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Synthesis, Characterization, and the Platinum-Catalyzed Ring-Opening Polymerization and Stereoselective Dimerization of Silicon-Bridged [1]Ferrocenophanes with Acetylenic Substituents

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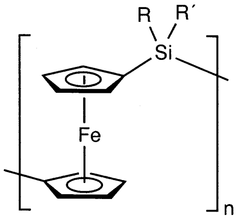
Reaction of the lithium acetylides LiC≡CR (R = Ph, *n*Bu) with the silicon-bridged [1]ferrocenophane Fe(η-C_5H_4)$_2$Si(Me)Cl (**2a**) at −78 °C was found to result in selective substitution of Cl, forming sila[1]ferrocenophanes with acetylenic substituents Fe(η-C_5H_4)$_2$Si(Me)C≡CR (**4**, R = Ph; **5**, R = *n*Bu). A similar reaction of sila[1]ferrocenophane Fe(η-C_5H_4)$_2$SiCl$_2$ (**2b**) with 2 equiv of LiC≡CPh resulted in the substitution of both Cl atoms, forming Fe(η-C_5H_4)$_2$Si(C≡CPh)$_2$ (**6**). Transition metal-catalyzed ring-opening polymerization of monomers **4**, **5**, and **6** resulted in the formation of high molecular weight ($M_n > 10^4-10^5$) polyferrocenylsilanes with acetylenic substituents, [Fe(η-C_5H_4)$_2$Si(Me)C≡CR]$_n$ (**7**, R = Ph; **8**, R = *n*Bu) and [Fe(η-C_5H_4)$_2$Si(C≡CPh)$_2$]$_n$ (**9**), respectively. The cyclic dimer [Fe(η-C_5H_4)$_2$Si(Me)C≡CPh]$_2$ (**10**) was isolated from the polymerization mixture derived from **4**. The dimer was shown to exist in the *cis* configuration by single-crystal X-ray diffraction. Detailed studies on the polymerization of **4** have shown that the ratio of high polymer **7** to cyclic dimer **10** formed in the reaction is highly solvent and concentration dependent. Pyrolysis of polymers **7** and **8** during thermogravimetric analysis (TGA) studies have resulted in the formation of black magnetic ceramics in the highest yields found to date for uncrosslinked polyferrocenylsilane homopolymers (2 h, 900 °C; **7**, 81%; **8**, 61%).

Introduction

Metal-containing polymers are of considerable interest, as such materials offer potential access to useful redox, magnetic, optical, preceramic, or catalytic properties[1] and functional supramolecular structures.[2] One class of metallopolymers, the polyferrocenylsilanes (PFSs) (**1**), have been synthesized via the ring-opening polymerization (ROP) of strained silicon-bridged [1]ferrocenophane monomers (**2**)[3] using thermal,[4] anionic,[5] and transition metal-catalyzed[6] methodologies.[7,8]



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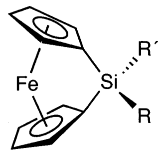

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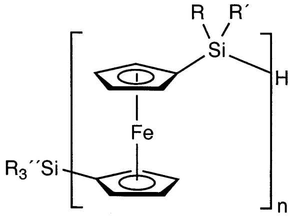

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Platinum-catalyzed ROP of sila[1]ferrocenophanes remains the most convenient route to polyferrocenylsilanes found to date.[6,9] The high temperatures utilized in thermal ROP make it undesirable for thermally sensitive substituents. Furthermore, a method of molecular weight control has yet to be found for the

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[1] See, for example: (a) Archer, R. D. *Inorganic and Organometallic Polymers*; Wiley-VCH: New York, 2001. (b) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (c) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (d) Manners, I. *Science* **2001**, *294*, 1664.

[2] See: (a) Massey, J. A.; Winnik, M. A.; Manners, I.; Chan, V. Z.-H.; Ostermann, J. M.; Enchelmaier, R.; Spatz, J. P.; Möller, M. *J. Am. Chem. Soc.* **2001**, *123*, 3147. (b) Steffen, W.; Kohler, B.; Altmann, M.; Scherf, U.; Stitzer, K.; zur Loye, H. C.; Bunz, U. H. F. *Chem. Eur. J.* **2001**, *7*, 117. (c) Park, C. M.; McAlvin, J. E.; Fraser, C. L.; Thomas, E. L. *Chem. Mater.* **2002**, *14*, 1225. (d) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromolecules* **2002**, *35*, 4560.

[3] The first sila[1]ferrocenophane **2** (R = R′ = Ph) was synthesized by Osborne and co-workers, see: (a) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27, (b) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402.

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

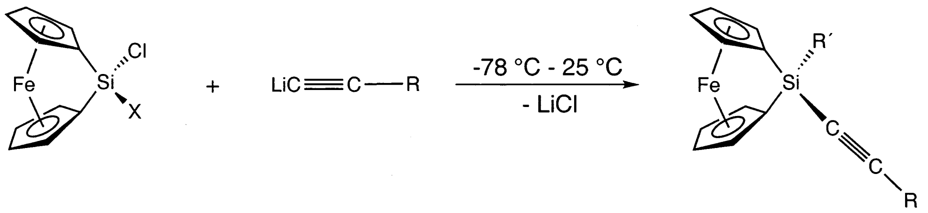
[5] (a) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102. (b) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797.

[6] (a) Ni, Y.; Rulkens, R.; Pudelski, J. K.; Manners, I. *Macromol. Rapid Commun.* **1995**, *16*, 637. (b) Reddy, N. P.; Yamashita, H.; Tanaka, M. *Chem. Commun.* **1995**, *22*, 2263.

[7] (a) Manners, I. *Chem. Commun.* **1999**, 857. (b) A range of other [1]ferrocenophanes with different bridging elements have been prepared that also undergo ROP. See: Manners, I. *Can. J. Chem.* **1998**, *76*, 371.

10.1021/om0204078 CCC: $22.00

Scheme 1. Reaction of 2a or 2b with Li[C≡CR]; Synthesis of 4 (R = Ph, R′ = Me), 5 (R = *n*Bu, R′ = Me), and 6 (R = Ph, R′ = C≡CPh)



2a: X = Me
2b: X = Cl

4: R = Ph, R′ = Me
5: R = *n*Bu, R′ = Me
6: R = Ph, R′ = CCPh

thermal ROP of sila[1]ferrocenophanes. Although extremely narrow polydispersities, molecular weight control, and access to interesting architectures such as block copolymers are all benefits of utilizing anionic-initiated ROP of sila[1]ferrocenophanes, the stringent monomer and solvent purity requirements make this method challenging to use.[5] On the other hand, transition metal-catalyzed ROP of sila[1]ferrocenophanes can be performed on a large scale using only reasonably pure monomer to give high yields of high molecular weight ($M_n > 10^5$) polymer with reasonable polydispersity indices (commonly 1.5−1.9).[6,9,10] Additionally, the molecular weight of the polyferrocenylsilane can be controlled by the addition of a species containing an Si-H functionality which can then “compete” with molecules of **2** for addition to the growing polymer chain, resulting in “capped” polyferrocenylsilanes, **3**.[10] Addition of silanes of differing reactivity has been found to lead to molecular weight control plots of differing slope.[11] Using silanes of differing architecture, block,[12] star,[10] and heteroatom-containing[13] polymers have also been prepared.

We have recently been studying the preparation of functional polyferrocenylsilanes.[14,15] We now report details of the synthesis and polymerization behavior of sila[1]ferrocenophanes with acetylenic substituents. Such species are of interest as precursors to polyferrocenylsilane homopolymers with high ceramic yields as a result of potentially efficient, thermally induced cross-linking chemistry. In addition, complexation of the acetylenic groups offers opportunities for further metallization of the ring-opened polymers.[16]

Results and Discussion

Recent developments on the substitution chemistry of sila[1]ferrocenophanes with Si−Cl bonds (e.g., **2a**) with organic nucleophiles[14] have allowed for the selective synthesis of sila[1]ferrocenophanes with a wide range of functionality not available by other methods.[17] We therefore decided to undertake the synthesis of sila[1]ferrocenophanes with acetylenic substituents through the reaction of Si−Cl bonds with lithium acetylides.

