

# Poly{ferrocene(phenylene)bis(silylenevinylene)}s via Platinum- and Rhodium-Catalyzed Hydrosilylation of Diethynylbenzenes with 1,1'-Bis(dimethylsilyl)ferrocene

Rajsapan Jain, Roger A. Lalancette, and John B. Sheridan\*

Department of Chemistry, Rutgers, The State University of New Jersey,  
University Heights, Newark, New Jersey 07102

Received October 26, 2004

Ferrocene-containing polymers with one and two ferrocenes per repeat unit have been prepared via hydrosilylation polymerization of dialkynes and ferrocene-containing bis-enynes with 1,1'-bis(dimethylsilyl)ferrocene (**1**) using Karstedt's catalyst (platinum-divinyltetramethyldisiloxane) and Rh(PPh<sub>3</sub>)<sub>3</sub>I. Addition of equivalent amounts of **1** and various dialkynes {RC≡C–X–C≡CR (R = H, SiMe<sub>3</sub>, X = C<sub>6</sub>H<sub>4</sub> (1,4- and 1,3-); R = H, X = SiMe<sub>2</sub>; R = Ph, X = nothing)} gave polymers **2a–f** with varying regiochemical distributions. All polymers were characterized using <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analyses. Novel ferrocene-containing bis-enynes (**4a,b**) were prepared by hydrosilylation addition of **1** to 2 equiv of 1,4-bis(trimethylsilyl)butadiyne and 1,4-bis(trimethylsilylethynyl)benzene, respectively. Desilylation of **4a,b** gave ferrocene-containing bis(enyne)s (**5a,b**) that were used as monomers for the synthesis of polymers with two ferrocenes per repeat unit (**6a,b**). The X-ray crystal structure of the bis(enyne) **4a** has also been described, and the redox behavior of polymers **2a–e** (Pt), **2a** (Rh), and **2c** (Rh) were studied using cyclic voltammetry. In all cases a single reversible redox wave was observed, attributed to the Fe(II)–Fe(III) redox couple of the ferrocene center.

## Introduction

In recent years there has been an enormous interest in the design and synthesis of metal-containing polymers linked via  $\pi$ -conjugated organic/inorganic bridges.<sup>1</sup> Many transition metals such as Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, and Au have been successfully incorporated into the backbone of polymers,<sup>1d</sup> with metallocenes and, in particular, ferrocene-containing polymers,<sup>1c,2,3</sup> as well as rigid-rod organometallic frameworks, being common.<sup>1c,2</sup> Most noteworthy are the well-defined high molecular weight poly(ferrocenylsilane)s prepared via the ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes,<sup>4</sup> in which electrochemical studies showed two reversible oxidation waves indicative of electronic interactions between adjacent Fe centers.<sup>1c,2a,b,4,5</sup>

Many types of polymer contain silicon in the backbone,<sup>1a,6,7</sup> and hydrosilylation is one of many useful synthetic approaches to such species.<sup>6</sup> For example, electroluminescent silicon-containing poly(phenylenevinylene)s (Si-PPV)s have been prepared via Wittig and Heck reactions as well as via hydrosilylation.<sup>7</sup> Recently, Mori and co-workers showed Rh(PPh<sub>3</sub>)<sub>3</sub>I to be a highly effective catalyst in hydrosilylation polyadditions to form (*E*) or (*Z*) type phenylenevinylene organosilicon polymers with good regiocontrol.<sup>8</sup>

\* To whom correspondence should be addressed. E-mail: jsheridn@newark.rutgers.edu.

(1) See for example: (a) *Inorganic and Organometallic Polymers II-Advanced Materials and Intermediates*; Wisian-Neilson, P., Alcock, H. R., Wynne, K. J., Eds.; ACS Symp. Ser. 572; Washington, DC, 1994. (b) Manners I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602, and references therein. (c) Nguyen, P.; Gómez-Elipse, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515, and references therein. (d) Sheats, J. E.; Carraher, C. E.; Pittman, C. U. *Metal Containing Polymer Systems*; Plenum: New York, 1985.

(2) (a) Manners I. *Adv. Organomet. Chem.* **1995**, *37*, 131, and references therein. (b) Manners I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602, and references therein. (c) Kingsborough, R. P.; Swager T. M. In *Progress in Inorganic Chemistry*; Karlin K. D., Ed.; 1999; Vol. 48, pp 123–233, and references therein.

(3) Gonsalves, K. E.; Chen, X. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Germany, 1995; Chapter 10, pp 497–527, and references therein.

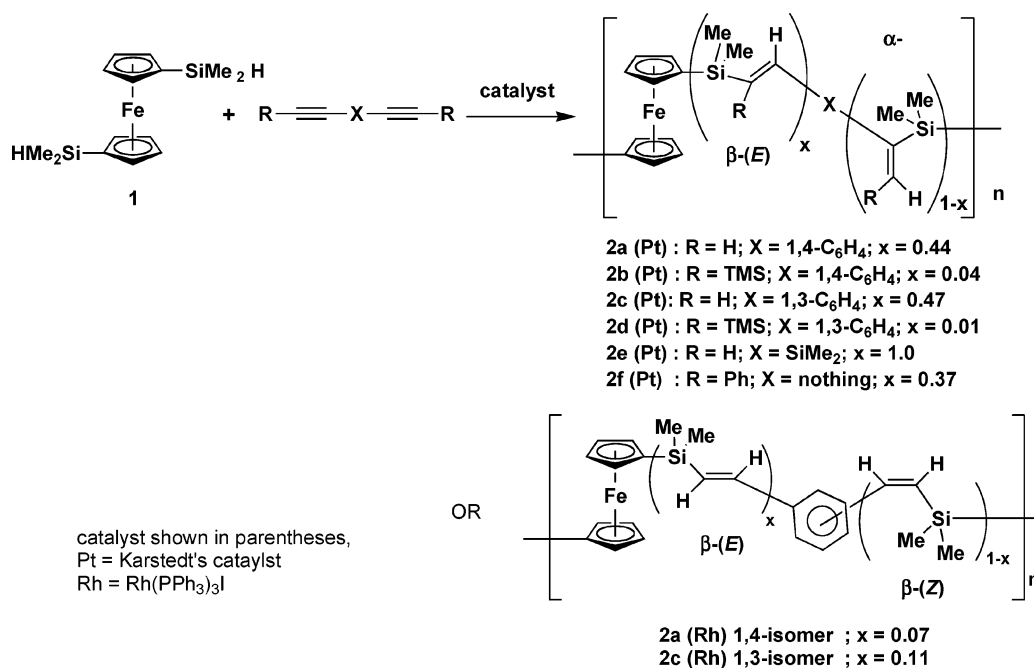
(4) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(5) (a) 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. (b) Manners, I. *J. Inorg. Organomet. Polym.* **1993**, *3*, 185. (c) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.

(6) See for example: (a) Pang Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671. (b) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y.; Hsu, J.-H.; Fann, W. *J. Am. Chem. Soc.* **1997**, *119*, 11321. (c) Yamashita, H.; Uchimaru, Y. *J. Chem. Soc., Chem. Commun.* **1999**, 1763. (d) Tsumura, M.; Iwahara, T.; Hirose, T. *Polym. J.* **1995**, *27*, 1048. (e) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society, Washington, D.C., 1990. (f) *Organosilicon Chemistry—From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Germany, 1994. (g) *Organosilicon Chemistry II—From Molecules to Materials*, edited by Auner, N.; Weis J. VCH: Germany, 1996. (h) *Organosilicon Chemistry III—From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Germany, 1998. (i) Hengge, E. In *Organosilicon Chemistry—From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Germany, 1994; pp 275–283. (j) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (k) Birot, M.; Pillot, J.-P.; Dunoguès. *Chem. Rev.* **1995**, *95*, 1443.

(7) (a) Kim, H. Y.; Ryu, M.-K.; Lee, S.-M. *Macromolecules* **1997**, *30*, 1236. (b) Jung, S.-H.; Kim, H. K.; Kim, S.-H.; Kim, Y. H.; Jeoung, S. C.; Kim, D. *Macromolecules* **2000**, *33*, 9277. (c) Kim, H. K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M.; Cho, S.-W.; Park, J.-W. *Macromolecules* **1998**, *31*, 1114. (d) Son, D. Y.; Bucca, D.; Keller, T. M. *Tetrahedron Lett.* **1996**, *37*, 1579. (e) Kim, D. S.; Shim, S. C. *J. Polym. Sci., Part A* **1999**, *37*, 2933. (f) Kim, D. S.; Shim, S. C. *J. Polym. Sci., Part A* **1999**, *37*, 2263.

Scheme 1



Hydrosilylation has also been used for the formation of oligosilicon species that serve as templates for organometallic polymers bearing transition metals such as Cr, Mo, and Co,<sup>9</sup> ferrocene-containing dendrimers,<sup>10</sup> and three-dimensional organometallic polymers such as poly(ferrocenyloctasilsesquioxane)s.<sup>11</sup> The grafting of vinylferrocene to a methylhydrosiloxane–dimethylsiloxane copolymer<sup>12</sup> and the modification of Si–H side groups of poly(ferrocenylsilane)s to form thermotropic liquid crystalline polymers are other examples.<sup>13</sup> Finally, hydrosilylation of diphenyl- and diethyldiethynylsilane with 1,1'-bis(methylphenylsilyl)ferrocene was reported to give poorly defined oligomeric species.<sup>14</sup>

We now report the incorporation of silyl, phenylenevinylene, and ferrocene groups into a polymer backbone via hydrosilylation polymerization using a Pt catalyst (Karstedt's catalyst) and RhI(PPh<sub>3</sub>)<sub>3</sub>. The products are poly{ferrocene(phenylene)bis(silylenevinylene)}s and are compared to model compounds, reported in the subsequent article.<sup>15</sup>

## Results and Discussion

**Platinum-Catalyzed Polymerizations.** Treatment of equimolar amounts of **1** and various dialkynes resulted in polymers **2a–f** (Pt) as orange powders or gums (Scheme 1).

