolyte $[fcSiMe\{CH_2CH_2CH_2N(CH_2CH_2CH_2SO_3Na)_2\}]_n$ (**21**). All three anionic polyelectrolytes **19**−**21** were obtained in 2−3 steps from **3** with 60−75% overall yields. The polyferrocenylsilane polyelectrolytes **13**, **14**, and **19**−**21** were readily soluble in water, making them potentially useful materials for a range of applications.

## Introduction

Polyelectrolytes represent an important class of macromolecules which possess ionic groups, and examples range from naturally occurring polymers such as nucleic acids to synthetic materials such as poly(allylamine hydrochloride), poly(sodium 4-styrenesulfonate), and poly(sodium acrylate).[1] These materials are of considerable importance for many industrial and technological applications.[2] Polyelectrolytes have attracted intense recent attention for the creation of electrostatic superlattices, which are multilayer structures generated by the sequential adsorption of polyion monolayers from aqueous solutions.[3] Interestingly, despite extensive studies on organic polyelectrolytes, examples of inorganic polyelectrolytes are rare.[4,5] This is especially the case for transition metal-containing polymers, which would also be expected to possess a range of attractive conductive, optical, redox, preceramic, catalytic, or other physical properties.[6,7]

Polyferrocenylsilanes (PFSs) **2** are an interesting class of high molecular weight metal-containing polymers which are readily accessible via the thermal, anionic, or transition metal-catalyzed ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes **1** (Scheme 1).[8,9] PFS materials are attracting current attention as a result of their redox activity and semiconductivity after oxidation,[9] and the observation that pyrolysis of PFS networks provides a route to nanostructured ceramic films, macroscopic shapes, and soft-lithographically patterned micrometer-scale structures with tunable magnetic properties.[10] In addition, we have shown that anionic and transition metal-catalyzed ROP routes provide access to PFS block copolymers which form phase-separated domains in the solid state and self-assembled micellar aggregates in solution.[11] PFS materials also offer potential applications in microsphere technology,[12] as radiation protective coatings,[13] as photonic band gap materials,[14] and as variable refractive index sensing materials.[15]

**Scheme 1**



Organometallic superlattices formed by the layer-by-layer assembly of PFS polyelectrolytes are of considerable interest and should possess a range of novel properties. With this and other potential applications in mind, our group has previously developed routes to the first examples of water-soluble PFS polyelectrolytes.[16] These materials were prepared via nucleophilic substitution reactions on poly(ferrocenylmethylchlorosi-

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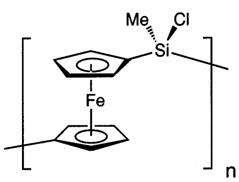
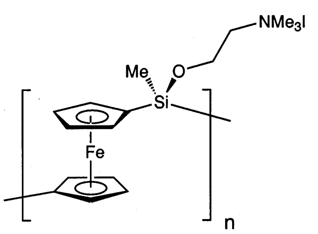
lane) **3** with alkoxide nucleophiles followed by quaternization, and a typical example is PFS **4**.[16] Subsequent reports have described a range of other PFS polyelectrolytes prepared via the ROP of dialkylaminophenyl-substituted silicon-bridged [1]ferrocenophane monomers.[17,18] In addition, we have demonstrated the use of such materials for the formation of well-characterized PFS electrostatic superlattices on primed Au, Si, and quartz substrates,[19] and PFS polyelectrolytes have also been recently prepared via the derivatization of halogenoalkyl-substituted PFS **5**.[20−22]



**3**



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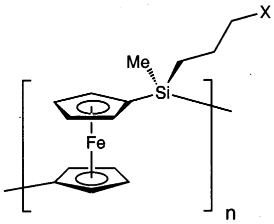


X = halogen

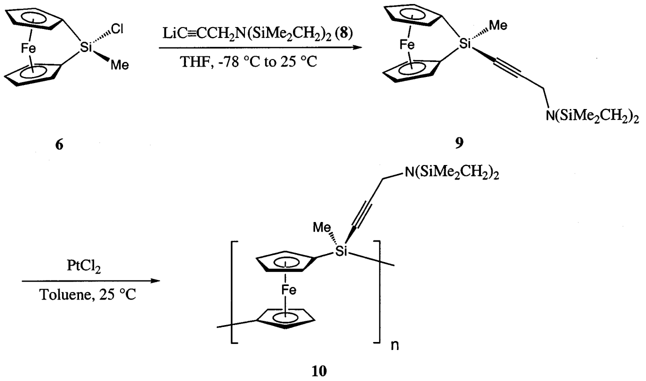
**5**

In this paper we report full details of our work on the synthesis and characterization of a series of PFS polyelectrolytes ultimately derived from the reactions of the substitutionally labile silicon-bridged [1]ferrocenophane **6** and PFS derivative **3** with protected aminoalkynyl nucleophiles.[23] We also report the unexpected synthesis and characterization of a monomer and polymer with cyclic silylamino substituents.

## Results and Discussion

**Synthesis and Characterization of the Silicon-Bridged [1]Ferrocenophane 9.** Our initial synthetic target was the protected aminopropynyl PFS **10** which, on silyl group removal, would be expected to function as a valuable precursor to PFS polyelectrolytes via quaternization or other derivatization techniques. To access this material, we viewed ROP of the silicon-bridged [1]ferrocenophane **9** as a feasible strategy. We prepared monomer **9** via nucleophilic substitution of the chlorine in [1]ferrocenophane **6** using a protected lithiated propynyl reagent **8** (Scheme 2). Ferrocenophane **6** was obtained in high yield (80−90%) from fcLi$_2$·TMEDA (fc = Fe($\eta$−C$_5$H$_4$)$_2$, TMEDA = tetramethylethylenediamine) and methyltrichlorosilane according to a literature procedure.[24] The lithium acetylide reagent **8** was prepared via the reaction of propargylamine and 1,2-bis(chlorodimethylsilyl)ethane in the presence of triethylamine to afford the acetylene HC≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$ (**7**) in 60−70% yield[25] followed by deprotonation of **7** with *n*-BuLi. Although the crude yield was quantitative by $^1$H and $^{13}$C NMR, the pure [1]ferrocenophane **9** was obtained as a red crystalline solid in low to moderate yield (30−60%) after recrystallization (hexanes, −55 °C) and vacuum sublimation (0.05 mmHg, 80 °C).

**Scheme 2**

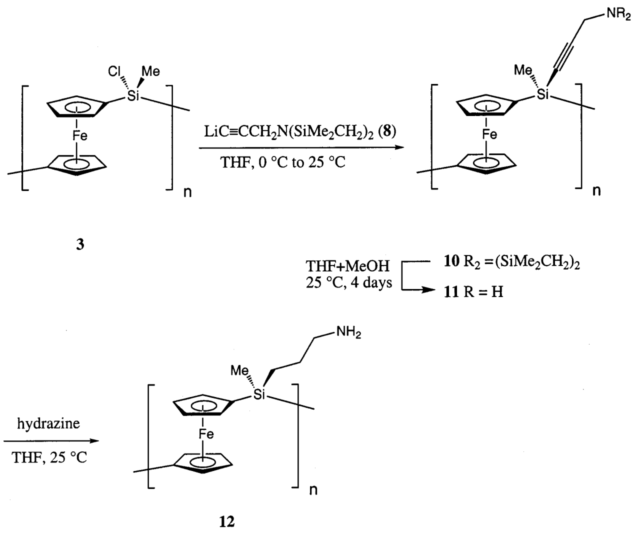


The protected aminopropynyl-substituted silicon-bridged [1]ferrocenophane **9** was characterized by $^{29}$Si, $^{13}$C, and $^1$H NMR analysis as well as high-resolution mass spectrometry, all of which afforded data consistent with the assigned structure. For example, the $^{29}$Si NMR spectrum of **9** showed two signals at −28.9 and 15.2 ppm, corresponding to the resonances for the bridging silicon and the cyclic disilyl protecting group, respectively. In comparison to the $^{29}$Si NMR resonance for ferrocenophane **6** ($\delta$ = 5.75 ppm), the resonance of the bridging silicon in **9** was shifted significantly upfield, consistent with the successful substitution of the chlorine side group by the acetylide. In the $^{13}$C NMR spectrum of **9**, the resonance for the ipso carbon on the cyclopentadienyl ring was observed at 32.2 ppm, upfield from the rest of Cp carbon resonances ($\delta$ = 75−79 ppm). This upfield chemical shift for the ipso carbon attached to the bridging silicon atom is characteristic of strained [1]ferrocenophanes.[26] Significantly, the resonance at $\delta$ = 110.8 ppm for the acetylenic carbon attached to the silicon atom in **9** was shifted downfield from that of the corresponding carbon in acetylene **7** ($\delta$ = 70.1 ppm). In addition, the characteristic resonance of the acetylenic proton ($\delta$ = 2.08 ppm) of **7** was not detected in the $^1$H NMR spectrum of **9**, again confirming successful replacement of the chlorine atoms in ferrocenophane **6**.