Synthesis and Characterization of Acetylide-Substituted Sila[1]ferrocenophanes 4−6. The addition of an ether solution of Li[C≡CPh] to a solution of **2a** in the same solvent at low temperature (−78 °C) was found to result in selective substitution of the Cl atom for a phenylacetylene group with formation of LiCl (Scheme 1) upon warming to 25 °C. After workup, the desired product **4** was obtained as a red crystalline solid in good (65%) yield after recrystallization from hexanes/toluene (ca. 50:50) at −30 °C.

The ^{1}H NMR spectrum was consistent with the assigned structure. Four separate resonances were observed in the Cp region ($\delta = 4.51$, 4.44, 4.40, and 3.91 ppm), which is characteristic of unsymmetrically substituted [1]ferrocenophanes. The resonance for the methyl group was observed at a chemical shift of $\delta = 0.61$ ppm (cf. **2a** $\delta = 0.52$ ppm).[18] A single resonance was observed in the ^{29}Si NMR spectrum at a chemical

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(8) For the recent work of other groups on [1]ferrocenophanes and the synthesis of ring-opened polyferrocenes, see, for example: (a) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (b) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (c) Mizuta, T.; Onishi, M.; Miyoshi, K. *Organometallics* **2000**, *19*, 5005. (d) Compton, D. L.; Brandt, P. F.; Rauchfuss, T. B.; Rosenbaum, D. F.; Zukoski, C. F. *Chem. Mater.* **1995**, *7*, 2342. (e) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (f) Brunner, H.; Klankermayer, J.; Zabel, M. *J. Organomet. Chem.* **2000**, *601*, 211. (g) Herberhold, M.; Hertel, F.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *582*, 352. (h) Antipin, M. Y.; Vorontsov, I. I.; Dubovik, I. I.; Papkov, V.; Cervantes-Lee, F.; Pannell, K. H. *Can. J. Chem.* **2000**, *78*, 1511. (i) Calleja, G.; Carré, F.; Cerveau, G.; Labbé, P.; Coche-Guérente, L. *Organometallics* **2001**, *20*, 4211. (j) Papkov, V. S.; Gerasimov, M. V.; Dubovik, I. I.; Sharma, S.; Dementiev, V. V.; Pannell, K. H. *Macromolecules* **2000**, *33*, 7107. (k) Espada, L.; Shadaram, M.; Robillard, J.; Pannell, K. H. *J. Inorg. Organomet. Polym.* **2000**, *10*, 169. (l) Barlow, S.; Rohl, A. L.; Shi, S.; Freeman, C. M.; O'Hare, D. *J. Am. Chem. Soc.* **1996**, *118*, 7578. (m) Sun, Q.; Lam, J. W. Y.; Xu, K.; Xu, H.; Cha, J. A. K.; Wong, P. C. L.; Wen, G.; Zhang, X.; Jing, X.; Wang, F.; Tang, B.-Z. *Chem. Mater.* **2000**, *12*, 2617.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4

Si(1)−C(1)	1.880(3)	C(13)−C(14)	1.440(4)	Si(1)−C(12)−C(13)	172.4(3)
Si(1)−C(6)	1.878(3)	Fe(1)−Si(1)	2.6917(9)	C(12)−C(13)−C(14)	177.7(3)
Si(1)−C(12)	1.834(3)	C(1)−Si(1)−C(6)	96.50(13)	α	20.53(14)
C(12)−C(13)	1.197(4)	C(11)−Si(1)−C(12)	112.35(14)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

Si(1)−C(1)	1.869(2)	C(12)−C(20)	5.11[a]	Si(1)−C(19)−C(20)	174.92(18)
Si(1)−C(6)	1.870(2)	Fe(1)−Si(1)	2.6408(6)	C(11)−C(12)−C(13)	178.8(2)
Si(1)−C(11)	1.827(2)	C(1)−Si(1)−C(6)	99.00(6)	C(19)−C(20)−C(21)	178.0(2)
Si(1)−C(19)	1.822(2)	C(11)−Si(1)−C(19)	112.36(9)	α	19.23(12)
C(11)−C(19)	3.03[a]	Si(1)−C(11)−C(12)	172.98(18)		

[a] Nonbonding distance.

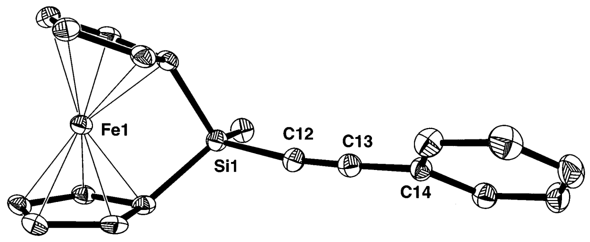

Figure 1. Molecular structure of **4** (thermal ellipsoids at 30% probability, hydrogen atoms have been removed for clarity).

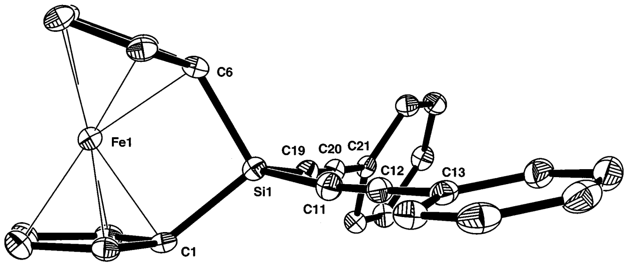

Figure 2. Molecular structure of **6** (thermal ellipsoids at 30% probability, hydrogen atoms have been removed for clarity).

shift of −27.8 ppm (cf. **2a** $\delta = 5.75$ ppm).[18] To further explore the structure of **4**, a single-crystal X-ray diffraction study was performed. The molecular structure of **4** is shown in Figure 1, and selected bond lengths and angles are given in Table 1.

The tilt-angle between the Cp rings of **4** (α) was found to be 20.53(14)°, which is within the normal range found for sila[1]ferrocenophanes (16−21°).[19] The Fe−Si distance of 2.6917(9) Å was also within the range of values obtained previously (ca. 2.55−2.75 Å). The acetylene moiety was observed to possess a slightly nonlinear geometry. The Si(1)−C(12)−C(13) angle was found to be 172.4(3)°, and the C(12)−C(13)−C(14) angle was 177.7(3)°.

The hexynyl-substituted sila[1]ferrocenophane **5** was isolated as a red crystalline solid in moderate (48%) yield from the analogous low-temperature reaction of Li[C≡C(CH$_2$)$_3$CH$_3$] with **2a**. The yield could be increased by further concentration of the supernatant and subsequent crystallization at −55 °C and was only a reflection of the dramatically increased solubility of **5** over **4**. Multinuclear NMR, MS, and EA were used to confirm the assigned structure.

The addition of 2 equiv of the lithium salt of phenylacetylene to a solution of **2b** in ether at low temperature was also performed (Scheme 1). This was found to result in the substitution of each of the Cl atoms for a phenylacetylene moiety, the first example of successful nucleophilic disubstitution of **2b**. After workup, the desired product, **6**, was isolated as a red crystalline solid in moderate (47%) yield from a dichloromethane/hexanes (25:75) solution at −30 °C. The ^{1}H NMR spectrum was in agreement with the assigned structure. In contrast to the cases of **4** and **5**, only two resonances were observed in the Cp region ($\delta = 4.49$, 4.43 ppm) of **6**, which is consistent with a symmetrical structure. A single resonance was observed in the ^{29}Si NMR spectrum at a chemical shift of −54.2 ppm. To further characterize the structure of **6**, a single-crystal X-ray diffraction study was performed. The molecular structure of **6** is shown in Figure 2, and selected bond lengths and angles are given in Table 2.

The tilt-angle, α, in **6** was found to be 19.23(12)°, which is slightly smaller than that found for **4** (20.53(14)°). Additionally, the Fe−Si distance was determined to be slightly shorter (for **4**, 2.6917(9) Å; for **6**, 2.6408(6) Å). The C(11)−Si(1)−C(19) angle was found to be 112.36(9)°. The nonbonding distance between the centroids of the acetylene substituents was found to be 4.07 Å.