**Poly{ferrocene(phenylene)bis(silylenevinylene)}s **2a,c** (Pt).** Poly{ferrocene(1,4-phenylene)bis(silylenevinylene)} (**2a** (Pt)) was isolated as an orange powder in 87% yield and was soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, THF, benzene, and *n*-hexane. It was characterized by <sup>1</sup>H (Figure 1), <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy (Table 1), MALDI-TOF mass spectrometry (Table 2), and elemental analysis and contained two randomly arranged  $\alpha$ - and  $\beta$ -(E) vinylene groups as previously reported for other Pt-catalyzed hydrosilylations.<sup>6a,7e,f,11,16</sup> The overall  $\alpha$ -/ $\beta$ -(E) ratio was determined as 0.56(1 - x)/0.44(x) (<sup>1</sup>H NMR) and is in close agreement with model compound **3a** (Pt) (Figure 2) ( $\alpha$ -/ $\beta$ -(E) ratio = 0.52/0.48).<sup>15</sup> Distinct olefinic peaks at  $\delta$  5.63, 5.88–5.90 for the  $\alpha$ -geminal protons and  $\delta$  6.63–6.71 and 7.01–7.07 for the two  $\beta$ -(E) vicinal protons concurred with assignments in model compounds **3a** (Pt) and **3d** (Pt).<sup>15</sup> Other spectral data were also in excellent agreement with these model compounds. Small aliphatic proton peaks at  $\delta$  1.29 and 2.13 arising from the hydrosilylation of the divinyltetramethyldisiloxane ligand of the catalyst were also observed. Lewis has documented that during an induction period the catalyst reacts with the silane in the presence of O<sub>2</sub> to form the hydrosilylated ligand and yellow colloidal Pt particles.<sup>17</sup>

The <sup>1</sup>H NMR spectrum of **2a** (Pt) showed both Si(Me)<sub>2</sub>X and C≡CH end group peaks at  $\delta$  0.21 and 2.76,

(8) (a) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Macromolecules* **2000**, *33*, 1115. (b) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Polyhedron* **2000**, *19*, 567. (c) Mori, A.; Takahisa, E.; Yamamura, Y.; Kato, T.; Mudalige, A. P.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Organometallics* **2004**, *23*, 1755.

(9) (a) Kuhnen, T.; Ruffolo, R.; Stradiotto, M.; Ulbrich, D.; McGlinchey, M. J.; Brook, M. A. *Organometallics* **1997**, *16*, 5042. (b) Kuhnen, T.; Stradiotto, M.; Ruffolo, R.; Ulbrich, D.; McGlinchey, M. J.; Brook, M. A. *Organometallics* **1997**, *16*, 5048.

(10) (a) Cuadrado, I.; Carmen, M. C.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (b) Garcia, B.; Casado, C. M.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *Organometallics* **1999**, *18*, 2349.

(11) Morán, M.; Casado, C. M.; Cuadrado, I. *Organometallics* **1993**, *12*, 4327.

(12) Inagaki, T.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1181.

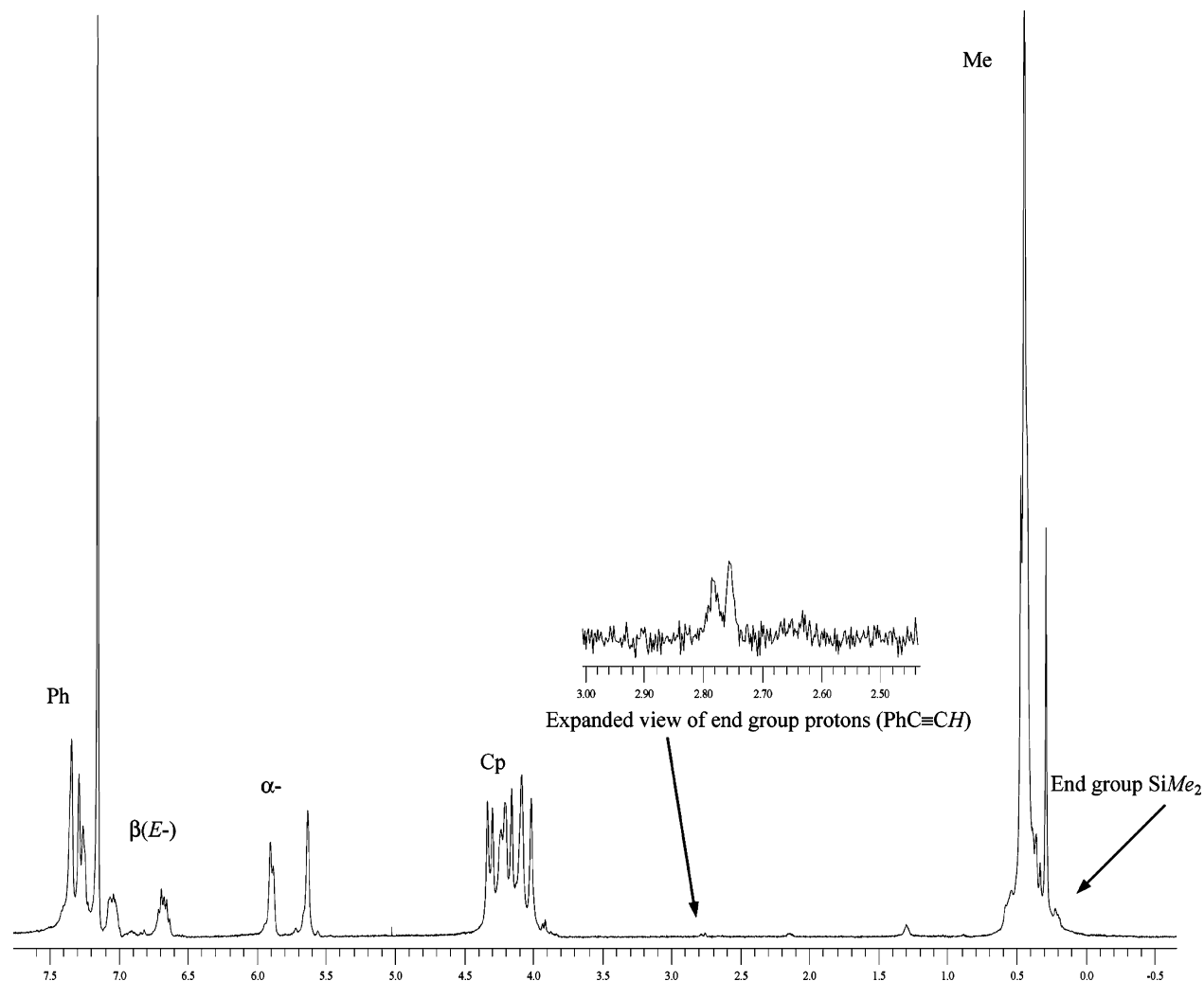
(13) (a) Liu, X.-H.; Bruce, D.; Manners, I. *J. Organomet. Chem.* **1997**, *548*, 49. (b) Liu, X.-H.; Bruce, D.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1997**, 289.

(14) Asatiani, L. P.; El-Agamey, A. A.; Diab, M. A. *J. Polym. Sci., Part A* **1983**, *21*, 2529.

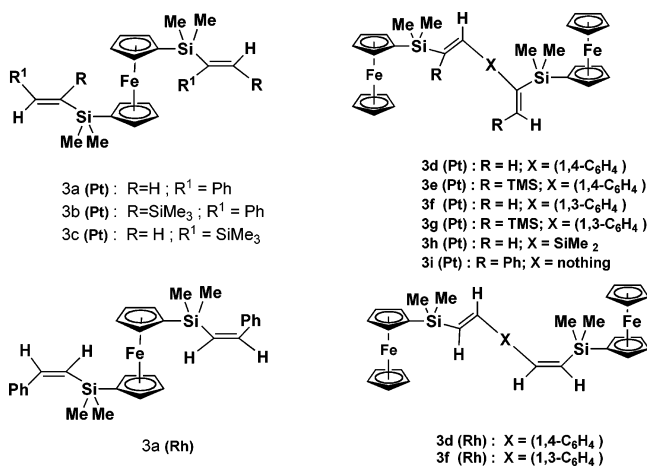
(15) Jain, R.; Choi, H.-J.; Sheridan, J. B.; Lalancette, R. A., following article in this issue.

(16) (a) Hiyami, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost B. M., Flemings, I., Eds.; Pergamon: Oxford, England, 1991; Vol. 8, pp 763–792, and references therein. (b) Chauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645*, 1.

(17) (a) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (b) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693.



**Figure 1.**  $^1\text{H}$  NMR spectrum of polymer **2a** (Pt).



**Figure 2.** Model compounds for poly{ferrocene(phenylene)-bis(silylenevinylene)}s.

respectively, confirming a linear AB type polymeric structure. The nature of X was not determined since no residual silane protons could be seen in the spectrum. The MALDI-TOF mass spectrum also confirmed an AB type polymer with a repeat unit of 428 mass units (the sum of the formula masses of the two monomers is 428). The heaviest species detected by this method had  $n = 17$  ( $M = 7295.3$ ) (Table 2), whereas GPC gave  $M_n$  as 9630, PDI = 3.2. Light scattering values were also

recorded [ $M_n = 11\,700$  (PDI = 2.4)]. Prolonged reflux of the reaction did not increase the molecular weight despite the fact that the alkynyl end group could still be detected in the  $^1\text{H}$  NMR spectrum, possibly due to decomposition of the silane end groups or their reaction with the catalyst ligand. Several reports describe hydrosilylation polymerizations that give cyclic structures;<sup>6d,18</sup> however the presence of end group signals appears to rule out such species in this case.

Similarly, polymer **2c** (Pt) derived from 1,3-diethynylbenzene and **1** was isolated as an orange sticky solid in 68% yield (Scheme 1). The sticky nature of related polymers with 1,3-substituted aryl groups has been reported previously as opposed to the powdery nature of the 1,4-polymers.<sup>18c,19,20</sup> Polymer **2c** (Pt) was fully characterized (Table 1) and has an  $\alpha$ -/ $\beta$ -(*E*) ratio of 0.53/0.47, consistent with that of **3a** (Pt) and **3f** (Pt).<sup>15</sup> End group peaks in the  $^1\text{H}$  NMR spectrum at  $\delta$  2.76 and  $\delta$  0.24 confirmed a linear AB type structure, and MALDI-TOF MS data showed the formula weight of the repeat unit to be 428, an (AB)<sub>*n*</sub> structure, and a degree of polymerization of 12 ( $M = 5139.69$ ) (Table 2).

(18) (a) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592. (b) Kim, C.; Choi, S. K.; Park, E.; Jung, I. *J. Kor. Chem. Soc.* **1997**, *41*, 88. (c) Tsumura, M.; Iwahara, T.; Hirose, T. *J. Polym. Sci., Part A* **1996**, *34*, 3155.

(19) Zhang, R.; Mark, J. E.; Pinhas, A. R. *Macromolecules* **2000**, *33*, 3508.

(20) Yoon, K.; Son, D. Y. *Macromolecules* **1999**, *32*, 5210.

