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Polyferrocenyldisiloxane from the Platinum-Catalyzed Reactions of Tertiary Bis(dimethylsilyl)ferrocene in a Polar Aprotic Solvent

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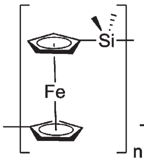
The development of high yield routes to polymers containing inorganic elements in the main chain continues to represent an important synthetic challenge. In the past 15 years, one of the most successful strategies toward this goal has been the ring-opening polymerization (ROP) of thermally or photochemically labile monomers.[1,2] The majority of these chain-growth inorganic polymers, such as polyferrocenylsilanes (**1**), are isolated in good yield with narrow polydispersities and high molecular weights ($> 1 \times 10^6$ Da). By contrast, only low to moderate molecular weight inorganic polymers have been prepared by step-growth polymerization methods. A variety of different condensation and coupling routes yielding low and moderate molecular weight polymetallocenes bearing a repeat unit of ferrocene and optionally a bridging group have been reported. These include the metal-mediated Ullmann coupling of dihaloferrocenes leading to low molecular weight ($< 1 \times 10^4$ Da) polyferrocenes (**2**)[3,4] and the polymerizations of 1,1′-ferrocenyl diacids[5] or 1,1′-bis(dimethylsilylamine)ferrocenes[6] with disilanols. This later process yields low molecular weight ($< 1 \times 10^4$ Da) hydrolytically unstable polyferrocenylsilyl esters (**3**) and thermally and moisture resistant moderate molecular weight (5.1×10^4 Da) polyferrocenylsiloxanes (**4**). More recently, the metal-catalyzed hydrosilylation reactions of 1,1′-bis(dimethylsilyl)ferrocene with alkynes[7] or alkenes[8] to prepare low molecular weight ($< 1 \times 10^4$ Da) materials such as poly{ferrocene(phenylene)bis(silylenevinylene)}s (**5**) have been disclosed.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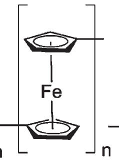
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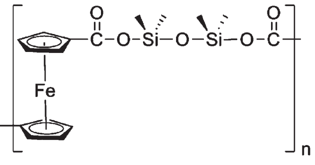
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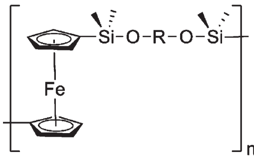
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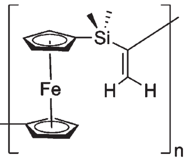
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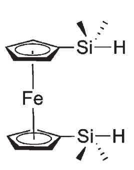
The redox-active ferrocene units of these polymers typically impart thermal and hydrolytic stability to the backbone, while the overall physical properties of these materials are dominated by the chemical nature of the bridging group. As a result, these polymetallocenes are often isolated in a wide range of physical forms ranging from gums and elastomers, to film forming materials, to insoluble powders.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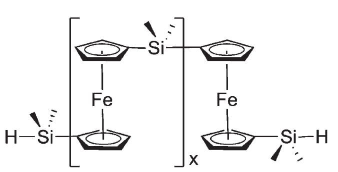
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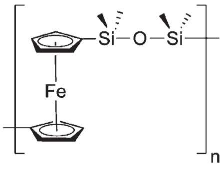
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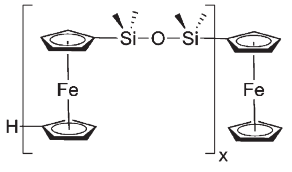
9a, x = 1, 9b, x = 2, 9c, x = 3

Our interest in polyferrocenes stems from the need to develop readily scalable step-growth routes to ferrocene polymers containing group 14 bridging elements. To that end, we have recently investigated the dehydrogenative coupling behavior of 1,1′-bis(dimethylsilyl)ferrocene, **6**, under solvent-free conditions which leads to the isolation of oligoferrocenylsilanes (**7a**, **7b**) containing a single silane bridge.[9] We now report an evaluation of the ambient and elevated temperature Pt-catalyzed reactions of **6** in two oxygen-containing polar aprotic solvents: DMF and DMSO (Scheme 1).