Transition Metal-Catalyzed Ring-Opening Polymerization of 4 and 5; Synthesis of Polyferrocenylsilanes 7 and 8 with Acetylenic Side Groups. The presence of acetylenic functionalities might be expected to hinder the metal-catalyzed ROP of [1]ferrocenophanes due to strong coordination to catalytically active species, or side reactions.[20] However, we found that acetylide-substituted sila[1]ferrocenophane **4** was readily polymerized in toluene solution via the addition of a solution of platinum-divinyltetramethyldisiloxane complex in xylene, hereafter referred to as the "Pt^0 catalyst" (ca. 0.3 mol % Pt). The reaction mixture was observed to gradually change color from red to deep orange and was allowed to stir for ca. 16 h. The polymerization mixture was precipitated into rapidly stirred methanol and was washed multiple times with hexanes (to remove low molecular weight species). After workup, the air- and moisture-stable **7** was obtained in high yield (93%) (Scheme 2). Analysis by gel permeation chromatography (GPC) of the light

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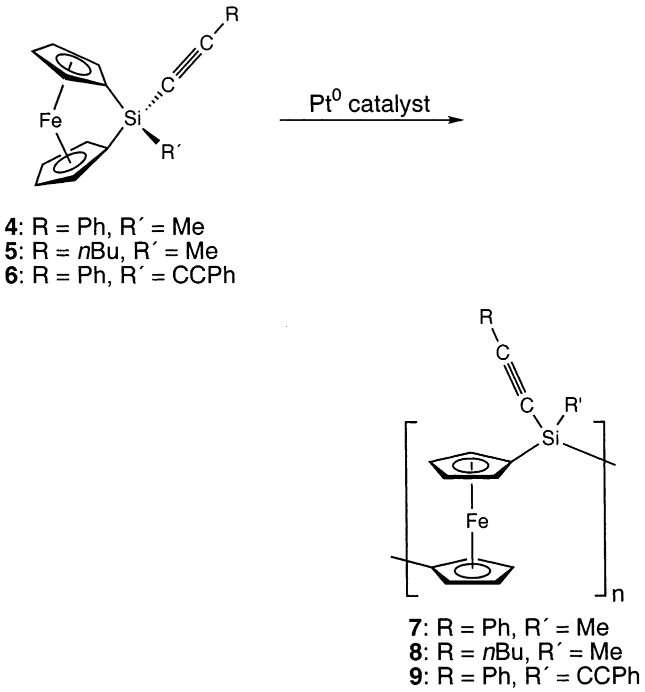
Scheme 2. Polymerization of 4−6 with a Pt^0 Catalyst; Synthesis of Polyferrocenylsilanes 7−9



orange polymer **7** gave a value for the M_n of 1.64×10^5 Da and a PDI of 1.6.[21]

The multinuclear NMR data were consistent with the formation of an atactic polymer. Five separate resonances were observed in the Cp region of the ^{1}H NMR spectrum ($\delta = 4.56-4.34$ ppm). The ^{13}C NMR spectrum showed a complicated pattern of resonances in the Cp region ($\delta = 74.8-73.0$ ppm) as well as a set of signals in a 1:2:1 intensity pattern due to triad resolution for the Si-Me resonance at ca. $\delta = -0.6$ ppm. The ^{29}Si NMR spectrum was also consistent with the formation of an atactic polymer.[22] A poorly resolved (even after 25 840 repetitions of a DEPT pulse sequence) but recognizable three signals in a 1:2:1 ratio due to triad resolution were detected centered at $\delta = -23.8$ ppm.

Analogous to the synthesis of **7**, a solution of the Pt^0 catalyst in xylene (ca. 0.3 mol % Pt) was added to a stirred toluene solution of **5**. The solution was again observed to gradually change color from red to deep orange, and the light orange fibrous material isolated was dried under high vacuum to give the air-stable polyferrocene **8** in good yield (67%) (Scheme 2). Analysis by GPC gave a value for the M_n of 1.21×10^6 and a PDI of 1.6.

The multinuclear NMR data were again consistent with the formation of an atactic polymer. Five separate resonances were observed in the Cp region of the ^{1}H NMR spectrum ($\delta = 4.56-4.32$ ppm). The ^{13}C NMR spectrum showed multiple resonances in the Cp region ($\delta = 74.5-72.8$ ppm) as well as the expected resonances corresponding to the hexynyl substituent. A resonance at $\delta = -0.2$ ppm for the methyl group on silicon was observed. Due to the atactic nature of the polymer, this signal did not appear as a singlet; however it was not fully resolved into individual signals. The ^{29}Si NMR spectrum was also consistent with the formation of an atactic polymer. Three poorly resolved signals in a 1:2:1 intensity ratio characteristic of triad resolution were observed at a chemical shift centered at $\delta = -25.2$ ppm. This polymer has previously been prepared from the reaction of Li[C≡C(CH$_2$)$_3$CH$_3$] with the Si−Cl functionalities on the backbone of polymer **1** (R = Me, R′ = Cl) synthesized via the thermal ROP of **2a**.[18] NMR spectral data for the polymers were very similar for the two methods of preparation. However, the major difference between the two methods was in the molecular weight (**8**: $M_n = 1.2 \times 10^6$; substitution onto **2a**, $M_n = 5.0 \times 10^4$) and PDI (**8**: 1.6; substitution onto **1** (R = Me, R′ = Cl), 2.6). The higher molecular weight and lower PDI achieved in this study clearly show the advantages of this new route over the previously reported synthesis of **8** from substitution onto PFS **1** (R = Me, R′ = Cl).

Transition Metal-Catalyzed Polymerization of 6; Synthesis of Polyferrocenylsilane 9 with Two Acetylenic Functionalities at Silicon. The polymerization of bis(phenylacetylenyl)sila[1]ferrocenophane **6** was also explored. Analogous to the previous polymerization studies, a solution of Pt^0 catalyst in xylene (ca. 0.3 mol % Pt) was added to a stirred C$_6$D$_6$ solution of **6**, that was then stirred for a further ca. 20 h. Ring-opened polymer **9** was isolated after workup as a light orange fibrous material in good yield (86%) (Scheme 2).

The multinuclear NMR data were consistent with the formation of **9**. Only two signals were observed in the Cp region ($\delta = 4.93$, 4.79 ppm), as is typical for symmetrically substituted polyferrocenylsilanes. The ^{29}Si NMR spectrum showed a single resonance at a chemical shift of $\delta = -44.3$ ppm (cf. monomer **6**, $\delta = -54.2$ ppm). In addition, GPC measurements showed that **9** was of high molecular weight ($M_n = 7.68 \times 10^4$, PDI = 1.5) but significantly lower than that of polymers **7** and **8**.

Isolation of Cyclic Dimer 10 Formed as a Byproduct from the ROP of 4. Interestingly, when the polymerization of **4** was conducted in THF instead of toluene, a red crystalline material, **10**, was isolated from the supernatant after precipitation of the polymer into hexanes. The ^{1}H NMR spectrum showed four multiplets in the Cp region (**10**, $\delta = 4.90$, 4.47, 4.33, 4.24 ppm; cf. **4**, $\delta = 4.51$, 4.44, 4.40, 3.91 ppm). The resonance corresponding to the Si-Me group was observed at a chemical shift of $\delta = 0.75$ ppm, which is downfield shifted from that of the monomer **4** ($\delta = 0.61$ ppm) and only slightly upfield from that of the high polymer **7** ($\delta = 0.81$ ppm). The ^{29}Si NMR spectrum showed a single resonance at a chemical shift of $\delta = -24.3$ ppm, which is again downfield shifted from that of the monomer **4** ($\delta = -27.8$ ppm) and only slightly upfield from the chemical shift of the silicon atoms in the backbone of the polymer **7** ($\delta = -23.8$ ppm). The EI mass spectrum of the material showed a peak at 656 amu, which corresponds to a M$^+$ ion for a cyclic dimer structure.

To confirm the nature of the product, a single-crystal X-ray diffraction study was performed on crystals isolated from slow evaporation of a saturated hexanes solution of **10**. See Figure 3a for the molecular structure of **10** and Table 3 for selected bond lengths and angles.