Table 1. NMR Spectroscopic Data for 2a–f (Pt), 2a–c (Rh), 4a, 4b, 5a, 5b, 6a, and 6b

product	$\delta$ , $^1\text{H}^a$	$\delta$ , $^{13}\text{C}\{\text{H}\}^a$	$\delta$ , $^{29}\text{Si}^{a,b}$
<b>2a (Pt)</b>	0.42–0.47 (br, 12H, Me), 4.01–4.33 (br, 8H, Cp), 6.63–6.71, 7.01–7.07 (br, 2H, $\beta$ -E), 5.63, 5.88–5.90 (br, 2H, $\alpha$ ), 7.22–7.40 (br, 4H, Ar), 0.21 (end group SiMe <sub>2</sub> ), 2.76 (end group C $\equiv$ CH) 0.35–0.44, 0.53–0.57 (br, 12H, SiMe <sub>2</sub> ) –0.01, –0.08, 0.02, 0.13 (br, 18H, SiMe <sub>3</sub> ), 3.87–4.28 (br, 8H, Cp), 6.52–6.55, 6.58–6.64, 7.90 (br, 2H, HC=CH), 6.79–6.83, 6.88–6.94, 7.38–7.42 (br, 4H, Ar), –0.15 (end group ArC $\equiv$ CSiMe <sub>3</sub> ), 0.24 (end group Fe(SiMe) <sub>2</sub> –C=C (Ar)SiMe <sub>3</sub> ), 4.45 (end group SiH)	–1.4, –1.2, –1.3 (Me), 70.4–70.5 (Cp <sub>ipso</sub> ), 71.9, 72.3, 73.7, 74.0 (Cp), 128.8, 143.3, 144.5 (C=C $\beta$ -E), 144.7, 152.8, 152.9 (C=C $\alpha$ -), 137.0, 138.5, 145.0 (Ar <sub>ipso</sub> ), 126.8, 127.2, 127.5 (Ar) –2.3 (SiMe <sub>2</sub> ), 0.6, 2.7 (SiMe <sub>3</sub> ), 70.0, 70.1 (Cp <sub>ipso</sub> ), 71.9, 73.7, 73.9, 74.1 (Cp), 142.9, 156.0, 157.0 (C=C $\beta$ -E), 144.2, 145.0, 166.0–166.7 (C=C $\alpha$ -), 140.4, 146.1 (Ar <sub>ipso</sub> ), 127.3–127.5 (Ar), 0.1, 0.2 (end group SiMe <sub>3</sub> ), 94.1 (end group ArC $\equiv$ C SiMe <sub>3</sub> ), 106.3 (end group ArC $\equiv$ CSiMe <sub>3</sub> ), 121.3 (end group Ar <sub>ipso</sub> ), 131.7 (end group Ar)	–9.2, –9.3 ( $\beta$ -E), –7.3 ( $\alpha$ -) –9.5, –9.8 (SiMe <sub>2</sub> ( $\alpha$ -)), –8.0 (SiMe <sub>2</sub> $\beta$ (E)), –7.7, –8.2 (SiMe <sub>3</sub> ( $\alpha$ -)), –2.9 (SiMe <sub>3</sub> $\beta$ (E)), –18.0 (end group C $\equiv$ CSiMe <sub>3</sub> )
<b>2b (Pt)</b>	0.42–0.47 (br, 12H, Me), 4.01–4.33 (br, 8H, Cp), 6.63–6.71, 7.01–7.07 (br, 2H, $\beta$ -E), 5.63, 5.88–5.90 (br, 2H, $\alpha$ ), 7.22–7.40 (br, 4H, Ar), 0.21 (end group SiMe <sub>2</sub> ), 2.76 (end group C $\equiv$ CH) 0.35–0.44, 0.53–0.57 (br, 12H, SiMe <sub>2</sub> ) –0.01, –0.08, 0.02, 0.13 (br, 18H, SiMe <sub>3</sub> ), 3.87–4.28 (br, 8H, Cp), 6.52–6.55, 6.58–6.64, 7.90 (br, 2H, HC=CH), 6.79–6.83, 6.88–6.94, 7.38–7.42 (br, 4H, Ar), –0.15 (end group ArC $\equiv$ CSiMe <sub>3</sub> ), 0.24 (end group Fe(SiMe) <sub>2</sub> –C=C (Ar)SiMe <sub>3</sub> ), 4.45 (end group SiH)	–1.4, –1.2, –1.3 (Me), 70.4–70.5 (Cp <sub>ipso</sub> ), 71.9, 72.3, 73.7, 74.0 (Cp), 128.8, 143.3, 144.5 (C=C $\beta$ -E), 144.7, 152.8, 152.9 (C=C $\alpha$ -), 137.0, 138.5, 145.0 (Ar <sub>ipso</sub> ), 126.8, 127.2, 127.5 (Ar) –2.3 (SiMe <sub>2</sub> ), 0.6, 2.7 (SiMe <sub>3</sub> ), 70.0, 70.1 (Cp <sub>ipso</sub> ), 71.9, 73.7, 73.9, 74.1 (Cp), 142.9, 156.0, 157.0 (C=C $\beta$ -E), 144.2, 145.0, 166.0–166.7 (C=C $\alpha$ -), 140.4, 146.1 (Ar <sub>ipso</sub> ), 127.3–127.5 (Ar), 0.1, 0.2 (end group SiMe <sub>3</sub> ), 94.1 (end group ArC $\equiv$ C SiMe <sub>3</sub> ), 106.3 (end group ArC $\equiv$ CSiMe <sub>3</sub> ), 121.3 (end group Ar <sub>ipso</sub> ), 131.7 (end group Ar)	–9.2, –9.3 ( $\beta$ -E), –7.3 ( $\alpha$ -) –9.5, –9.8 (SiMe <sub>2</sub> ( $\alpha$ -)), –8.0 (SiMe <sub>2</sub> $\beta$ (E)), –7.7, –8.2 (SiMe <sub>3</sub> ( $\alpha$ -)), –2.9 (SiMe <sub>3</sub> $\beta$ (E)), –18.0 (end group C $\equiv$ CSiMe <sub>3</sub> )
<b>2c (Pt)</b>	0.42–0.47 (br, 12H, Me), 4.00–4.32 (br, 8H, Cp), 6.68–6.74, 7.02–7.06 (br, 2H, $\beta$ -E), 5.64, 5.85–5.91 (br, 2H, $\alpha$ ), 7.11–7.55 (br, 4H, Ar), 0.24 (end group SiMe <sub>2</sub> ), 2.76 (end group C $\equiv$ CH) 0.33–0.47, 0.48–0.55 (br, 12H, SiMe <sub>2</sub> ) –0.09, 0.01–0.05, 0.15 (br, 18H, SiMe <sub>3</sub> ), 3.90–4.28 (br, 8H, Cp), 6.55–6.67, 7.94 (br, 2H, HC=CH), 6.86–6.95, 7.06–7.10, 7.36–7.43 (br, 4H, Ar), –0.13, –0.12 (end group ArC $\equiv$ CSiMe <sub>3</sub> ), 0.22 (end group Fe(SiMe) <sub>2</sub> –C=C (Ar)SiMe <sub>3</sub> ), 0.30 (end group SiMe <sub>2</sub> ), 4.50 (end group SiH)	–1.5, –1.1, –1.3 (Me), 70.3 (Cp <sub>ipso</sub> ), 71.9, 72.1, 73.6, 73.8, 74.0 (Cp), 144.6, 144.9, 128.8, 129.0 (C=C $\beta$ -E), 145.0, 153.3, 153.4 (C=C $\alpha$ -), 138.6, 139.0, 145.0 (Ar <sub>ipso</sub> ), 125.2–127.5 (Ar) –2.3, –1.6 (SiMe <sub>2</sub> ), 0.6, 2.7 (SiMe <sub>3</sub> ), 69.7, 70.3 (Cp <sub>ipso</sub> ), 72.0, 73.8–74.0 (Cp), 145.4, 145.5, 165.4–166.3 (C=C $\alpha$ -), 145.8 (Ar <sub>ipso</sub> ), 126.1, 127.8, 129.8 (Ar), 0.04, 0.2 (end group SiMe <sub>3</sub> ), 94.2 (end group ArC $\equiv$ C SiMe <sub>3</sub> ), 106.1 (end group ArC $\equiv$ CSiMe <sub>3</sub> ), 123.2 (end group Ar <sub>ipso</sub> ), 131.4 (end group Ar)	–9.3, –9.4 ( $\beta$ -E), –7.4, –7.5 ( $\alpha$ -) –9.6, –9.9 (SiMe <sub>2</sub> ( $\alpha$ -)), –7.9 (SiMe <sub>2</sub> $\beta$ (E)), –7.1, –7.6 (SiMe <sub>3</sub> ( $\alpha$ -)), –2.8 (SiMe <sub>3</sub> $\beta$ (E)), –17.8 (end group C $\equiv$ CSiMe <sub>3</sub> )
<b>2d (Pt)</b>	0.29 (br, s, 6H, Me), 0.37 (s, 12H, Me), 4.11–4.31 (br, 8H, Cp), 6.95, 7.09 (br, 4H, $\beta$ -E), $^3J = 22.5$ Hz), 2.11, 2.14 (end group Si–C $\equiv$ CH), 0.25 (end group Si(Me) <sub>2</sub> H), 6.79, 7.22 (end group, d, $^3J_{\text{H-H}} = 22.5$ Hz, $\beta$ (E-)), 4.48 (end group SiH)	–3.0, –1.7 (Me), 70.0 (Cp <sub>ipso</sub> ), 72.0, 73.6 (Cp), 149.4, 151.8 (C=C $\beta$ -E), 146.6, 153.0 (end group C=C $\beta$ -E), 88.1 (end group SiC $\equiv$ CH), 95.4 (end group SiC $\equiv$ CH), –1.9 (end group SiMe <sub>2</sub> H)	–10.7, –14.7
<b>2e (Pt)</b>	0.23, 0.31, 0.40 (br, 6H, Me), 0.46–0.47, 0.60, 0.01 (br, 6H, Me), 3.98–4.34 (br, 8H, Cp), 6.73, 6.90, 6.99, 8.06 (br, 2H, HC=CH), 7.04–7.11, 7.46–7.55, 7.69–7.70 (br, 10H, Ar)	–1.6, –1.0, –0.6, –2.1, –3.1, 1.6 (Me), 68.7, 70.0 (Cp <sub>ipso</sub> ), 71.6–72.1, 73.8–74.8 (Cp), 131.6, 137.3–138.9, 145.6, 146.2, 148.4 (C=C), 140.2, 142.7, 142.9 (Ar <sub>ipso</sub> ), 127.4, 128.6, 129.2, 129.7 (Ar), 91.6 (end group C $\equiv$ CAr), 101.7 (end group C $\equiv$ CAr)	–3.8, –4.7, –6.2, –6.5
<b>2f (Pt)</b>	0.46 (br, 6H, $\beta$ -E), Me), 0.39 (br, 6H, $\beta$ -Z), Me), 4.12, 4.15, 4.25, 4.31 (br, 8H, Cp), 6.68, 7.02 (br d, 2H, $\beta$ -E), $^3J = 19$ Hz), 6.12, 7.42 (br d, 2H, $\beta$ -Z), $^3J = 15$ Hz), 7.26, 7.35 (br, 4H, Ar), 4.69 (end group SiH), 3.32 (end group poly-ArC $\equiv$ CH)	–1.4, 0.3 (Me), 71.8 (Cp <sub>ipso</sub> ), 71.9, 72.0, 73.8 (Cp), 129.0, 144.5 (C=C $\beta$ -E), 132.2, 146.8 (C=C $\beta$ -Z), 137.9, 139.7 (Ar <sub>ipso</sub> ), 126.6, 127.5, 128.4 (Ar), –2.8 (end Si(Me) <sub>2</sub> )	–9.2 ( $\beta$ -E)), –13.2 ( $\beta$ -Z)), –18.2 (end group SiMe <sub>2</sub> )
<b>2a (Rh)</b>	0.46 (br, 6H, $\beta$ -E), Me), 0.37 (br, 6H, $\beta$ -Z), Me), 4.10, 4.13, 4.24, 4.28 (br, 8H, Cp), 6.71, 7.05 (br d, 2H, $\beta$ -E), $^3J = 19$ Hz), 6.12, 7.42 (br d, 2H, $\beta$ -Z), $^3J = 15$ Hz), 7.26, 7.35 (br, 4H, Ar), 4.69 (end group SiH), 3.32 (end group poly-ArC $\equiv$ CH)	–1.3, 0.3 (Me), 71.7 (Cp <sub>ipso</sub> ), 71.9, 72.0, 73.7, 73.9 (Cp), 128.9, 144.8 (C=C $\beta$ -E), 132.5, 146.9 (C=C $\beta$ -Z), 138.5, 140.2 (Ar <sub>ipso</sub> ), 126.2, 127.7, 128.9 (Ar), –2.8 (end group Si(Me) <sub>2</sub> )	–9.2 ( $\beta$ -E)), –13.2 ( $\beta$ -Z)), –18.3 (end group SiMe <sub>2</sub> )
<b>2c (Rh)</b>	0.46 (br, 6H, $\beta$ -E), Me), 0.37 (br, 6H, $\beta$ -Z), Me), 4.10, 4.13, 4.24, 4.28 (br, 8H, Cp), 6.71, 7.05 (br d, 2H, $\beta$ -E), $^3J = 19$ Hz), 6.12, 7.46 (br d, 2H, $\beta$ -Z), $^3J = 15$ Hz), 7.09–7.13, 7.30–7.31, 7.40 (br, 4H, Ar), 0.27 (end group Si(Me) <sub>2</sub> ), 4.69 (end group SiH), 3.32 (end group poly-ArC $\equiv$ CH)	–1.3, 0.3 (Me), 71.7 (Cp <sub>ipso</sub> ), 71.9, 72.0, 73.7, 73.9 (Cp), 128.9, 144.8 (C=C $\beta$ -E), 132.5, 146.9 (C=C $\beta$ -Z), 138.5, 140.2 (Ar <sub>ipso</sub> ), 126.2, 127.7, 128.9 (Ar), –2.8 (end group Si(Me) <sub>2</sub> )	–6.1 (SiMe <sub>2</sub> ), –8.3 (SiMe <sub>3</sub> -C=C), –18.7 (SiMe <sub>3</sub> -C $\equiv$ C)
<b>4a</b>	0.49 (s, 12H, SiMe <sub>2</sub> ), 0.24, 0.31 (s, 36H, SiMe <sub>3</sub> ), 4.21, 4.35 (t, 8H, Cp), 6.87 (s, 2H, CH=CH) –0.16, 0.24 (s, 36H, SiMe <sub>3</sub> ), 0.30 (s, 12H, SiMe <sub>2</sub> ), 3.86, 4.11 (t, 8H, Cp), 6.51 (s, 2H, CH=CH), 6.78–6.80, 7.37–7.39 (m, 8H, Ar)	–0.8, 0.0 (SiMe <sub>3</sub> ), –2.2 (SiMe <sub>2</sub> ), 68.8 (Cp <sub>ipso</sub> ), 72.4, 74.0 (Cp), 104.4, 108.4 (C $\equiv$ C), 145.3, 156.4 (C=C), 0.1, 0.2 (SiMe <sub>3</sub> ), –2.4 (SiMe <sub>2</sub> ), 69.7 (Cp <sub>ipso</sub> ), 72.0, 73.7 (Cp), 94.1, 106.3 (C $\equiv$ C), 145.0, 166.0 (C=C), 121.3, 146.1 (Ar <sub>ipso</sub> ), 131.7 (Ar)	–6.1 (SiMe <sub>2</sub> ), –8.3 (SiMe <sub>3</sub> -C=C), –18.7 (SiMe <sub>3</sub> -C $\equiv$ C)
<b>4b (bis-<math>\alpha</math>) (major)</b>	–0.15 (s, 9H, $\alpha$ , SiMe <sub>3</sub> ), –0.02 (s, 9H, $\beta$ -E), SiMe <sub>3</sub> ), 0.23, 0.24 (s, 18H, C $\equiv$ C–SiMe <sub>3</sub> ), 0.34 (s, 6H, $\alpha$ , SiMe <sub>2</sub> ), 0.48 (s, 6H, $\beta$ -E), SiMe <sub>2</sub> ), 3.93, 4.04, 4.19, 4.21 (t, 8H, Cp), 6.54 (s, 1H, $\alpha$ ), 7.71 (s, 1H, $\beta$ -E)), 6.80–6.89, 7.30–7.32, 7.40 (m, 8H, Ar)	–7.9 (SiMe <sub>2</sub> -C=C, $\alpha$ -), –18.1 (SiMe <sub>3</sub> -C=C), –9.6 (SiMe <sub>2</sub> -C=C, $\beta$ -E)), –18.0 (SiMe <sub>3</sub> -C $\equiv$ C, $\beta$ -E)), –8.3 (SiMe <sub>2</sub> , $\beta$ -E)).	–7.9 (SiMe <sub>2</sub> -C=C, $\alpha$ -), –18.1 (SiMe <sub>3</sub> -C=C, $\beta$ -E)), –18.0 (SiMe <sub>3</sub> -C $\equiv$ C, $\beta$ -E)), –8.3 (SiMe <sub>2</sub> , $\beta$ -E)).