After 24 h, the ambient temperature Pt-catalyzed DMF solutions of **6** showed no changes (^{1}H NMR spectroscopy) but upon heating were observed to darken in color and increase in viscosity over the reaction period (7 days). Analysis of these reaction mixtures (^{1}H NMR) confirmed the absence of Si−H groups and appearance of new resonances corresponding to the polyferrocenyldisiloxane **8**, linear oligoferrocenyldisiloxanes **9a**−**c**, and cyclic ferrocenyldisiloxanes **10** and **11a**−**c**. The ^{1}H NMR (400 MHz, $CDCl_3$ solution) spectrum for isolated polymer **8** (vide infra) is shown in Figure 1 and displays two characteristic broad Cp proton resonances at $\delta_H = 4.24$ and 4.09 ppm and a single methyl resonance at $\delta_H = 0.40$ ppm integrating in the expected ratio (1:1:3). The ^{29}Si NMR chemical shift resonance at $\delta_{Si} = +0.48$ ppm is also typical of other model ferrocenyldisiloxanes.[10]

The DMF reaction mixtures using different catalyst ratios were likewise precipitated into an excess of MeOH. The recovered gummy polymer products (**8**) ranged in absolute molecular weights from 1×10^4 to 1×10^5 Da (Figure 2 and Table 1).

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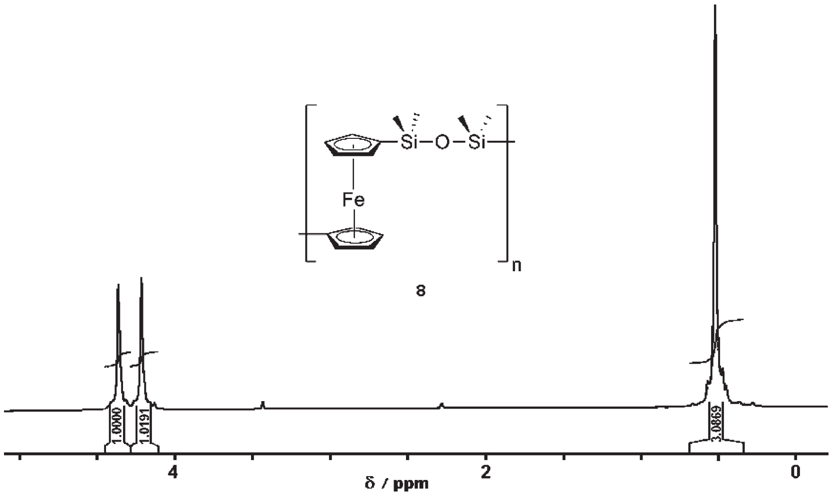
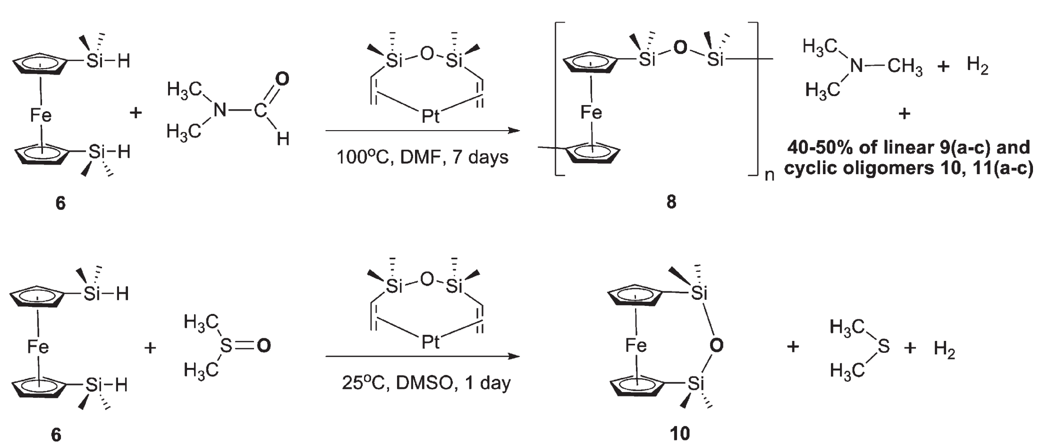
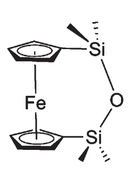


Figure 1. The 400 MHz ^1H NMR ($CDCl_3$) of polymer **8**.

Scheme 1. Overall reactions of 6 in DMF and DMSO Solvents Leading to the Polyferrocenyldisiloxane 8 and the Disiloxane-Bridged [3]Ferrocenophane 10



Low molecular weight linear ferrocenyldisiloxanes **9** and cyclic ferrocenyldisiloxanes **10** and **11** were also detected (MALDI-TOF MS) in crude reaction mixtures and recovered in a 40−50% yield from the supernatant solution following precipitation. Additionally, there was no evidence (NMR, MS) of either inter- or intramolecular dehydrogenative coupling to give the bridged disilane **12** or polymer **13**.



