The Nature of the Active Catalyst in Late Transition Metal-Mediated Ring-Opening Polymerization (ROP) Reactions: Mechanistic Studies of the Platinum-Catalyzed ROP of Silicon-Bridged [1]Ferrocenophanes

Karen Temple,[†] Frieder Jäkle,[†] J. B. Sheridan,*,[‡] and Ian Manners*,[†]

Contribution from the Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, Ontario, M5S 3H6, Canada, and Department of Chemistry, Rutgers University, The State University of New Jersey, University Heights, Newark, New Jersey, 07102

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Abstract: Current mechanisms for the transition metal-catalyzed ring-opening polymerization (ROP) of [1]-ferrocenophanes and related strained species such as cyclic carbosilanes invoke a homogeneous mechanism. In this paper we describe experiments which indicate that the Pt(0)-catalyzed ROP of silicon-bridged [1]-ferrocenophanes proceeds mainly by a heterogeneous mechanism with colloidal platinum as the catalyst. Mechanistic studies were initiated to elucidate the fate of the ferrocenylsilane component of the precatalyst, fcPt(1,5-cod)SiMe₂ (**4**) (fc = Fe(η^5-C₅H₄)₂), a proposed intermediate in the catalytic cycle for fcSiMe₂ (**1a**) with Pt(1,5-cod)₂ as the initiator. The ring-opened addition product Et₃SifcSiMe₂H (**6**) was isolated in high yield from the Pt(0)-catalyzed ROP of **1a** in the presence of 35-fold excess of Et₃SiH. Species **6** and Et₃SiH were subsequently employed as capping agents in the Pt(0)-catalyzed ROP of fcSiMePh (**1b**) to generate model oligomers, Et₃SifcSiMe₂(fcSiMePh)ₙH (**10**, $n \approx 20$) and Et₃Si(fcSiMePh)ₙH (**8**, $n \approx 7$), respectively. Copolymerization of a mixture of **1a** and **1b** using Pt(0) catalyst afforded a random copolymer (fcSiMe₂-*r*-fcSiMePh)ₙ (**9**). Comparative end-group analysis of **8**, **9**, and **10** was performed with the oligoferrocenylsilane synthesized via the ROP of **1b** in the presence of Et₃SiH initiated by the precatalyst **4**. Significantly, this revealed that the ferrocenyldimethylsilane component of **4** is *not* incorporated into the resultant polymer backbone which possessed the structure Et₃Si(fcSiMePh)ₙH (**8**). Similarly, the ROP of **1a** in the presence of Et₃SiH initiated by the precatalyst fcPt(1,5-cod)Sn(ᵗBu)₂ (**11**) gave end-capped oligomers Et₃Si(fcSiMe₂)ₙH (**5**), devoid of Sn(ᵗBu)₂ groups. The observations that the ferrocenylsilane and ferrocenylstannane components of **4** and **11** are not incorporated into the polyferrocene products and that, in addition, mercury was found to significantly retard ROP, indicates that the previously proposed homogeneous ROP mechanism is incorrect and that colloidal platinum is the main catalyst. A new heterogeneous mechanism for the platinum-mediated ROP of silicon-bridged [1]ferrocenophanes is proposed which is likely to have important implications for the metal-catalyzed ROP mechanisms for related species such as silacyclobutanes.

Introduction

Transition metal-catalyzed polymerization reactions are of widespread and growing importance in organic polymer synthesis. Recent innovations in this area include the development of late transition metal catalysts and metal-mediated atom transfer radical polymerization (ATRP) procedures that have revolutionized synthetic approaches to well-defined polyolefin architectures.[1] In contrast, metal-catalyzed routes to polymers containing inorganic elements have been much less explored. Early developments in this area were reported in the mid 1960s when it was demonstrated that the ROP of cyclic carbosilanes is catalyzed by a variety of late transition metal complexes.[2,3]

The resulting polycarbosilanes offer considerable potential as precursors to β-SiC ceramics and functionalized materials.[4] More recently, the transition metal-catalyzed dehydrocoupling of silanes and stannanes and the demethanative coupling of germanes have provided mild routes to σ-conjugated polymers based on Group 14 elements.[5−7] In addition, we have reported the rhodium-catalyzed heteronuclear dehydrocoupling of phosphine−borane adducts to afford high-molecular weight poly-phosphinoboranes [PRR′−BH₂]ₙ.[8,9] Catalytic processes involving the dehydrocoupling of silanols and silanes have also been developed.[10,11]

[†] University of Toronto.

[‡] Rutgers University.

(1) See, for example: (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 849. (b) Maynard, H. D.; Okada, S. Y.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6239. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169 and references therein. (d) Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2340. (e) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601.

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Despite the potential wealth of interesting properties associated with transition metal-based macromolecules, synthetic routes to these materials remain relatively elusive.[12] As a contribution to solving this problem, we have previously shown that strained [1]ferrocenophanes (e.g., **1a**) function as very convenient precursors to high-molecular weight polymetallocenes via thermal and anionic ROP.[13−15]

1a (R = R' = Me)
1b (R = Me, R' = Ph)

2a (R = R' = Me)
2b (R = Me, R' = Ph)
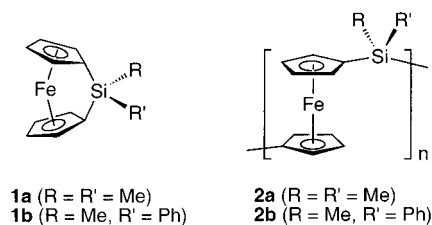
In view of the catalytic activity of Pt(0) complexes toward cyclic carbosilanes,[2,3] the transition metal-catalyzed ROP of the strained silicon-bridged [1]ferrocenophane (**1a**) has also been explored. Thus, in 1995, it was discovered that a variety of late transition metal complexes catalyze the ROP of **1a**, thereby offering a mild and convenient route to high polymer **2a** and, in some cases, with the cyclic dimer, [fcSiMe$_2$]$_2$ (fc = Fe(η^5-C$_5$H$_4$)$_2$), as a byproduct.[16,17] Catalysts include a variety of platinum and palladium complexes ranging from Pt(1,5-cod)$_2$, Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex), PtCl$_2$ and PdCl$_2$ to Rh(I) complexes, such as [Rh(coe)$_2$-(μ-Cl)]$_2$ (coe = cyclooctene). Moreover, the synthetic methodology has grown in importance as molecular weight control and access to block copolymers are possible.[18,19]

Since this discovery, efforts have been directed at unraveling the mechanism of these reactions. Previous mechanistic con-

Scheme 1
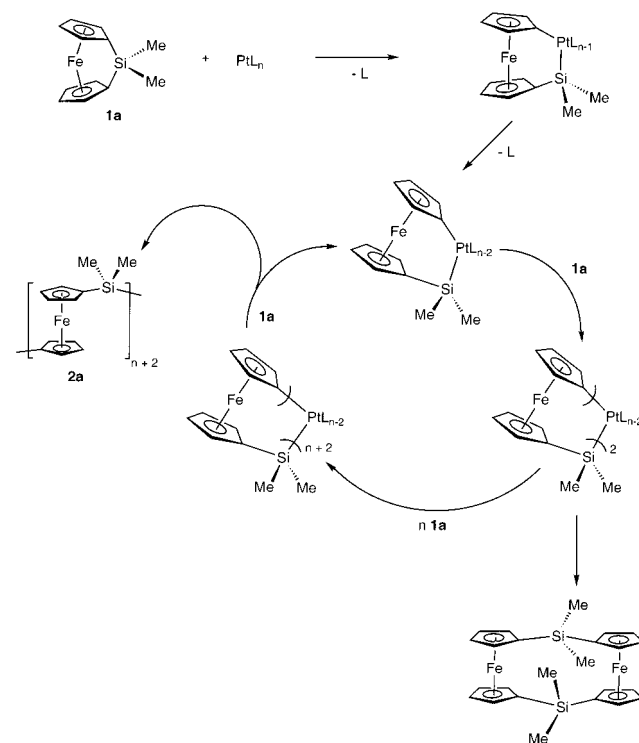
siderations for the transition metal-catalyzed ROP of cyclic carbosilanes has led to the suggestion of a homogeneous mechanism which involves an initial insertion of the metal into the strained Si−C bond of the heterocycle.[20,21] Indeed, Tanaka et. al. have reported oxidative-addition of a silacyclobutane to Pt(PEt$_3$)$_3$ affording the corresponding 2-platina-1-silacyclopentane containing a skeletal Pt(PEt$_3$)$_2$ fragment, and have observed the Pt(1,5-cod) analogue by NMR spectroscopy during the ROP.[21] Propagation was suggested to proceed through sequences of oxidative-addition and reductive-elimination processes involving the Si−C bonds or via σ-bond metathesis of the Pt−Si and Si−C bonds.[21] In light of this work, we previously proposed that the metal-mediated ROP of [1]silaferrocenophanes might proceed in an analogous manner (Scheme 1).[22,23]

Significantly, we have reported the oxidative-addition of Pt(PEt$_3$)$_3$ and Pt(1,5-cod)$_2$ to **1a** to afford the corresponding [2]platinasilaferrocenophanes, **3** and **4**.[22,24,25] We postulated that following dissociation of the remaining 1,5-cod ligand from the initial [2]platinasilaferrocenophane intermediate, consecutive oxidative-additions and reductive-eliminations (or σ-bond metathesis processes) at the metal center could lead to the formation of high-molecular weight **2a**.[26]

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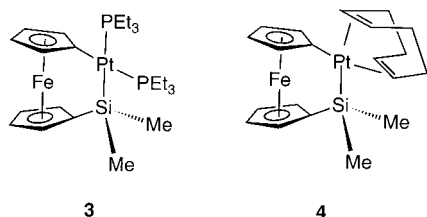(13) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

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(22) Sheridan, J. B.; Temple, K.; Lough, A. J.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 711.