<b>5a</b>	0.27 (s, 18H, SiMe <sub>3</sub> ), 0.47 (s, 12H, SiMe <sub>2</sub> ), 3.18 (s, 2H, C≡C-H), 4.17, 4.29 (t, 8H, Cp), 6.88 (s, 2H, CH=CH)	-0.8 (SiMe <sub>3</sub> ), -2.4 (SiMe <sub>2</sub> ), 68.6 (Cp <sub>ipso</sub> ), 72.3, 74.0 (Cp), 86.1, 87.6 (C≡C-H), 144.3, 157.2 (C=C)	-8.5 (SiMe <sub>3</sub> -C=C), -5.5 (SiMe <sub>2</sub> )
<b>5b (bis-α) (major)</b>	-0.15 (s, 18H, SiMe <sub>3</sub> ), 0.31 (s, 12H, SiMe <sub>2</sub> ), 2.71 (s, 2H, C≡C-H), 3.88, 4.13 (t, 8H, Cp), 6.54 (s, 2H, CH=CH), 6.81, 7.37 (d, 8H, Ar)	0.2 (SiMe <sub>3</sub> ), -2.4 (SiMe <sub>2</sub> ), 72.0, 73.8 (Cp), 69.6 (Cp <sub>ipso</sub> ), 77.7, 84.0 (C≡C-H), 145.1, 165.9 (C=C), 120.3, 146.3 (Ar <sub>ipso</sub> ), 131.8 (Ar)	-7.9 (SiMe <sub>3</sub> ), -9.6 (SiMe <sub>2</sub> )
<b>5b (β-(E)-α) (minor)</b>	-0.14 (s, 9H, α-, SiMe <sub>3</sub> ), 0.00 (s, 9H, β-(E), SiMe <sub>3</sub> ), 0.36 (s, 6H, α-, SiMe <sub>2</sub> ), 0.50 (s, 6H, β-(E), SiMe <sub>2</sub> ), 2.71, 2.72 (s, 2H, C≡C-H), 3.94, 4.05, 4.20, 4.24 (t, 8H, Cp), 6.56 (s, 1H, α-), 7.73 (s, 1H, β-(E)), 6.84, 6.88, 6.90, 7.27, 7.28, 7.39 (br, 8H, Ar)	-0.1 (C=C-SiMe <sub>3</sub> , α-), 2.3 (C=C-SiMe <sub>3</sub> , β-(E)), -2.4 (SiMe <sub>3</sub> , α-), -0.8 (SiMe <sub>2</sub> , β-(E)), 69.6 (Cp <sub>ipso</sub> ), 72.0, 73.8, 72.1, 74.1 (Cp), 77.7, 84.0 (C≡C-), 145.1, 165.9 (C=C-), 78.1, 83.9 (C=C-β-(E)), 147.5, 155.9 (C=C-β-(E)), 120.3, 121.4, 143.5, 146.3 (Ar <sub>ipso</sub> ), 131.8 (Ar)	-7.9 (SiMe <sub>3</sub> -C=C, α-), (SiMe <sub>2</sub> , β-(E)), -9.6 (SiMe <sub>2</sub> , α-), -2.9 (SiMe <sub>3</sub> -C=C, β-(E)),
<b>6a</b>	0.22-0.23 (br, 18H, SiMe <sub>3</sub> ), 0.44-0.45, 0.57-0.58 (br, 24H, SiMe <sub>2</sub> ), 4.16-4.18, 4.32, 4.36-4.37 (br, 16H, Cp), 6.57 (br s, 2H, SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> ), 6.35, 7.23 (br d, 4H, CH=C(H)-SiMe <sub>2</sub> -Fc, β-(E)), <sup>3</sup> J <sub>H-H</sub> = 19.0 Hz), 3.20 (end group C≡CH), 4.42 (end group SiH)	-1.3, -0.5 (SiMe <sub>2</sub> , α-), 0.7 (SiMe <sub>3</sub> ), 70.2, 71.0 (Cp <sub>ipso</sub> ), 72.0, 72.1, 73.6, 74.2 (Cp), 149.3, 162.7 SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> ), 133.0, 147.6 CH=C(H)-SiMe <sub>2</sub> -Fc), 86.0, 87.6 (end groups C≡CH), -2.3 (end group Si(Me) <sub>2</sub> )	-8.2 (SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> ), -10.8 (SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> ), -9.5 CH=C(H)-SiMe <sub>2</sub> -Fc, β-(E)), -5.6, -9.7 (end groups SiMe <sub>2</sub> ), -8.6 (end group SiMe <sub>3</sub> ), -17.1 (end group SiH)
<b>6b</b>	-0.07 to -0.01 (br, 18H, SiMe <sub>3</sub> ), 0.33-0.55 (br, 24H, SiMe <sub>2</sub> ), 3.84-4.31 (br, 16H, Cp's) 5.59-5.64, 5.88-5.90 (br, 2H, α-), 6.61, 7.90 (br, 2H, SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> , α-, β-(E)), 6.62-6.67, 7.03, 7.07 (br, 2H, CH=C(H)-SiMe <sub>2</sub> -Fc, β-(E)), 6.98-7.00, 7.18-7.46 (br, 8H, Ar)	-2.2, -0.6 (SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> , α-, β-(E)), -1.4 to -1.1 CH=C(H)-SiMe <sub>2</sub> -Fc, α-, β-(E)), 0.4, 2.5 (SiMe <sub>3</sub> ), 68.6, 69.9 (Cp <sub>ipso</sub> ), 71.9-72.0, 73.7-73.9 (Cp), 128.2, 144.8, 145.7, 166.4 (C=C, Ar <sub>ipso</sub> ), 136.4 (Ar <sub>ipso</sub> ), 126.3, 126.7, 126.8 (Ar), 100.2, 114.5 (end group C≡C)	-2.7 (SiMe <sub>3</sub> -C=C, β-(E)), -7.9, -8.3 [(SiMe <sub>3</sub> -C=C, α-); (SiMe <sub>2</sub> -C=C, α-)], -9.2 to -9.5 [(SiMe <sub>2</sub> -C=C(H)-SiMe <sub>3</sub> ; CH=C(H)-SiMe <sub>2</sub> -Fc, β-(E))]