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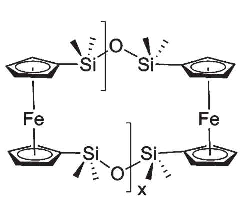
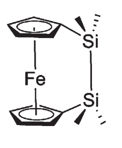


11a, x = 1, 11b x = 2, 11c, x = 3



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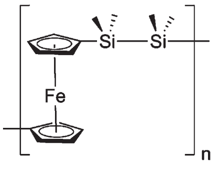

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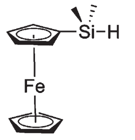

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A recent report[11] of the dehydrocoupling of **6** to yield the disilane bridged polymer **13** using a Fe catalyst (DMF) has been found to be in error. Our current efforts,[12] a reinterpretation of the original report,[13] and others[14] have now correctly identified the polyferrocenyldisiloxane **8** as the main product of those reactions, along with detectable quantities of NMe_3 and $H_2(g)$.[11] It is of interest to note that ambient Fe-catalyzed (1:25 [cat.]/[monomer]) UV-irradiated polymerizations of **6** yields low molecular weight polymer **8** in high yield after 24 h, whereas the thermally Pt-catalyzed reactions of **6** (1:92, 1:209, 1:357 [cat.]/[monomer]) in DMF convert more slowly over a longer period (in lower yield) to give substantially higher molecular weight polymer products. The mechanism of oxygen atom abstraction and subsequent polymerization to **8** with both the Pt and Fe catalysts in DMF requires further investigation, as it appears to occur without proceeding through a silanol intermediate.[15] By contrast, the byproduct of the Pt-catalyzed coupling reactions of **6** in DMSO-d_6 solution at both ambient and elevated temperature (100 °C) have resonances that have been identified (NMR) as free H_2 (s, $\delta_H = 5.53$ ppm) and the residual deuterated dimethyl sulfide (br s, $\delta_H = 2.04$ ppm).[16]

Plausible reaction schemes for the coupling of **6** in DMF and DMSO as solvents are shown in Scheme 1. Surprisingly, the disiloxane-bridged [3]ferrocenophane **10** was isolated as the exclusive product of the ambient and higher temperature reactions carried out in DMSO solution. At elevated temperatures, elimination of $H_2(g)$ in the presence of the Pt catalyst likely results in the reduction of DMF to NMe_3.[11] Similarly, in DMSO solutions, the reaction proceeds with the evolution of $H_2(g)$ and the subsequent reduction of DMSO to Me_2S. This type of solvent

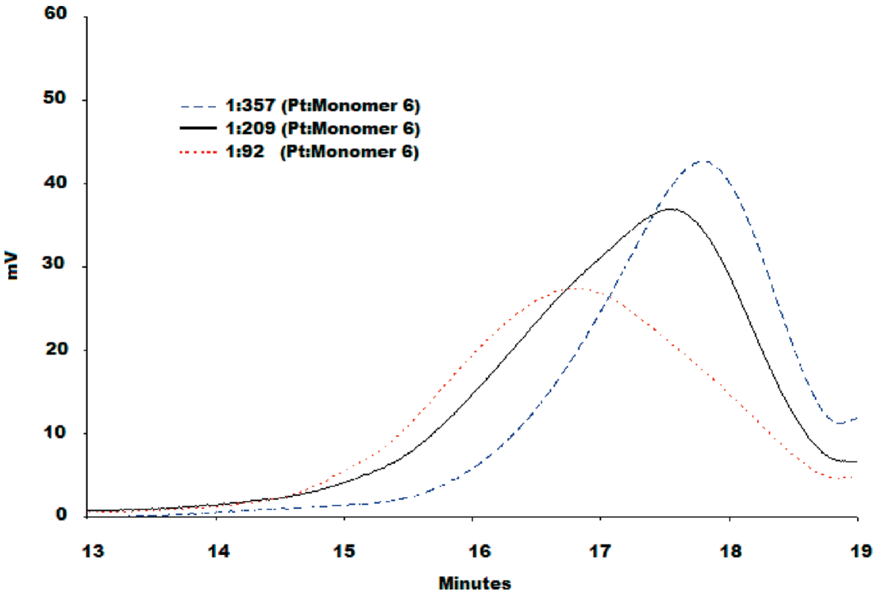

Figure 2. GPC traces of polymer **8** prepared at three catalyst concentration ratios.