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(21) See the Experimental Section for details on the GPC procedure.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for 10

Si(1)−C(1)	1.845(3)	C(1)−Si(1)−C(11)	116.18(13)	C(22)−C(23)−C(24)	176.7(3)
Si(2)−C(6)	1.848(3)	C(6)−Si(2)−C(16)	112.32(13)	C(31)−C(32)−C(33)	177.8(3)
Si(1)−C(11)	1.848(3)	C(21)−Si(1)−C(22)	107.96(15)	α_1	−10.3(3)
Si(2)−C(16)	1.851(3)	C(30)−Si(2)−C(31)	107.07(14)	α_2	1.7(2)
C(22)−C(23)	1.203(4)	Si(1)−C(22)−C(23)	173.1(3)		
C(31)−C(32)	1.203(4)	Si(2)−C(31)−C(32)	176.4(3)		

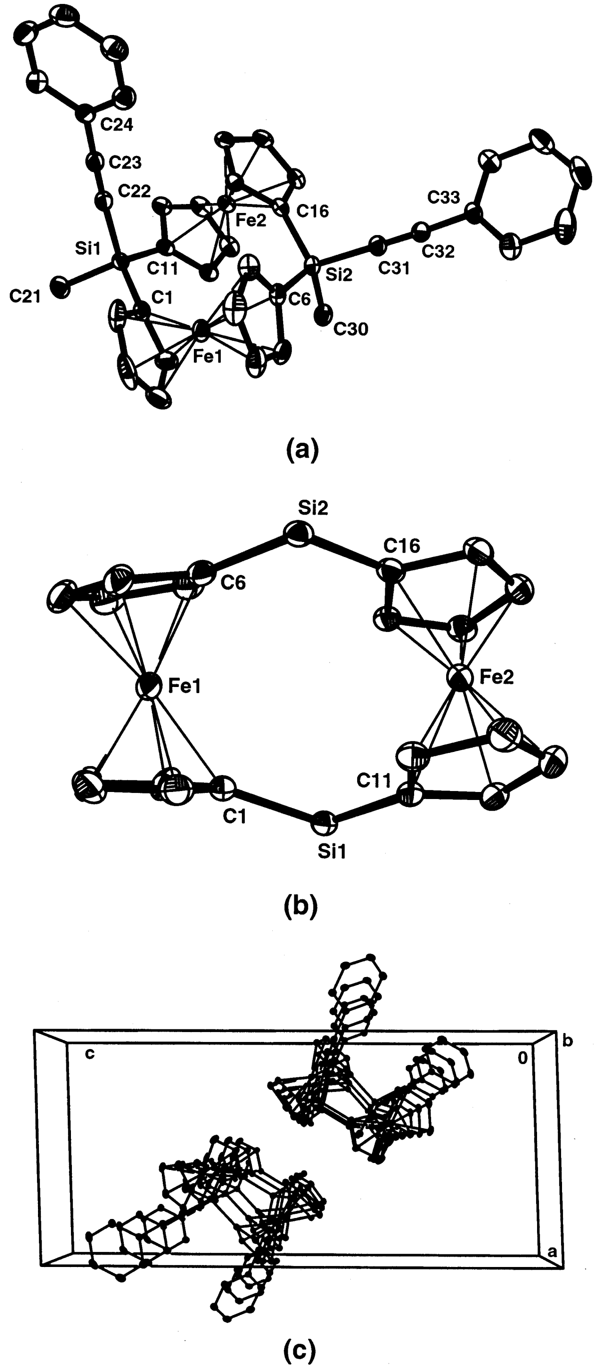

Figure 3. (a) Molecular structure of **10** (thermal ellipsoids at 30% probability, hydrogen atoms have been removed for clarity). (b) The ferrocene unit (left) showing a ring tilt of −10.3(3)° (thermal ellipsoids at 30% probability, substituents on silicon and hydrogen atoms removed for clarity). (c) Cell-packing diagram for **10** down the *a* axis (thermal ellipsoids at 10% probability, hydrogen atoms have been removed for clarity).

Table 4. Summary of the Results Obtained for the Polymerization of 4 in Toluene, CH_2Cl_2, and THF

solvent (volume)[a]	polymer:dimer[b]	M_n (Da × 10^5)[c]	M_w (Da × 10^5)[c]	PDI[c]
toluene (1 mL)	11.3:1	3.40	6.04	1.8
toluene (2 mL)	9.9:1	4.00	6.58	1.7
CH_2Cl_2 (1 mL)	9.9:1	3.27	5.41	1.7
THF (1 mL)	5.9:1	2.74	4.68	1.7
THF (4.5 mL)	1.9:1	1.79	3.08	1.8
THF (20 mL)	0.7:1	1.43	2.32	1.6

[a] Volume/50 mg of **4**. [b] Obtained from an average of the values obtained from integration of both the Me and Ph ^{1}H NMR signals arising from **7** and **10** in reaction mixtures of the polymerization of **4**. [c] Obtained from GPC analysis of isolated **7**.

The X-ray data confirmed the molecular structure of **10** to be a cyclic dimer existing in the conformation where the substituents on Si are in a *cis* orientation and the molecule in the *anti*-conformation (i.e., that in which the ring resembles the chair conformation of cyclohexane). A similar dimer (**11**) has been reported in the reaction mixture when **2** (R = R′ = Me) has been polymerized via metal-catalyzed ROP.[6a] The X-ray structure of **11** was obtained after synthesis by a separate route.[23] The Si−C_{ipso} distances in **10** (av = 1.85 Å) are slightly but significantly shorter than the corresponding distances in **4** (av = 1.88 Å). The C_{ipso}−Si−C_{ipso} angles in **10** of 116.18(13)° and 112.32(13)° are substantially more obtuse than the corresponding angle in **4** (96.50(13)°), indicating a loss of ring strain in the transition from monomer to cyclic dimer. Of particular interest is the fact that there is significant tilting of the Cp rings of **10** in the solid state structure. One of the ferrocene units (containing Fe2) possesses virtually planar rings (ring tilt = 1.7(2)°), and the other (containing Fe1) has a ring tilt of 10.3(3)° in the manner opposite that found in [1]ferrocenophanes (see Figure 3b). The dimethyl analogue **11** shows a symmetric ring tilt of 4.9(3)° in the manner opposite that found in [1]ferrocenophanes.[23] The unsymmetrical tilting found in the solid state structure of **10** is then most likely due to a factor other than the conformational requirements of the ring. Also of note are the torsional angles indicating the twisting of the Cp rings within each ferrocene unit. For the ferrocene moiety with an α angle of 1.7° the Cp rings were measured to be rotated 76.2° with respect to each other. The Cp rings of the other ferrocene unit were rotated by 34.5° with respect to each other. This is also in contrast to dimer **11**, which displays torsional angles of only 13.2(5)°.[23] The most likely cause of this structural distortion in **10** lies in the preference of the phenylacetylene moieties to pack efficiently in the solid state, so that they are aligned down the *a* axis (see Figure 3c).

As the initial results for the polymerization of **4** were intriguing, especially with respect to the fact that only

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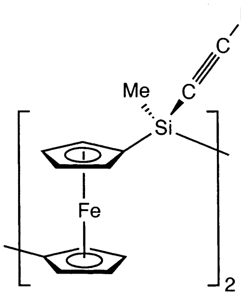
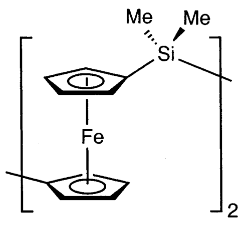
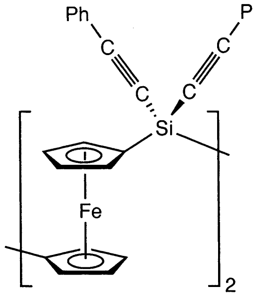
(23) (a) Zechel, D. L.; Foucher, D. A.; Pudelski, J. K.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1995**, 1893. (b) The structure of **11** was reported independently by an alternate route, see: Park, J.; Seo, Y.; Cho, S.; Whang, D.; Kim, K.; Chang, T. *J. Organomet. Chem.* **1995**, *489*, 23. The analogue with bridging $SiCl_2$ groups has also been structurally characterized and shown to possess a small symmetric ring tilt of 3.5°. See ref 8i.



10



11



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the *cis* form of cyclic dimer **10** was isolated, we decided to investigate this reaction further. Emphasis was placed on determining if the dimer was formed stereoselectively (or if the isolation of the *cis* form was due to differential crystallization) and if there was indeed a solvent and concentration effect on the ratio of dimer **10** to polymer **7**.

Detailed Studies of the ROP of 4: Influence of Solvent and Concentration on the Ratio of High Polymer 7 to Cyclic Dimer 10. We first decided to explore the influence of the nature of solvent on the ratio of high polymer **7** to cyclic dimer **10** and the molecular weight of the isolated polymer **7**. A series of polymerizations (2−3 per solvent) were set up using a constant ratio of monomer **4**, solvent volume, and catalyst. The solvents selected were toluene, CH_2Cl_2, and THF. The results of this study are summarized in Table 4.

