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Highly Active Cationic Rhodium(I) Precatalysts for the Ambient Temperature Ring-Opening Polymerization of [1]Silaferrocenophanes and Tetramethyldisilacyclobutane

Karen Temple, Sebastian Dziadek, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada

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The cationic rhodium(I) complexes [Rh(1,5-cod)$_2$]A (A = OTf, PF$_6$, 1,5-cod = 1,5-cyclooctadiene) have been shown to exhibit high catalytic activity for the transition metal-mediated ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes (e.g., fcSiMe$_2$ (**1a**), fc = Fe(η^5-C$_5$H$_4$)$_2$), to quantitatively afford high molecular weight ($M_n > 10^5$) polyferrocenylsilanes (e.g., [fcSiMe$_2$]$_n$ (**2a**)). However, prolonged exposure of the resulting polyferrocene solution to the catalyst resulted in a dramatic molecular weight decline. Transition metal-catalyzed ROP of tetramethyldisilacyclobutane (**6**) and copolymerization of this species with **1a** also proved readily feasible with [Rh(1,5-cod)$_2$]OTf forming high molecular weight polycarbosilane homopolymer (**7**) ($M_n = 4.20 \times 10^5$ to 1.08×10^6, PDI = 1.39−2.08) and poly(carbosilane-*r*-ferrocenylsilane) (**8**) copolymer ($M_n = 4.63 \times 10^5$, PDI = 1.86), respectively. While [Rh(1,5-cod)(dmpe)]PF$_6$ (dmpe = bis(dimethylphosphinoethane)) proved less active as a ROP catalyst, this species represents the first phosphine-ligated catalyst for the ROP of **1a**, and moreover, in this case no subsequent depolymerization of the resulting poly(ferrocenyldimethylsilane) (**2a**) was detected. The cleavage of the polyferrocene backbone in the presence of [Rh(1,5-cod)$_2$]OTf was modeled through the catalytic reaction of Fc$_2$SiMe$_2$ (Fc = Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)) with the rhodium complex (9 mol %), which resulted in Cp−Si bond cleavage affording ferrocene as the sole, isolable product. The presence of 1,5-cod inhibited the catalytic activity of both [Rh(1,5-cod)$_2$]OTf and [Rh(1,5-cod)(dmpe)]PF$_6$, suggesting that elimination of a 1,5-cod ligand is necessary to generate the true active catalytic species. The addition of dmpe effectively arrested the catalytic activity with [Rh(1,5-cod)(dmpe)]PF$_6$; this is presumably a result of the displacement of the 1,5-cod ligand by dmpe, which would generate catalytically inactive [Rh(dmpe)$_2$]PF$_6$.

Introduction

The incorporation of main group and transition elements into polymer chains continues to attract attention due to the interesting physicochemical properties of the resulting materials.[1] Synthetic routes to inorganic polymers have traditionally employed condensation and ionically-initiated ring-opening polymerization (ROP) processes.[1,2] However, key synthetic advances involving the polymerization of silanes, germanes, and stannanes using transition metal catalysis have recently gained much attention.[3−5] In addition, our group has recently reported a rhodium-mediated route for the formation of polyphosphinoboranes.[6,7]

An area of significant recent interest concerns polyferrocenes (e.g., **2a**), which are readily accessible via the ROP of strained [1]metallocenophanes (e.g., **1**) and their analogues.[8−11] Due to the unique backbone comprised of alternating repeat units of ferrocene and silicon, these

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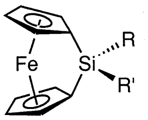
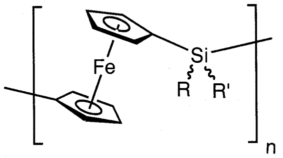
polymers exhibit electrochromism and redox activity and become semiconducting upon doping.[9,12,13] As a result of such physical properties, these materials are attracting attention as charge dissipation coatings, variable refractive index sensing materials, and magnetic ceramic precursors over a range of length scales.[14−19] In addition to the previously reported thermal, anionic, and cationic ROP routes,[10,20,21] the ambient temperature transition metal-catalyzed polymerization promoted by a variety of Pt and Pd complexes, as well as the Rh(I) complex $[Rh(coe)_2(\mu\text{-}Cl)]_2$ (coe = cyclooctene), provides a mild and more convenient route to these novel materials.[22−25] Moreover, this facile synthetic methodology also permits molecular weight control and access to complex polymer architectures, such as block, star, and graft copolymers.[24−26]