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> External reference SiMe<sub>4</sub> (0.00 ppm).

**Poly[ferrocene(phenylene)bis(silylene(trimethylsilyl)vinylene)s, 2b,d (Pt).** Oligomers **2b (Pt)** and **2d (Pt)** were respectively prepared from 1,4-bis(trimethylsilyl)ethynylbenzene and 1,3-bis(trimethylsilyl)ethynylbenzene and **1** in 75% and 70% yields (Scheme 1). In these reactions, attack of the silane on the internal carbon of the alkyne (*syn* addition) (due to the bulky TMS group) led to mostly  $\alpha$ -geometry ( $1 - x > 0.96$ ) in the oligomers, in close agreement with model compounds **3b (Pt)**, **3e (Pt)**, and **3g (Pt)**.<sup>15</sup>

Using end group analysis the average number of repeat units was determined to be quite low ( $n = 4$ ), but Kim and co-workers have recorded similar trends in the hydrosilylation of bulky dialkynes such as 4,4'-diethynylbiphenyl with Ph<sub>2</sub>SiH<sub>2</sub>, where only four repeat units were present in the oligomer.<sup>7e</sup> The <sup>1</sup>H NMR spectrum of **2b** shows olefinic peaks at  $\delta$  6.55, 6.58–6.64 {cf. **3b (Pt)**, **3e (Pt)**}<sup>15</sup> assigned to major  $\alpha$ -isomers, and a peak corresponding to the end group, C≡CSiMe<sub>3</sub>, was clearly detected in the <sup>29</sup>Si DEPT NMR spectrum at  $\delta$  -18.0.

Polymer **2d (Pt)** was similarly characterized and showed end group SiMe<sub>3</sub> protons {attached to alkene ( $\delta$  0.22)} {attached to alkyne ( $\delta$  -0.13 to -0.12)} as well as a signal for the end group SiMe<sub>2</sub>H protons at  $\delta$  0.30. In this case, end group silyl proton SiMe<sub>2</sub>H was seen as a very small peak at  $\delta$  4.5. GPC analysis gave a  $M_n$  value of 1710 (PDI = 1.73), and the MALDI-TOF MS data were similar to that of **2b (Pt)** with (AB)<sub>*n*</sub> ( $n = 2-4$ ) and (AB)<sub>*n*</sub> - A ( $n = 2-8$ ) patterns (A = dialkyne) (Table 2).

**Polymers from Nonaryl Alkynes.** Poly{ferrocene-tris(dimethylsilylene)bis(vinylene)}, **2e (Pt)**, was prepared from diethynyl(dimethyl)silane and **1** as a sticky orange solid in 85% yield (Scheme 1) and had a regiochemical distribution that was exclusively  $\beta$ (E-); that is, Si adds only to terminal alkynyl carbons.<sup>9a</sup> End group analysis of the alkynyl protons gave an average value for  $n$  of 11 ( $M_n \approx 4500$ ), whereas GPC gave  $M_n = 3520$  (PDI = 3.84) and MALDI-TOF MS (Figure 3) showed a maximum value of  $n = 12$  and an (AB)<sub>*n*</sub> type structure with both alkynyl and silane end groups (Table 2).

Hydrosilylation polymerization of 1,4-diphenylbutadiene with **1** gave **2f (Pt)** as an orange powder in 52% yield (Scheme 1). Whereas the model compound **3i** results from exclusive attack of the silane at the phenyl-substituted carbons of the diene, in the case of the polymer another isomeric form resulting from *syn* addition was also observed (Table 1). MALDI-TOF MS confirmed an exclusive (AB)<sub>*n*</sub>-A type structure (A = dialkyne) with the highest molecular weight species having  $n = 10$  ( $M = 5249.03$ ) (Table 2); in contrast GPC analysis gave  $M_n = 1860$  (PDI = 1.74).

**Hydrosilylation Polymerizations Using Iodotris-(triphenylphosphine)rhodium(I).** Treatment of equimolar amounts of **1** and 1,4-diethynylbenzene in THF at room temperature with Rh(I) as the catalyst afforded **2a (Rh)** as an orange powder in 62% yield (Scheme 1). The polymerization was extremely slow (13 days), and at the end of the reaction the thick THF slurry of crude **2a (Rh)** was precipitated into methanol. Three different regioisomers were present in **2a (Rh)** { $\beta$ (-Z),  $\beta$ (-E), and  $\alpha$ -} in a 0.93(1 -  $x$ ):0.07( $x$ ):trace ratio. The hydrosilylation of 1,4-diethynylbenzene with 1,4-

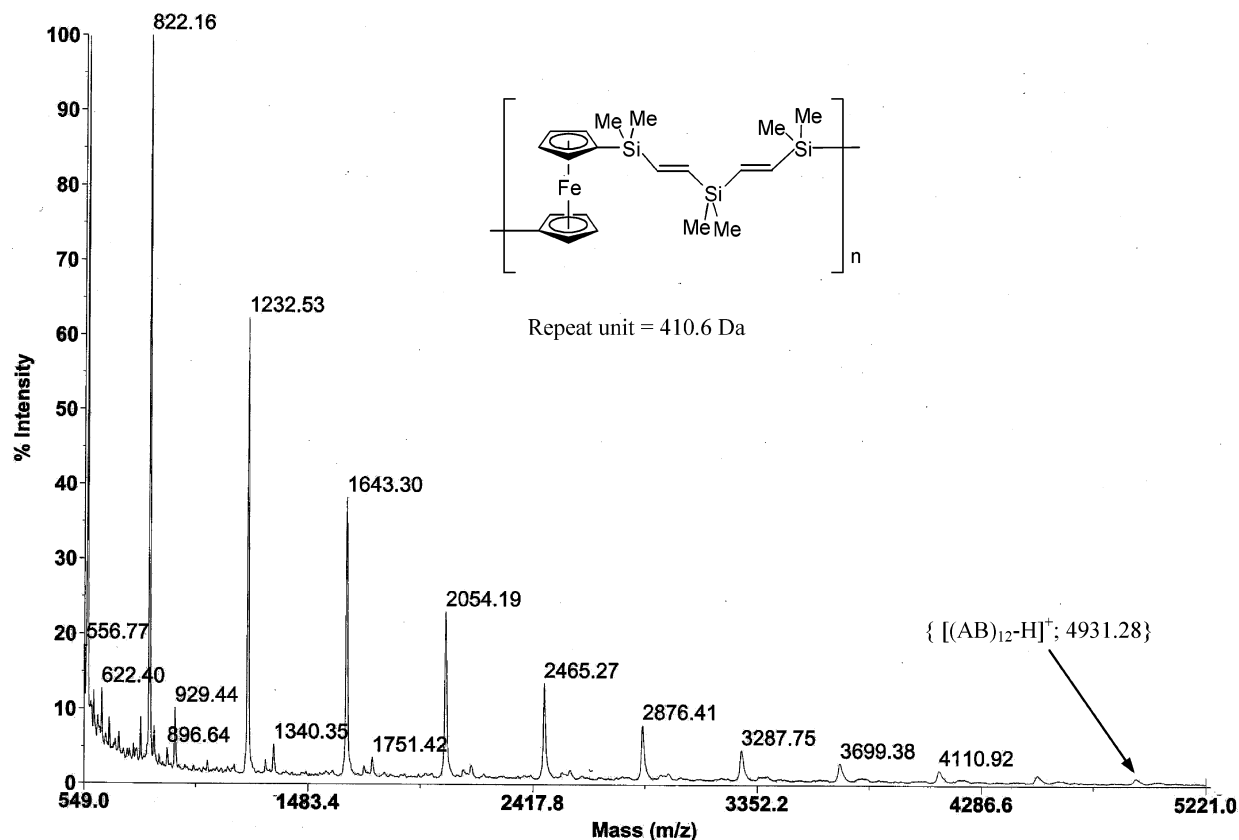


Figure 3. MALDI-TOF MS of polymer **2e** (Pt).