The results of this study clearly show that the product distribution arising from **7** is highly solvent dependent. The levels of cyclic dimer **10** are highest when the polymerization is conducted in THF, which is presumably why this red crystalline material was not observed to form from the supernatants of the precipitation steps of the initial studies of the polymerization carried out in toluene. The molecular weight of the isolated polymer **7** was not significantly different (within GPC error, ca. 10%) for polymerizations conducted in toluene and CH_2Cl_2; however, in the case of THF, significantly lower molecular weight material was isolated.

The transition metal-catalyzed ROP of **4** was also conducted at two concentrations in toluene and three in THF. The results of this study (summarized in Table 4) indicate that there is a significant concentration dependence for the product distribution. This effect was observed for both THF and toluene. Interestingly, even when the polymerization was carried out at extreme dilution in THF (50 mg/20 mL), a small amount of high polymer **7** was formed (ca. 31% yield by ^{1}H NMR), although at this concentration unreacted monomer **4** is present (ca. 25% yield) even after 22 h. The major component of the reaction mixture was the *cis* form of cyclic dimer **10** (ca. 44% yield). Importantly, no other species were detectable in either the ^{1}H or ^{29}Si NMR spectrum.[24] Since no signals within the NMR detection limit assignable to the *trans* form of cyclic dimer **10** were observed under any experimental conditions studied, we conclude that the dimerization is highly stereoselective, strongly favoring the *cis* form.

Detailed Studies of the ROP of 6; Influence of the Presence of Two Phenyl Acetylene Substituents. As high polymer **7** was shown to be atactic, the only step that appears to proceed with stereoselectivity in the polymerization of **4** is the formation of the cyclic dimer, **10**. It is likely that the geometry of an intermediate or transition state highly favors addition of a molecule of **4** in one particular orientation due to the steric asymmetry of its substituents: the long rigid phenyl acetylene group and the small, approximately spherical methyl group. If the second addition of a molecule of **4** to the site for the initiated polymer chain (presumably at the surface of a Pt colloid)[9] is less favorable in the *trans* configuration for steric reasons, then the polymerization of **6** should proceed much less efficiently than the polymerization of **4**, as two long rigid phenyl acetylene substituents are present. We therefore examined the ROP of **6** in further detail to evaluate any evidence for such behavior.

(i) Polymerization of 6 in Toluene and THF. To allow a quantitative comparison of the ROP behavior of **6** with that of **4**, a polymerization study was performed under conditions identical to that previously used for the latter in toluene (Table 4, entry 2). After 18.5 h, analysis by ^{1}H NMR spectroscopy showed the presence of three sets of signals in the Cp region (the resonances in the Ph region were overlapping and, therefore, not resolvable into the individual components of the product mixture). The most intense set ($\delta = 4.93$, 4.79 ppm) was assigned to the high polymer **9**, and signals corresponding to unreacted monomer **6** ($\delta = 4.49$, 4.43 ppm) were also observed. A new set of signals observed at chemical shifts of $\delta = 5.10$ and 4.33 were also detected and were assigned to a cyclic dimer **12** (cf. **10** $\delta = 4.90$, 4.47, 4.33, 4.24 ppm). Integration of the resonances gave a ratio of 9.8:0.95:1 for the reaction mixture components **9**:**6**:**12**. The ratio of polymer to dimer was similar to the value obtained for the polymerization of **4** in toluene at the same dilution after 16 h (ratio of polymer **7** to dimer **10** was 9.9:1); however, two important differences were noted. First, the presence of residual monomer after a period of ca. 20 h was observed only in the case of the polymerization of **4** at high dilution in THF. Second, the molecular weight of the polymer **9** isolated from the ROP of **6** was substantially lower than that of **7** formed under identical conditions, and the distribution was found to be bimodal in nature (**9**: fraction 1: $M_n = 5.9 \times 10^4$, PDI = 2.1, $DP_n = 1.4 \times 10^2$; smaller fraction 2: $M_n = 1.8 \times 10^3$, PDI = 1.5, $DP_n = 4$; **7**: $M_n = 4.0 \times 10^5$, PDI = 1.7, $DP_n = 1.2 \times 10^3$).

In the case of the polymerization of **4**, changing the solvent to THF and diluting the reaction mixture was

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[24] We have previously found that the *cis* and *trans* forms of the cyclic dimers formed in the metal-catalyzed ROP of **2a** have significantly different ^{1}H and ^{29}Si NMR spectra. See: ref 18.

observed to increase the amount of cyclic dimer **10**. We therefore performed a ROP experiment for a dilute solution of **6** in THF. Upon stirring for 18.5 h, no color change was noted. Analysis by ^{1}H NMR spectroscopy of the product mixture showed that the major component was unreacted **6** with smaller resonances assigned to polymer **9**. Integration of the signals showed that the ratio of monomer **6** to polymer **9** was 8.2:1; that is, the conversion to polymer was only ca. 11%. Upon dropwise addition of the reaction mixture into stirred hexanes, very little precipitate was observed to form, and only trace amounts of high polymer **9** were isolated. The molecular weight of this isolated polymer was shown to be low compared to that of **7** formed under similar conditions and the distribution was bimodal (fraction 1: $M_n = 2.7 \times 10^4$, PDI = 1.6, DP$_n$ = 65; smaller fraction 2: low molecular weight oligomers, $M_n < 1000$).

(ii) Polymerization of 6 in C_6D_6 Monitored by NMR. The results of the aforementioned polymerization studies of **6** suggested that the ROP proceeded with less efficiency than that of **4**. To provide convincing additional support for this assertion, we undertook a comparative investigation of the polymerization of **6** and **4** using ^{1}H NMR to monitor the course of the reaction.

A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a solution of **4** in C_6D_6 in an NMR tube. After a 40 min period, an ^{1}H NMR spectrum was taken, and integration of the Ph resonances showed a 6.2:1.0:1.2 ratio for the components **7**:**4**:**10** present in the product mixture. This corresponds to a ca. 88% conversion of monomer **4** into dimer **10** and high polymer **7** at this time. An additional NMR spectrum taken after 3 h 40 min showed that no residual **4** was present, and the ratio of **7** to **10** was 5.0:1.

When an analogous experiment was performed with **6**, after 40 min, ^{1}H NMR analysis involving integration of the Cp resonances showed a 1:2.7:0.1 ratio between the components **9**:**6**:**12** present in the product mixture. This corresponds to a ca. 29% conversion of monomer **6** into dimer **12** and high polymer **9** at this time. After 2 h 40 min NMR showed a ratio for **9**:**6**:**12** of 1.0:1.4:0.1, corresponding to a ca. 44% conversion of **6** into products. An additional NMR spectrum after a 24 h period showed the ratio of **9**:**6**:**12** to be 8.5:1.3:1.1, corresponding to a ca. 88% conversion to products. The same conversion for **4** was achieved after 40 min.

These results confirmed that the polymerization of **6** proceeds much slower than the polymerization of **4** under identical conditions. The results for the ROP of **6** in toluene also show that, in comparison to the ROP of **4**, the molecular weight of the resultant polyferrocenylsilane is significantly lower. Very low conversion of **6** into oligomers/polymer was observed in dilute THF solution, which is again different from the polymerization of **4** under analogous conditions which proceeds with ca. 75% conversion. We tentatively explain the stereoselective formation of the *cis* dimer **10** from **4** in terms of the existence of a sterically preferred mode of addition of the second molecule of monomer **4** to the site for the growing polymer chain. Clearly, this effect is more pronounced at the initial stage of chain growth than at the later stages in the polymerization, as high polymer **7** is atactic. We propose that this might be a consequence of the reduction of steric hindrance at the active catalytic center as the metallamacrocyclic polyferrocenylsilane chains grow larger.[9] In the case of **6**, there is no preferred mode of addition, as two acetylenic substituents are present. The result is a more sluggish ROP process.