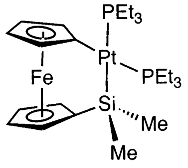


1a: R = R' = Me
1b: R = Me, R' = Et
1c: R = Me, R' = Ph



2a: R = R' = Me
2b: R = Me, R' = Et
2c: R = Me, R' = Ph

Since the discovery of transition metal-catalyzed ROP of **1a** in 1995,[22,23] efforts have been directed at unraveling the mechanisms of these reactions.[27−32] The insertion of a platinum fragment into a strained Si−C bond has been proposed as the first step in the mechanism. With this in mind, we and Sheridan have reported the oxidative-addition of $Pt(PEt_3)_3$ and $Pt(1,5\text{-cod})_2$ to **1a**, affording the corresponding [2]platinaferrocenophanes, **3** and **4**, respectively.[29−31] With a labile 1,5-cod ligand, **4** proved an equally effective catalyst for the ROP of **1a** as its parent compound, $Pt(1,5\text{-cod})_2$. In contrast, the absence of catalytic activity for **3** was attributed to the presence of more strongly coordinating phosphine ligands. 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. Furthermore, when used in conjunction with $BH_3{\cdot}THF$ cocatalyst, which serves as a phosphine ligand abstraction agent, complex **3** becomes catalytically active, affording low molecular weight, cyclic polymers.[32] Recent mechanistic studies point to the formation of platinum colloids as the active catalytic species.[27]



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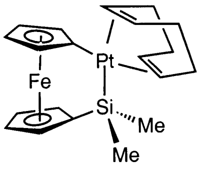

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ROP of **1a** with platinum catalysts normally requires ca. 24 h to reach high conversion (ca. 100%). With this in mind, we have recently examined cationic organorhodium complexes with the intention of developing a more active catalytic system. In this paper we report the high catalytic activity of the cationic Rh(I) complexes $[Rh(1,5\text{-cod})_2]A$ (1,5-cod = 1,5-cyclooctadiene, A = OTf, PF_6) for the ROP of [1]silaferrocenophanes (**1a**−**1c**) and also tetramethyldisilacyclobutane (**6**). In addition, the discovery of the first effective ROP catalyst bearing phosphine ligands, namely, $[Rh(1,5\text{-cod})dmpe]PF_6$ (dmpe = bis(dimethylphosphino)ethane), is described.

Results and Discussion

Transition Metal-Catalyzed ROP of 1a Using $[Rh(1,5\text{-cod})_2]A$ (A = OTf, PF_6) as a Precatalyst. The transition metal-mediated ROP of [1]silaferrocenophanes (e.g., **1a**) by platinum complexes normally requires ca. 24 h to reach 100% conversion. Therefore, we explored the catalytic potential of $[Rh(1,5\text{-cod})_2]A$ with the hopes of discovering a more efficient catalyst. Thus, on addition of catalytic amounts of $[Rh(1,5\text{-cod})_2]A$ (ca. 1 mol %) to **1a** in toluene, the solution immediately became highly viscous and changed from the initial red color to amber, characteristic of polyferrocenylsilane formation.

Analysis of the reaction mixture by ^1H NMR spectroscopy confirmed ROP to be 100% completed within 2 min.[33] The resulting polymer was immediately iso-

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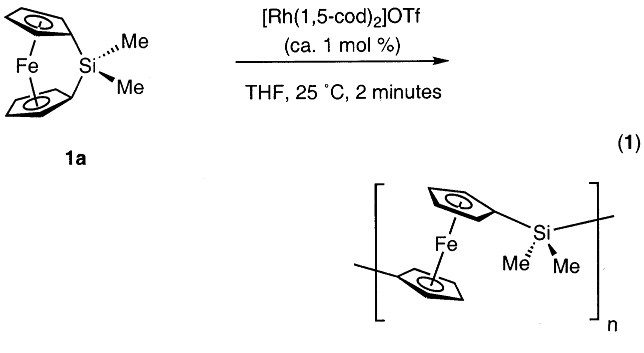
[33] The ambient-temperature Rh(I)-catalyzed polymerizations of **1a**−**1c** dissolved in C_6D_6 to give a 0.25 M solution with 1.4 mol % [Rh-(1,5-cod)2]OTf are complete (100% conversion) by ^1H NMR spectroscopy by the time the spectrum can be run (ca. 2 min). Similar concentrations using the Pt(0) catalysts result in 80% polymer within 2 h and require 24 h to reach full conversion. When reactions are performed in CH_2Cl_2, enough heat is generated during the polymerization to cause the solution to reflux.



lated by precipitation into hexanes, affording a fibrous orange polymer of high molecular weight. Generally, M_n values ranged between 1.00×10^5 and 1.94×10^5, although values up to $M_n = 4.81 \times 10^5$ have also been observed, with corresponding PDI values falling between 1.40 and 2.10 by GPC analysis.