Table 2. MALDI-TOF MS Data of Polymers  $\{[(AB)_n\text{-H}]^+\}$  and/or  $\{[(AB)_n\text{-A-H}]^+\}$  Where A Is the Dialkyne and B Is 1

polymer (repeat unit Da)	MS (Da) data
<b>2a</b> (Pt) (428.5)	858.0, 1287.2, 1715.0, 2145.5, 2575.2, 3004.3, 3434.2, 3863.5, 4292.4, 4723.1, 5152.1, ..., 7296.3 $\{[(AB)_{17}\text{-H}]^+\}$
<b>2c</b> (Pt) (428.5)	858.0, 1286.5, 1715.0, 2143.3, 2571.8, 3000.0, 3428.0, 3856.7, 4284.6, 4713.1, 5140.7 $\{[(AB)_{12}\text{-H}]^+\}$
<b>2b</b> (Pt) (572.9)	844.5, 1146.7, 1417.2, 1719.6, 1990.0, 2292.4, 2562.6, 2865.3, 3135.5, 3363.5 $\{[(AB)_6\text{-H}]^+\}$
<b>2d</b> (Pt) (572.9)	844.2, 1146.7, 1417.3, 1719.8, 1990.4, 2292.4, 2563.0, 3136.11, 3709.8, 4282.8, 4855.9 $\{[(AB)_8\text{-A-H}]^+\}$
<b>2e</b> (Pt) (410.6)	822.2, 1232.5, 1643.3, 2054.2, 2465.3, 2876.4, 3287.8, 3699.4, 4110.9, 4523.0, 4931.3, 5343.6 $\{[(AB)_{13}\text{-H}]^+\}$
<b>2f</b> (Pt) (504.6)	708.4, 1213.0, 1717.6, 2222.0, 2726.7, 3231.3, 3736.1, 4240.6, 4745.5, 5250.0 $\{[(AB)_{10}\text{-A-H}]^+\}$
<b>6a</b> (849.2)	850.2, 1699.2, 2548.6, 3398.6, 4248.9, 5099.4, 5950.6, 6801.4, 7652.3 $\{[(AB)_9\text{-H}]^+\}$
<b>6b</b> (1001.4)	1002.9, 2004.3, 3007.4, 4007.6, 5009.5, 6011.8 $\{[(AB)_6\text{-H}]^+\}$
<b>2a</b> (Rh) (428.5)	857.2, 1285.4, 1713.4, 2141.5, 2569.6, 3000.6, 3429.1, 3858.3, 4287.1, 4715.2, 5143.9 $\{[(AB)_{12}\text{-H}]^+\}$
<b>2c</b> (Rh) (428.5)	857.8, 1286.6, 1715.0, 2143.9, 2572.3, 3429.1, 5142.1, ..., 7284.4 $\{[(AB)_{17}\text{-H}]^+\}$

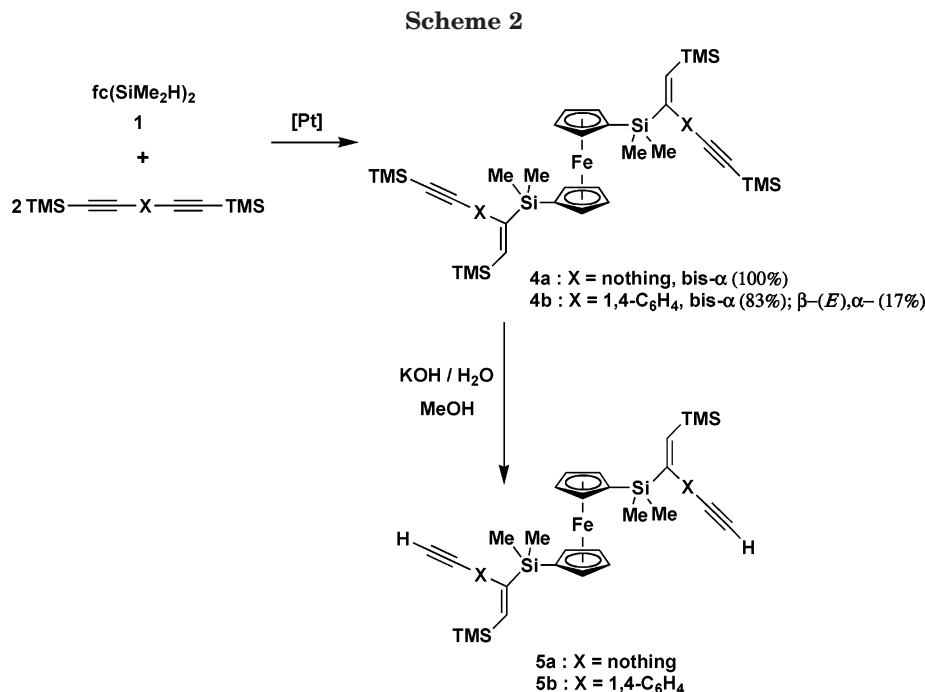
1,3-bis(dimethylsilyl)benzene using  $\text{Rh}(\text{PPh}_3)_3\text{I}$  also results in a similar  $\beta\text{-}(Z)\text{:}\beta\text{-}(E)$  distribution of 0.96:0.04 and 0.91:0.09, respectively.<sup>8a</sup>

The  $^1\text{H}$  NMR spectrum of **2a** (Rh) shows the  $\beta\text{-}(Z)$  olefinic protons as two broad doublets at  $\delta$  6.12, 7.42 with methyl protons of this isomer as a broad singlet at  $\delta$  0.39 [cf. **3a** (Rh), **3d** (Rh)].<sup>15</sup> Two types of end group protons at  $\delta$  4.69 (Si-H) and 3.32 (C $\equiv$ CH) are indicative of a noncyclic  $(\text{AB})_n$  type polymer. Other assignments for **2a** (Rh) were in good agreement with model compounds **3a** (Rh), **3d** (Rh), and polymer **2a** (Pt). For example, the  $^{29}\text{Si}$  DEPT NMR clearly shows the  $\beta\text{-}(Z)$  Si at  $\delta$  -13.2,  $\beta\text{-}(E)$  at  $\delta$  -9.2, and  $\alpha$ - at  $\delta$  -7.3 ppm with the end group Si-H at  $\delta$  -18.2. End group analysis gave the average value of  $n$  as 16, GPC data had  $M_n$  = 4660 with an unusually high PDI of 14.8, and

MALDI-TOF MS confirmed an  $(\text{AB})_n$  type structure with the largest detectable  $n = 12$  ( $M = 5142.9$  Da, Table 2).

Polymer **2c** (Rh) was obtained similarly as a sticky orange solid, in 76% yield from **1** with 1,3-diethynylbenzene (Scheme 1), and has a similar isomeric ratio to **2a** (Rh). The NMR data for **2c** (Rh) showed  $\beta\text{-}(Z)$ -olefinic protons that matched those of model compound **3f** (Rh)<sup>15</sup> and  $\beta\text{-}(E)$ -olefin signals like those of polymer **2c** (Pt). MALDI-TOF MS gave the highest detectable value for  $n$  in a  $(\text{AB})_n$  type structure of 17 (7283.4 Da, Table 2) (GPC;  $n = 5$ ,  $M_n = 3650$ ; PDI = 2.69).

Unfortunately, reaction of **1** with 1,4-bis(trimethylsilylethynyl)benzene using  $[\text{Rh}(\text{PPh}_3)_3\text{I}]$  gave **2b** in 49% yield ( $M_n = 2450$ ; PDI = 1.89, GPC) that was indistinguishable from **2b** (Pt). Thus, under reflux conditions the Rh catalyst does not display any different specificity.<sup>8a</sup>

**Table 3. Cyclic Voltammetric Data<sup>a</sup>**

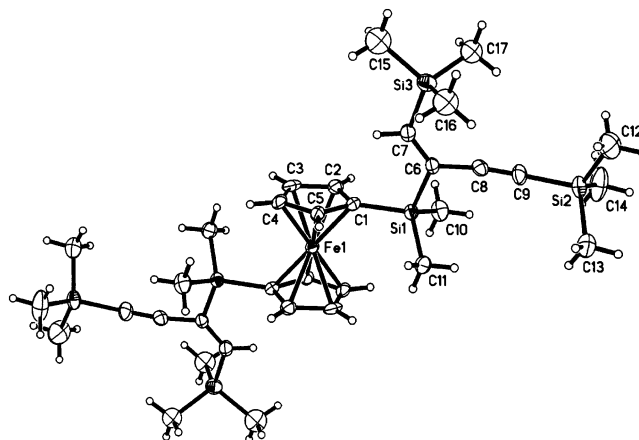
polymer	$E_{pa}$ (V)	$E_{pc}$ (V)	$E^\circ$ (V)
<b>2a (Pt)</b>	0.20	0.13	0.17
<b>2b (Pt)</b>	0.25	0.15	0.20
<b>2c (Pt)</b>	0.20	0.13	0.17
<b>2d (Pt)</b>	0.31	0.13	0.22
<b>2e (Pt)</b>	0.23	0.12	0.18
<b>2a (Rh)</b>	0.20	0.13	0.17
<b>2c (Rh)</b>	0.23	0.15	0.19
ferrocene	0.21	0.06	0.14

<sup>a</sup> Measured in a THF solution containing ca. 1 mM of the monomer unit and 0.1 M of [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub>. Sweep rate = 50 mV s<sup>-1</sup>.

**Syntheses of Ferrocene-Containing Bis(enyne)s and Polymers with Two Ferrocenes per Repeat Unit.** Attempted hydrosilylation polymerization of 1,4-bis(trimethylsilyl)butadiyne with **1** failed to proceed beyond the formation of the single adduct HSi(Me)<sub>2</sub>Fc-Si(Me)<sub>2</sub>C(TMS)=CH-C≡C-TMS {Fc = ( $\eta$ -C<sub>5</sub>H<sub>4</sub>)Fe-( $\eta$ -C<sub>5</sub>H<sub>4</sub>)}. This single hydrosilylated product was characterized only by GC-MS ([M]<sup>+</sup> = 496) and <sup>1</sup>H NMR spectroscopy and has a characteristic septet centered at  $\delta$  4.66 for Si(Me)<sub>2</sub>H. A similar sluggish reaction was observed in the synthesis of polymer **2f (Pt)**, although prolonged reaction time did eventually lead to polymerization in that case.