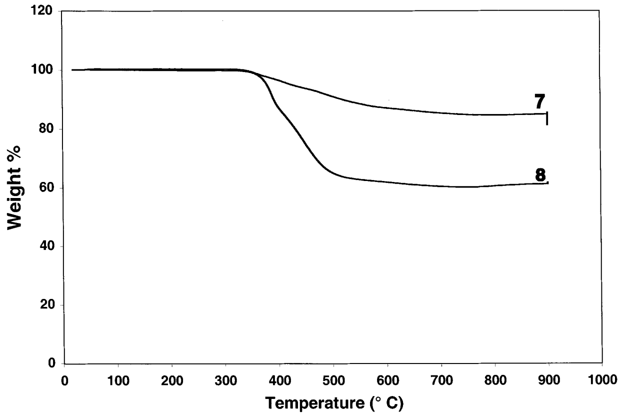

Figure 4. TGA traces of polymers **7** and **8**.

Thermogravimetric Analysis (TGA) Studies of Compounds 7 and 8. Polyferrocenylsilanes have been shown to be of utility in the formation of shaped and patterned ceramics which display tunable magnetic properties via pyrolysis.[8m,25−27] However, to date, the pyrolysis of soluble polyferrocenylsilane homopolymers has produced ceramic materials only in relatively low yield.[27] The high ceramic yields needed for shape retention in the pyrolysis process have been achieved only through the use of thermally polymerizable cross-linkable monomers (e.g., **2**, R, R′ = μ-(CH$_2$)$_3$).[25] Unfortunately, the cross-linked polymer network formed initially is insoluble, which does not lend well to solution or melt-processing techniques.

As acetylenic groups have been shown to provide an effective site for thermal cross-linking of organometallic oligomers and polymers[28] while leaving the precursor polymer soluble at ambient temperature, we decided to investigate the pyrolysis of PFSs **7** and **8** by TGA under an N$_2$ flow.

As shown in Figure 4, relatively high ceramic yields are formed in each case (for **7**, 81%; for **8**, 61%). In both cases, the temperature at which significant weight loss begins is ca. 350 °C, and the temperature at which loss of volatile material ceases is ca. 600 °C. As expected, the ceramic yield of the polymer containing phenyl substituents was higher than that containing the aliphatic butyl group. Encouragingly, both ceramics took the shape of the polymer initially placed in the TGA pan,

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(25) MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I. *Science* **2000**, *287*, 1460.

(26) Ginzburg, M.; MacLachlan, M. J.; Yang, S. M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Herber, R. H.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 2625.

(27) (a) Ceramic yields of 45% (1000 °C, 4 h) have been detected for poly(ferrocenylmethylvinylsilane). See: Petersen, R.; Foucher, D. A.; Tang, B.-Z.; Lough, A.; Raju, N. P.; Greedan, J. E.; Manners, I. *Chem. Mater.* **1995**, *7*, 2045. (b) The insoluble PFS poly(ferrocenyldihydrosilane) has a ceramic yield of 63% at 1000 °C. See: Pudelski, J. K.; Rulkens, R.; Foucher, D. A.; Lough, A. J.; Macdonald, P. M.; Manners, I. *Macromolecules* **1995**, *28*, 7301.

(28) See: (a) Corriu, R. J. P.; Devylder, N.; Guerin, C.; Henner, B.; Jean, A. *J. Organomet. Chem.* **1996**, *509*, 249. (b) Houser, E. J.; Keller, T. M. *Macromolecules* **1998**, *31*, 4038.

and both were attracted to a bar magnet, which is highly interesting for potential materials applications.[25]

Summary

Sila[1]ferrocenophanes with acetylenic substituents (**4**−**6**) have been prepared in good yields from silicon-bridged [1]ferrocenophanes with Si−Cl moieties. These monomers have been shown to undergo facile transition metal-catalyzed ROP in the presence of a platinum catalyst to give high molecular weight polyferrocenylsilanes (**7**−**9**) with acetylenic substituents. Significantly, the presence of C≡C bonds in the monomers led to no detrimental effects on the ROP process. Cyclic dimer **10** was isolated from the polymerization mixture derived from **4** and was shown to possess an interesting solid state structure whereby one of the ferrocene moieties possessed a ring tilt of −10.3(3)°. The ratio of cyclic dimer **10** to high polymer **7** was shown to be highly solvent dependent, with the most dimer formed in THF solution at dilute concentrations. Work is currently underway in our laboratory which aims to explore the reactivity of monomers **4**−**6** and polymers **7**−**9** toward transition metal complexes with the goal of producing highly metallized monomers and polymers as well as ceramics derived therefrom.

Experimental Section

The Pt^0 catalyst used in these studies, platinum-divinyltetramethyldisiloxane complex (2.1−2.4 wt % in xylene), was obtained from Gelest and used as purchased. Phenylacetylene and 1-hexyne were obtained from Aldrich, distilled under partial vacuum, and stored under an atmosphere of N_2. **2a** and **2b** were synthesized according to literature procedures.[18]

Most reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox. Solvents were distilled from Na and stored under N_2. The air- and moisture-stable polymers **7**−**9** and cyclic dimer **10** were handled under air with ACS grade solvents after workup. ^1H NMR spectra (400 MHz), ^{13}C NMR spectra (100.4 MHz), and ^{29}Si NMR spectra (79.3 MHz) were recorded on a Varian Unity 400 spectrometer. All solution ^1H and ^{13}C NMR spectra were referenced internally to protonated solvent shifts. ^{29}Si NMR spectra were referenced externally to $SiMe_4$. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in electron impact (EI) mode. The calculated isotopic distribution for each ion was in agreement with experimental values. Molecular weight estimates were obtained via gel-permeation chromatography (GPC) using a Waters Associates 2690 Separations Module equipped with a column heater, Ultrastyragel columns with pore sizes of 10^3−10^5 Å, an in-line degasser, and a differential refractometer. The GPC possesses a triple detection system (refractive index, light scattering, viscosity) such that absolute molecular weights are reported. A flow rate of 1.0 mL/min was used, and the eluent was THF. Polystyrene standards purchased from American Polymer Standards were used for calibrating the instrument response. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer TGA-7 analyzer under nitrogen at a heating rate of 10 °C/min. Elemental analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ.

Synthesis of 4. In a typical reaction, *n*BuLi (2.2 mL, 1.6 M in hexanes, 3.5 mmol) was added dropwise to a stirred 0 °C solution of phenylacetylene (0.39 g, 3.8 mmol) in 25 mL of Et_2O, and the reaction mixture was allowed to stir for an additional 15 min. In a separate flask **2a** (1.0 g, 3.8 mmol) was dissolved in Et_2O (50 mL), and the resulting solution was cooled to ca. −78 °C, and the LiC≡CPh suspension was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred for a further 1 h period, and filtered to remove the white (LiCl) precipitate, and all volatile material was removed under high vacuum. The red solid was recrystallized from hexanes/toluene (ca. 50:50) at −30 °C to give **4**, yield: 0.75 g (65%).

For **4**: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ 7.50−7.47 (m, 2 H, Ph), 6.95−6.92 (m, 3 H, Ph), 4.51 (m, 2 H, Cp), 4.44 (m, 2 H, Cp), 4.40 (m, 2 H, Cp), 3.91 (m, 2 H, Cp), 0.61 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 132.5, 129.2, 128.6 (Ph), 123.0 (*ipso*-Ph), 107.7 (Ph*C*CSi), 89.7 (PhC*C*Si), 78.21, 78.17, 76.7, 74.6 (Cp), 30.4 (*ipso*-Cp), −3.0 (Me); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −27.8; MS (70 eV, EI) *m*/*z* (%) 328 (100) [M^+], 313 (13) [$M^+ - CH_3$]. Anal. Calcd for $C_{19}H_{16}FeSi$: C 69.51, H 4.92. Found: C 69.13, H 4.39.

Synthesis of 5. In a typical reaction, *n*BuLi (11.3 mL, 1.6 M in hexanes, 18.1 mmol) was added dropwise to a stirred 0 °C solution of 1-hexyne (1.56 g, 2.18 mL, 19.0 mmol) in 30 mL of Et_2O and allowed to stir for a further 15 min. In a separate flask **2a** (5.0 g, 19.0 mmol) was dissolved in Et_2O (200 mL) and cooled to ca. −78 °C, and the LiC≡CBu suspension was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h, followed by removal of all volatile material under high vacuum. The residue was dissolved in a minimal amount of hexanes, filtered through a fritted glass disk to remove the LiCl, and crystallized at −55 °C to give **5**, yield: 2.67 g (48 %). The yield could be increased by concentration of the supernatant and subsequent crystallization at −55 °C.