In contrast to the platinum catalytic systems, failure to isolate **2a** within ca. 2 h led to significant apparent decreases in molecular weight as measured by GPC. The results are rather dramatic. Specifically, addition of [Rh(1,5-cod)$_2$]A to **1a** in either toluene, THF, or CH_2Cl_2 was accompanied by the normal rapid increase in solution viscosity indicative of high polymer formation. After 2 h, a marked decrease in viscosity was observed, irrespective of the counterion or solvent employed. Precipitating aliquots at selected time intervals revealed a continuous decrease in the molecular weights as indicated by GPC (Table 1).

It is important to bear in mind that partial oxidation of polyferrocenes can cause artificially low apparent molecular weights to be observed by GPC in THF due to the associated decrease in the hydrodynamic radius.[34] However, attempts to reduce samples of **2a** generated using [Rh(1,5-cod)$_2$]OTf with a 10% v/v solution of hydrazine in MeOH only occasionally resulted in partial regeneration of the higher molecular weight fraction (Table 1). Similar results were observed with [Rh(1,5-cod)$_2$]PF$_6$ as a precatalyst. This indicated that although some degree of oxidation appears to occur, the decline in molecular weight is real and chain cleavage is observed.

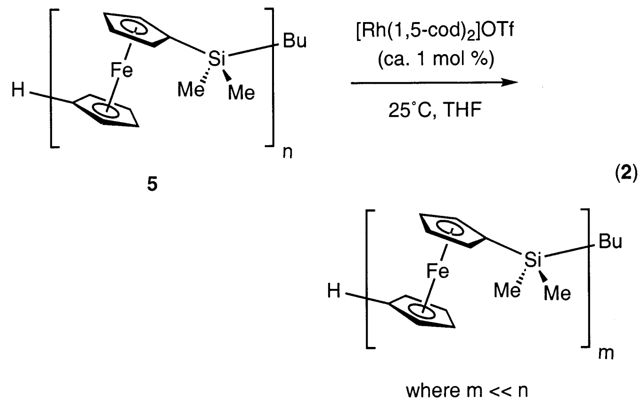


Table 1. Influence of Prolonged Reaction Times on the GPC-Derived Molecular Weights of Polyferrocenylsilane 2a Formed from the [Rh(1,5-cod)]$_2$A-Catalyzed ROP of 1a in THF

A	time (h)	M_n	PDI
OTf	0.25	1.00×10^5	1.90
	4	1.50×10^4	1.67
	20	oligomers[a]	
	20[b]	7.90×10^3	1.15
	20[b]	1.01×10^5 [d]	1.22
PF$_6$	0.25	1.78×10^5	2.05
	2	1.60×10^5	2.01
	48	3.60×10^4	1.64
	48[c]	1.95×10^5	2.14

[a] Oligomers soluble in hexanes at 25 °C, $M_n < 1.5 \times 10^3$. [b] After reduction of polymer, isolated after 20 h, by treatment with hydrazine (7.90×10^3:1.01×10^5 = 1:2). [c] After reduction of polymer, isolated after 48 h, by treatment with hydrazine. [d] This experiment was repeated several times and the $M_n \approx 10^5$ peak was often not observed.

In an effort to gain more insight into the cause of the decreasing molecular weights, we turned our attention to the reaction of [Rh(1,5-cod)$_2$]OTf (ca. 1 mol %) with narrow polydispersity samples of polyferrocenylsilane **5** ($M_n = 1.10 \times 10^5$, PDI = 1.12).[21] Importantly, molecular weights decreased in a fashion similar to that observed for the poly(ferrocenyldimethylsilane) generated using rhodium(I) precatalysts (Table 2).

Reduction of the polymer by treatment with hydrazine again resulted in a bimodal distribution with partial regeneration of a high molecular weight fraction ($M_n \approx 1.2 \times 10^5$, PDI ≈ 1.2), in addition to a low molecular weight fraction ($M_n \approx 1.4 \times 10^4$, PDI ≈ 2.5). To investigate the ability of the triflate anion to react with the silicon−carbon bonds of a polyferrocenylsilane, sodium triflate was added to a THF solution of monodisperse **5**. No decrease in molecular weight or broadening of the molecular weight distribution was observed over a period of 11 days.