Table 1. Molecular Weights and Thermal Transitions for Silicon-Containing Ferrocene Polymers

polymer	[cat.] (mmol)	ratio [cat.]/[**6**]	M_w	M_n	PDI	T_g/T_m (°C)[f]
8[a]	0.041 (Pt);	1:81	12 620	8 390	1.50	−25/np
8[a]	0.009 (Pt);	1:357	50 040	34 590	1.45	−28/np
8[a]	0.017 (Pt);	1:209	103 740	92 300	1.12	−30/np
8[a]	0.037 (Pt);	1:92	80 290	41 280	1.94	−27/np
8[b]	0.20 (Fe);	1:25	8 870	6 560	1.35	nr/nr
4[c]			46 800	18 080	2.59	nr/75−80
1[d]			87 100	76 700	1.14	33/143
PDMS[e]			> 300 000			−120/np

[a] This work. [b] Reference 11. [c] Reference 6. [d] Reference 18. [e] Reference 19. [f] np = not present, nr = not reported.

reduction in the presence of organosilanes (R_nSiH_{4-n}) with a Pt catalyst at ambient temperature in DMSO has been previously reported by Lukevits and co-workers, who described the stoichiometric conversion of such organosilanes to disiloxanes.[17] Attempts at the preparation of disiloxanes from the ambient Pt-catalyzed reactions of silanes in DMF by these same workers were unsuccessful.

As shown in Table 1, modest molecular weights of polymer **8** were obtained using DMF as the reaction media. Condensation polymerizations (including the one used to produce polymer **4**)[6] typically eliminate small molecule species (e.g., H_2O, MeOH, or $HNMe_2$) and yield polymers with polydispersities > 2.0. The GPC traces (Figure 2) of **8** at different catalyst concentrations were monomodal and the polydispersities (Table 1) < 2.0. Despite the elimination of H_2(g) small molecule during the reaction, the metal-mediated behavior suggests a chain-growth polymerization rather than a condensation pathway. Unfortunately, the extended reaction periods and high temperatures required for polymerizations in DMF render these protocols unsuitable for a high yield synthesis of **8**. Polymer **8** was invariably isolated as an amorphous dark brown-orange sticky gum in a 50−60% yield. By comparison, the semicrystalline polyferrocenylsiloxanes **4** prepared by Pittman and co-workers contained less flexible spacer groups and were isolated as powders.[6] Glass transitions (T_g's) were not reported for these ferrocenyldisiloxane polymers. The T_g (−28 ± 3 °C) recorded for **8** is considerably lower than the T_g (33 °C) observed for dimethylpolyferrocenylsilane[18] (**1**) but still > 90 °C higher when compared to the parent dimethylsiloxane polymer (PDMS).[19]

Analysis of the supernatant residues from the reaction of **6** (DMF) indicates that there is a significant amount (up to 40−50%) of oligoferrocenyldisiloxanes **9**, **10**, and **11** also formed in these reactions. These materials are likely the result of the reaction of the Si−H groups of **6** with end-capping species, such as the monosilylated ferrocenylsilane **14**. Alternatively, such products may result due to ring-closure (backbiting) of the growing polymer chains which could prematurely terminate these reactions. No Si−H bonds were observed in the analysis of these reaction mixtures (^1H NMR). The MALDI-TOF MS (see Supporting Information, Figure 11S) of the reaction mixture revealed a series of linear oligomeric ferrocenyldisiloxanes **9** with up to eight ferrocene units along with detectable traces of other cyclics which were not isolated. Similar phenyl end-capped oligoferrocenylsiloxanes were first reported by Schaaf in the 1960s but were not characterized by NMR methods.[20] To better quantify the nature of these residuals, as well as to assist in the modeling of polymer **8**, a series of oligoferrocenylsiloxanes **9a**−**c** were isolated from the Pt-catalyzed reaction of equimolar amounts of **6** and **14** (DMF). Additionally, **9a** was prepared (54% yield) from the Pt-catalyzed reaction of **14** (DMF) at elevated temperature. Initial purification by column chromatography removed unreacted starting materials and separated the crystalline biferrocene **9a**. Identification of **9a** was made by comparison of the ^1H and ^{29}Si NMR spectra with that of published data for this compound.[21,22] A further separation of the higher molecular weight oligomeric materials from the Pt-catalyzed equimolar reactions of **6** and **14** (DMF) by preparative TLC afforded the trimer **9b** and tetramer **9c** (Figure 3) in decreasing relative yields. Oligomers **9b** and **9c** were readily characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and further confirmed via HR-MS.