For **5**: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ 4.51 (m, 2 H, Cp), 4.45 (m, 2 H, Cp), 4.38 (m, 2 H, Cp), 3.90 (m, 2 H, Cp), 2.07 (tr, $J(H_{CH2}, H_{CH2}) = 6.8$ Hz, 2 H, CH_2-italic: $C\mathit{H_2}CH_2CH_2CH_3$), 1.33 (m, 4 H, $CH_2C\mathit{H_2}C\mathit{H_2}CH_3$), 0.76 (tr, $J(H_{CH3}, H_{CH2}) = 7.2$ Hz, 3 H, $CH_2CH_2CH_2C\mathit{H_3}$), 0.58 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 110.2 (*C*CSi), 80.2 (C*C*Si), 78.1, 78.0, 76.6, 74.7 (Cp), 31.2 (*ipso*-Cp), 30.7 ($\mathit{C}H_2CH_2CH_2CH_3$), 22.1 ($CH_2\mathit{C}H_2CH_2CH_3$), 19.8 ($CH_2CH_2\mathit{C}H_2CH_3$), 13.6 ($CH_2CH_2CH_2\mathit{C}H_3$), −2.8 (Me); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −29.1; MS (70 eV, EI) *m*/*z* (%) 308 (100) [M^+]. Anal. Calcd for $C_{17}H_{20}FeSi$: C 66.22, H 6.55. Found: C 66.07, H 6.47.

Synthesis of 6. *n*BuLi (6.6 mL, 1.6 M in hexanes, 10.6 mmol) was added dropwise to a stirred 0 °C solution of phenylacetylene (1.2 mL, 10.9 mmol) in ca. 25 mL of Et_2O and allowed to stir for an additional 15 min. In a separate flask **2b** (1.53 g, 5.4 mmol) was dissolved in Et_2O (ca. 50 mL) and cooled to ca. −78 °C, and the LiC≡CPh suspension was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred for a further 1 h period, and filtered to remove the white precipitate, and all volatile material was removed under high vacuum. The red solid was recrystallized from CH_2Cl_2/hexanes (25:75) at −30 °C to give **6**, yield: 1.05 g (47%).

For **6**: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ 7.42−7.40 (m, 4 H, Ph), 6.95−6.86 (m, 6 H, Ph), 4.49 (m, 4 H, Cp), 4.43 (m, 4 H, Cp); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 132.7, 129.5, 128.5 (Ph), 122.5 (*ipso*-Ph), 108.1, (Ph*C*CSi), 86.9 (PhC*C*Si), 78.7, 75.6 (Cp), 28.2 (*ipso*-Cp); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −54.2; MS (70 eV, EI) *m*/*z* (%) 414 (100) [M^+].

Polymerization of 4. In a typical reaction, a solution of Pt^0 catalyst in xylenes (ca. 0.3 mol % Pt) was added to a stirred solution of **4** (1.5 g, 4.6 mmol) in toluene (ca. 25 mL). After 1 h time a color change from red to orange was noted. The reaction mixture was allowed to stir for ca. 20 h, after which time the solution was precipitated into stirred methanol. The light orange precipitate was washed three times with hexanes and was dried under high vacuum to give the light orange powder **7**, yield: 1.4 g (93%).

For **7**: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ 7.58−7.57 (m, 2 H, Ph), 6.96−6.95 (m, 3 H, Ph), 4.56 (br s, 4 H, Cp), 4.51 (br s, 1 H, Cp), 4.50 (br s, 1 H, Cp), 4.37 (br s, 1 H, Cp), 4.34 (br s, 1 H, Cp), 0.81 (s, 3 H, Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20 °C) δ 132.3, 128.9, 128.7 (Ph), 123.7 (*ipso*-Ph), 106.8, (Ph*C*CSi), 93.5 (PhC*C*Si), 74.8−73.0 (m, Cp), 69.1 (*ipso*-Cp), −0.6 (Me); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −23.8 (3 poorly resolved signals in a 1:2:1 intensity pattern due to atacticity of polymer); UV−vis (25 °C, THF) λ 447 nm, ϵ 1.7 × 10^2 L mol^{-1} cm^{-1}; GPC $M_n = 1.64 \times 10^5$; $M_w = 2.61 \times 10^5$; PDI = 1.6. Anal. Calcd for $(C_{19}H_{16}FeSi)_n$: C 69.51, H 4.92. Found: C 69.80, H 4.53.

Polymerization of 5. In a typical reaction, Pt^0 catalyst in xylenes (ca. 0.3 mol % Pt) was added to a stirred solution of **5** (0.30 g, 0.97 mmol) in toluene (ca. 2 mL). After 1 h time a color change from red to orange was noted. The reaction mixture was allowed to stir a further 18 h, after which time the solution was precipitated into stirred methanol. The light orange precipitate was washed three times with hexanes and was dried under high vacuum to give the orange gummy polymer **8**, isolated yield: 0.20 g (67%).

For **8**: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 4.56, 4.54, 4.48, 4.35, 4.32 (br s, Cp), 2.17, (br tr, 2 H, $CH_2CH_2CH_2CH_3$), 1.52−1.36 (m, 4 H, $CH_2CH_2CH_2CH_3$), 0.84 (br m, 3 H, $CH_2CH_2CH_2CH_3$), 0.79 (br s, 3 H, Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20 °C) δ 108.8 (Bu*C*CSi), 83.4 (BuC*C*Si), 74.5, 74.2, 72.8 (Cp), 69.8 (*ipso*-Cp), 31.1 ($CH_2CH_2CH_2CH_3$), 22.3 ($CH_2CH_2CH_2CH_3$), 20.0 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$), −0.2 (m, Me); ^{29}Si{^{1}H} NMR (79.3 MHz, C_6D_6, 20 °C) δ −25.2 (3 poorly resolved signals in a 1:2:1 intensity pattern due to atacticity of polymer); GPC $M_n = 1.21 \times 10^6$; $M_w = 1.80 \times 10^6$; PDI = 1.6. The GPC trace and the molecular weight value did not change significantly upon dilution of the sample, which rules out artifacts caused by aggregation.

Polymerization of 6. In a typical reaction, a solution of Pt^0 catalyst in xylenes (ca. 0.3 mol % Pt) was added to a stirred solution of **6** (0.050 g, 0.12 mmol) in C_6D_6 (ca. 1 mL). After 1 h time a color change from red to orange was noted. The reaction mixture was allowed to stir for ca. 20 h, after which time the solution was precipitated into stirred methanol. The light orange precipitate was washed three times with hexanes and was dried under high vacuum to give the light orange powder **9**, yield: 43 mg (86%).

For **9**: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 7.56−7.50 (m, 4 H, Ph), 6.94−6.88 (m, 6 H, Ph), 4.93 (br s, 4 H, Cp), 4.79 (br s, 4 H, Cp); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20 °C) δ 132.5, 129.1, 128.6 (Ph), 123.2 (*ipso*-Ph), 107.2, (Ph*C*CSi), 90.6 (PhC*C*Si), 75.4, 74.3 (Cp), 66.9 (*ipso*-Cp); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −44.3; GPC (polystyrene calibration) $M_n = 7.68 \times 10^4$; $M_w = 1.13 \times 10^5$; PDI = 1.5.

Cyclic Dimer 10 Isolated as a Byproduct of the Polymerization of 4. In one case, a significant amount of red crystalline material was obtained from condensation of the hexanes washes from the precipitation of the polymerization reaction mixture. The yield of high molecular weight polymer isolated was correspondingly lower. For this experiment, 0.46 g (1.4 mmol) of **4** was dissolved in THF (ca. 5 mL). Pt^0 catalyst (ca. 0.3 mol % Pt) was added to the stirred solution, and the reaction mixture was allowed to stir for a further 16 h. Precipitation into stirred hexanes followed by three hexanes washes resulted in the isolation of a light orange precipitate, which was dried under high vacuum to give 0.26 g (57% yield) of the high polymer **7**. Condensation of the supernatant from the initial precipitation along with the collected hexanes washes resulted in the isolation of a red crystalline material, **10**: yield = 0.10 g (22%). Crystals of suitable quality for single-crystal X-ray diffraction were grown from slow evaporation of a saturated hexanes solution of **10** at 25 °C.