**ROP of the Silicon-Bridged [1]Ferrocenophane 9; Synthesis and Characterization of Protected Aminopropynyl PFS 10.** The silicon-bridged [1]ferrocenophane **9** was converted to PFS **10** via transition metal-catalyzed ROP at room temperature in toluene with a catalytic amount of PtCl$_2$ (Scheme 2). Thermal ROP of the cyclic monomer was also achieved by heating a solution of **9** in xylene at reflux (ca. 140 °C). Precipitation of the reaction mixture into methanol afforded polymer **10** as an orange-yellow fibrous solid.

The polyferrocenylsilane **10** was characterized by $^{29}$Si, $^{13}$C, and $^1$H NMR spectroscopy. The $^{29}$Si NMR of **10** showed two signals at 14.9 and −24.8 ppm, corresponding to the silicon environments in the protecting group and the main chain of the polymer, respectively. The latter was analogous to the $^{29}$Si signal of −24.9 ppm observed for the previously reported hexynyl PFS [fcSiMe{C≡C(CH$_2$)$_3$CH$_3$}]$_n$.[24] In the $^{13}$C NMR spectrum of polymer **10**, the signal for the ipso carbons ($\delta$ = 69.4 ppm) was shifted significantly downfield from that in **9** ($\delta$ = 32.2 ppm). This observation was in agreement with previous reports that the release of ring strain in ferrocenophane monomers via ROP leads to a downfield shift of the ipso carbon signals.[24,26] As with the $^{13}$C NMR spectrum of ferrocenophane **9**, two resonances charac-

**Scheme 3**



teristic of the acetylenic carbons from the aminopropynyl substituents on the polyferrocenylsilane **10** were detected ($\delta = 84.7$, 109.3 ppm). The $^1$H NMR data for PFS **10** were also consistent with the assigned structure.

**Alternative Synthesis of the Protected Aminopropynyl PFS 10.** We have previously reported that the chlorines of PFS **3** could be successfully substituted in a reaction with organolithium reagents such as the lithium acetylide $LiC{\equiv}C(CH_2)_3CH_3$ to yield the hexynyl PFS $[fcSiMe\{C{\equiv}C(CH_2)_3CH_3\}]_n$.[24] In all cases complete substitution of chlorines was achieved without any detectable significant chain cleavage and consequential molecular weight decline. We therefore explored the use of an analogous approach with PFS **3** to prepare the aminopropynyl polymer **10** by using lithium acetylide **8** as the nucleophile. Polymer **3** was obtained via $PtCl_2$-catalyzed ROP of monomer **6** in high yield (>90%).[24] Deprotonation of acetylene **7** with *n*-butyllithium followed by reaction of lithium acetylide **8** with polymer **3** in THF at room temperature for 16 h afforded polymer **10** as an orange-yellow fibrous solid (Scheme 3). Complete substitution of the chlorine side groups of **3** was confirmed by $^{29}$Si NMR. The cyclic disilyl protecting groups of the amine functionalities in polymer **10** were found to remain intact under the substitution reaction conditions, as demonstrated by $^1$H, $^{13}$C, and $^{29}$Si NMR. GPC analysis of polymer **10** showed that the material possessed a molecular weight of $M_w = 304{,}100$ with a polydispersity index of 1.48. PFS **10** was soluble in common organic solvents such as THF, benzene, dichloromethane, and hexanes. The cyclic disilyl protecting groups on the polymer slowly hydrolyzed in air over a period of several weeks to give a cross-linked material. Therefore, the polymer was kept under a nitrogen atmosphere for long-term storage.

The synthesis of polymer **10** through nucleophilic substitution of the chlorinated PFS **3** by lithium acetylide **8** was found to be a more convenient route in comparison to the ROP of monomer **9**. The latter method proved to be challenging as purification of **9** formed in the reaction of ferrocenophane **6** with acetylide **8** was not straightforward and the isolated yield was generally moderate (30–60%). By comparison, polymer **10** could be obtained in excellent yield (ca. 80%) via acetylide substitution of the readily accessible chlorinated PFS **3** and was easily purified via precipitation into methanol.

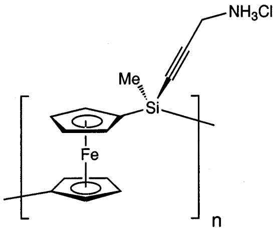
**Synthesis and Characterization of Deprotected Aminopropynyl PFS 11.** The cyclic disilyl protecting groups for the amine functionalities present in polymer **10** were removed under mild conditions by stirring a solution of the polymer in a mixture of solvents (THF: methanol, volume ratio ca. 3:1) at room temperature for 4 days. Precipitation into hexanes afforded the aminopropynyl PFS **11** as an orange-yellow fibrous solid. Complete removal of the protecting groups was demonstrated by $^{29}$Si, $^{13}$C, and $^1$H NMR analysis. The polymer was soluble in THF and dichloromethane but only slightly soluble in methanol.

Polymer **11** was characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. In the $^{29}$Si NMR spectrum of **11**, no signal corresponding to the cyclic disilyl groups (at $\delta = 14.9$ ppm for **10**) was detected, which indicated that complete removal of the protecting groups had taken place. The only observed signals in the $^{29}$Si NMR spectrum of **11** were three resonances in an approximate 1:2:1 ratio centered at $-23.18$ ppm and these corresponded to the silicon atoms in the main chain. The peaks at lower and higher field were found at $-23.16$ and $-23.20$ ppm, respectively, and the latter resonance overlapped partially with the major central signal. The observation of three resonaces has been reported previously for the chlorinated PFS **3** and was explained in terms of triad resolution for the atactic polymer.[24] A similar explanation for PFS **11** appears likely in the present work. The $^1$H and $^{13}$C NMR of **11** were also consistent with the assigned structure.

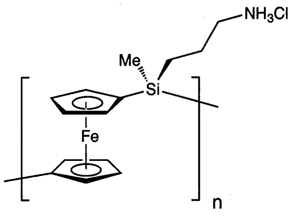
**Synthesis and Characterization of the Aminopropyl PFS 12.** A convenient synthesis of the aminopropyl polymer **12** was accomplished through reduction of the aminopropynyl polymer **11** with hydrazine in THF (Scheme 3). Thus, overnight reaction of polymer **11** with hydrazine hydrate in THF under air at room temperature followed by precipitation of the reaction mixture into hexanes afforded polymer **12** as a yellow powder. This material was fairly soluble in dichloromethane and in THF, but was only slightly soluble in methanol.