The addition of one further equivalent of diyne to the single adduct HSi(Me)<sub>2</sub>-Fc-Si(Me)<sub>2</sub>C(TMS)=CH-C≡C-TMS did however give further hydrosilylated product **4a** as an orange solid in 45% yield (Scheme 2). The attack of the silane was *syn* at the internal carbon bearing no trimethylsilyl group (i.e., bis- $\alpha$  product), as previously documented in the Pt- and Rh-catalyzed hydrosilylation of 1,4-bis(trimethylsilyl)butadiyne with HSiCl<sub>2</sub>Me and HSiR<sub>3</sub> (R = Me, Et, Ph).<sup>21</sup> Product **4a** was fully characterized by GC-MS, <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si

NMR spectroscopy, elemental analysis, and X-ray crystallography from crystals grown from *n*-hexane at -78 °C (Figure 4).



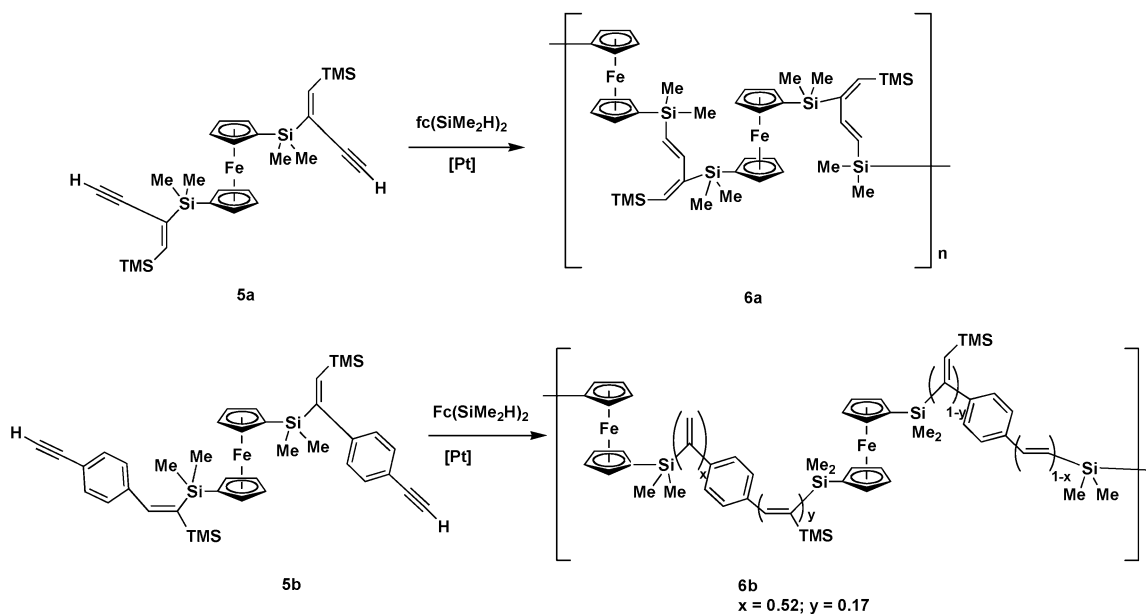
**Figure 4.** Molecular structure of **4a**, showing the atom-numbering scheme and using 30% probability thermal ellipsoids. Bond lengths (Å): C6-C7 1.356(9), C6-C8 1.451(9), C8-C9 1.202(9), Si1-C10 1.852(7), Si1-C6 1.881(7), Si3-C7 1.880(7), C9-Si2 1.826(8). Bond angles (deg): C6-C8-C9 171.6(7), Si2-C9-C8 177.9(7), C7-C6-C8 121.5(6), C7-C6-Si1 126.0(5), C8-C6-Si1 112.4(5).

Complex **4a** is a good candidate for further hydrosilylation polymerization if the trimethylsilyl groups are removed. Thus, desilylation of **4a** with KOH in methanol gave **5a** as an orange solid in 87% yield (Scheme 2). Noteworthy features are a [M]<sup>+</sup> of 546 in the GC-MS, the alkynyl protons at  $\delta$  3.18 in the <sup>1</sup>H NMR spectrum, and the alkynyl carbons ( $\delta$  86.1, 87.6) in the <sup>13</sup>C NMR spectrum (Table 1). The trimethylsilyl group attached to the double bond was not removed and is seen as a signal in the <sup>29</sup>Si NMR spectrum at  $\delta$  -8.5.

With complex **5a** in hand, an oligomer with two ferrocenes per repeat unit can be accessed from equimolar amounts of **1** and **5a**. The product, **6a**, was isolated as an orange sticky solid in 86% yield (Scheme

(21) (a) Bock, H.; Seidl, H. *J. Am. Chem. Soc.* **1968**, *90*, 5694. (b) Marciniec, B., Eds. *Comprehensive Handbook on Hydrosilylation*; Pergamon: Oxford, 1992, and references therein. (c) Kusumoto, T.; Hiyama, T. *Chem Lett.* **1985**, 1405.

Scheme 3



3). The regiochemistry was exclusively  $\beta$ -(*E*) due to the bulky alkenyl substituent on the internal carbon of **5a**. Hydrosilylation of the double bonds was not observed, consistent with the fact that enynes show greater susceptibility of the triple bond toward hydrosilylation.<sup>6f,9a,22</sup> Full characterization of **6a** was completed using  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopy, as well as MALDI-TOF MS (Tables 1 and 2).

Having established a method to incorporate two ferrocene units in the backbone per repeat unit, this method was applied to another system. First, 2 equiv of 1,4-bis(trimethylsilylethynyl)benzene was reacted with **1** to give **4b** as an orange solid in 41% yield (Scheme 2). Two inseparable isomers, bis- $\alpha$  (**4b**, major) and  $\alpha$ , $\beta$ -(*E*) (**4b**, minor) in a 0.83/0.17 ratio, were formed. Mixture **4b** was fully characterized using  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopy (Table 1). Removal of the terminal trimethylsilyl groups from **4b** gave **5b** in 96% yield (Scheme 2), again as two isomeric forms in the same 0.8/0.2 ratio.

The aryl-based ferrocenyl bis(enyne) (**5b**) was then reacted with **1** and Karstedt's catalyst in THF for 3 days to afford oligomer **6b**. In contrast to the exclusive formation of the  $\beta$ -(*E*) regiochemistry in oligomer **6a**, a ratio of  $0.48(1-x)$   $\{\beta$ -(*E*) $\}$  and  $0.52(x)$  ( $\alpha$ -) was obtained, very similar to that of polymers **2a** (Pt) and **2c** (Pt) as well as model compound **3a** (Pt).<sup>15</sup>

### Electrochemical Studies

Cyclic voltammetry was used to investigate electronic interactions between iron centers in the poly{ferrocene(phenylene)bis(silylenevinylene)}s {**2a–e** (Pt), **2a,c** (Rh)}, and the results were compared to the model compounds 1,1'-bis{dimethyl(phenylvinylene)silyl}ferrocenes (**3a–c**) and bis{ferrocenylsilylenevinylene}phenylenes (**3d–i**). For all polymer samples, a single reversible redox wave was observed (Fe(II)–Fe(III) redox couple) and the anodic potential ( $E_{\text{pa}}$ ), cathodic potential

( $E_{\text{pc}}$ ), and average potential ( $E^\circ$ ) are listed in Table 3. The presence of a single wave suggests no interaction between the metal centers and may be due to ineffective redox-matching between the spacer groups and the ferrocene units, as suggested by Swager and co-workers.<sup>23</sup> Moreover, the organosilicon spacer may be too long, permitting only very weak and unresolvable electronic interactions between iron centers.<sup>24</sup>

### Conclusions

Hydrosilylation polymerization of 1,1'-bis(dimethylsilyl)ferrocene (**1**) and dialkynes leads to characterizable low molecular weight polymers and oligomers in which ferrocene and silylenevinylene phenylene groups form the backbone. The new polymers were fully characterized and compared to model complexes. Electrochemical studies indicate little electronic interaction between adjacent metal centers in the polymer backbone.

### Experimental Section

**Materials.** Karstedt's catalyst (platinum-divinyltetramethyldisiloxane complex; 3–3.5% Pt concentration in vinyl-terminated poly(dimethylsiloxane)) was purchased from Gelest, Inc. (Tullytown, PA). All alkynes used were purchased from GFS Chemicals, Inc. (Columbus, OH) and were used as received. 1,1'-Bis(dimethylsilyl)ferrocene (**1**),<sup>25</sup> 1,4-diethynylbenzene,<sup>26</sup>  $\text{Rh}(\text{PPh}_3)_3\text{I}$ ,<sup>27</sup> and diethynyl(dimethyl)silane<sup>28</sup> were prepared using previously described literature methods.

**Equipment.** The preparation, purification, and reactions of all complexes described were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques

(23) Zhu, S. S.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 8713.

(24) Long, N. J.; Martin, A. J.; Vilar, R.; White, A. J. P.; Williams, D. J.; Younus M. *Organometallics* **1999**, *18*, 4261.

(25) Corriu, R. J. P.; Devylder, N.; Guérin, C.; Henner, B.; Jean, A. *Organometallics* **1994**, *13*, 3194.

(26) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synth.* **1980**, 627.

(27) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. (A)* **1966**, 1711.

(28) Kraihanzel, C. S.; Losee, M. L. *J. Organomet. Chem.* **1967**, *10*, 427.

(22) Marciniak, B. *Appl. Organomet. Chem.* **2000**, *14*, 527, and references therein.



unless otherwise stated. Hydrosilylation experiments were carried out with a trace amount of air to promote catalysis. Solvents were dried over Na/benzophenone (THF) and CaH<sub>2</sub> (*n*-hexane, CH<sub>2</sub>Cl<sub>2</sub>) and were freshly distilled prior to use. NMR spectra were recorded on Varian VXR-400S (400 MHz) and Varian Unity Inova (500 MHz) NMR Fourier transform spectrometers. The solvent used for NMR studies was C<sub>6</sub>D<sub>6</sub> as purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Gas chromatography–mass spectrometry (GC-MS) was performed on a Hewlett-Packard HP 6890 series gas chromatograph connected to a HP 5973 mass selective detector. Elemental analyses were performed by Robertson Microlit Laboratories, Inc. (Madison, NJ). Chromatography was performed on silica gel (100–200 mesh, purchased from Fisher Scientific Co., or Sorbent Technologies, Atlanta, GA). Filtrations used Celite purchased from Fisher that was preheated and dried before use. MALDI-TOF mass spectrometry was performed on a Perspective (PE) Biosystems Voyager System 6078 MALDI linear/reflectron time-of-flight mass spectrometer, equipped with a pulsed nitrogen laser (337 nm). The instrument was operated in the linear, positive-ion, high-voltage (20 kV) mode. Molecular weight distributions were analyzed by gel permeation chromatography using a Waters Associates 2690 separations unit, with Ultrastayragel columns with a pore size between 500, 10<sup>3</sup>, and 10<sup>5</sup> Å, and a Waters 410 differential refractometer. Polystyrene standards purchased from Aldrich were used for calibration purposes. Cyclic voltammetry studies were performed using a platinum wire counter electrode, a gold wire working electrode, and a Ag/AgCl reference electrode connected to a EG&G Princeton Applied Research potentiostat Model 273. Measurements were conducted at ambient temperature under nitrogen in THF using 0.1 M [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub> as supporting electrolyte. Sample concentrations were 1.0 mM, and cyclic voltammograms were recorded at sweep rates of 50–200 mV s<sup>-1</sup>. Under these conditions ferrocene has the following potentials: *E*<sub>pc</sub> 0.06 V; *E*<sub>pa</sub> 0.21 V; *E*<sup>o</sup> 0.14 V.