For **7**: $M_n = 1.69 \times 10^5$; $M_w = 2.75 \times 10^5$; PDI = 1.6.

For **10**: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 7.41−7.39 (m, 4 H, Ph), 6.95−6.84 (m, 6 H, Ph), 4.90 (m, 4 H, Cp), 4.47 (m, 4 H, Cp), 4.33 (m, 4 H, Cp), 4.24 (m, 4 H, Cp), 0.75 (s, 6 H, Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20 °C) δ 132.2, 128.6, 128.5 (Ph), 123.8 (*ipso*-Ph), 106.4, (Ph*C*CSi), 94.2 (PhC*C*Si), 75.6, 74.2, 71.9, 71.4 (Cp), 69.3 (*ipso*-Cp), 2.8 (Me); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −24.3; UV−vis (25 °C, THF) λ 467 nm, ϵ 3.6 × 10^2 L mol^{-1} cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 656 (41) [M$^+$]. Anal. Calcd for $C_{38}H_{32}Fe_2Si_2$: C 69.51, H 4.92. Found: C 69.66, H 4.83.

Polymerization of 4 in Toluene, CH_2Cl_2, or THF. A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a stirred solution of **4** (50 mg, 0.15 mmol) in the appropriate solvent (toluene, 1 or 2 mL; CH_2Cl_2, 1 mL; THF, 1 or 4.5 mL). The polymerizations were allowed to stir for a further 16 h at room temperature. A sample was taken at this time for analysis by ^{1}H NMR spectroscopy. The remaining reaction mixture was precipitated into stirred methanol, the supernatant discarded, and the fibrous orange polymer washed twice with fresh methanol and dried under high vacuum. The polymerization was performed twice at each concentration. Yields: $\mathbf{7}_{\mathbf{tol-1mL}}$ = 27 mg (72%); $\mathbf{7}_{\mathbf{tol-2mL}}$ = 30 mg (80%); $\mathbf{7}_{\mathbf{CH2Cl2-1mL}}$ = 21 mg (56%); $\mathbf{7}_{\mathbf{THF-1mL}}$ = 17 mg (45%); $\mathbf{7}_{\mathbf{THF-4.5mL}}$ = 15 mg (40%).[29]

Polymerization of 4 in Dilute THF Solution. A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a stirred solution of **4** (50 mg, 0.15 mmol) in THF (20 mL). The polymerization was allowed to stir for a further 22 h at room temperature before all volatile material was removed under high vacuum. The residue was taken up in C_6D_6 and analyzed by NMR (^{1}H, ^{29}Si). Spectroscopic yields (^{1}H NMR): $\mathbf{7}_{\mathbf{20mL}}$ = 31%; $\mathbf{10}_{\mathbf{20mL}}$ = 44%; unreacted **4** = 25%.

Polymerization of 6 in Toluene. A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a stirred solution of **6** (25 mg, 0.06 mmol) in toluene (1 mL). The polymerization was allowed to stir for a further 18.5 h at room temperature, whereupon the color was observed to change from red to orange. A sample was taken at this time for analysis by ^{1}H NMR spectroscopy. The remaining reaction mixture was precipitated into stirred hexanes, the supernatant discarded, and the fibrous orange polymer washed twice with fresh hexanes and dried under high vacuum. Isolated yield: $\mathbf{9}_{\mathbf{1mL}}$ = 10 mg (53%).[29] $M_{n1} = 5.9 \times 10^4$, $M_{w1} = 1.3 \times 10^5$, PDI = 2.1; $M_{n2} = 1.8 \times 10^3$, $M_{w2} = 2.7 \times 10^3$, PDI = 1.5.

Polymerization of 6 in THF. A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a stirred solution of **6** (50 mg, 0.12 mmol) in THF (5 mL). The polymerization was allowed to stir for a further 18.5 h at room temperature, whereupon the color was observed to remain red during this period of time. A sample was taken at this time for analysis by ^{1}H NMR spectroscopy. The remaining reaction mixture was precipitated into stirred hexanes, the supernatant discarded, and a very small amount of orange polymer was isolated on a fritted glass disk. This material was washed with fresh hexanes and dried under high vacuum. Yield: $\mathbf{9}_{\mathbf{5mL}}$ = trace. $M_{n1} = 2.7 \times 10^4$, $M_{w1} = 4.4 \times 10^4$, PDI = 1.6; $M_{n2} = 8.1 \times 10^2$, $M_{w2} = 1.9 \times 10^3$, PDI = 2.3.

Polymerization of 4 in C_6D_6 Monitored by NMR. A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a solution of **4** (25 mg, 0.08 mmol) in C_6D_6 (0.5 mL) in an NMR tube. The contents of the tube were mixed well and the tube placed in a sonication bath to ensure adequate mixing of the components. After a 40 min period, a ^{1}H NMR spectrum was taken, and integration of the Ph resonances showed a 6.2:1.0:1.2 ratio between the **7**:**4**:**10** present in the product mixture. This corresponds to a ca. 88% conversion of monomer **4** into dimer **10** and high polymer **7** at this time. An additional NMR spectrum taken after 3 h 40 min showed that no residual **4** was present, and the ratio of **7** to **10** was 5.04:1.

Polymerization of 6 in C_6D_6 Monitored by NMR. A solution of Pt^0 catalyst in xylenes (ca. 0.3 mol %) was added to a solution of **6** (8 mg, 0.02 mmol) in C_6D_6 (0.5 mL) in an NMR tube. The contents of the tube were mixed well and the

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(29) These yields are calculated on the basis of the fact that 25% of the solution was removed for analysis by ^{1}H NMR spectroscopy.

Table 5. Crystal Data and Structure Refinement

	4	**6**	**10**
formula	$C_{19}H_{16}FeSi$	$C_{26}H_{18}FeSi$	$C_{38}H_{32}Fe_2Si_2$
M_r	328.26	414.34	656.52
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/c$
a, Å	10.5076(3)	14.5767(3)	12.2437(3)
b, Å	12.2932(5)	10.45430(10)	9.5283(3)
c, Å	23.8440(9)	13.1120(3)	26.9516(6)
α, deg	90	90	90
β, deg	90	92.2280(10)	91.824(2)
γ, deg	90	90	90
V, $Å^3$	3079.98(19)	1996.62(6)	3142.63(14)
Z	8	4	4
ρ_{calc}, g cm^{-3}	1.416	1.378	1.388
μ(Mo Kα), mm^{-1}	1.046	0.823	1.026
$F(000)$	1360	856	1360
cryst size, mm	0.30 × 0.24 × 0.13	0.30 × 0.20 × 0.18	0.23 × 0.20 × 0.02
θ-range, deg	3.07−27.48	2.80−27.53	2.62−25.01
no. of reflns collected	14 891	20 743	17 513
no. of ind reflns	3521	4568	5513
abs corr	multiscan	multiscan	semiempirical
max. and min. transmn coeff	0.8760 0.7443	0.8659 0.7903	0.9798 0.7983
no. of params refined	192	254	382
GoF on F^2	1.020	1.032	1.037
R1[a] ($I > 2\sigma(I)$)	0.0445	0.0346	0.0401
wR2[b] (all data)	0.1179	0.0926	0.0910
peak/hole (e $Å^{-3}$)	0.420/−0.397	0.285/−0.394	0.267/−0.399

[a] $R1 = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

tube placed in a sonication bath to ensure adequate mixing of the components. After a 40 min period, a ^{1}H NMR spectrum was taken, and integration of the Cp resonances showed a 1:2.7:0.11 ratio between the **9**:**6**:**12** present in the product mixture. This corresponds to a ca. 29% conversion of monomer **6** into dimer **12** and high polymer **9** at this time. An NMR spectrum taken after 2 h 40 min showed a ratio for **9**:**6**:**12** of 1.0:1.4:0.10, corresponding to a ca. 44% conversion of **6** into products. An additional NMR spectrum after a 24 h period showed the composition to consist of a ratio of 8.5:1.3:1.1 for **9**:**6**:**12**, corresponding to a ca. 88% conversion to products.

X-ray Structural Characterization. A summary of selected crystallographic data are given in Table 5. Data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A combination of 1° phi and omega (with kappa offsets) scans was used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[30]

The structures were solved and refined using the SHELXTL\PC V5.1[31] package. Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-190582 (**4**), CCDC-190583 (**6**), and CCDC-190584 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for compounds **4**, **6**, and **10** including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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