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(25) Reddy, N. P.; Choi, N.; Shimada, S.; Tanaka, M. *Chem. Lett.* **1996**, 649.

3   **4**

In the proposed homogeneous mechanism, the ferrocenophane fragment of the precatalyst is incorporated into the polymer. This paper describes detailed mechanistic studies with particular emphasis on tracing the fate of the [2]platinasilaferrocenophane during the catalytic ROP of [1]silaferrocenophanes.

Results and Discussion

We have previously shown complex **4** to be an equally effective catalyst for the ROP of **1a** as the precursor, Pt(1,5-cod)$_2$.[22] Indeed, complex **4** has been detected in situ by ^{1}H NMR spectroscopy during the ROP of **1a** with Pt(1,5-cod)$_2$, suggesting involvement in the catalytic cycle. In contrast, **3** does not catalyze the ROP of **1a**, a fact attributed to the presence of more strongly coordinating phosphine ligands.[24] The importance of facile dissociation of the remaining ligands was convincingly illustrated by the complete lack of polymer formation when catalytic amounts of **4** were added to **1a** in neat 1,5-cod.[22] Furthermore, when used in conjunction with the phosphine abstraction reagent H$_3$B·THF, complex **3** is rendered catalytically active affording low-molecular weight, cyclic polymers.[23]

We have also shown that the addition of varying amounts of Et$_3$SiH to the Pt(0)-catalyzed reactions permits excellent chain-length control and yields the end-capped polymer **5** (eq 1).[18] In fact, desired molecular weights can be effectively targeted over the range $M_n = 2000-45\,000$. Significantly, the amount of Et$_3$-SiH added and the observed M_n do not accurately correlate with the molecular weight expected based on the actual stoichiometric monomer:Et$_3$SiH ratio used. In particular, the observed M_n value is greater than expected from the initial ratio of **1a**:Et$_3$SiH, suggesting that **1a** is more reactive than Et$_3$SiH toward the catalytic center. We previously proposed that oxidative-addition of the Si–H functionality to the catalytic center competes with the addition of the strained Si–Cp bond of **1a**. As the concentration of monomer decreases, Et$_3$SiH addition to the growing metallomacrocycle with the ensuing reductive-elimination was suggested to lead to the observed Et$_3$Si–C and Si–H chain ends.[18]

(1)

5
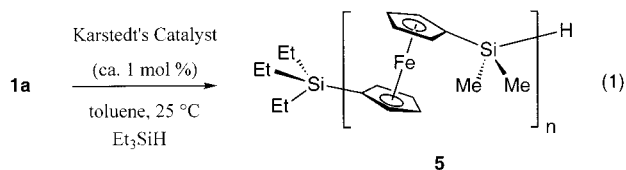
The starting point for the chemistry discussed in this paper involved an attempt to determine if a mono-addition product (i.e., **5** where $n = 1$) could be isolated when the platinum-catalyzed ROP reactions were conducted in the presence of a large excess of Et$_3$SiH.

1. Platinum-Catalyzed ROP of fcSiMe$_2$ (1a) in the Presence of a Large Excess of Et$_3$SiH: Synthesis and Characterization of Ring-Opened Addition Products Et$_3$SifcSiMe$_2$H (6) and Et$_3$Si(fcSiMe$_2$)$_2$H (7). Reaction of **1a** with a 35-fold

excess Et$_3$SiH in the presence of a catalytic amount of Pt(1,5-cod)$_2$ resulted in a color change from red to orange indicating the consumption of **1a**. Removal of the solvent afforded a highly viscous, deep red oil. Purification via column chromatography afforded the ring-opened mono-addition product **6** (87% yield), the end-capped dimer **7** (10% yield), and a very small quantity of higher oligomers (eq 2).

(2)

6 (major)

+

7 (minor)
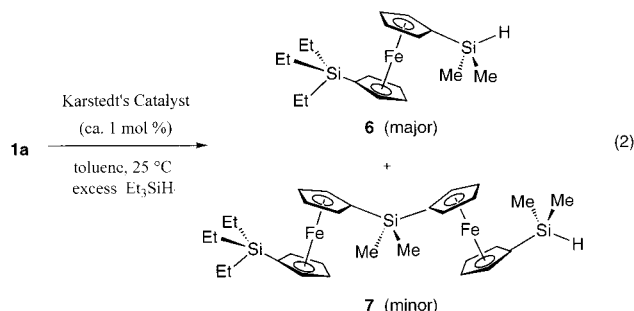
Multinuclear NMR spectroscopy and mass spectrometry confirmed the proposed structure of compound **6**. Significantly, the ^{29}Si NMR spectrum[27] showed signals corresponding to two silicon environments, namely Et$_3$*Si*fc ($\delta = 2.1$) and fc*Si*Me$_2$H ($\delta = -18.6$).

The ^{1}H NMR spectrum showed a heptet at $\delta = 4.70$, typical of Si–H groups, assigned to the Si–H proton of the fcSiMe$_2$*H* moiety. Further upfield, a doublet at $\delta = 0.28$ was assigned to the adjacent methyl groups, fcSi*Me*$_2$H. In addition, triplet and quartet resonances ($\delta = 1.06$ and 0.75) were attributed to the methyl and methylene protons of the triethylsilyl group, respectively. As expected, the protons of the cyclopentadienyl ligands were observed at four different frequencies. The ^{13}C NMR and mass spectra provided further evidence for the proposed structure, and the latter showed the presence of the molecular ion ($m/z = 358$).

The end-capped dimer (**7**) was also fully characterized by NMR and mass spectrometry. Thus, three resonances were observed in the ^{29}Si NMR spectrum, consistent with the formation of an Et$_3$SiH-capped dimer. The fc*Si*Me$_2$H and Et$_3$*Si*fc end groups were observed at $\delta = -18.6$ and 2.1, respectively, while the interior silicon atom was found to resonate at $\delta = -6.8$. The ^{1}H NMR spectrum showed distinctive resonances at $\delta = 0.28$ and 0.54, observed in a 1:1 ratio respectively, attributed to the terminal fcSi*Me*$_2$H and internal fcSi*Me*$_2$fc units of a dimeric structure. A characteristic heptet due to the Si–H moiety was observed at $\delta = 4.70$ and interestingly, eight unique sets of protons of the cyclopentadienyl ligands gave rise to resonances between $\delta = 4.02-4.28$. Analysis by ^{13}C NMR spectroscopy also showed eight signals for the corresponding carbon atoms between $\delta = 71.5-73.9$. Importantly, on comparison with **6**, an additional signal was detected upfield at $\delta = -0.7$ clearly due to the interior methyl groups. Mass spectrometric analysis provided further confirmation of the assigned structure with the detection of a molecular ion ($m/z = 600$).

Significantly, the recent isolation of the [2]platinasilaferrocenophane (**4**) and now also the ring-opened addition product (**6**) appeared to offer a unique opportunity to gain insight into the mechanism of the ROP of silicon-bridged [1]ferrocenophanes. Thus, we anticipated that end-group analysis of the resulting low-molecular weight end-capped oligo(ferrocenylsilane) from the ROP of **1b** using **4** as a precatalyst in the

(26) Manners, I. *Polyhedron* **1996**, *15*, 4311.

(27) See Supporting Information
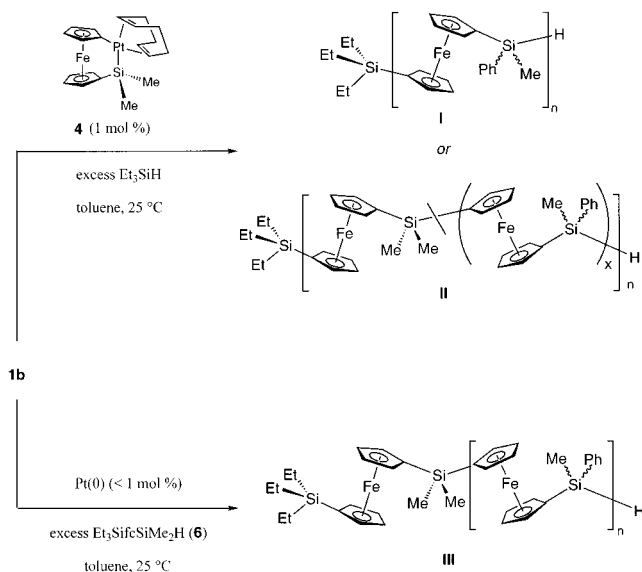
Scheme 2

presence of Et$_3$SiH as the capping agent would allow us to probe whether the ferrocenylsilane component of **4** becomes incorporated into the resulting polymer. The previously proposed mechanism (Scheme 1) predicts that the product should possess structure **III** in which the fcSiMe$_2$ component of **4** is indeed incorporated and is located at a terminal position (Scheme 2). On the other hand, alternative structures in which no incorporation takes place (structure **I**) or even a random incorporation of the fcSiMe$_2$ group (structure **II**) might also be envisaged. The use of Et$_3$SifcSiMe$_2$H (**6**) as a chain-capping agent for the ROP of **1b** catalyzed by Karstedt's catalyst would be expected to lead to a model oligo(ferrocenylmethylphenylsilane) of structure **III** with a fcSiMe$_2$ unit as the penultimate group. Moreover, ROP of **1b** catalyzed by Pt(1,5-cod)$_2$ in the presence of Et$_3$SiH as the capping agent would be expected to yield a product with structure **I**. Although structure **II** would be difficult to synthesize, the key structural elements should be present in a random copolymer formed by the ROP of a mixture of **1a** and **1b** under similar conditions. NMR data for each of these species would be expected to allow the possible product structures **I**−**III**, that might arise from the ROP of **1b** using Et$_3$SiH and **4**, to be convincingly distinguished.