Our investigation found that the reaction **6** with Karstedt's catalyst in DMF solutions at elevated temperatures yielded a linear polyferrocenyldisiloxane **8** and shorter chain linear and cyclic oligoferrocenylsiloxanes **9a**−**c**, **10**, and **11a**−**c**. Polymerization

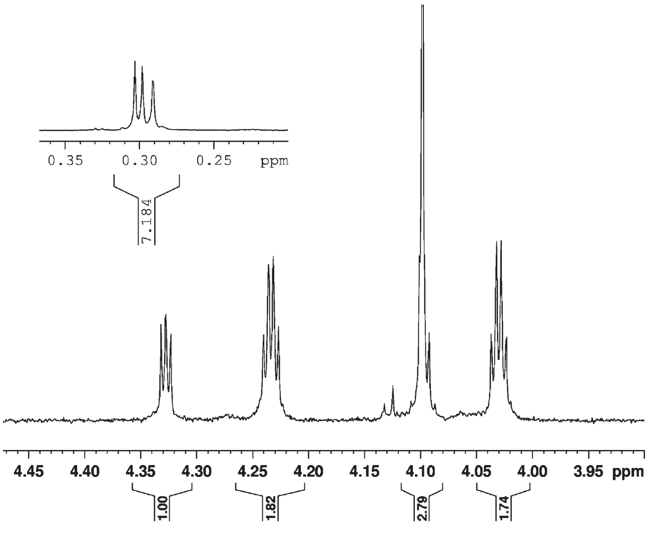

Figure 3. The 400 MHz ^{1}H NMR (CDCl$_3$) of **9c** of the Cp and methyl regions (inset).

is consistent with a concomitant oxidation of the ferrocenylsilane and the stoichometric reduction of the solvent. The Pt-catalyzed coupling reactions of **6** in DMSO solutions proceed much more quickly than in DMF solutions under ambient or elevated temperatures. These reactions lead exclusively to the intramolecular cyclization to **10** rather than polymerization or partial conversion to **8** in DMSO. Absolute molecular weights for the polyferrocenyldisiloxanes (**8**) range from 12.5 to 103 kDa and are isolated as low-T_g polymeric gums. Future efforts will be directed to the coupling of other hydride-containing group 14 ferrocene monomers, the influence of a broad range of different coupling catalysts, and the use of other 1,4-type silane monomers in polar aprotic solvents to optimize yields of such metal-containing siloxane polymers.

Experimental Section

Equipment and Procedures. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. ^{1}H and ^{13}C were referenced internally to the deuterated solvent resonances, while ^{29}Si was referenced to TMS. Mass spectrometry were performed at the University of Toronto AIMS Laboratory with a Waters GC TOF mass spectrometer with EI/CI sources mass spectrometer in electron impact mode. The calculated isotopic distribution for each ion was in agreement with experimental values. Elemental analysis was performed by Analest laboratories at the University of Toronto. Absolute molecular weights of the polyferrocenylsiloxane **8** were determined by gel permeation chromatography (GPC) using a Viscotek Triple model 302 detector system equipped with a refractive index detector (RI), a four capillary differential viscometer (VISC), a right angle (90°) laser light scattering detector ($\lambda_0 = 670$ nm), and a low angle (7°) laser light scattering detector. GPC columns were calibrated versus polystyrene standards (American Polymer Standards). A flow rate of 1.0 mL/min was used with ACS grade THF as the eluent.

Materials. Solvents were dried by standard procedures prior to use. Dimethylchlorosilane and Karstedt's catalyst (2.0% in xylenes) were purchased from Sigma-Aldrich and used as received. Dilithioferrocene·TMEDA was prepared according to a literature procedure.[23] 1,1′-Bis(dimethylsilyl)ferrocene (**6**), isolated as a red oil, was prepared by a previous literature route[23] and purity confirmed in relation to previously published data.[24] Product **6** was purified by multiple vacuum distillations (150 °C, $P = 5\times10^{-3}$ mmHg) to remove unreacted ferrocene and **14**. For **6**: ^{29}Si NMR (C$_6$D$_6$): $\delta_{Si} = -18.58$ (s, *Si*Me$_2$H); $R_f = 0.82$ (3:1 *n*-hexane/CH$_2$Cl$_2$). Product **14** was also isolated as a red oil, and the characterization data for this product were in good agreement with published values.[25,26] For **14**: ^{29}Si NMR (C$_6$D$_6$): $\delta_{Si} = -18.38$ (s, *Si*Me$_2$H); $R_f = 0.82$ (3:1 *n*-hexane/CH$_2$Cl$_2$).

