

# Reinvestigation of the Rosenberg Synthesis of Silyleneferrocenylene Polymers

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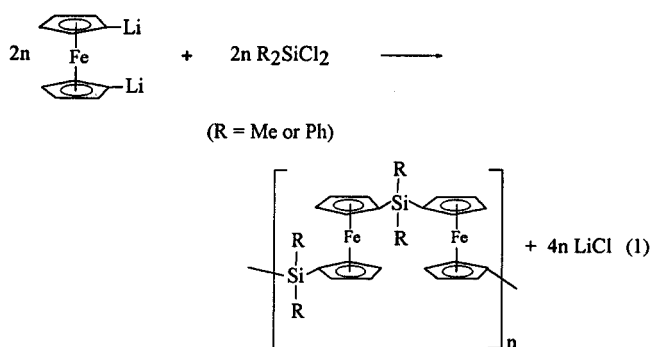
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**Summary:** Reinvestigation of the original Rosenberg synthesis of silyleneferrocenylene polymers shows that no condensation–polymerization occurs in the reaction of dilithioferrocene (**1**) and dimethyldichlorosilane (**2a**) in the THF/hexane solvent mixture specified. These experimental conditions result in the direct formation of [1](dimethylsilylene)ferrocenophane (**3a**). Differing work up conditions result in differing products, and those reported produce a mixture of ferrocenylene- and ferrocenylsiloxanes. The addition of **1** to **2a** in THF also produced the ferrocenophane as the most abundant product, whereas the reverse addition of **2a** to **1** resulted in the formation of ferrocenophane at low temperatures and a polymeric material at high temperatures. Similar results were obtained upon replacing **2a** by diphenyldichlorosilane (**2b**), suggesting that the results are general.

## Introduction

There is currently interest in the formation and study of ferrocene containing group 14 organometallic polymers, with ferrocenyl as a pendant group<sup>1</sup> and ferrocenylene<sup>2–5</sup> as an integral part of the polymer backbone. Non-group 14 containing ferrocenylene poly-

mers also have been reported.<sup>6</sup> Silyleneferrocenylene polymers were first reported as low molecular weight materials by Rosenberg.<sup>7</sup> The polymers were synthesized by the reaction of 1,1'-dilithioferrocene (**1**) and a dichlorosilane, Me<sub>2</sub>SiCl<sub>2</sub> (**2a**) and Ph<sub>2</sub>SiCl<sub>2</sub> (**2b**), eq 1, presumably via a polycondensation salt-elimination reaction.



For use in the reaction with Me<sub>2</sub>SiCl<sub>2</sub>, 1,1'-dilithioferrocene was obtained by treatment of 1,1'-bis(chloromercurio)ferrocene with *n*-butyllithium at 0 °C in a 2:1 THF:hexane solvent mixture. Dimethyldichlorosilane (**2a**) was added directly to the dilithioferrocene solution by syringe while maintaining the reaction mixture at 0 °C, and the resulting mixture was stirred at this temperature for 45 min. Following distillation of the solvents (no temperature specified), the di-*n*-butylmercury formed in the transmetalation reaction was removed by steam distillation. Subsequent trituration of the residue with methanol, drying at 60 °C for a week, and final heating to constant weight at 120 °C completed the polymer separation and isolation procedure.

We have revisited this reaction, with the aid of modern analytical tools, since the initial products from this process may not have been the reported polymer. Possibly, the steam distillation could have provided a range of alternative reaction products. Furthermore, the final heating to constant weight at 120 °C could be the step responsible for polymer formation by the thermal ring-opening of any ferrocenophane that had survived the previous treatments.

(5) Hmyene, M.; Yasser, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *6*, 564.

(6) (a) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (b) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (c) Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5503. (d) Neef, C. J.; Glatzhofer, D. T.; Nicholas, K. M. Southwest Regional Meeting of the American Chemical Society, Ft. Worth, TX, Nov. 1994. (e) *Ibid.* Joint Southeast/Southwest Regional Meeting of the American Chemical Society, Memphis, TN, Nov. 1995.