2. Preparation of Model Oligomers and Polymers from the Transition Metal-Catalyzed ROP of 1b.

(a) Platinum-Catalyzed ROP of 1b in the Presence of Et$_3$SiH: Synthesis and Characterization of a Model End-Capped Oligo(ferrocenylmethylphenylsilane) (8) with Structure I. Addition of Karstedt's catalyst (1 mol %) to a toluene solution of complex **1b** and Et$_3$SiH (1:2 mole ratio) resulted in an amber polymer **8** in high yield (94%) (eq 3).
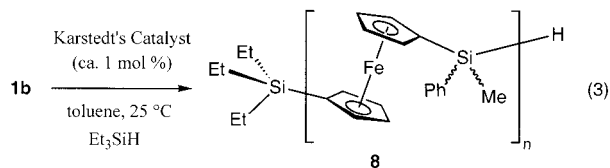

GPC analysis revealed that **8** possessed a monomodal distribution with M_n and PDI values of 2000 and 1.49, respectively. In the ^{29}Si NMR spectrum, the chain ends, fc*Si*MePhH and Et$_3$*Si*fcSiMePh, gave signals at $\delta = -18.2$ and 2.5 respectively, while those of the interior silicon centers were

of intermediate value ($\delta = -10.9$). Importantly, ^{1}H NMR spectroscopy provided distinctive shifts associated with the end-groups of **8**. With the introduction of chiral silicon centers, the methyl protons of the fcSi*Me*PhH chain end gave rise to a multiplet at $\delta = 0.47$. In turn, the Si−H resonance for the fcSiMePh*H* end-group was observed at $\delta = 5.10$, significantly downfield from the fcSiMe$_2$*H* end group of **6** found at $\delta = 4.70$. The ^{13}C NMR spectrum also provided distinctive shifts associated with the fcSiMePhH chain end. Thus, the broad resonance at $\delta = -4.3$ was attributed to the fcSi*Me*PhH carbon atoms while the methyl groups of the interior of the chain (fcSi*Me*Phfc) were observed downfield from $\delta = -3.2(5)$ to $-3.3(4)$.

These results demonstrate that the presence of Et$_3$SiH in the ROP of **1b** catalyzed by Pt(0) catalysts served to cap the growing polymer leading to the formation of low-molecular weight **8**. Moreover, the characteristic NMR resonances of **8** provide valuable data with which to characterize the fcSi-MePhH end group and to investigate if structure **I** results from the ROP of **1b** catalyzed by **4** in the presence of Et$_3$SiH.

(b) Synthesis and Characterization of a Poly(ferrocenyldimethylsilane-*r*-ferrocenylmethylphenylsilane) Random Copolymer (9) to Model Structure II. To determine relevant NMR resonances associated with the switching groups of structure **II**, we undertook the synthesis of a random copolymer from monomers **1a** and **1b**. Thus, using Pt(1,5-cod)$_2$ as the catalyst, the red-colored toluene solution containing equimolar amounts of **1a** and **1b** became highly viscous and amber in color. Precipitation into hexane after 4 d afforded an orange-colored elastomer **9** in high yield (86%) (eq 4).
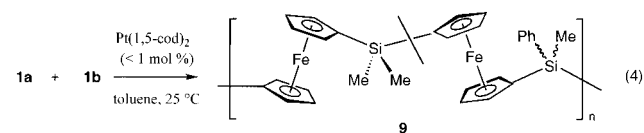
Significantly, GPC analysis revealed a monomodal distribution of high-molecular weight polymer ($M_n = 576\,000$, PDI = 1.49) consistent with a copolymer rather than a mixture of two homopolymers. The presence of distinct switching groups, particularly in the ^{13}C and ^{29}Si NMR spectra, offered clear evidence for the formation of a random microstructure as opposed to a blend or block architecture. Most convincing was the ^{29}Si NMR spectrum. Two major resonances were observed at $\delta = -10.8$ and -6.5, arising from segments of fc*Si*MePhfc and fc*Si*Me$_2$fc units, respectively, in addition to other significant resonances in the same regions associated with switching groups. Importantly, as we have been unable to resolve triads for the atactic poly(ferrocenylmethylphenylsilane) homopolymer **2b** by high-resolution ^{29}Si NMR spectroscopy, the presence of multiple resonances for **9** is clearly due to switching groups. In the ^{13}C NMR spectrum multiple switching groups appeared between $\delta = -3.2$ and -3.0 (fc*Si*Me*PhfcSiMe$_2$) and $\delta = -0.7$ and -0.6 (fcSiMePhfcSi*Me$_2$*). These reside close to the corresponding methyl environments detected in the homopolymers **2b** and **2a** (cf.: **2b**: $\delta = -3.2$ and **2a**: $\delta = -0.6$). By integration of the methyl resonances in the ^{1}H NMR spectrum, we found that **1a** and **1b** were incorporated into the resulting polymer in a 1.25:1 mol ratio, quite close to the original monomer feed of 1:5:1. The cyclopentadienyl region of the ^{13}C NMR spectrum also showed evidence for switching groups. The data for **9** were expected to be useful in the assessment of whether the product from the ROP of **1b** by **4** in the presence of Et$_3$SiH coincides with structure **II**.

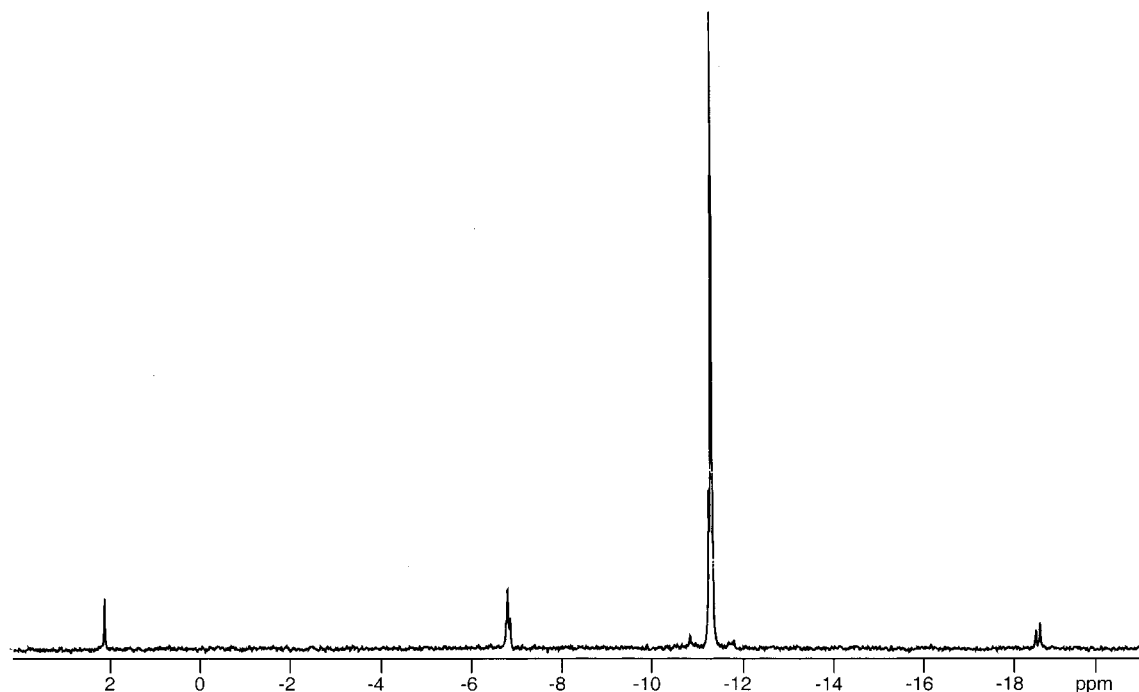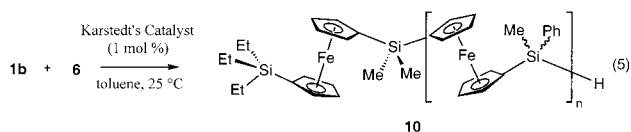**Figure 1.** ^{29}Si NMR spectrum (C_6D_6) of $Et_3SifcSiMe_2(fcSiMePh)_nH$ (**10**).

(c) ROP of 1b Catalyzed by Pt(0) in the Presence of $Et_3SifcSiMe_2H$: Synthesis and Characterization of a Model Oligoferrocenylsilane (10) with Structure III. Using the mono-addition product (**6**) as the end-capping silane for the Pt(0)-catalyzed ROP of **1b**, should provide model oligomers of structure **III** for comparative end-group analysis with those synthesized using Et_3SiH and **4**. A catalytic amount of Karstedt's catalyst was therefore added to a toluene solution containing $Et_3SifcSiMe_2H$ and **1b** in a 1:4 mole ratio. The resulting polymer **10** was isolated in 60% yield, ($M_n = 6200$ and PDI = 1.49) (eq 5).

Multinuclear NMR and mass spectrometric data confirmed that **10** was an $Et_3SifcSiMe_2fcSiMePh-$ and $-fcSiMePhH$ end-capped oligo(ferrocenylmethylphenylsilane). The most definitive evidence was provided by the ^{29}Si NMR spectrum (Figure 1).