Characterization of polymer **12** was performed using $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. In the $^1$H NMR spectrum in $CD_2Cl_2$, a significant upfield shift was observed for the methylene protons adjacent to the amino groups ($\delta = 2.66$ ppm) in comparison to that in the aminopropynyl polymer **11** ($\delta = 3.55$ ppm). In addition, two new proton resonances were detected for polymer **12** at 0.9 and 1.5 ppm, corresponding to the methylene protons in the aminopropyl side chains which are $\alpha$- and $\beta$- to Si, respectively. The $^{13}$C NMR of polymer **12** was also consistent with the assigned structure. Thus, two new resonances corresponding to the $SiCH_2CH_2$ carbons appeared at 13.5 ppm ($\alpha$- to Si) and 29.2 ppm ($\beta$- to Si) while no acetylenic carbon signals were detected, which indicated that reduction was complete. The methylene carbons adjacent to the amino groups gave rise to a resonance at 46.2 ppm, shifted significantly downfield from those in polymer **11** ($\delta = 32.8$ ppm). In comparison with the $^{29}$Si NMR resonance for **11** detected at $-23.2$ ppm, PFS **12** showed a single resonance at $-3.4$ ppm, which was in accordance with the chemical shifts observed previously for alkyl-substituted PFS derivatives.[26]

**Synthesis and Characterization of the Cationic Water-Soluble Polyelectrolytes 13 and 14.** PFSs **13** and **14** with quaternary ammonium substituents were



**13**



**14**

readily obtained through protonation of the amino polymers **11** and **12**, respectively. Addition of 1 equiv of HCl (1 M solution in ether) to a solution of PFS **11** in dichloromethane afforded the cationic polymer **13** as an orange-yellow powder. Polymer **14** was similarly obtained using an analogous procedure. Both PFSs **13** and **14** were very soluble in water and their solutions remained clear orange-yellow over a period of several months. The polymers were also soluble in methanol, but were insoluble in common organic solvents such as THF and dichloromethane.

The cationic polyelectrolytes **13** and **14** were characterized by $^{1}$H, $^{13}$C, and $^{29}$Si NMR spectroscopy and, in the case of **14**, also by elemental analysis. In the $^{1}$H NMR spectrum of polymer **13** in $CD_3OD$, the resonance of the methylene protons adjacent to the ammonium groups was detected at 3.9 ppm, which was downfield-shifted from that in the amino polymer **11** ($\delta = 3.4$ ppm). This result is in accordance with our previous observations that the methylene protons adjacent to the amino groups were less shielded after the amino groups had been quaternized.[16] The absence of any signals around 3.4 ppm in the spectrum of polymer **13** confirmed that protonation of the amino polymer **11** by HCl had proceeded to completion. Similar results were also obtained for polymer **14** (see Figure 1a). Notably, the $^{1}$H NMR spectra of both polymers **13** and **14** in $D_2O$ at 20 °C clearly exhibited the resonances of the cyclopentadienyl protons in the region of 3.9−4.6 ppm, which indicated that the backbones were more solvated and flexible in water than those for the PFSs with alkylammonium substituents reported previously.[16] This is probably due to more extensive solvation of **13** and **14** as a result of the presence of more hydrophilic $-NH_3^+$ substituents. The $^{13}$C NMR spectra of polymers **13** and **14** (see Figure 1b) also supported the assigned structures and the $^{29}$Si NMR spectra (in $D_2O$) showed the expected singlet resonances which were found at −23.8 and −4.9 ppm, respectively.

Although direct estimates of the molecular weights of polyelectrolytes are difficult to obtain and were not achieved for **13** and **14**, we anticipate that the values are close to that of the sample of the PFS precursor **10** ($M_w \approx$ 75,000−300,000). The PFSs are derived from **10** via reactions such as treatment with hydrazine which have previously been shown to lead to no detectable main chain cleavage. Moreover, samples of **13** and **14** form viscous solutions in water and show substantial hydrodynamic radii ($R_H$ > 30 nm) by dynamic light scattering which is typical behavior for high molecular weight polyelectrolyte materials.

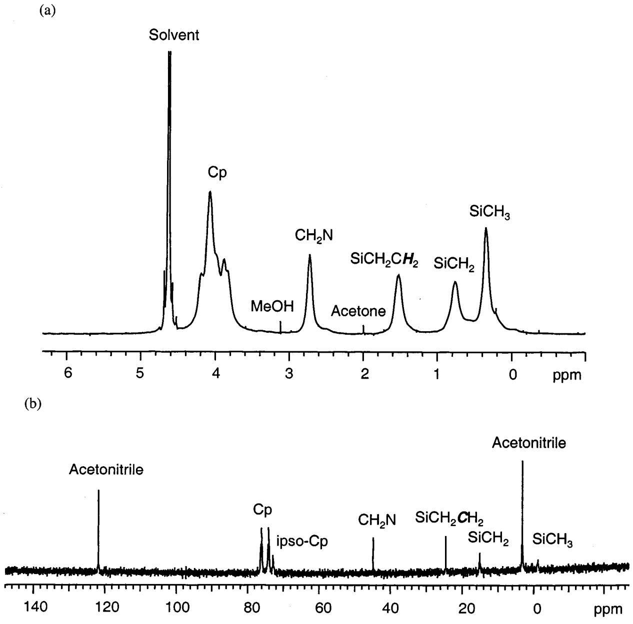
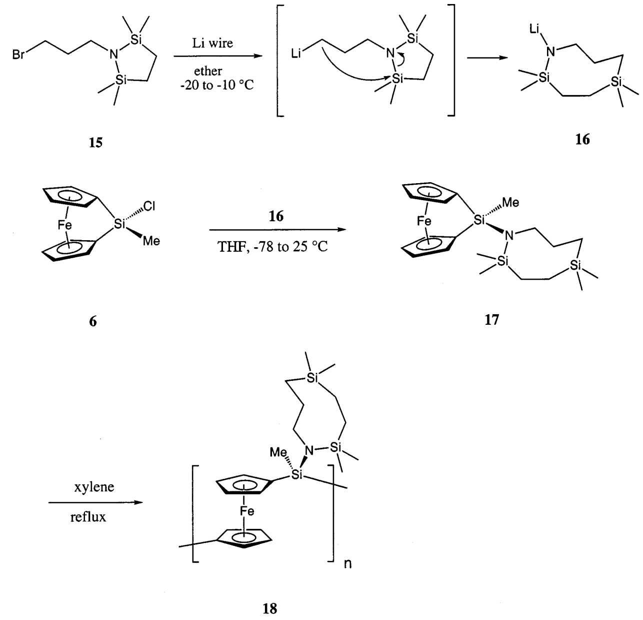


**Figure 1.** (a) $^{1}$H (400 MHz) and (b) $^{13}$C (100 MHz) NMR spectra of polymer **14** in $D_2O$ (at 80 °C).

**Scheme 4**



**Unexpected Synthesis and Structural Characterization of the Silicon-Bridged [1]Ferrocenophane 17.** We also attempted to synthesize an analogue of silicon-bridged [1]ferrocenophane **9** via substitution of the chlorine side group in ferrocenophane **6** by the *saturated* aminopropyllithium species $LiCH_2CH_2CH_2N(SiMe_2CH_2)_2$ rather than with the propynyl derivative **8**. Such species could also ultimately function as a precursor to PFSs **12** and **14** following ROP and side group modifications. However, although the protected amino derivative $BrCH_2CH_2CH_2N(SiMe_2CH_2)_2$ (**15**) was successfully prepared from 3-bromopropylamine hydrobromide and 1,2-bis(chlorodimethylsilyl)ethane in the presence of triethylamine and a catalytic amount of 4-*N*,*N*′-(dimethylamino)pyridine,[25,27] attempted lithiation of **15** using lithium metal followed by reaction with **6** did not yield the desired product. Instead, the novel ferrocenophane **17** was obtained as the only isolable ferrocene-containing product from the reaction mixture (Scheme 4). It has been reported in the literature that Grignard reagent $BrMgCH_2CH_2CH_2N(SiMe_2CH_2)_2$ can be generated successfully from the reaction of bromide **15** with magnesium metal.[28] Previous reports have also indicated that the cyclic disilyl protecting group was

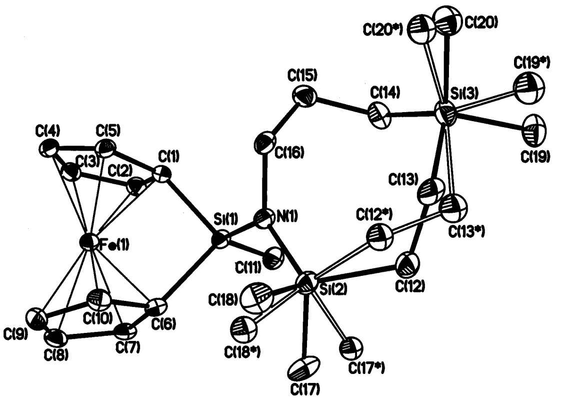


**Figure 2.** Crystal structure of the silicon-bridged [1]ferrocenophane **17** in which the major rotamer is 67% of the fractional occupancy and the minor rotamer (depicted by hollow bonds) is 33%.

stable to organolithium reagents.[25] However, in our case, lithiation of the bromide **15** appears to have led to a subsequent rearrangement and ring expansion process to form the amide **16** which then reacted with **6** to yield **17** (Scheme 4).[29] Ferrocenophane **17** was isolated as a red crystalline solid and was characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR which gave spectra in agreement with the assigned structure. However, to provide conclusive proof of the structure of **17**, a single-crystal X-ray diffraction study was performed.