In an effort to probe the generality of the [Rh(1,5-cod)$_2$]OTf precatalyst for the ROP of [1]silaferrocenophanes, we also investigated the Rh-mediated ROP behavior of the unsymmetrically substituted monomer **1b** and **1c**. Similar rates of polymerization were observed for monomers **1a** and **1b**.[33] In contrast, steric effects appeared to play a role in the ROP of **1c**, which proceeded at a noticeably slower rate. Trends in molecular weight decline for polyferrocenylsilane **2b** with respect to reaction time paralleled that observed with **2a,** while the decline detected for polymer **2c** over time was less dramatic. It should be noted that molecular weights remained more uniform in the case of **2c**, reaching a plateau typically around $M_n = 5 \times 10^4$ after 24 h. This may be a consequence of the bulkier phenyl groups, which may inhibit chain cleavage reactions in ring-opened polymer **2c**.

Transition Metal-Catalyzed ROP of 1a Using [Rh(1,5-cod)dmpe]OTf as a Precatalyst. In sharp contrast to the dramatic decrease in the observed molecular weights with [Rh(1,5-cod)$_2$]A precatalysts, substitution of a 1,5-cod ligand for dmpe affords an effective catalyst for the ROP of **1a** without subsequent

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(34) Gómez-Elipe, P.; Temple, K.; Manners, I. Unpublished work. Gel-permeation chromatography gives molecular weight data based on the hydrodynamic size of the polymer molecules. Oxidation of the main chain ferrocene units leads to contraction of the polymer coils due to poorer polymer/solvent interactions, and so an apparent decrease in molecular weight is detected. If the oxidized polymer is reduced back to the neutral material, the original hydrodynamic size and GPC-derived molecular weight is restored. For an introduction to GPC, see: Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman and Hall: New York, 1991; pp 211−221.

Table 2. Influence of [Rh(1,5-cod)$_2$]OTf on the GPC-Derived Molecular Weights of Polyferrocenylsilane 5

	time (h)					
	0	44	66	102	$102^{a,b}$	
M_n	1.10×10^5	4.80×10^4	3.40×10^4	2.50×10^4	1.2×10^5	1.4×10^4
PDI	1.12	1.48	1.59	1.80	1.20	2.51

[a] After reduction by treatment of the polymer with hydrazine. [b] Bimodal molecular weight distribution with an approximate molecular weight (M_n) 2:1 ratio of the fractions of 1.2×10^5:1.4×10^4.

chain cleavage. Thus, **1a** underwent metal-catalyzed ROP initiated by [Rh(1,5-cod)dmpe]OTf in C_6D_6 to afford high polymer **2a** with quantitative conversion attained after 4 h ($M_n = 1.0 \times 10^5$, PDI = 1.94).[35] Equally important, prolonged exposure of the polymer to the catalyst solution over 1 week had no significant effect on the resulting molecular weight.

In light of the inability of Wilkinson's catalyst, Rh(PPh_3)$_3$Cl, to induce ROP of **1a**,[22] the catalytic activity of [Rh(1,5-cod)dmpe]OTf is significant. This further contrasts with Pd and Pt systems, where strongly binding phosphine ligands hinder catalytic ROP activity,[29] although Tanaka and co-workers have demonstrated catalytic dimerization reactions with Pd phosphine complexes.[28] Thus, [Rh(1,5-cod)dmpe]OTf represents the first phosphine-ligated catalyst to produce high molecular weight polymer **2a**.