Particularly noteworthy is the signal at $\delta = -6.9$ due to a fc*Si*Me₂fcSiMePh switching group. This is upfield ($\sim$0.5 ppm) from that of the fc*Si*Me₂fc units present in the interior of the main chain of the corresponding homopolymer (cf. **2a**: $\delta = -6.4$) and is in agreement with the resonance of a similar switching group detected in the random copolymer **9** ($\delta = -6.6$ (fc*Si*Me₂fcSiMePh)). The major resonance at $\delta = -11.3(3)$ was attributed to the interior fc*Si*MePhfc units, with a shoulder at $\delta = -11.2(8)$ assigned to the fcSiMe₂fc*Si*MePh switching group. Two signals at $\delta = -18.5$ and -18.6 were in agreement with the formation of diastereomeric end-groups (fc*Si*MePhH), while the resonance at $\delta = 2.1$ correlated to the opposite chain terminus, namely the Et_3SifcSiMe₂ end-group (cf. **8** and **5**).[18] Of considerable significance in the ^1H NMR spectrum is the signal at $\delta = 0.53$, suggesting that the fcSi*Me₂* component of **6** was indeed incorporated into the polymer backbone. Two distinct resonances at $\delta = 0.49$ and 5.10 were assigned to the fcSi*Me*Ph*H* chain end. Similarly in the ^{13}C NMR spectrum, the

resonances centered at $\delta = -0.6$ were attributed to the SiMe₂ moiety of the $Et_3SifcSiMe_2fcSiMePh$ switching group. Significantly, the random copolymer (**9**) showed switching groups between $\delta = -0.7$ and -0.6.

The supernatant from the initial precipitation was analyzed by mass spectroscopy and also revealed the presence of short oligomers with structures consistent with the presence of an $Et_3SifcSiMe_2$ chain end. Thus, ion peaks were observed for $Et_3SifcSiMe_2(fcSiMePh)_3H$ ($m/z = 1270$), $Et_3SifcSiMe_2(fcSiMePh)_2H$ ($m/z = 966$), $Et_3SifcSiMe_2fcSiMePhH$ ($m/z = 663$) in addition to unreacted silane, $Et_3SifcSiMe_2H$, ($m/z = 358$).

3. Investigations into the Fate of the Ferrocenylsilane Fragment of 4 During the ROP of 1b.

(a) ROP of 1b Catalyzed by [2]Platinasilaferrocenophane 4 in the Presence Et_3SiH. The synthesis of oligo- and polyferrocene models by the ROP of **1b** catalyzed by Pt(0)-precatalysts in the presence of varying amounts of Si−H end-capping agents has clearly demonstrated that the unique resonances assigned to the possible end/switching groups present in the proposed structures **I−III** are indeed observable by multinuclear NMR. Thus, NMR analysis should demonstrate whether the ferrocenylsilane component of the precatalyst **4** is indeed incorporated into the polymer backbone during the ROP of **1b** catalyzed by [2]platinasilaferrocenophane **4** in the presence of Et_3SiH.

Thus, reaction of **1b** and Et_3SiH (1:1.5 mol ratio) with a catalytic amount of **4** (1 mol %) over a 24 h period gave an orange polymeric material (94%). The isolated polymer possessed a monomodal molecular weight distribution with $M_n = 4900$ and PDI = 1.54 as determined by GPC analysis. Further purification, using column chromatography, afforded the corresponding polyferrocene with $M_n = 5000$ and PDI = 1.12. This molecular weight was sufficiently low that detection of any skeletal SiMe₂ units derived from **4** would be possible.

Significantly, the NMR spectral data was consistent with the structure in which the SiMe₂ units of **4** were *not* incorporated into the resulting polymer. For example, the ^{29}Si NMR spectrum of the product showed major resonances at $\delta = 2.1$, -11.2,
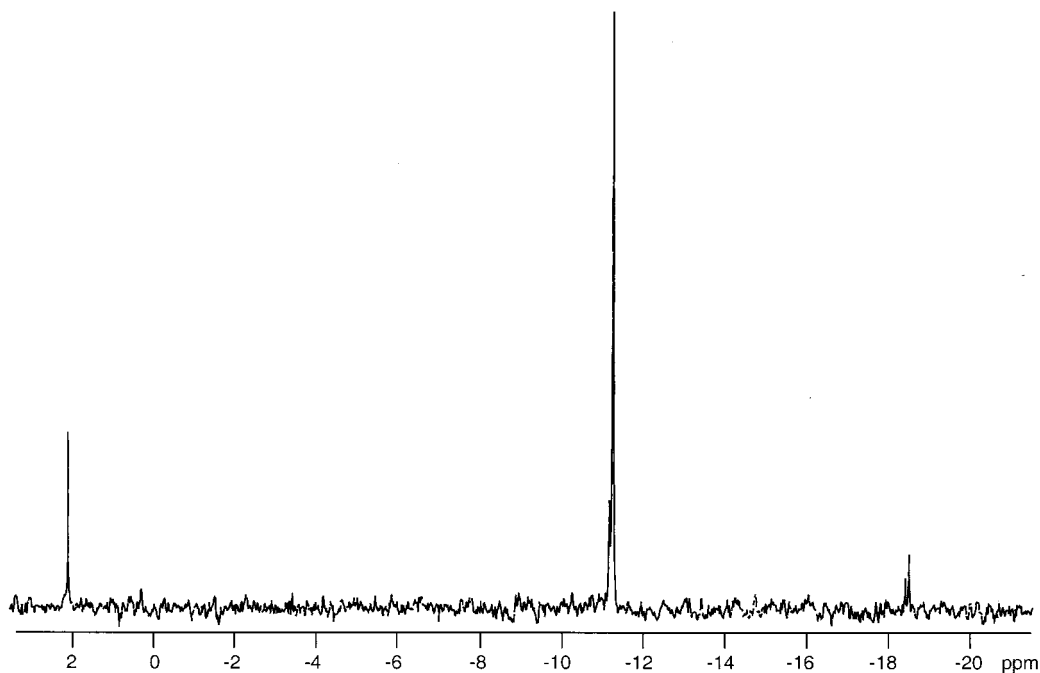
Figure 2. ^{29}Si NMR spectrum (C_6D_6) of $Et_3Si(fcSiMePh)_nH$ (**8**) synthesized via the ROP of **1b** by **4** in the presence of Et_3SiH.

and −18.5, −18.4 assignable to Et_3Si, interior fc*Si*MePhfc and end group fc*Si*MePhH environments, respectively (Figure 2). However, the signal in the range of $\delta = -6.9$ to −6.4 for the $SiMe_2$ group was absent, confirming that the ferrocenylsilane component of **4** was not incorporated into the polymer.

Moreover, the ^1H and ^{13}C NMR spectra were in excellent agreement with those of **8**, clearly indicating the formation of the Et_3SiH end-capped oligo(ferrocenylmethylphenylsilane) of structure **I** (Scheme 2). Again, no ^1H or ^{13}C NMR signals typical of an $Et_3SifcSiMe_2fc$ group were observed, further confirming that the ferrocenylsilane component of the precatalyst is not present.

The supernatant obtained from the initial precipitation was also analyzed for the presence of ferrocenylsilane units. Noticeably, the ^{29}Si NMR spectrum of the supernatant residue was also devoid of any signals between $\delta = -6.4$ and −6.9. Both the ^1H and ^{13}C NMR spectra were identical with the higher-molecular weight oligomer fraction with the exception of multiple signals due to the presence of short chains of different molecular weight. Mass spectrometry was also consistent with the assigned structure (**8**) of the low molecular weight species.[27] Thus, peaks of significant intensity were detected at $m/z = 1637$ ($Et_3Si(fcSiMePh)_5H$), 1333 ($Et_3Si(fcSiMePh)_4H$), 1028 ($Et_3Si-(fcSiMePh)_3H$), and 724 ($Et_3Si(fcSiMePh)_2H$). Significantly, no signals indicative of short oligomeric chains possessing ferrocenyldimethylsilane repeat units were detected.

Consequently, the accumulative evidence leads to the conclusion that the ferrocenylsilane component of the precatalyst does not become incorporated into the polymer chain nor into the oligomeric byproducts. Indeed, the resulting polymer has structure **I**, which is identical to the Et_3SiH end-capped poly-(ferrocenylmethylphenylsilane) (**8**) prepared from the ROP of **1b** using Karstedt's catalyst (eq 6).