An X-ray quality single crystal of **17** was obtained after recrystallization from hexanes at −55 °C followed by vacuum sublimation at 75 °C. The molecular structure is shown in Figure 2. Although compound **17** possesses a bulky cyclic silylamino substituent attached to the bridging silicon atom of the ferrocenophane via a Si−N bond, a close examination of structural parameters reveals many similarities to the structure of the dimethyl ferrocenophane analogue **1** ($R = R' = Me$).[30] For example, the ring-tilt angle $\alpha$ between the two planes of the cyclopentadienyl ligands in **17** is 21.0(2)°, which is comparable to that of 20.8(5)° in **1** ($R = R' = Me$). Further comparison of the structures of the two compounds shows that the C(ipso)−Si−C(ipso) bond angle $\theta$ in **17** (95.01(12)°) is close to that in **1** ($R = R' = Me$) ($\theta = 95.7(4)°$), while the Fe−Si distance in **17** (2.7216(9) Å) is slightly longer than that in the dimethyl analogue **1** (2.690(3) Å).

**Thermal ROP of the Silicon-Bridged [1]Ferrocenophane 17; Synthesis and Characterization of PFS 18.** The unusual ferrocenophane **17** was found to be resistant to transition metal-catalyzed ROP in the presence of Karstedt's catalyst or $PtCl_2$. After the monomer and the catalyst were stirred in toluene for 24 h at room temperature, only unreacted **17** was recovered from the reaction mixture. However, thermal ROP of **17** was readily achieved by heating a solution of the monomer in xylene at reflux (ca. 140 °C). Precipitation of the crude product in methanol gave polymer **18** as a light brown fibrous solid. The polymer was soluble in common organic solvents such as hexanes, benzene, THF, and dichloromethane and was characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. The $^1$H NMR spectrum showed that the resonances of $fcSiCH_3$ ($\delta = 1.04$ ppm) and the methylene groups adjacent to the nitrogen atoms ($\delta = 3.27$ ppm) in polymer **18** were shifted notably downfield from those of the corresponding protons in monomer **17** ($\delta = 0.52$ and $\delta = 3.08$ ppm, respectively). We have previously observed that the ROP of silicon-bridged [1]ferrocenophanes generally leads to a downfield shift of the signal for the methyl group substituted at the bridging silicon atom.[24,26] A downfield shift was also detected in the $^{13}$C NMR spectrum for the same methyl group in polymer **18** ($\delta = 2.9$ ppm) in comparison to that in monomer **17** ($\delta = 0.9$ ppm). The $^{29}$Si NMR spectrum of **18** showed three signals, as expected for the assigned structure.

**Synthesis and Characterization of Anionic Polyelectrolyte 19.** Anionic polyelectrolytes generally possess functional groups such as sulfonate or carboxylate moieties. Numerous reports in the literature have shown that sulfonate groups can be attached to polymers possessing tertiary amine functionalities via ring opening of 1,3-propane sultone by the dialkylamino groups.[31] The resulting materials, polybetaines, contain both the positively charged quaternary ammonium and negatively charged sulfonate moieties in each repeat unit. We anticipated that the same procedure might be applied to the preparation of anionic macromolecules with only negatively charged sulfonate functionalities if the starting polymers, such as PFSs **11** or **12**, contained primary amino groups. However, reactions of polymer **11** with 1,3-propane sultone in various solvents (THF, dichloromethane, DMF, and methanol) led only to the precipitation of a polymer product, which was found to be insoluble in water or any of the common organic solvents. When the reaction was carried out in the presence of triethylamine and a catalytic amount of 4-*N*,*N'*-(dimethylamino)pyridine using low molecular weight PFS **11** ($M_w \leq 10{,}000$), a water-soluble polyelectrolyte was produced. Unfortunately, the synthesis was not consistently reproducible when higher molecular weight PFS **11** was used. Often most of the polymer precipitated out as an insoluble material. Similar results were also obtained for PFS **12**. We suspect that the $H^+$ ions generated during the ring-opening reaction of 1,3-propane sultone with the primary amino groups may protonate other unreacted amino functionalities in PFSs **11** and **12**. Interaction of the positively and negatively charged polymer segments might then lead to the precipitation of insoluble solids.

The aforementioned problem was completely circumvented by using PFS **10** as the starting material in which the primary amino groups were protected by the cyclic disilyl moiety. Reaction of **10** in a mixture of solvents (dichloromethane:methanol, 2:1 by volume) with 1,3-propane sultone in the presence of an excess amount of diisopropylethylamine for 4 days afforded the desired product (Scheme 5). The reaction mixture remained a clear orange-colored solution throughout the reaction, and solvent removal followed by precipitation of the crude product into an acetone solution containing sodium hexafluorophosphate or sodium tetraphenylborate for cation-exchange purposes afforded polymer **19** as an orange-yellow powder in high yield (≥ 90%). The polymer was highly soluble in water but insoluble in methanol, THF, or dichloromethane. An amount of >300 mg of the polymer can easily dissolve in 1 mL of water within 5−10 min at room temperature and the clear orange-yellow solution remains stable with no discoloration or precipitation after periods of several months.

Polymer **19** was fully characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. The $^1$H and $^{13}$C NMR spectra recorded in $D_2O$ are shown in Figure 3. The resonances for all expected proton and carbon environments, in-

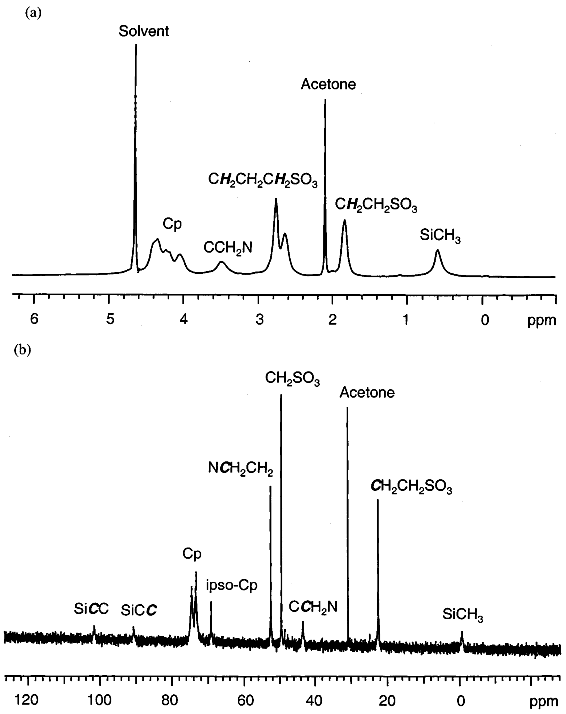
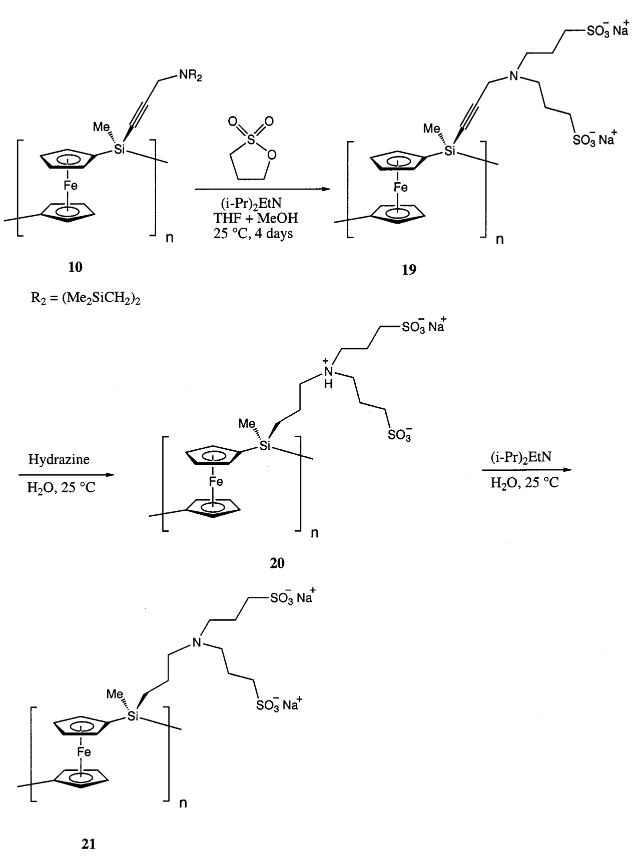