(7) Rosenberg, H. U.S. Patent 3,426,053, filed August 31, 1966, patented February 4, 1969.

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(1) (a) Lin, J.; Wen, X.; Du, Z. *J. Shandong Univ.* **1987**, *22*, 100; *Chem. Abstr.* **1988**, *109*, 74041e. (b) Du, Z.; Wen, X.; Lin, J. *J. Shandong Univ.* **1987**, *22*, 115; *Chem. Abstr.* **1988**, *108*, 56695w. (c) Pannell, K. H.; Rozell, J. M.; Zeigler, J. M. *Macromolecules* **1988**, *21*, 276. (d) Diaz, A.; Seymour, M.; Pannell, K. H.; Rozell, J. M. *J. Electrochem. Soc.* **1990**, *137*, 503. (e) Pannell, K. H.; Rozell, J. M.; Vincenti, S. P. *224 Silicon-Based Polymer Science: A Comprehensive Resource*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; Chapter 20. (f) Pannell, K. H.; Dementiev, V. V.; Diaz, A. F. *Transition Metal-Containing Silicon-Based Polymers. The Polymeric Materials Encyclopedia. Synthesis, Properties and Applications*; Salomone, J. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1996; Vol. 6, p 4133.

(2) (a) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Tang, B.-Z.; Foucher, D. A.; Lough, A.; Coombs, N.; Sodhi, R.; Manners, I. *J. Chem. Soc. Chem. Commun.* **1993**, 523. (c) Foucher, D. A.; Ziembinski, R.; Tang, B.-Z.; Macdonald, P. M.; Massey, J.; Jaeger, C. R.; Vansco, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878. (d) Foucher, D. A.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vansco, G. J.; Manners, I. *Macromolecules* **1994**, *27*, 3992. (e) Zechel, D. L.; Hultsch, K. C.; Rulkens, R.; Balaishis, D.; Ni, Y.; Pudelski, J. K.; Lough, A. L.; Manners, I.; Foucher, D. A. *Organometallics* **1996**, *15*, 1972. (f) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131. (g) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102.

(3) (a) Nguyen, M. T.; Diaz, A. F.; Dementiev, V. V.; Sharma, H.; Pannell, K. H. *SPIE Proc.* **1993**, *1910*, 230. (b) Nguyen, M. T.; Diaz, A. F.; Dementiev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389. (c) Dementiev, V. V.; Cervantes-Lee, F.; Párkányi, L.; Sharma, H. K.; Pannell, K. H.; Nguyen, M.-T.; Diaz, A. F. *Organometallics* **1993**, *12*, 1983. (d) Nguyen, M. T.; Diaz, A. F.; Dementiev, V. V.; Pannell, K. H. *Chem. Mater.* **1994**, *6*, 952. (e) Pannell, K. H.; Dementiev, V. V.; Li, H.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A. F. *Organometallics* **1994**, *13*, 3644. (f) Kapoor, R. N.; Crawford, G. M.; Mahmoud, J.; Dementiev, V. V.; Nguyen, M. T.; Diaz, A. F.; Pannell, K. H. *Organometallics* **1995**, *14*, 4944.

(4) (a) Tanaka, M.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334. (b) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263.