(b) ROP of 1a Catalyzed by fcPt(1,5-cod)Sn(^tBu)_2 (11) in the Presence of Et_3SiH. In an effort to further confirm the lack of incorporation of the ferrocenophane component of the precatalyst into the resulting polymer chain, we also prepared an oligoferrocene via the ROP of **1a** catalyzed by an analogue of **4**, the [2]platinastannaferrocenophane fcPt(1,5-cod)Sn(^tBu)_2
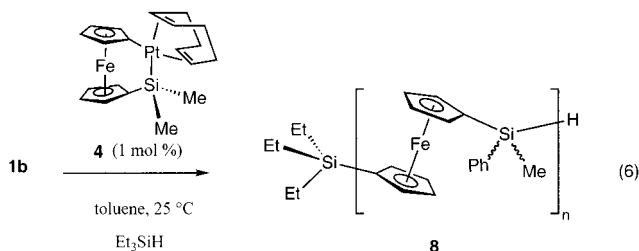

(**11**), in the presence of an excess of Et_3SiH.[28] The polymeric product was isolated after 4 d in good yield (79%), ($M_n = 3800$, PDI = 1.21) (eq 7).
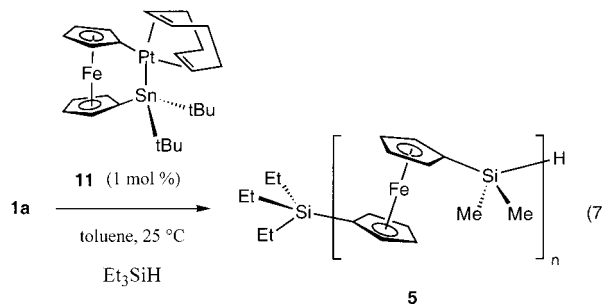
The ^1H NMR spectrum of the isolated polymer showed no ferrocenylstannane resonances. Instead, the spectrum was in full agreement with the formation of a Et_3SiH end-capped oligo-(ferrocenyldimethylsilane) **5**. The ^{13}C NMR spectrum of the purified polymer also showed no *tert*-butyl resonances which would normally be observed between $\delta = 25.0$ and 32.0. In addition, the ^{29}Si NMR spectrum of the product possessed only three signals at $\delta = -18.6$, −6.8, and 2.1, corresponding to the fc*Si*Me_2H terminus, the interior fc*Si*Me_2fc units, and the opposite chain end, Et_3SifcSiMe_2, respectively. Analysis of the supernatant using ^1H NMR spectroscopy revealed a single resonance at $\delta = 1.54$ ($^3J(^{117/119}Sn-H) = 75$ Hz) attributed to

(28) Jäkle, F.; Rulkens, R.; Zech, G.; Foucher, D.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 2117.
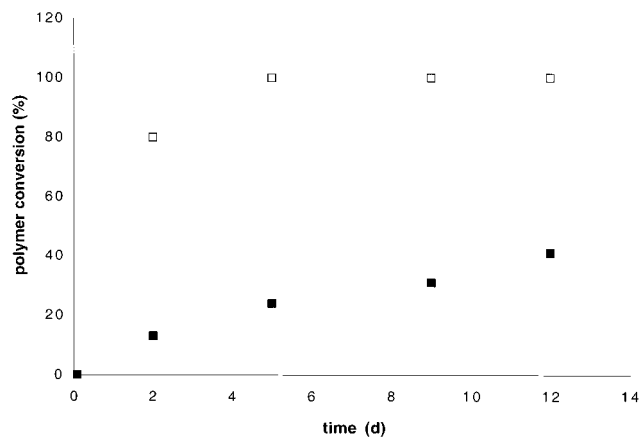
Figure 3. Effect of mercury on the ROP of **1a** in the presence and absence of Hg. (■)with Hg; (□) without Hg.

Table 1. Effects of Mercury on the Molecular Weight Control of Polyferrocenylsilanes **5** and **2a**[a]

ratio of monomer to silane	M_n	PDI	mercury
25:1	32 700	1.51	×
	65 600	1.55	√
50:1	51 000	1.79	×
	27 400	1.66	√
75:1	84 400	1.69	×
	27 200	1.68	√
no silane	55 300	1.53	×
	121 500	1.45	√

[a] √ = mercury present; × = mercury absent.

[t]Bu protons of the remaining amounts of precatalyst, in addition to other resonances associated with **11**.

Thus, through comparative end group analysis of polyferrocenylsilane formed using the precatalyst **11** in the presence of Et$_3$SiH, we have again clearly demonstrated that the ferrocenophane component of the precatalyst does not become incorporated into the resultant polymer.

4. The Fate of the Platinum from Precatalyst 4 in the Mechanistic Cycle. Mechanistic evidence points to the loss of both 1,5-cod ligands from the Pt(1,5-cod)$_2$ precatalyst during the ROP of [1]silaferrocenophanes.[22,23] Moreover, the absence of both the ferrocenylsilane fragment and platinum from the precatalyst **4** in the resulting polymer chains prompts immediate questions concerning their fate and hence, the true nature of the catalytic species. As with many catalytic cycles, the active catalyst may be either homogeneous or heterogeneous.[29] Mercury is a well-known poison for heterogeneous platinum that inhibits such catalytic cycles by forming an alloy with the zerovalent metal.[30] We therefore investigated the nature of the catalytic species through a series of inhibition reactions with mercury. In a typical experiment, following the addition of mercury to a solution of **1a**, a catalytic amount of Pt(1,5-cod)$_2$ (≪1 mol %) was injected, and the NMR tube was immediately shaken vigorously for 2 min.[31] The progress of the polymerizations was monitored by ^{1}H NMR spectroscopy. The polymerization was strongly inhibited by the presence of mercury as shown in Figure 3. In fact, after prolonged reaction times approaching 2 weeks, the percent conversion to polymer reached only 40%. In contrast, ROP of **1a** reached high conversions (>80%) after 2 days in the control reactions.

We also investigated the effect of mercury on the ROP of **1a** in the presence of Et$_3$SiH. Following a similar protocol, both **1a** and the appropriate amount of Et$_3$SiH were added to an NMR tube containing mercury followed by a catalytic amount of Pt-

(1,5-cod)$_2$ (≪1 mol %). Mercury again proved an effective inhibitor of the polymerization over a range of Et$_3$SiH concentrations (Figure 4), while maintaining constant initial concentrations of **1a**, Pt(1,5-cod)$_2$ and Hg. These studies indicate that colloidal platinum is the main active catalyst in the ROP reactions.[32]

Table 1 summarizes the corresponding molecular weight data. Noticeably, in the presence of mercury molecular weight control is lost. This contrasts with the ability of Et$_3$SiH to cap the growing chain end to achieve predetermined molecular weights when Hg is absent (see Table 1). Importantly, while mercury does serve to dramatically inhibit the ROP, polyferrocenylsilane (**2a** or **5**) still very slowly forms in both the absence and presence of Et$_3$SiH. Thus, while it is clear that the major catalytic species is colloidal in nature we cannot rule out the presence of a minor homogeneous component.[29,33]

Summary and Conclusions

Through comparative end-group analysis between the products from the ROP of **1b** in the presence of Et$_3$SiH using the [2]platinasilaferrocenophane precatalyst **4** and oligomeric models, we have found that the ferrocenophane component of the precatalyst does not become incorporated into the growing polymer. This finding was substantiated by a study of the ROP of **1a** catalyzed by the [2]platinastannaferrocenophane, fcPt-(1,5-cod)Sn([t]Bu)$_2$ (**11**), in which the lack of *tert*-butyl resonances confirmed the absence of the fcSn([t]Bu)$_2$ unit in the resulting polymer. In each case additional support was provided by the isolation of short chains from the residual supernatant solutions that possessed end-groups that were consistent with those of the corresponding higher-molecular weight oligomers. In addition, inhibition of the polymerization cycle by mercury poisoning points to colloidal platinum as the major catalytic species in the ROP of **1a**. On the basis of these results a revised *heterogeneous* mechanism for the ROP of [1]silaferrocenophanes can be proposed (Schemes 3 and 4).

Thus, ROP of **1a** using Pt(1,5-cod)$_2$ is proposed to proceed through the initial formation of the [2]platinasilaferrocenophane (**4**) via oxidative-addition to the zerovalent platinum complex.[15]

(29) For recent studies aimed at elucidating the homogeneous or heterogeneous nature of late transition metal catalysts, see: (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Weddle, K. S.; Aiken, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653. (c) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693. (d) Reference 3d.

(30) For papers concerning the use of mercury as a poison for heterogeneous late transition metal catalysts, see: (a) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P.; Sowinski, A. F.; Izumi, A. N.; More, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819. (b) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891. (c) Weddle, K. S.; Aiken, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653. (d) Reference 29c. (e) Reference 3d. (f) Young, R. J.; Grushin, V. V. *Organometallics* **1999**, *18*, 294.

(31) This procedure is similar to that outlined by Stein et. al. in ref 29c.