**Figure 3.** (a) $^1$H (400 MHz) and (b) $^{13}$C NMR (100 MHz) spectra of polymer **19** in $D_2O$.

**Scheme 5**



cluding the Cp rings, were clearly detected, which indicated that the polymer is well-solvated in water. Resonances for the protecting groups were not detected, which indicated that complete removal of the cyclic disilyl group had taken place. Integration of the signals in the $^1$H NMR spectrum demonstrated that for each nitrogen atom per repeat unit two propylsulfonate moieties were present. Therefore, even in acidic conditions where the tertiary amine moieties were protonated in the presence of an excess amount of glacial acetic acid, the polymer still dissolved in water and remained as an anionic polyelectrolyte. The resonances in both $^1$H and $^{13}$C NMR spectra were in accordance with the assigned structure for PFS **19**. The $^{29}$Si NMR spectrum of **19** in $D_2O$ exhibited a single resonance at −24.7 ppm, corresponding to the silicon in the PFS main chain bonded to methyl and acetylenic substituents. Although, as with the case of the cationic PFSs **13** and **14**, a direct estimate of the molecular weight of anionic polyelectrolyte **19** was not made, the polymer forms viscous solutions in water which show substantial hydrodynamic radii ($R_H$ > 50 nm) by dynamic light scattering which is consistent with a high molecular weight material.

**Reduction of 19; Synthesis and Characterization of Anionic Polyelectrolytes 20 and 21.** In a procedure analogous to the synthesis of the aminopropyl PFS **12**, the acetylenic moiety in polymer **19** was conveniently reduced in the presence of hydrazine to give polymer **20**. Deprotonation of **20** with diisopropylethylamine afforded polymer **21**. Both polymers were obtained as yellow powders which were highly soluble in water.

PFSs **20** and **21** were characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR in $D_2O$. As with the case of the anionic PFS **19**, the resonances for all proton and carbon environments in **20** and **21** were detected, indicating the polymers are well-solvated in water. In the $^1$H spectrum of polymer **20**, the characteristic chemical shift of the methylene protons adjacent to the acetylenic group in polymer **19** ($\delta$ = 3.50 ppm) was not observed, which suggests complete reduction of the carbon−carbon triple bonds in the latter. In addition, two new chemical shifts were detected at 0.95 and 1.75 ppm, corresponding to the methylene protons in the propyl side chains which are $\alpha$ and $\beta$ to the main chain Si in PFS **20**, respectively. The methylene protons $\gamma$ to the Si are buried in the region of 2.80−3.30 ppm. Although the ammonium protons were not directly observed in the spectrum recorded in $D_2O$, the presence of a protonated nitrogen was evident from the downfield shift of the $NCH_2$ protons in the propylsulfonate moieties in **20** ($\delta$ = 3.12 ppm) in comparison with that in PFS **19** ($\delta$ = 2.65 ppm). The $^{13}$C and $^{29}$Si NMR of the polymer were also consistent with the assigned structure.

Deprotonation of polymer **20** with diisopropylethylamine yielded polymer **21**. Analysis of the $^1$H spectra of polymers **20** and **21** showed that the resonances of the $NCH_2$ protons in the propylsulfonate moieties was shifted significantly upfield from 3.12 ppm in polymer **20** to 2.70 ppm in polymer **21**, indicating successful removal of the ammonium protons in polymer **20**. The $^{13}$C and $^{29}$Si NMR spectra of polymer **21** were also consistent with the assigned structure.

## Summary

Facile syntheses of both cationic and anionic PFS polyelectrolytes **13**, **14**, and **19**−**21** have been achieved and these materials were readily soluble in water and remained stable in this solvent even after a period of several months. The PFSs were readily synthesized from polymer **10** which is conveniently available via substitution reactions on the chlorinated PFS **3**. A novel PFS **18** was also prepared by means of the ROP of a ferrocenophane precursor with a cyclic silylamino substituent formed via an unexpected rearrangement/ring-expansion process. Further studies of the applications of the PFS polyelectrolyte materials in layer-by-layer assembly processes and other areas will be reported shortly.[33]

## Experimental Section

**Materials.** 1,2-Bis(chlorodimethylsilyl)ethane was purchased from Gelest Inc., $PtCl_2$ from Strem Chemicals, Inc., and all other reagents from Aldrich. The reagents were used as received. Compounds $[fcSiMeCl]_n$ (**6**),[24] fcSiMeCl (**3**),[24] and $BrCH_2CH_2CH_2N(SiMe_2CH_2)_2$ (**15**)[25,27] were synthesized according to literature procedures. Solvents were dried according to standard methods.

**Equipment.** All manipulations of air-sensitive materials were performed under a nitrogen atmosphere either in an Innovative Technology glovebox or by standard Schlenk line techniques. $^1H$, $^{13}C$, and $^{29}Si$ NMR spectra were recorded on Varian spectrometers (Unity 500, Unity 400, Gemini 300, Mercury 300, or Gemini 200) and referenced to residual protonated solvent ($^1H$) or deuterated solvent ($^{13}C$) unless otherwise specified. Mass spectra were obtained with the use of a VG 70−250S mass spectrometer operating in electron impact (EI) mode. Elemental analyses were performed by Quantitative Technologies Inc., Whitehorse, NJ. Molecular weights were determined by gel permeation chromatography (GPC) using a Waters Associates 2690 separation module equipped with a column heater, in-line degasser, a high-performance liquid chromatograpy (HPLC) pump, and an autosampler. The separation module was equipped with a Waters 410 differential refractometer as the concentration detector and, connected in parallel, a Viscotek T60A dual detector consisting of a right-angle laser light-scattering detector with a laser source of 670 nm and a four-capillary differential viscometer. Software from Viscotek was used to analyze the data. Columns from Polymer Laboratories with pore sizes of $5 \times 10^2$, $1 \times 10^4$, and $1 \times 10^5$ Å were used with THF as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards purchased from Aldrich and Viscotek were used for calibration.[32]

**Synthesis of $HC{\equiv}CCH_2N(SiMe_2CH_2)_2$ (7).** To a solution of propargylamine (10.00 g, 0.182 mol) in 300 mL of dichloromethane at 25 °C under nitrogen was added triethylamine (54.0 mL, 0.387 mol). The mixture was cooled to 0 °C and a solution of 1,2-bis(chlorodimethylsilyl)ethane (39.10 g, 0.182 mol) in 100 mL of dichloromethane was added via a cannula slowly into the reaction flask. A white precipitate formed immediately. The reaction mixture was stirred at 25 °C overnight. The precipitate was filtered and the filtrate was concentrated on a rotavap. To the residue was added 100 mL of hexanes and the resulting precipitate was filtered off. The filtrate was concentrated, dried over calcium hydride overnight, and distilled under high vacuum. The acetylene **7** was obtained as a clear colorless oil (50−55 °C/0.05 mmHg; 23.69 g, 0.120 mol, 66%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 0.084 (s, 12H, $NSi(CH_3)_2$), 0.69 (s, 4H, $NSiCH_2$), 2.08 (t, $J = 2.4$ Hz, 1H, $C{\equiv}CH$), 3.54 (d, $J = 2.4$ Hz, 2H, $NCH_2C{\equiv}CH$). $^{13}C$ NMR ($C_6D_6$, 100 MHz): $\delta$ −0.5 ($NSi(CH_3)_2$), 8.3 ($NSiCH_2$), 30.6 ($NCH_2$), 70.1 ($C{\equiv}CH$), 85.2 ($C{\equiv}CH$).