**Table 1. Product Distribution from Steam Distillation of 3a and *n*-Bu<sub>2</sub>Hg<sup>a</sup>**

compd (retention time, min)	<sup>29</sup> Si NMR (δ ppm)	<i>m/z</i> (%)	% yield	ref
ferrocene (5.3)		186 (100, [M] <sup>+</sup> ); 121 (70, [C <sub>5</sub> H <sub>5</sub> Fe] <sup>+</sup> )	13	
FcSiMe <sub>2</sub> OMe (7.2)	11.91	274 (65, [M] <sup>+</sup> ); 259 (42, [M - Me] <sup>+</sup> ); 186 (78, [FcH] <sup>+</sup> ); 121 (82, [C <sub>5</sub> H <sub>5</sub> Fe] <sup>+</sup> )	27	8
( <i>η</i> <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub> Fe(SiMe <sub>2</sub> ) <sub>2</sub> O (7.6)	1.03	316 (100, [M] <sup>+</sup> ); 301 (82, [M - Me] <sup>+</sup> ); 186 (60, [FcH] <sup>+</sup> ); 121 (68, [C <sub>5</sub> H <sub>5</sub> Fe] <sup>+</sup> )	25	9
( <i>η</i> <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub> Fe(SiMe <sub>2</sub> O) <sub>2</sub> SiMe <sub>2</sub> (8.0)	0.48, -21.3	390 (35, [M] <sup>+</sup> ); 375 (14, [M - Me] <sup>+</sup> ); 348 (100, [Fc(SiMe <sub>2</sub> O) <sub>2</sub> Me] <sup>+</sup> ); 316 (11, [M - SiMe <sub>2</sub> O] <sup>+</sup> ); 301 (46); 186 (46); 121 (68)	9	9
( <i>η</i> <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub> Fe(SiMe <sub>2</sub> O) <sub>3</sub> SiMe <sub>2</sub> (8.8)		464 (10, [M] <sup>+</sup> ); 374 (41); 301 (25); 243 (19); 186 (46)	1	9
( <i>η</i> <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub> Fe(SiMe <sub>2</sub> O) <sub>4</sub> SiMe <sub>2</sub> (9.5)		538 (3, [M] <sup>+</sup> ); 496 (4, [Fc(SiMe <sub>2</sub> O) <sub>4</sub> Me] <sup>+</sup> ); 448 (100); 316 (25); 301 (20)	2	9
FcSiMe <sub>2</sub> Fc (12.5)		428 (51, [M] <sup>+</sup> ); 413 (8, [M - Me] <sup>+</sup> ); 363 (21, [M - C <sub>5</sub> H <sub>5</sub> ] <sup>+</sup> ); 121 (92)	1	8
FcSiMe <sub>2</sub> OSiMe <sub>2</sub> Fc (13.1)	0.48	502 (100, [M] <sup>+</sup> ); 437 (18, M - C <sub>5</sub> H <sub>5</sub> ] <sup>+</sup> ); 316 (10); 301 (90)	13	9-11

<sup>a</sup> Relative products and their distributions were determined *via* GC/MS and GC analysis, respectively, of the reaction product mixtures. Our experimental retention times provide relative product elution times. An unknown material with a retention time of 8.2 min [*m/e* 300 (70); 285 (4); 243 (100); 186 (46)] was also obtained in 6% relative abundance, possibly (*η*<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>FeSiMe<sub>2</sub>SiMe<sub>2</sub>.

## Results and Discussion

We repeated the Rosenberg procedure up to the point of removal of the solvents. In our procedure, the solvents were removed *in vacuo* at room temperature and the resulting residue was analyzed by <sup>29</sup>Si, <sup>13</sup>C, and <sup>1</sup>H NMR spectroscopy. The observable products at this stage were [1](dimethylsilylene)ferrocenophane (**3a**) and di-*n*-butylmercury. There was no evidence for the formation of significant amounts of polymeric material.

We used two different procedures for the removal of the di-*n*-butylmercury. Distillation at 0.001 mmHg left a residue of [1](dimethylsilylene)ferrocenophane.<sup>2,3</sup> Steam distillation, as used by Rosenberg, yielded a mixture of known materials (see Table 1) that were identified by comparison of their NMR and GC/MS properties with those reported in the literature or with those of authentic materials.<sup>8-11</sup>

Steam distillation of [1](dimethylsilylene)ferrocenophane in the presence and absence of di-*n*-butylmercury and LiCl gave similar product distributions which differed slightly in the amount of ferrocenylenesiloxane materials. The difference is probably due to the presence of the mercury salts formed during this procedure which could facilitate siloxane formation in the former sample.