(32) While it is common to view colloids by TEM, the presence of the electron-rich Fe centers has made resolution of colloidal particles difficult. For imaging of polyferrocenes by TEM, see: Massey, J. A.; Temple, K.; Cao, L.; Rharbi, Y.; Raez, J.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 11577. Moreover, in agreement with Stein and co-workers (see ref 29c), we believe the preparation of the sample may in itself induce decomposition of the platinum complex.
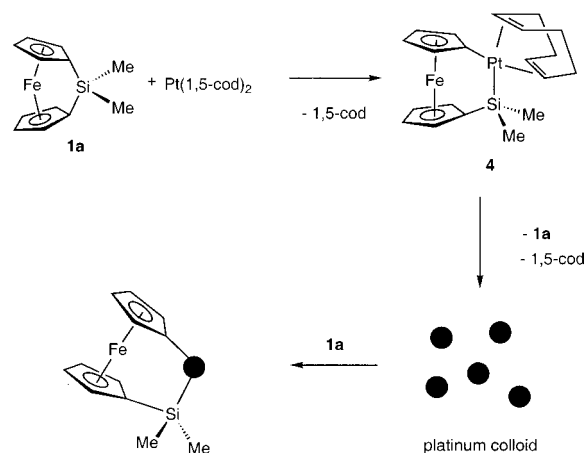
(33) It is also possible that the quenching of catalytic activity by mercury is not 100% efficient, and thus the catalyst may be entirely heterogeneous.
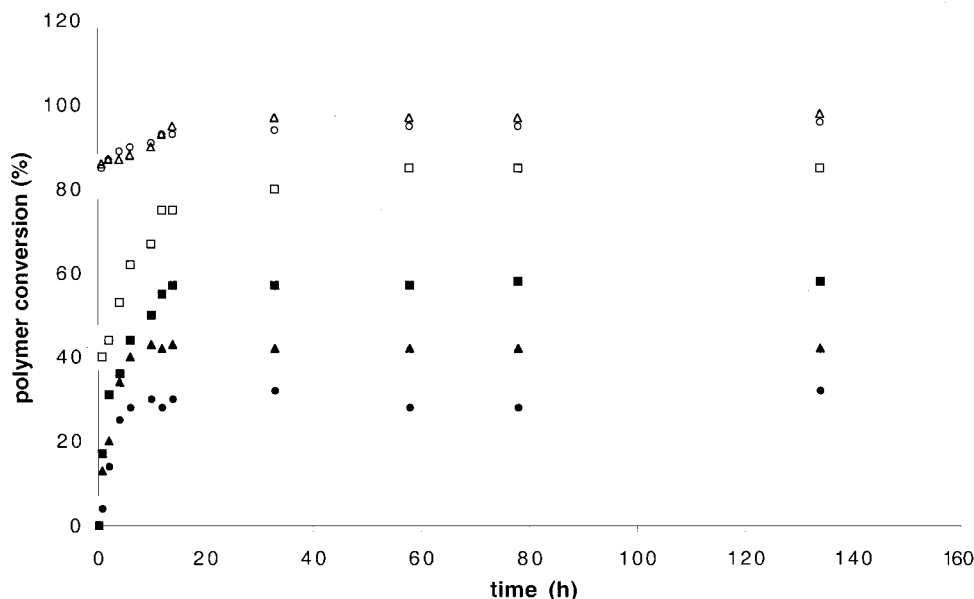
Figure 4. Effect of mercury on the ROP of **1a** in the presence and absence of Hg. Ratio of **1a**: Et$_3$SiH: (■) 75:1 with Hg; (□) 75:1 without Hg; (▲) 50:1 with Hg; (△) 50:1 without Hg; (●) 25:1 with Hg; (○) 25:1 without Hg.
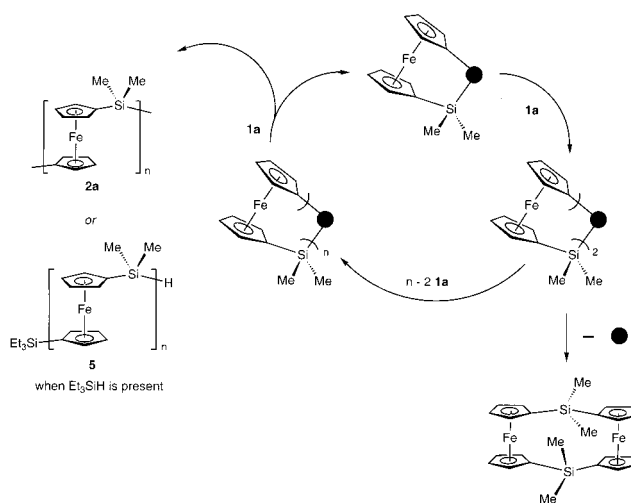
Scheme 3

Scheme 4

Indeed, complex **4** has been detected in situ by ^{1}H NMR spectroscopy during the ROP of **1a** in both the presence and absence of Et$_3$SiH.[22,34] Moreover, complex **4** functions as an effective ROP precatalyst, but in the presence of excess 1,5-cod all catalytic activity is arrested.[22] Thus, the elimination of the remaining 1,5-cod ligand appears essential for ROP and is proposed to lead to the formation of the platinum colloids as the principal catalytic component (Scheme 3). Subsequent oxidative-addition and reductive-elimination (or σ-bond metathesis) chemistry at the colloid surface is proposed to explain the observed products (Scheme 4). The inhibition of the ROP of **1a** by mercury supports this proposition.

The reactivity and polymerization behavior of [1]silaferrocenophanes closely mimics that observed for the cyclic carbosilanes. As noted above, the strained Si−C bonds of silacyclobutanes undergo oxidative-addition reactions to platinum-(0) centers affording products analogous to **4**.[21] However, despite the broad interest in polycarbosilanes,[4] the mechanism for their synthesis via metal-catalyzed ROP has remained virtually unexplored.[21] It is highly likely that our results on silaferrocenophanes also have direct implications for the ROP of cyclic carbosilanes and also other related species.

Another interesting recent contribution to the chemistry of the latter is that of Neckers and co-workers who discovered the photoinduced ROP of cyclic carbosilanes in the presence of Pt-(acac)$_2$.[3d] In this case, mercury inhibition studies confirmed that platinum colloids served as a catalytic species. However, they also observed significant retardation by homogeneous inhibitors, thus leading to the conclusion that both a homogeneous and a heterogeneous mechanism operate. Indeed, we cannot dismiss the possibility of a minor homogeneous component to the overall mechanism for the transition metal-catalyzed ROP of **1a**, for while mercury clearly inhibits ROP, polymer does very slowly form. Future work will address this issue and will also focus on the now even more intriguing question of the fate of the ferrocenylsilane component of precatalyst **4** in the polymerization cycle.

Experimental Section

(34) Temple, K.; Manners, I. *Unpublished results.*

Compounds **1a**, **1b**, **4**, and **11** were synthesized as described in the literature.[13,22,28,35]

Equipment. All reactions and manipulations were performed under an inert atmosphere (prepurified N₂) using either standard Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies), except for the polymers **5**, **8**, **9**, and **10**, for which manipulations were carried out in air. The reactions were monitored by ¹H NMR. Solution NMR spectra were recorded on a Varian XL 400 instrument. ¹H NMR spectra (400 MHz) were referenced to residual protonated solvent, and ¹³C NMR spectra (100.5 MHz) were referenced to the NMR active carbons of the deuterated solvent. ²⁹Si NMR (79.5 MHz) spectra were referenced externally to TMS utilizing a normal (proton decoupled) pulse sequence. All NMR shifts are reported in ppm. Molecular weight distributions were analyzed by gel permeation chromatography using a Waters Associates 2690 Separations Unit. Ultrastyragel columns with a pore size between 500, 10³, and 10⁵ Å, and a Waters 410 differential refractometer were used. A flow rate of 1.0 mL/min was used, and samples were dissolved in a THF solution. Polystyrene standards purchased from Aldrich were used for calibration purposes.

Synthesis and Characterization of the Ring-Opened Addition Products Et₃SifcSiMe₂H (6) and Et₃Si(fcSiMe₂)₂H (7). Complex **1a** (2.00 g, 8.26 mmol) was dissolved in toluene (.~15 mL). To this red-colored solution, Et₃SiH (46 mL, 290 mmol) was added followed by a catalytic amount of Pt(1,5-cod)₂ (<1 mol %). After stirring for 24 h at room temperature, the solvent was removed under high vacuum giving a red-colored oil. The products were then passed through an alumina column which had been deactivated with NEt₃. Cyclohexane was used as the elutent. Both **6** and **7** were isolated as deep red oils.

Compound 6: Yield: 2.57 g (87%). ¹H NMR (δ, C₆D₆): 0.28 (d, 6H, fcSi*Me₂*H), 0.75 (q, 6H, fcSi(C*H₂*CH₃)₃), 1.06 (t, 9H, fcSi-(CH₂C*H₃*)₃), 4.02 (t, 2H, Et₃Si*fc*SiMe₂H), 4.07 (t, 2H, Et₃Si*fc*SiMe₂H), 4.22 (t, 2H, Et₃Si*fc*SiMe₂H), 4.24 (t, 2H, Et₃Si*fc*SiMe₂H), 4.70 (heptet, 1H, Et₃SifcSiMe₂*H*). ¹³C NMR (δ, C₆D₆): −2.9 (fcSi*Me₂*H), 5.0 ((CH₃-*CH₂*)₃Sifc), 8.1 ((*CH₃*CH₂)₃Sifc), 67.9 (ipso-C, Et₃Si*fc*SiMe₂H), 69.8 (ipso-C, Et₃Si*fc*SiMe₂H), 71.5 (Et₃Si*fc*SiMe₂H), 71.9 (Et₃Si*fc*SiMe₂H), 73.7 Et₃Si*fc*SiMe₂H), 73.8 Et₃Si*fc*SiMe₂H). ²⁹Si NMR (δ, C₆D₆): −18.6 (fc*Si*Me₂H), 2.1 (Et₃*Si*fc). MS (EI, 70 eV) *m/z* [%] 358 [100; M⁺].

Compound 7: Yield: 0.25 g (10%). ¹H NMR (δ, C₆D₆): 0.28 (d, 6H, fcSi*Me₂*H), 0.54 (s, 6H, fcSi*Me₂*fc) 0.75 (q, 6H, fcSi(C*H₂*CH₃)₃), 1.06 (t, 9H, fcSi(CH₂C*H₃*)₃), 4.02 (t, 2H, Cp), 4.06 (t, 2H, Cp), 4.09 (t, 2H, Cp), 4.10 (t, 2H, Cp), 4.22 (t, 2H, Cp), 4.24 (m, 4H, Cp), 4.28 (t, 2H, Cp), 4.70 (heptet, 1H, fcSiMe₂*H*). ¹³C NMR (δ, C₆D₆): −2.9 (H*Me₂*-Sifc), −0.7 (fcSi*Me₂*fc), 5.0 ((CH₃*CH₂*)₃Sifc), 8.1 ((*CH₃*CH₂)₃Sifc), 68.1 (ipso-C, Cp), 69.7 (ipso-C, Cp), 71.5 (Cp), 71.6 (Cp), 71.7 (Cp), 71.9 (Cp), 73.4 (Cp), 73.7(1) (Cp), 73.7(3) (Cp), 73.9 (Cp). ²⁹Si NMR (δ, C₆D₆): −18.6 (fc*Si*Me₂H), −6.8 (fc*Si*Me₂fc), 2.1 (Et₃*Si*fc). MS (EI, 70 eV) *m/z* [%] 600 [100; M⁺].