**Synthesis of $fcSiMe\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\}$ (9).** To a solution of acetylene **7** (2.84 g, 14.4 mmol) in 50 mL of THF at −78 °C was added *n*-BuLi (8.56 mL of a 1.6 M solution in hexanes, 13.7 mmol). The solution was warmed to 0 °C and added via a cannula to a solution of the chlorinated ferrocenophane **6** (3.60 g, 13.7 mmol) in 100 mL of THF cooled to −78 °C. The reaction mixture was warmed slowly to 25 °C and stirred for 4 h before the solvent was removed under high vacuum. The residue was dissolved in hexanes and filtered to remove the lithium chloride salt. Recrystallization at −55 °C followed by sublimation under high vacuum (0.05 mmHg) at 75−80 °C afforded ferrocenophane **9** as a dark red crystalline solid (3.41 g, 8.04 mmol, 59%). $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 0.21 (s, 12H, $NSi(CH_3)_2$), 0.59 (s, 3H, $fcSiCH_3$), 0.76 (s, 4H, $NSiCH_2$), 3.57 (s, 2H, $NCH_2$), 3.90, 4.38, 4.47, 4.54 (4m, 4 × 2H, Cp). $^{13}C$ NMR ($C_6D_6$, 100 MHz): $\delta$ −2.6 ($fcSiCH_3$), 0.1 ($NSi(CH_3)_2$), 8.7 ($NSiCH_2$), 31.1 ($NCH_2$), 32.2 (*ipso*-Cp), 75.1, 76.8, 78.4, 78.5 (Cp), 82.1 ($SiC{\equiv}CCH_2$), 110.8 ($SiC{\equiv}CCH_2$). $^{29}Si$ NMR ($C_6D_6$, 79 MHz): $\delta$ −28.9 ($SiC{\equiv}C$), 15.2 ($NSi$). HRMS for $C_{20}H_{29}FeNSi_3$: calcd 423.0957; found 423.0944.

**Synthesis of $[fcSiMe\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\}]_n$ (10).** To a solution of the amino propyne **7** (5.64 g, 28.6 mmol) in 50 mL of THF at −78 °C under nitrogen was added *n*-BuLi (17.2 mL of 1.6 M solution in hexanes, 27.8 mmol) dropwise. After the addition was complete, the reaction mixture was stirred for 5 min at 0 °C before the resulting acetylide solution was added via a cannula dropwise to a solution of polymer **3** (5.00 g, 19.0 mmol of Si−Cl) in 200 mL of THF at 0 °C. The reaction mixture was warmed to 25 °C and stirred for 24 h. The orange-red solution was then concentrated to ca. 80 mL and precipitated into methanol to afford polymer **10** as an orange-yellow fibrous solid (6.32 g, 14.9 mmol, 79%). Ring-opening polymerization of monomer **9** in xylene at reflux for 16 h or at 25 °C in toluene over 24 h with a catalytic amount of $PtCl_2$ also afforded polymer **10**. $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ 0.25 (s, 12H, $NSi(CH_3)_2$), 0.79, 0.82 (2s, 7H, $NSiCH_2$, $fcSiCH_3$), 3.67 (s, 2H, $NCH_2$), 4.28, 4.35, 4.48, 4.49, 4.57 (br, 8H, Cp). $^{13}C$ NMR ($C_6D_6$, 75 MHz): $\delta$ −0.5 ($fcSiCH_3$), −0.1 ($NSi(CH_3)_2$), 8.4 ($NSiCH_2$), 32.0 ($NCH_2$), 69.39, 69.43 (*ipso*-Cp), 72.8, 74.2, 74.4 (Cp), 84.7 ($SiC{\equiv}CCH_2$), 109.3 ($SiC{\equiv}CCH_2$). $^{29}Si$ NMR ($C_6D_6$, 79 MHz): $\delta$ −24.8 ($fcSi$), 14.9 ($NSi$). GPC: $M_w = 304100$, PDI = 1.48.

**Synthesis of $[fcSiMe(C{\equiv}CCH_2NH_2)]_n$ (11).** A solution of the polymer **10** (1.10 g, 2.60 mmol) in 120 mL of THF and 40 mL of methanol was stirred at 25 °C for 4 days. The product was isolated by solvent removal, dissolution in THF, and precipitation into hexanes to give polymer **11** as an orange-yellow fibrous solid (0.62 g, 2.2 mmol, 85%). $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 0.64 (s, 3H, $fcSiCH_3$), 1.46 (s, 2H, $NH_2$), 3.55 (s, 2H, $NCH_2$), 4.10, 4.13, 4.20, 4.23, 4.37, 4.39 (m, 8H, Cp). $^1H$ NMR ($CD_3OD$, 400 MHz): $\delta$ 0.52 (br, 3H, $fcSiCH_3$), 1.19 (br, $NH_2$), 3.41 (br, 2H, $NCH_2$), 3.9−4.4 (m, 8H, Cp). $^{13}C$ NMR ($CD_2Cl_2$, 100 MHz): $\delta$ −1.23, −1.20 ($fcSiCH_3$), 32.8 ($NCH_2$), 69.13, 69.15 (*ipso*-Cp), 72.61, 72.69, 72.73, 73.87, 73.97, 74.21, 74.30 (Cp), 84.9 ($SiC{\equiv}CCH_2$), 108.9 ($SiC{\equiv}CCH_2$). $^{29}Si$ NMR ($CD_2Cl_2$, 79 MHz): $\delta$ −23.20, −23.18, −23.16 (1:2:1).

**Synthesis of $[fcSiMe(CH_2CH_2CH_2NH_2)]_n$ (12).** A solution of the polymer **10** (5.20 g, 12.3 mmol) in a mixture of the solvents THF (1.1 L) and methanol (0.4 L) was stirred at 25 °C for 4 days. Solvent removal followed by dissolution in THF and precipitation into hexanes gave a gum which was redissolved in ca. 100 mL of THF. Hydrazine hydrate (10 mL) was added to the polymer solution and the reaction mixture was stirred under air for 2 days. Precipitation into hexanes afforded a gummy material, which was redissolved in THF, filtered through Celite, and precipitated into hexanes. Polymer **12** was isolated as a light-yellow powder (2.05 g, 7.19 mmol, 58%). $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 0.48 (s, 3H, $fcSiCH_3$), 0.90 (m, 2H, $fcSiCH_2$), 1.31 (br, 2H, $NH_2$), 1.49 (br, 2H, $SiCH_2CH_2$), 2.66 (t, $J = 6.4$ Hz, 2H, $CH_2NH_2$), 3.98, 4.01, 4.05, 4.22 (m, 8H, Cp). $^{13}C$ NMR ($CD_2Cl_2$, 100 MHz): $\delta$ −3.0 ($fcSiCH_3$), 13.5 ($fcSiCH_2$), 29.2 ($SiCH_2CH_2$), 46.2 ($CH_2NH_2$), 71.1 (*ipso*-Cp), 71.58, 71.68, 73.70, 73.73, 73.79, 73.83 (Cp), $^{29}Si$ NMR ($CD_2Cl_2$, 79 MHz): $\delta$ −3.4.