**General Synthesis of 2a–f (Pt).** The general syntheses of 2a–f (Pt) are illustrated by the synthesis of 2a (Pt) below.

**Preparation of 2a (Pt).** Karstedt's catalyst (1 drop) was added to a solution of 1,4-diethynylbenzene (0.188 g, 1.49 mmol) and 1,1'-bis(dimethylsilyl)ferrocene (**1**) (0.451 g, 1.49 mmol) in THF (7 mL) along with a trace of air and refluxed for 2 days. Drying in vacuo, dissolution in a minimum amount of THF (3.5 mL), and precipitation into methanol gave **2a (Pt)** as a bright orange precipitate, which was washed with methanol (3 × 20 mL) and dried under vacuum overnight, yield 0.556 g, 87%. *M*<sub>n</sub> = 9630; *M*<sub>w</sub>/*M*<sub>n</sub> = 3.2 (RI detector) and *M*<sub>n</sub> = 11 700; *M*<sub>w</sub>/*M*<sub>n</sub> = 2.4 (light scattering). Anal. Calcd for (C<sub>24</sub>H<sub>28</sub>Si<sub>2</sub>Fe)<sub>n</sub>: C, 67.27; H, 6.59. Found: C, 65.86; H, 6.94.

**2b (Pt):** reflux, 2 days; orange powder; yield 75% *M*<sub>n</sub> = 1920; *M*<sub>w</sub>/*M*<sub>n</sub> = 1.73. Anal. Calcd for (C<sub>30</sub>H<sub>44</sub>Si<sub>4</sub>Fe)<sub>n</sub>: C, 62.90; H, 7.74. Found: C, 60.32; H, 7.83.

**2c (Pt):** room temperature, 4 days; orange sticky solid; yield 68% *M*<sub>n</sub> = 9120; *M*<sub>w</sub>/*M*<sub>n</sub> = 21.7. Anal. Calcd for (C<sub>24</sub>H<sub>28</sub>Si<sub>2</sub>Fe)<sub>n</sub>: C, 67.27; H, 6.59. Found: C, 67.05; H, 6.52.

**2d (Pt):** reflux, 2 days; orange powder; yield 70% *M*<sub>n</sub> = 1710; *M*<sub>w</sub>/*M*<sub>n</sub> = 1.73. Anal. Calcd for (C<sub>30</sub>H<sub>44</sub>Si<sub>4</sub>Fe)<sub>n</sub>: C, 62.90; H, 7.74. Found: C, 62.67; H, 7.55.

**2e (Pt):** room temperature, 4 days; orange sticky solid; yield 85% *M*<sub>n</sub> = 3520; *M*<sub>w</sub>/*M*<sub>n</sub> = 3.84. Anal. Calcd for (C<sub>20</sub>H<sub>30</sub>Si<sub>3</sub>Fe)<sub>n</sub>: C, 58.51; H, 7.37. Found: C, 55.75; H, 7.20.

**2f (Pt):** room temperature, 4 days; orange powder; yield 52% *M*<sub>n</sub> = 1860; *M*<sub>w</sub>/*M*<sub>n</sub> = 1.74.

**Preparation of 2a (Rh).** Iodotris(triphenylphosphine)-rhodium(I) (2 mg) was added to a solution of 1,4-diethynylbenzene (0.028 g, 0.218 mmol) and **1** (0.066 g, 0.222 mmol) in THF (5 mL) and stirred at room temperature for 13 days. Drying in vacuo, dissolution in a minimum of THF (0.5 mL), and precipitation into methanol (40 mL) gave a bright orange precipitate. Washing with methanol (3 × 10 mL) and drying

under vacuum overnight gave polymer **2a (Rh)** as an orange solid (yield 0.058 g, 62%). *M*<sub>n</sub> = 4660; *M*<sub>w</sub>/*M*<sub>n</sub> = 14.8. Anal. Calcd for (C<sub>24</sub>H<sub>28</sub>Si<sub>2</sub>Fe)<sub>n</sub>: C, 67.27; H, 6.59. Found: C, 65.38; H, 6.18.

Polymer **2c (Rh)** was similarly prepared from 1,3-diethynylbenzene at room temperature over 4 days as a sticky orange solid in 76% yield. *M*<sub>n</sub> = 3,650; *M*<sub>w</sub>/*M*<sub>n</sub> = 2.69. Anal. Calcd for (C<sub>24</sub>H<sub>28</sub>Si<sub>2</sub>Fe)<sub>n</sub>: C, 67.27; H, 6.59. Found: C, 66.14; H, 6.91.

**Preparation of 4a.** Karstedt's catalyst (1 drop) was added to a solution of 1,4-bis(trimethylsilyl)butadiyne (0.060 g, 0.31 mmol) and **1** (0.047 g, 0.155 mmol) in THF (7 mL) with a trace of air and stirred at room temperature for 2 days. Drying in vacuo, chromatography on silica gel (70–100 μm, 21 × 2 cm) loading with 0.5 mL of hexane and eluting with hexane, followed by evaporation in vacuo gave **4a** as an orange solid (yield 0.048 g, 45%). *m/z* = 690 (M<sup>+</sup>). Anal. Calcd for C<sub>34</sub>H<sub>58</sub>Si<sub>6</sub>Fe: C, 59.08; H, 8.46. Found: C, 59.00; H, 8.39.

**Preparation of 4b.** Karstedt's catalyst (1 drop) was added to a solution of 1,4-bis(trimethylsilyl)ethynylbenzene (0.277 g, 1.02 mmol) and **1** (0.155 g, 0.513 mmol) in THF (10 mL) with a trace of air and refluxed for 2 days. Drying in vacuo gave an orange oil, which was chromatographed on silica gel (70–100 μm, 30 × 3 cm) loading with 1.5 mL of hexane and eluting with hexane. Evaporation of solvent in vacuo gave **4b** as an orange oil (yield 0.176 g, 41%).

**Preparation of 5a.** A solution of KOH (0.008 g, 0.142 mmol) in water (0.5 mL) was added to a solution of **4a** (0.048 g, 0.069 mmol) in methanol (15 mL) and stirred for 1 day at room temperature. Evaporation to dryness, extraction with hexane (3 × 10 mL), filtration through Celite, and removal of hexane in vacuo followed by chromatography on silica gel (70–100 μm, 15 × 2 cm) loading with 0.5 mL of hexane and eluting with hexane gave **5a** as an orange solid (yield 0.033 g, 87%). *m/z* = 546 (M<sup>+</sup>). Anal. Calcd for C<sub>28</sub>H<sub>42</sub>Si<sub>4</sub>Fe: C, 61.50; H, 7.74. Found: C, 62.01; H, 7.04.

Compound **5b** was prepared similarly from **4b** over 2 days in 96% yield.

**Preparation of Polymer 6a.** Karstedt's catalyst (1 drop) was added to a solution of **5a** (0.028 g, 0.051 mmol) and **1** (0.016 g, 0.052 mmol) in THF (2 mL) with a trace of air and stirred at room temperature for 2 days. Drying in vacuo gave a sticky orange solid, which was dissolved in a minimum of THF (0.4 mL) and precipitated into methanol to give a sticky orange precipitate. Washing with methanol (3 × 10 mL) and drying under vacuum overnight gave polymer **6a** as a sticky orange solid (yield 0.038 g, 86%).

Polymer **6b** was prepared similarly from **5b** at room temperature over 3 days in 59% yield.

**X-ray Crystal Structure Determination.** Crystals of **4a** were mounted on a glass fiber using cyanoacrylate cement. Intensity data were collected on a Siemens P4 diffractometer at 296 K, using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The θ–2θ scan technique was applied with variable scan speeds. The intensities of three standard reflections were measured every 97 reflections, and corrections were applied. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied to the data set. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods to minimize Σw(F<sub>o</sub> – F<sub>c</sub>)<sup>2</sup>, where w<sup>-1</sup> = σ<sup>2</sup>(F) + g(F)<sup>2</sup>. Hydrogen atoms were included in calculated positions (C–H from 0.93 to 0.98 Å depending on type of bonding). Crystal data, data collection, and least-squares parameters are listed in Table 2. All calculations were performed and graphics created using SHELXTL-97.

**MALDI-TOF MS of Polymers.** Approximately 1–2 mg of polymer was dissolved in 1 μL THF and added to 1 μL of the matrix in THF (mix). The matrix solution was prepared by dissolving 23 mg of 1,8,9-anthracenetriol (dithranol) (MW = 226.23 g/mol) in 1 mL of THF (0.1 mol/L) + 1 μL of 5 g/L THF solution of silver trifluoroacetate (MW = 220.88 g/mol) + 10

$\mu\text{L}$  of trifluoroacetic acid (1%). Finally, 1  $\mu\text{L}$  of the mix was spotted on a stainless steel target plate and air-dried prior to acquisition.

**Acknowledgment.** We are grateful to Prof. Ian Manners and Dr. Kevin Kulbaba at the University of Toronto for the collection of GPC data on some of the polymer samples and Prof. James Schlegel of this department for electrochemical measurements. We thank the National Science Foundation for GPC and electrochemical instrumentation at Rutgers–Newark provided through the NSF-MRI program (MRI 0116066). We are

also grateful to Dr. Hong Li of the mass spectrometry facility in the Department of Biochemistry at the University of Medicine and Dentistry of New Jersey in Newark, NJ, for assistance with MALDI-TOF spectrometry.

**Supporting Information Available:** Tables of crystallographic data for **4a (Pt)** and selected  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra and MALDI-TOF mass spectra of the polymers reported are available free of charge via the Internet at <http://pubs.acs.org>.

OM049166P