Synthesis and Characterization of Et₃SiH End-Capped Oligo-(methylphenylferrocenylsilane) (8). Ferrocenophane **1b** (0.50 g, 1.64 mmol) and Et₃SiH (382 mg, 3.29 mmol) were dissolved in toluene (7.0 mL). To this solution, a catalytic amount of Karstedt's catalyst (1 mol %) was injected. While the reaction stirred for 2 d, the color changed from red to orange. The polymer was then precipitated into hexanes (200 mL) and filtered at −78 °C. A small amount of benzene (~3 mL) was then added to dissolve the product which after drying under high vacuum was isolated as a red oil. Yield: 470 mg (94%). ¹H NMR (δ, C₆D₆): 0.47 (m, fcSi*Me*PhH), 0.72, (s, fcSi*Me*Phfc), 0.74 (s, fcSi*Me*Phfc), 0.76 (s, fcSi*Me*Phfc), 0.80 (m, fcSi(C*H₂*CH₃)₃), 1.03 (t, fcSi(CH₂C*H₃*)₃), 3.97 (br, Cp, *fc*SiMePh,), 4.06 (br, Cp, *fc*SiMePh), 4.14 (br, Cp, *fc*SiMePh), 4.21(br, Cp, *fc*SiMePh), 5.10 (m, br, fcSiMePh*H*), 7.24 (br, fcSiMe*Ph*), 7.75 (br, fcSiMe*Ph*). ¹³C NMR (δ, C₆D₆): −4.3 (s, fcSi*Me*PhH), −3.3(4) (s, fcSi*Me*Phfc), −3.3(0) (s, fcSi*Me*Phfc), −3.2(5) (s, fcSi*Me*Phfc), 4.9 (fcSi(*CH₂*CH₃)₃), 8.2 (s, fcSi-(CH₂*CH₃*)₃), 70.2 (m, ipso-C, *fc*SiMePh), 72.0 (Cp, *fc*SiMePh), 72.4 (Cp, *fc*SiMePh), 74.2 (m, Cp, *fc*SiMePh), 74.4 (m, Cp, *fc*SiMePh), 128.1 (fcSiMe*Ph*), 129.3 (fcSiMe*Ph*), 134.6 (fcSiMe*Ph*), 138.8 (ipso-C, fcSiMe*Ph*). ²⁹Si NMR (δ, C₆D₆): −18.2 (m, fc*Si*MePhH), −10.9 (fc*Si*MePh), 2.5 (Et₃*Si*fc). GPC Analysis: M_n = 2000, PDI = 1.49.

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Synthesis and Characterization of Poly(ferrocenyldimethylsilane-*r*-ferrocenylmethylphenylsilane) Copolymer (9). Ferrocenophanes **1a** (72 mg, 0.30 mmol) and **1b** (61 mg, 0.20 mmol) were dissolved in toluene (~5 mL) to give a red-colored solution. The catalyst, Pt(1,5-cod)₂ (<1 mol %) was then added. The reaction was allowed to stir for 4 d during which time the solution turned amber in color and became highly viscous. The polymer was then precipitated into hexanes (~150 mL) and filtered to afford an orange-colored polymer. Yield: 115 mg (86%). ¹H NMR (δ, C₆D₆): 0.54 (br, fcSi*Me₂*fc), 0.76 (br, fcSi*Me*Phfc), 4.10−4.26 (br, SiMe₂*fc*SiMe₂, SiMePh*fc*SiMePh and switching groups), 7.26 (br, fcSiMe*Ph*), 7.75 (br, fcSiMe*Ph*). ¹³C NMR (δ, C₆D₆): −3.2-(1) (s, fcSi*Me*Phfc), −3.1(5) to −3.0 (m, fcSiMePhfcSiMe₂, switching groups), −0.7 to −0.6 (m, fcSi*Me₂*fcSiMePh, switching groups), −0.5 (s, fcSi*Me₂*fc), 70.2 (ipso-C, SiMePh*fc*SiMePh), 71.8 (Cp, SiMe₂*fc*SiMe₂), 71.9 (ipso-C, *fc*SiMe₂), 72.0 (Cp, SiMePh*fc*SiMePh), 72.2−72.4 (m, Cp, SiMePh*fc*SiMePh and switching groups), 72.6 (Cp, SiMe₂*fc*SiMe₂), 74.1−74.5 (m, Cp, SiMePh*fc*SiMePh and switching groups), 128.0 (s, fcSiMe*Ph*), 129.3 (s, fcSiMe*Ph*), 134.7 (s, fcSiMe*Ph*), 138.8 (s, fcSiMe*Ph*). ²⁹Si NMR (δ, C₆D₆): −11.0 to −10.6 (fc*Si*MePhfc and switching groups), −6.4 to −6.6 (fc*Si*Me₂fc and switching groups). GPC Analysis: M_n = 576 000, PDI = 1.49.

Synthesis and Characterization of Et₃SifcSiMe₂(fcSiMePh)ₙH (10). Complex **1b** (750 mg, 2.47 mmol) and Et₃SifcSiMe₂H (**6**) (220 mg, 0.61 mmol) were dissolved in toluene (5 mL). To the resulting deeply red-colored solution, the catalyst Karstedt's catalyst (<1 mol %) was added. The color immediately changed to orange. After stirring at room temperature for 2 days, the polymer was precipitated into hexanes (~150 mL) and filtered at −78 °C. The orange-colored polymer was then redissolved in benzene (~10 mL). After all volatile material was removed under high vacuum, an extremely viscous, deep red polymer was isolated. Yield: 0.58 g (60%). ¹H NMR (δ, C₆D₆): 0.49 (t, fcSi*Me*PhH), 0.53 (s, Et₃SifcSi*Me₂*fc), 0.72, (s, fcSi*Me*Phfc), 0.74 (s, fcSi*Me*Phfc), 0.76 (s, fcSi*Me*Phfc), 0.80 (m, fcSi(C*H₂*CH₃)₃), 1.07 (t, fcSi(CH₂C*H₃*)₃), 3.99 to 4.15 (br, Cp, SiMePh*fc*SiMePh and Et₃-SifcSiMe₂*fc*), 4.23 to 4.28 (br, Cp, Et₃Si*fc*SiMe₂fc), 5.10 (m, fcSiMe*Ph*H), 7.24 (br, fcSiMe*Ph*), 7.72 (br, fcSiMe*Ph*). ¹³C NMR (δ, C₆D₆): −4.2 (fcSi*Me*PhH), −3.3(4) (s, fcSi*Me*Phfc), −3.3(0) (s, fcSi*Me*Phfc), −3.2(5) (s, fcSi*Me*Phfc), −0.6 (m, Et₃SifcSi*Me₂*fc), 5.0 (s, fcSi-(*CH₂*CH₃)₃), 8.2 (s, fcSi(CH₂*CH₃*)₃), 70.3 (m, ipso-C, *fc*SiMePh), 71.6 to 71.8 (m, Cp and ipso-C, Et₃Si*fc*SiMe₂fcSiMePh), 72.0 (s, Cp, *fc*SiMePh), 72.4 (s, Cp, *fc*SiMePh), 73.5−73.8 (m, Cp, Et₃Sifc-SiMe₂*fc*SiMePh), 74.2 (s, Cp, *fc*SiMePh), 74.5 (s, Cp, *fc*SiMePh) 127.9 (s, fcSiMe*Ph*), 129.3 (s, fcSiMe*Ph*), 134.6 (s, fcSiMe*Ph*), 138.9 (s, ipso-C, fcSiMe*Ph*). ²⁹Si NMR (δ, C₆D₆): −18.6 (s, fc*Si*MePhH), −18.5 (s, fc*Si*MePhH), −11.3(3) (fc*Si*MePhfc), −11.2(8) (switching group), −6.9 (s, Et₃Sifc*Si*Me₂fcSiMePh), 2.1 (s, Et₃*Si*fcSiMe₂fcSiMePh). GPC Analysis: M_n = 6200, PDI = 1.49. The supernatant was passed through an alumina column and analyzed by mass spectrometry. MS (EI, 70 eV) *m/z* 663 (Et₃SifcSiMe₂fcSiMePhH), 966 (Et₃SifcSiMe₂(fcSiMePh)₂H), 1270 (Et₃SifcSiMe₂(fcSiMePh)₃H).