There was no significant formation of silyleneferrocenylenes polymers in the reaction between **1** and **2a** in THF:hexane at 0 °C as specified in the patent. Any polymer produced probably resulted from thermal ring-opening polymerization of [1](dimethylsilylene)ferrocenophane initially formed. The heating responsible for this could have been applied during the initial solvent distillation after completion of the reaction of the dilithioferrocene with dimethyldichlorosilane or the final heating to constant weight at 120 °C. The characterization of the Rosenberg polymer was limited to elemental analysis. The reported data (Anal. Calcd for C<sub>12</sub>H<sub>14</sub>FeSi: C, 59.50; H, 5.84; Fe, 23.06; Si, 11.60. Found: C, 59.01; H, 5.64; Fe, 22.45; Si, 7.42.) suggest that the polymer (isolated as a black, brittle material not characteristic of the normal form of this polymer) was not a silyleneferrocenylenes but probably contained significant amounts of oxygen in the form of siloxane units.

We repeated the reaction between dilithioferrocene (**1**) and diphenyldichlorosilane (**2b**) in a THF:hexane mixture. As described in the patent for this reaction, **1** was formed *via* the reaction of ferrocene and *n*-butyllithium in the presence of tmeda,<sup>12</sup> and solvent extraction, not steam distillation, was used for product separation. In our hands, the use of the THF:hexane solvent mixture resulted in the sole formation of [1](diphenylsilylene)ferrocenophane, **3b**,<sup>2c,13</sup> in essentially quantitative yield.

Hmyene et al. have reported the synthesis of a low molecular weight dimethylsilyleneferrocenylenes polymer directly by the reaction of dilithioferrocene (**1**) and dimethyldichlorosilane (**2a**) in THF at 60 °C.<sup>5</sup> No precise experimental details, spectroscopic data (apart from noting that the UV-vis spectrum was identical to that reported for the high molecular weight form), nor yield were provided. We performed this reaction using two procedures: addition of dimethyldichlorosilane, **2a**, to dilithioferrocene, **1**, and addition of **1** to **2a**. Addition of **2a** by syringe to a THF solution of **1** at room temperature led to the predominant formation of [1]-(dimethylsilylene)ferrocenophane, **3a**. Approximately 30% by weight of the crude reaction product was polymeric material (presumably that isolated previously). When the reaction was performed in refluxing THF, only polymeric material was produced. The reverse addition of a THF solution of **1** to **2a** resulted in the formation of ferrocenophane **3a** almost exclusively (>90%), regardless of the temperature of addition.

The low temperature reactions between dilithioferrocene and dimethyl- and diphenyldichlorosilanes yielded no useful amounts of polymeric silyleneferrocenylenes, regardless of the solvent combination. Only at elevated temperatures and with the addition of R<sub>2</sub>SiCl<sub>2</sub> to the dilithioferrocene can useful amounts of polymeric material be obtained. This latter reaction probably involves anionic ring opening of the initially formed ferrocenophane since the dilithioferrocene will always be present in this mode of addition.<sup>2f</sup>

## Experimental Section

All manipulations were carried out under an argon atmosphere or high vacuum. 1,1'-Bis(chloromercurio)ferrocene was purchased from Strem Chemicals, and Me<sub>2</sub>SiCl<sub>2</sub> and Ph<sub>2</sub>SiCl<sub>2</sub>

- (8) Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10*, 954.  
 (9) Angelakos, C.; Zamble, D. B.; Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994**, *33*, 1709.  
 (10) Rausch, M. D.; Schloemer, G. C. *Org. Prep. Proced.* **1969**, *1*, 131.  
 (11) Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501.

- (12) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.  
 (13) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27.

were purchased from Gelest, Inc. and distilled before use. NMR spectra were recorded on Bruker NR 200 MHz and 250 MHz spectrometers in  $C_6D_6$ ; GC/MS analysis was performed using a Hewlett Packard 5890 Series II instrument, using a cross-linked methylsilicone column with the following operating temperatures: injection 250 °C, column 270 °C, detector 280 °C.