**Synthesis of $[fcSiMe(C{\equiv}CCH_2NH_3Cl)]_n$ (13).** To a solution of the polymer **11** (129 mg, 0.46 mmol) in 7.0 mL of dichloromethane at 25 °C under nitrogen was added a solution of HCl (0.46 mL of 1.0 M solution in ether, 0.46 mmol) dropwise. The reaction mixture was stirred for 5 min and the precipitate was collected by suction filtration under nitrogen. Repeated washing of the precipitate with dichloromethane followed by drying under high vacuum gave polymer **13** as an orange-yellow powder (117 mg, 0.37 mmol, 80%). $^1H$ NMR ($D_2O$, 200 MHz): $\delta$ 0.55 (br, 3H, $fcSiCH_3$), 3.78 (br, 2H, $CH_2N$), 3.9−4.6 (m, br, 8H, Cp). $^1H$ NMR ($CD_3OD$, 400 MHz): $\delta$ 0.58 (br, 3H, $fcSiCH_3$), 3.93 (br, 2H, $CH_2N$), 4.0−4.6 (m, br, 8H, Cp). $^{13}C$ NMR ($D_2O$, 100 MHz, $\delta_{ref(acetonitrile)} = 121.7$): $\delta$ 1.1 ($fcSiCH_3$), 32.3 ($NCH_2$), 70.2 (*ipso*-Cp), 75.3, 76.5 (Cp), 93.6

($\mathrm{SiC{\equiv}}C\mathrm{CH_2}$), 100.4 ($\mathrm{Si}C\mathrm{{\equiv}CCH_2}$). $^{29}$Si NMR ($\mathrm{D_2O}$, 99 MHz, 50 °C): $\delta = -23.8$.

**Synthesis of [fcSiMe(CH$_2$CH$_2$CH$_2$NH$_3$Cl)]$_n$ (14).** To a solution of the aminopropyl polymer **12** (110 mg, 0.39 mmol) in a mixture of 5 mL of dichloromethane and 2.5 mL of methanol at 25 °C under nitrogen was added HCl (0.40 mL of 1.0 M solution in ether, 0.40 mmol) dropwise. The solution turned cloudy during the addition and 9.0 mL of methanol was added to dissolve the precipitated polymer. The reaction solution was stirred for 10 min before the solvents were removed in vacuo. The residue was dried at 90 °C under high vacuum (0.05 mmHg) for 16 h, dissolved in 1 mL of methanol, and precipitated into 20 mL of acetone containing 1 drop of hydrazine hydrate. The ammonium polymer **14** was obtained as a yellow-orange powder (100 mg, 0.31 mmol, 80%). $^1$H NMR ($\mathrm{D_2O}$, 400 MHz): $\delta$ 0.43 (br, 3H, $\mathrm{fcSiC}H_3$), 0.83 (br, 2H, $\mathrm{fcSiC}H_2$), 1.59 (br, 2H, $\mathrm{SiCH_2C}H_2$), 2.80 (br, 2H, $\mathrm{C}H_2\mathrm{N}$), 3.90−4.40 (m, br, 8H, Cp). $^{13}$C NMR ($\mathrm{D_2O}$, 100 MHz, $\delta_{\mathrm{ref(acetonitrile)}} = 121.7$, 80 °C): $\delta$ −1.1 ($\mathrm{fcSi}C\mathrm{H_3}$), 15.1 ($\mathrm{fcSi}C\mathrm{H_2}$), 24.5 ($\mathrm{SiCH_2}C\mathrm{H_2}$), 44.8 ($C\mathrm{H_2N}$), 72.8 (*ipso*-Cp), 74.1, 76.1 (Cp). $^{29}$Si NMR ($\mathrm{D_2O}$, 99 MHz, 50 °C): $\delta$ −4.9. Anal. Calcd for $(\mathrm{C_{14}H_{20}ClFeNSi})_n$ $(321.71)_n$: C, 52.26; H, 6.27; N, 4.35. Found: C, 51.95; H, 6.60; N, 3.84.

**Synthesis of fcSiMe{N(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_2$SiMe$_2$} (17).** To a suspension of lithium wire pieces (743 mg, 107 mmol) in 20 mL of ether at 25 °C was added a solution of bromide **15** (3.33 g, 11.9 mmol) in 5.0 mL of ether. Upon initiation of the lithiation, the reaction flask was cooled to −20 °C. After the mixture was stirred for 2 h at −20 to −10 °C, the solid in the reaction mixture was removed and the colorless organolithium filtrate was collected in a Schlenk round-bottom flask cooled at −20 °C. From this organolithium solution 16.4 mL was taken (ca. 2 equiv for each Si−Cl bond) and added dropwise to a solution of ferrocenophane **6** (1.00 g, 3.81 mmol) in 50 mL of THF at −78 °C. The reaction was warmed slowly to 25 °C over ca. 3 h. Filtration of the reaction mixture followed by removal of the solvent under high vacuum gave a dark red residue which was dissolved in 50 mL of hexanes and filtered again to remove any remaining lithium salt. Evaporation of hexanes, heating the viscous residual oil to 80 °C under high vacuum (0.05 mmHg), recrystallization at −55 °C, and sublimation at 75 °C under high vacuum gave **17** as a red crystalline solid (0.480 g, 1.12 mmol, 29%). $^1$H NMR ($\mathrm{C_6D_6}$, 400 MHz): $\delta$ −0.02 (s, 6H, $\mathrm{CH_2Si(C}H_3)_2\mathrm{CH_2}$), 0.32 (s, 6H, $\mathrm{NSi(C}H_3)_2\mathrm{CH_2}$), 0.52 (s, 3H, $\mathrm{fcSiC}H_3$), 0.75 (s, 4H, $\mathrm{NSiC}H_2\mathrm{C}H_2\mathrm{Si}$), 0.84 (m, 2H, $\mathrm{SiC}H_2\mathrm{CH_2CH_2N}$), 1.84 (m, 2H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2N}$), 3.08 (t, $J = 9.0$ Hz, 2H, $\mathrm{SiCH_2CH_2C}H_2\mathrm{N}$), 3.87, 4.11, 4.34, 4.42 (4 × m, 4 × 2H, Cp). $^{13}$C NMR ($\mathrm{C_6D_6}$, 75 MHz): $\delta$ −2.8 ($\mathrm{CH_2Si(}C\mathrm{H_3)_2CH_2}$), 0.2 ($\mathrm{NSi(}C\mathrm{H_3)_2CH_2}$), 0.9 ($\mathrm{fcSi}C\mathrm{H_3}$), 10.1, 10.4 ($\mathrm{Si}C\mathrm{H_2}C\mathrm{H_2SiN}$), 12.6 ($\mathrm{Si}C\mathrm{H_2CH_2CH_2N}$), 27.3 ($\mathrm{SiCH_2}C\mathrm{H_2CH_2N}$), 38.0 (*ipso*-Cp), 44.5 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2N}$), 76.0, 76.1, 77.4, 77.6 (Cp). $^{29}$Si NMR ($\mathrm{C_6D_6}$, 79 MHz): $\delta$ −9.1, 3,7, 5.4. HRMS for $\mathrm{C_{20}H_{33}FeNSi_3}$: calcd 427.1270; found 427.1261.