ROP of 1b Catalyzed by [2]Platinasilaferrocenophane 4 in the Presence of Et₃SiH. Complex **1b** (1.00 g, 3.29 mmol) was dissolved in toluene (5 mL). Prior to the addition of the catalyst, fcPt(1,5-cod)-SiMe₂ (<1 mol %), Et₃SiH (558 mg, 4.81 mmol) was added. The resulting red-colored solution was stirred at room temperature over a 24 h period during which time the color changed to orange. The reaction mixture was then precipitated into hexanes (.~150 mL) and filtered at −78 °C. The orange-colored polymer was taken up in benzene. After removal of the residual solvent, an orange polymer was obtained. Similarly, removal of the solvent from the −78 °C precipitation afforded an orange oil which was analyzed as the supernatant. Yield: 1.46 g (94%). GPC Analysis: M_n = 4900, PDI = 1.54. The polymer was then passed through an alumina column deactivated with triethylamine initially using cyclohexane as the eluting solvent and gradually increasing the amount of CH₂Cl₂.

cyclohexane:CH₂Cl₂ = 80:20: ¹H NMR (δ, C₆D₆): 0.49 (m, fcSi*Me*PhH), 0.72, (s, fcSi*Me*Phfc), 0.74 (s, fcSi*Me*Phfc), 0.76 (s, fcSi*Me*Phfc), 0.79 (m, fcSi(C*H₂*CH₃)₃), 1.06 (t, fcSi(CH₂C*H₃*)₃), 3.99 to 4.21 (br, Cp, SiMePh*fc*SiMePh), 5.09 (m, fcSiMePh*H*), 7.24 (br, fcSiMe*Ph*), 7.72 (br, fcSiMe*Ph*). ¹³C NMR (δ, C₆D₆): −4.2 (fcSi*Me*PhH), −3.3(4) (s, fcSi*Me*Phfc), −3.3(0) (s, fcSi*Me*Phfc), −3.2(5) (s,

fcSi*Me*Phfc), 5.0 (s, fcSi(*CH₂*CH₃)₃), 8.3 (s, fcSi(CH₂*CH₃*)₃), 70.3 (m, ipso-C, Cp), 72.0 (s, Cp, *fc*SiMePh), 72.4 (s, Cp *fc*SiMePh), 74.2 (s, Cp *fc*SiMePh), 74.5 (s, Cp *fc*SiMePh), 127.9 (s, fcSiMe*Ph*), 129.3 (s, fcSiMe*Ph*), 134.6 (s, fcSiMe*Ph*), 138.9 (s, ipso-C, fcSiMe*Ph*), ²⁹Si NMR (δ, C₆D₆): −18.5 (s, fc*Si*MePhH), −18.4 (s, fc*Si*MePhH), −11.2-(4) (fc*Si*MePhfc), −11.1(9) (switching group), 2.1 (s, Et₃*Si*fcSiMePh). GPC Analysis: M_n = 5000, PDI = 1.12.

The Supernatant. Following isolation of the crude polymer from the reaction mixture, the resulting supernatant was characterized after removal of the hexanes under vacuum. ¹H NMR (δ, C₆D₆): 0.49 (m, fcSi*Me*PhH), 0.72, (s, fcSi*Me*Phfc), 0.74 (s, fcSi*Me*Phfc), 0.76 (s, fcSi*Me*Phfc), 0.80 (m, fcSi(C*H₂*CH₃)₃), 1.07 (t, fcSi(CH₂C*H₃*)₃), 3.99 to 4.15 (br, Cp, SiMePh*fc*SiMePh), 4.20 to 4.30 (br, Cp, Et₃Si*fc*SiMe₂-fc switching groups), 5.09 (m, fcSiMePh*H*), 7.24 (br, fcSiMePh*H*), 7.72 (br, fcSiMe*Ph*). ¹³C NMR (δ, C₆D₆) −4.2 (s, fcSi*Me*PhH), −3.3(4) (s, fcSi*Me*Phfc), −3.3(0) (s, fcSi*Me*Phfc), −3.2(5) (s, fcSi*Me*Phfc), 5.0 (s, fcSi(*CH₂*CH₃)₃), 8.1 (s, fcSi(CH₂*CH₃*)₃), 69.8 to 70.6 (m, ipso-C, Cp), from 71.6 to 71.9 (switching groups), 72.0 (br, Cp), 72.2 (br, Cp), 73.8 to 74.8 (switching groups), 74.2 (br, Cp), 74.4 (br, Cp) 127.9 (br, fcSiMe*Ph*), 129.3 (s, fcSiMe*Ph*), 134.6 to 134.8 (s, fcSiMe*Ph*), 138.7 to 138.8 (m, fcSiMe*Ph*). ²⁹Si NMR (δ, C₆D₆): −18.5 (s, fc*Si*MePhH), −18.4 (s, fc*Si*MePhH), −11.3 (fc*Si*MePhc), −11.2 (switching group, fc*Si*MePhfc), 2.1 (s, Et₃*Si*fc). MS (EI, 70 eV) *m/z* 1637 (Et₃Si-(fcSiMePh)₅H), 1333 (Et₃Si(fcSiMePh)₄H), 1028 (Et₃Si(fcSiMePh)₃H), 724 (Et₃Si(fcSiMePh)₂H), 420 (Et₃SifcSiMePhH).

ROP of 1a Catalyzed by fcPt(1,5-cod)Sn(ᵗBu)₂ (11) in the Presence of Et₃SiH. Ferrocenophane **1a** (0.204 g, 0.84 mmol) and Et₃SiH (0.096 g, 0.83 mmol) were dissolved in toluene (.∼2 mL). fcPt-(1,5-cod)Sn(tBu)₂ (**11**) (16 mg, 0.03 mmol %) was dissolved in toluene (.∼1 mL). This solution was then added to the **1a**/Et₃SiH mixture. After the reaction was allowed to stir at room temperature for 4 d, the resulting oligomer was precipitated into hexanes (200 mL) at −78 °C, filtered, and dried under vacuum. Yield: 162 mg (79%).

Isolated polymer: ¹H NMR (δ, C₆D₆): 0.28 (d, fcSi*Me₂*H), 0.54 (s, fcSi*Me₂*fc), 0.77 (q, fcSi(C*H₂*CH₃)₃), 1.07 (t, fcSi(CH₂C*H₃*)₃), 4.10 (m, *fc*SiMe₂fc), 4.26 (m, *fc*SiMe₂fc), 4.69 (m, *H*SiMe₂fc). ¹³C NMR (δ, C₆D₆): −2.8 (fcSi*Me₂*H), −0.6 (fcSi*Me₂*fc), 5.0 ((CH₃*CH₂*)₃Sifc), 8.1 ((*CH₃*CH₂)₃Sifc), 71.7 (s, Cp, *fc*SiMe₂), 71.8 (s, ipso-C, *fc*SiMe₂H), 73.6 (s, Cp, *fc*SiMe₂H). ²⁹Si NMR (δ, C₆D₆): −18.6 (fc*Si*Me₂H), −6.8 (fc*Si*Me₂fc), 2.1 (Et₃*Si*fc). GPC Analysis: M_n = 3800, PDI = 1.21.

Supernatant fraction: ¹H NMR (δ, C₆D₆): 0.27 (d, fcSi*Me₂*H), 0.53 (s, fcSi*Me₂*fc), 0.74 (q, fcSi(C*H₂*CH₃)₃), 1.05 (t, fcSi(CH₂C*H₃*)₃), 1.54 (s, $^3J^{(117/119}$Sn−H) = 56 Hz), 1.78 (m, C*H₂* of 1,5-cod), 4.06 (m, switching groups and Pt(1,5-cod)*fc*Sn'Bu₂), 4.09 (br, fcSiMe₂fc), 4.24 (br, fcSiMe₂fc), 4.37 (m, br, Pt(1,5-cod)*fc*Sn'Bu₂), 4.46 (m, br, Pt(1,5-cod)*fc*Sn'Bu₂), 4.69 (m, *H*Me₂Sifc). ¹³C NMR (δ, C₆D₆): −2.9 (s, fcSi*Me₂*H) −0.6 (s, fcSi*Me₂*fc), 5.0 (fcSi(*CH₂*CH₃)₃), 8.1 (s, fcSi(CH₂-*CH₃*)₃), 33.2 ('Bu), 31.6 (*C*H₂ of 1,5-cod), 27.8 (*C*H₂ of 1,5-cod), 71.7

(m, Cp, *fc*SiMe₂), 71.8 (ipso-C, *fc*SiMe₂), 73.6 (m, Cp, *fc*SiMe₂). ²⁹Si NMR (δ, C₆D₆): −18.2 (s, fc*Si*Me₂H), −6.4 (fc*Si*Me₂fc), 2.5 (s, Et₃-*Si*fcSiMe₂). While not all of the ¹³C NMR resonances associated with **11** were resolved, conclusive evidence for the presence of this species in the crude reaction mixture may be found in the ¹H NMR spectrum. GPC Analysis: M_n = 800, PDI = 1.80.

The Effect of Mercury on the Pt(0)-Catalyzed ROP of 1a. A typical experiment involved **1a** (0.05 g, 0.21 mmol) dissolved in 0.7 mL of C₆D₆ to which Hg (0.2 g, 1.0 mmol) was added. To this reaction mixture, a catalytic amount of Pt(1,5-cod)₂ (≪1 mol %) was added and the reaction shaken vigorously for 1 min. The progress of the polymerization was monitored by ¹H NMR spectroscopy. Yield: with Hg 12 mg (24%); without Hg 41 mg (82%). GPC Analysis: with Hg M_n 55 300, PDI = 1.53; without Hg M_n 121 500, PDI = 1.45.

The Effect of Mercury on the Pt(0)−Catalyzed ROP of 1a in the Presence of Et₃SiH. A series of experiments using varying ratios of **1a**:Et₃SiH were conducted in the presence of mercury. A typical experiment involved **1a** (0.05 g, 0.21 mmol) and Et₃SiH (0.50 mg, 100 μL of a 5 mg/mL solution, 4.2 μmol) dissolved in 0.7 mL of C₆D₆ to which Hg (0.2 g, 1.0 mmol) (or in the case of the controls, no mercury) was added. To this reaction mixture, a catalytic amount of Pt(1,5-cod)₂ (≪1 mol %) was added and the reaction shaken vigorously for 1 min. The progress of the polymerization was monitored by ¹H NMR spectroscopy. Yield: with Hg 26 mg (52%); without Hg 24 mg (49%). GPC Analysis: ratio of monomer:silane = 25:1 with Hg M_n 65 600, PDI = 1.55; without Hg M_n 32 700, PDI = 1.51; monomer:silane = 50:1 with Hg M_n 27 400, PDI = 1.55; without Hg M_n 51 000, PDI = 1.79; monomer:silane = 75:1 with Hg M_n 27 200, PDI = 1.68; without Hg M_n 84 400, PDI = 1.69.

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