**Reaction between 1,1'-Dilithioferrocene and  $Me_2SiCl_2$  in THF/hexane.** In a 250 mL Schlenk flask 6.9 g (0.01 mol) of 1,1'-bis(chloromercurio)ferrocene was placed in a solvent mixture consisting of 130 mL of THF and 63 mL of hexanes. To this mixture was added slowly by syringe 26 mL (0.041 mol) of *n*-butyllithium solution (1.6 M in hexanes) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then at room temperature for 1 h. The chocolate-colored 1,1'-dilithioferrocene formed was used directly. While the solution of 1,1'-dilithioferrocene was maintained at 0 °C, 1.29 g (0.01 mol) of  $Me_2SiCl_2$  was added slowly by syringe with stirring. The reaction mixture was maintained at 0 °C for another 45 min. During this time, the color of the solution changed from chocolate-brown to red. The mixture was stirred overnight at room temperature. The solvents were removed under vacuum, 0.001 mmHg.  $^{13}C$  and  $^{29}Si$  NMR spectral analysis of an aliquot showed, by comparison with authentic materials, the mixture to be comprised of [1](dimethylsilylene)ferrocenophane,  $^{29}Si$  NMR  $\delta$  -4.8 ppm,<sup>2a,3b</sup> with traces of (dimethylsilyl)ferrocenylene polymer,  $^{29}Si$  NMR  $\delta$  -6.3 ppm,<sup>2a,3b</sup> 1,1'-bis(chlorodimethylsilyl)ferrocene,  $^{29}Si$  NMR  $\delta$  22.8 ppm,<sup>14</sup> (chlorodimethylsilyl)ferrocene,  $^{29}Si$  NMR  $\delta$  22.2 ppm,<sup>8</sup> and ferrocene,  $^{13}C$  NMR  $\delta$  68.2 ppm. After removal of the solvents, the red liquid residue was subjected to steam distillation to remove di-*n*-butylmercury and ferrocene. The color of the residue in contact with steam changed from red to orange and finally to brown. The residue was extracted with 200 mL of methylene chloride, and the extracts were dried over  $Na_2SO_4$  and filtered. The methylene chloride was removed on a rotary evaporator. The residual red oil was treated with 100 mL of methanol, but no polymer precipitated. After evaporation of the methanol, a red oil was obtained. The NMR and GC/MS data of this material were recorded, and the results obtained are presented in the Table 1.

**Reaction between 1,1'-Dilithioferrocene and  $Ph_2SiCl_2$  in THF/hexane.** To 1,1'-dilithioferrocene-tmeda,<sup>12</sup> obtained from 4.8 g (0.025 mol) of ferrocene, 34 mL (0.054 mol) of *n*-butyllithium (1.6 M in hexanes), and 8 mL of tmeda in 80 mL of hexanes, was added 50 mL of THF and 32 mL of hexanes. Dichlorodiphenylsilane 6.5 g (0.025 mol) was added by syringe at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then stirred at room temperature overnight. The solvents were removed under vacuum, and the red residue was extracted with 100 mL of benzene. The extracts were filtered. Benzene was removed under vacuum, and a red solid was obtained. The NMR spectrum of this material showed it to be [1](diphenylsilylene)ferrocenophane,<sup>2c,13</sup> **3b**.  $^1H$  NMR (ppm,  $C_6D_6$  solvent): 4.10 ( $C_5H_4$ ), 4.40 ( $C_5H_4$ ), 7.16–7.22 (m,  $C_6H_5$ ), 8.02 (m,  $C_6H_5$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  31.1 (*ipso*-C of  $C_5H_4$ ), 77.1 ( $C_5H_4$ ), 78.3 ( $C_5H_4$ ), 128.6, 130.6, 134.7, 135.1 ( $C_6H_5$ ).  $^{29}Si$  NMR ( $C_6D_6$ ):  $\delta$  -11.4.