General Synthesis and Characterization of the Polyferrocenyldisiloxane 8 Prepared in DMF. In a 50 mL round-bottom flask equipped with condenser and stir bar, **6** (1.00 g, 3.31 mmol) in 10 mL of DMF and Karstedt's catalyst in xylenes (400 mg, 0.041 mmol of Pt) was added. The mixture was heated to 100 °C and left for 7 days. Initial purification was achieved by precipitation of the DMF solutions into an excess of MeOH. Further purification to remove traces of DMF was carried out by successive precipitation of CH$_2$Cl$_2$ solutions of crude **8** into an excess of MeOH. Polymer **8** was thus recovered as orange-brown sticky elastomer. Yield = 0.480 g (48%). Absolute M_w = 12, 620; M_n = 8390, PDI = 1.50. For **8**: isolated as gummy solid. ^{1}H NMR (C$_6$D$_6$): $\delta_H = 0.40$ (s, 12H, Si*Me*$_2$OSi*Me*$_2$), 4.09 (br s, 4H, Cp), 4.24 (br s, 4H, Cp). ^{13}C NMR (C$_6$D$_6$): $\delta_C = 1.37$ (s, 4C, Si*Me*$_2$), 68.49 (s, 2C *ipso*-Cp), 71.78 (s, 4C, Cp), 71.86 (s, 4C, Cp). ^{29}Si NMR (C$_6$D$_6$): $\delta_{Si} = 0.48$ (s, *Si*Me$_2$O*Si*Me$_2$). Anal. Calcd for C$_{14}$H$_{20}$OSi$_2$Fe: C 53.16, H 6.37%. Found: C 52.74, H 6.36%.

General Synthesis and Characterization of the Cyclic Ferrocenyldisiloxane 10 Prepared in DMSO at Elevated Temperature. In a 50 mL round-bottom flask equipped with condenser and stir bar, compound **6** (1.05 g, 3.32 mmol) in 10 mL of DMSO and Karstedt's catalyst in xylenes (0.041 mmol Pt) was added. The mixtures were heated to 100 °C and left for 2 days. After cooling the reaction mixture, a significant amount of crystalline materials was observed in the flask. GPC analysis of the reaction mixture did not detect polymer **8**. Purification was achieved by precipitation of the DMSO solutions into an excess of cold MeOH. This MeOH was removed (in vacuo), and 0.82 g of the crystalline solid **10** was recovered (78% yield). Analysis by HR-MS of the crystalline material confirmed compound **10** to be the exclusive product. Characterization data for **10** were in good agreement with published values.[10,21] ^{29}Si NMR (C$_6$D$_6$): $\delta_{Si} = -0.10$ (s, *Si*Me$_2$O*Si*Me$_2$). HR-MS EI$^+$: calcd for C$_{20}$H$_{14}$OSi$_2$Fe: 316.0402; found 316.0394 g mol^{-1}.

Synthesis and Characterization of the Cyclic Ferrocenyldisiloxane 10 prepared in Deutrated DMSO-*d*$_6$ at Ambient Temperature. In a Wilmad sealable NMR tube, 50 mg of compound **6** (0.016 mmol) in 1 mL of DMSO-*d*$_6$ (99%) and Karstedt's catalyst in xylenes (0.0002 mmol of Pt) was added. The ambient mixture was monitored by ^{1}H NMR several times over a 24 h period. ^{1}H NMR spectroscopy showed the loss of the Si−H resonance at $\delta_H = 4.65$ ppm and the detection of new resonances at $\delta_H = 5.53$ ppm (free H$_2$) and 2.05 ppm for the dimethyl sulfide as well as new peaks attributed to the cyclic ferrocenyldisiloxane **10**. No polymer (**8**) was detected in the work-up of the NMR solution.

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Supporting Information Available: A more detailed experimental section; NMR and MS spectral data for the oligomeric compounds **9a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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