**Synthesis of [fcSiMe{N(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_2$SiMe$_2$}]$_n$ (18).** A solution of monomer **17** (1.0 g, 2.3 mmol) in 5 mL of xylene was heated at reflux overnight. The reaction mixture was precipitated in methanol to afford polymer **18** as a light brownish fibrous solid (0.7 g, 1.6 mmol, 70%). $^1$H NMR ($\mathrm{C_6D_6}$, 400 MHz): $\delta$ 0.06 (s, 6H, $\mathrm{CH_2Si(C}H_3)_2\mathrm{CH_2}$), 0.24 (s, 6H, $\mathrm{NSi(C}H_3)_2\mathrm{CH_2}$), 0.79 (br, 6H, $\mathrm{NSiC}H_2\mathrm{C}H_2\mathrm{Si}$ and $\mathrm{SiC}H_2\mathrm{CH_2CH_2N}$), 1.04 (s, 3H, $\mathrm{fcSiC}H_3$), 1.71 (br, 2H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2N}$), 3.27 (br, 2H, $\mathrm{SiCH_2CH_2C}H_2\mathrm{N}$), 4.3−4.7 (m, 8H, Cp). $^{13}$C NMR ($\mathrm{C_6D_6}$, 100 MHz): $\delta$ −2.4 ($\mathrm{CH_2Si(}C\mathrm{H_3)_2CH_2}$), 1.9 ($\mathrm{NSi(}C\mathrm{H_3)_2CH_2}$), 2.9 ($\mathrm{fcSi}C\mathrm{H_3}$), 10.0, 10.9 ($\mathrm{Si}C\mathrm{H_2}C\mathrm{H_2SiN}$), 12.8 ($\mathrm{Si}C\mathrm{H_2CH_2CH_2N}$), 27.4 ($\mathrm{SiCH_2}C\mathrm{H_2CH_2N}$), 46.4 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2N}$), 71.7, 72.2, 73.4, 74.6, 74.9, 75.2, 75.4 (Cp). $^{29}$Si NMR ($\mathrm{C_6D_6}$, 79 MHz): $\delta$ −2.93, 3.96, 7.09.

**Synthesis of [fcSiMe{C≡CCH$_2$N(CH$_2$CH$_2$CH$_2$SO$_3$Na)$_2$}]$_n$ (19).** To a solution of **10** (2.51 g, 5.93 mmol, $M_\mathrm{w} = 304100$, PDI = 1.48) in 130 mL of dichloromethane and 30 mL of methanol at 25 °C was added diisopropylethylamine (2.59 mL, 14.9 mmol) followed by a solution of 1,3-propane sultone (1.88 g, 15.4 mmol) in 20 mL of methanol. The clear orange solution was stirred for 4 days before the solvents were removed under high vacuum. The residue was dissolved in methanol and precipitated into 1000 mL of acetone containing sodium hexafluorophosphate (5.00 g, 29.8 mmol). The polymer was redissolved in distilled water and precipitated into acetone. Suction filtration followed by drying under high vacuum afforded polymer **19** as a yellow powder (3.13 g, 5.50 mmol, 93%). $^1$H NMR ($\mathrm{D_2O}$, 400 MHz): $\delta$ 0.59 (br, 3H, $\mathrm{fcSiC}H_3$), 1.84 (br, 4H, $\mathrm{C}H_2\mathrm{CH_2SO_3}$), 2.65, 2.77 (br, 8H, $\mathrm{C}H_2\mathrm{CH_2C}H_2\mathrm{SO_3}$), 3.50 (br, 2H, $\mathrm{C{\equiv}CC}H_2\mathrm{N}$), 3.90−4.60 (m, br, 8H, Cp). $^{13}$C NMR ($\mathrm{D_2O}$, 100 MHz, $\delta_{\mathrm{ref(acetone)}} = 215.9$): $\delta$ −0.77 ($\mathrm{fcSi}C\mathrm{H_3}$), 22.4 ($C\mathrm{H_2CH_2SO_3}$), 43.4 ($\mathrm{C{\equiv}C}C\mathrm{H_2N}$), 49.5 ($C\mathrm{H_2SO_3}$), 52.5 ($\mathrm{N}C\mathrm{H_2CH_2CH_2SO_3}$), 69.1 (*ipso*-Cp), 73.3, 74.5 (Cp), 90.6 ($\mathrm{SiC{\equiv}}C\mathrm{CH_2}$), 101.6 ($\mathrm{Si}C\mathrm{{\equiv}CCH_2}$). $^{29}$Si NMR ($\mathrm{D_2O}$, 79 MHz): $\delta$ −24.7.

**Synthesis of [fcSiMe{CH$_2$CH$_2$CH$_2$NH(CH$_2$CH$_2$CH$_2$SO$_3$)(CH$_2$CH$_2$CH$_2$SO$_3$Na)}]$_n$ (20).** To a solution of **19** (0.34 g, 0.60 mmol) in 8 mL of distilled water at 25 °C was added 0.40 mL of hydrazine hydrate. The clear orange solution was stirred under air for 2 days before the polymer product was precipitated by addition to 250 mL of acetone. Suction filtration followed by drying under high vacuum afforded polymer **20** as a yellow powder (0.31 g, 0.56 mmol, 94%). $^1$H NMR ($\mathrm{D_2O}$, 400 MHz): $\delta$ 0.58 (br, 3H, $\mathrm{fcSiC}H_3$), 0.95 (br, 2H, $\mathrm{fcSiC}H_2$), 1.75 (br, 2H, $\mathrm{SiCH_2C}H_2$), 2.06 (br, 4H, $\mathrm{C}H_2\mathrm{CH_2SO_3}$), 2.92, 3.12 (br, 10H, $\mathrm{C}H_2\mathrm{CH_2C}H_2\mathrm{SO_3}$ and $\mathrm{NCH_2}$), 3.90−4.60 (m, br, 8H, Cp). $^{13}$C NMR ($\mathrm{D_2O}$, 125 MHz, $\delta_{\mathrm{ref(acetone)}} = 215.9$): $\delta$ −2.8 ($\mathrm{fcSi}C\mathrm{H_3}$), 12.8 ($\mathrm{fcSi}C\mathrm{H_2}$), 19.3 ($\mathrm{SiCH_2}C\mathrm{H_2}$), 20.0 ($C\mathrm{H_2CH_2SO_3}$), 48.7 ($C\mathrm{H_2SO_3}$), 51.9 ($\mathrm{N}C\mathrm{H_2CH_2CH_2SO_3}$), 56.5 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2N}$), 70.6 (*ipso*-Cp), 72.1, 74.0 (Cp). $^{29}$Si NMR ($\mathrm{D_2O}$, 79 MHz): $\delta$ −5.4.

**Synthesis of [fcSiMe{CH$_2$CH$_2$CH$_2$N(CH$_2$CH$_2$CH$_2$SO$_3$Na)$_2$}]$_n$ (21).** To a solution of **20** (90 mg, 0.16 mmol) in 1 mL of distilled water at 25 °C was added 0.28 mL of diisopropylethylamine (1.6 mmol). The reaction mixture was stirred overnight before precipitation of the polymer by addition to 20 mL of acetone. Suction filtration followed by drying under high vacuum afforded polymer **21** as a yellow powder (80 mg, 0.14 mmol, 86%). $^1$H NMR ($\mathrm{D_2O}$, 400 MHz): $\delta$ 0.61 (br, 3H, $\mathrm{fcSiC}H_3$), 0.94 (br, 2H, $\mathrm{fcSiC}H_2$), 1.67 (br, 2H, $\mathrm{SiCH_2C}H_2$), 1.98 (br, 4H, $\mathrm{C}H_2\mathrm{CH_2SO_3}$), 2.70, 2.92 (br, 10H, $\mathrm{NCH_2}$ and $\mathrm{C}H_2\mathrm{CH_2C}H_2\mathrm{SO_3}$), 3.80−4.70 (m, br, 8H, Cp). $^{13}$C NMR ($\mathrm{D_2O}$, 100 MHz, $\delta_{\mathrm{ref(acetone)}} = 215.6$): $\delta$ −2.9 ($\mathrm{fcSi}C\mathrm{H_3}$), 12.7 ($\mathrm{fcSi}C\mathrm{H_2}$), 19.8 ($\mathrm{SiCH_2}C\mathrm{H_2}$), 20.6 ($C\mathrm{H_2CH_2SO_3}$), 48.7 ($C\mathrm{H_2SO_3}$), 51.7 ($\mathrm{N}C\mathrm{H_2CH_2CH_2SO_3}$), 57.0 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2N}$), 70.5 (*ipso*-Cp), 72.0, 73.8 (Cp). $^{29}$Si NMR ($\mathrm{D_2O}$, 79 MHz): $\delta$ −5.5.

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**Supporting Information Available:** Details of X-ray structure determination and tables of X-ray diffraction data for crystal **17** and comparison of structure features of selected silicon-bridged [1]ferrocenophanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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