One gram of **3b** was redissolved in 15 mL of benzene, and following the Rosenberg procedure, methanol was added

dropwise to precipitate any polymer. No polymer was obtained, and the treatment resulted in the formation of a mixture of  $FcSiPh_2OMe$  and  $FcSiPh_2OH$ ,<sup>11</sup> as determined by NMR and GC/MS.  $FcSiPh_2OMe$ :  $^1H$  NMR (ppm,  $C_6D_6$ ) 3.53 (OMe), 4.05 ( $C_5H_5$ ), 4.22, 4.25 ( $C_5H_4$ ), 7.22–7.24, 7.79–7.80 (Ph).  $^{13}C$  NMR:  $\delta$  51.5 (OMe), 66.4 (*ipso* C,  $C_5H_4$ ), 69.1, 71.6, 74.8 (Fc), 128.3, 130.1, 135.5, 135.9 (Ph).  $^{29}Si$  NMR:  $\delta$  -7.42. MS: *m/e* 398 ( $M^+$ , 100), 333 (9), 321 (5), 121 ( $C_5H_5Fe$ , 14).  $FcSiPh_2OH$ :  $^1H$  NMR (ppm,  $C_6D_6$ ) 2.06 (OH), 3.99 ( $C_5H_5$ ), 4.21–4.24 ( $C_5H_4$ ), 7.20–7.78 (Ph).  $^{13}C$  NMR:  $\delta$  67.4, 68.9, 71.7, 74.4 (Fc), 128.4, 130.0, 135.0, 137.3 (Ph).  $^{29}Si$  NMR:  $\delta$  -9.58. IR ( $cm^{-1}$ ,  $CCl_4$ ): 3678 (free OH), 3422 (v bd, H bonded OH).

**Reactions between 1,1'-Dilithioferrocene and  $Me_2SiCl_2$  in THF. (a) High-Temperature Reaction.** The slow addition (45 min) of dimethyldichlorosilane (2.07 g, 0.016 mol) in THF to a refluxing THF solution of 1,1'-dilithioferrocene-tmeda (0.016 mol) was followed by reflux for 7 h. Analysis of the product obtained subsequent to removal of THF showed the absence of (dimethylsilylene)ferrocenophane and only the formation of (dimethylsilylene)ferrocenylene polymer. This material was dissolved in toluene and precipitated by addition of hexane to yield 0.4 g of the polymer;  $M_w$  (GPC) 90 000,  $M_n$  65 000,  $M_w/M_n$  = 1.38. The NMR data of the sample were in total accord with published data.<sup>2a,3b</sup>  $^1H$  NMR (ppm,  $C_6D_6$  solvent): 0.52 (SiMe), 4.10, 4.26 ( $C_5H_4$ ).  $^{13}C$  NMR:  $\delta$  -0.60 (SiMe), 71.7, 73.6 ( $C_5H_4$ ).  $^{29}Si$  NMR:  $\delta$  -6.26.

The reverse addition of 1,1'-dilithioferrocene (0.016 mol) in THF to a refluxing solution of 2.07 g (0.016 mol) of dimethyldichlorosilane in THF, with similar time periods, resulted mainly in the formation of [1](dimethylsilylene)ferrocenophane (>90%), along with traces of (dimethylsilylene)ferrocenylene polymer, 1,1'-bis(chlorodimethylsilyl)ferrocene, ferrocene, and (chlorodimethylsilyl)ferrocene.

**(b) Low-Temperature Reaction.** A reaction with the same amounts of material as above, involving addition of dimethyldichlorosilane to a THF solution of 1,1'-dilithioferrocene-tmeda at room temperature, resulted in the formation of a mixture of (1,1'-dimethylsilylene)ferrocenophane and (dimethylsilylene)ferrocenylene polymer. The relative yields of the two products varied from experiment to experiment, depending upon the rate of addition and the degree to which the reaction warmed up due to the exothermic nature of the salt-elimination reaction. When local warming was apparent, the relative yield (NMR analysis) of polymer increased to a maximum of 35%.

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**Supporting Information Available:**  $^{29}Si$  and  $^{13}C$  NMR spectra of addition of **2a** to **1** and  $^{13}C$  NMR spectrum of addition of **1** to **2a** (4 pages). Ordering information is given on any current masthead page.

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(14) Zechel, D. L.; Foucher, D. A.; Pudelski, J. K.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1995**, 1893.