Inhibition of Catalytic Activity via the Addition of 1,5-cod or dmpe. Mechanistic studies of the Pt(1,5-cod)$_2$-catalyzed polymerization of **1a** have shown initial insertion to afford **4** with the loss of 1,5-cod followed by dissociation of the second ligand prior to polymerization. Evidence for the second step was provided by the complete lack of polymer formation when the polymerization of **1a** was initiated by **4** in neat 1,5-cod.[30] Further evidence pointing to the necessary elimination of the remaining ligands on platinum lies in the inability of **3** to induce ROP of **1a** in the absence of the phosphine ligand abstracting BH_3·THF complex as a cocatalyst.[32] Consequently, the effect of 1,5-cod on the catalytic activity of [Rh(1,5-cod)$_2$]OTf and [Rh(1,5-cod)dmpe]OTf and dmpe on that of [Rh(1,5-cod)dmpe]OTf was expected to provide insight into the ROP mechanism for the Rh catalysts. Thus, equimolar amounts of **1a** and 1,5-cod were dissolved in C_6D_6 to which [Rh(1,5-cod)$_2$]OTf (<1 mol %) was added. After 12 h at room temperature, the formation of less than 5% of polymer **2a** was detected by ^{1}H NMR spectroscopy. In the case of [Rh(1,5-cod)dmpe]OTf, the addition of 1 equiv of either 1,5-cod or dmpe completely inhibited formation of polymer **2a** under similar experimental conditions. Therefore these studies for the rhodium-based catalysts also point to the necessary elimination of weakly coordinated 1,5-cod before catalytic activity is achieved. With excess dmpe, the anticipated displacement of the 1,5-cod ligand in [Rh(1,5-cod)dmpe]OTf by the diphosphine to yield [Rh(dmpe)$_2$]OTf arrested catalytic activity. Indeed, when small quantities of [Rh(dmpe)$_2$]OTf were added to a solution of **1a** in C_6D_6, no polymer was detected after 1 week at room temperature.

Polymerization of Disilacyclobutane (6) and the Copolymerization of 1a and 6 Catalyzed by [Rh(1,5-cod)$_2$]OTf. Silacyclobutanes possess ring strain, which also renders them effective as ROP monomers. The resulting polycarbosilanes represent an important class of inorganic polymers that attract interest as ceramic precursors to β-SiC.[1] Transition metal-catalyzed polymerization of cyclic carbosilanes by Pt(IV) complexes was discovered in the 1960s. Numerous other precatalysts have been explored for the metal-mediated ROP of silacyclobutanes ranging from anionic species such as $IrCl_6^{2-}$ and $RuCl_6^{2-}$ to neutral organorhodium complexes typically bearing phosphine ligands.[36] In the case of the Ru catalyst, polymers were of low molecular weight, while the Ir complexes resulted in low conversion. Neutral rhodium-based systems generated intractable gums, with Wilkinson's catalyst proving most effective, affording 50% conversion after 4 h.[37] Recently, Neckers and co-workers reported the discovery of a highly active catalyst, Pt(acac)$_2$, which photocatalyzes the ROP of **6**, affording high molecular weight polymer within 15 min.[38,39] Nonetheless, H_2PtCl_6 presently remains the general catalyst of choice despite requiring elevated reaction temperatures.[40]

The ROP of **1a** appears to mirror the polymerization of sila- and disilacyclobutanes in a number of key respects. Tanaka and co-workers isolated 1-platina-2-silacyclopentanes via the oxidative-addition of Pt(PEt_3)$_3$ to a variety of silacyclobutanes.[41] Indeed, complexes **3** and **4** model analogous insertions of platinum fragments into the strained Si−C bond of **1a**. As a result of the impressive catalytic rate for the polymerization of **1a**, we therefore decided to investigate the ability of [Rh(1,5-cod)$_2$]OTf to initiate the ROP of **6**. Thus, catalytic amounts of [Rh(1,5-cod)$_2$]OTf (<1 mol %) were added to a solution of $[CH_2SiMe_2]_2$ in $CDCl_3$ at room temperature. A pronounced increase in viscosity was noted after only 45 min, and ^{1}H NMR spectroscopy revealed the appearance of new resonances appearing at $\delta = 0.04$ and -0.25, consistent with the formation of polymer **7**. Integration of the signals indicated an 85% conversion to polymer at that time. Isolation of the resulting polymer **7** via precipitation into MeOH afforded a white fibrous material of very high molecular weight in 80%

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[35] [Rh(1,5-cod)(dmpe)]PF_6 proved less efficient as a catalyst than [Rh(1,5-cod)$_2$]PF_6, displaying ROP rates similar to those observed with Pt(0) catalysts.

[36] For examples of transition metal-catalyzed ROP of carbosilanes, see: (a) Kriner, W. A. *J. Polym. Sci., Part A-1* **1966**, *4*, 444. (b) Cundy, C. S.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 445, and references therein. (c) Poletaev, V. A.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1973**, *208*, 1112. (d) Lienhard, M.; Ruskin, I.; Verdecia, G.; Wiegand, C.; Apple, T.; Interrante, L. V. *J. Am. Chem. Soc.* **1997**, *119*, 12020. (e) Peckham, T. J.; Nguyen, P.; Bourke, S. C.; Wang, Q.; Harrison, D. G.; Zoricak, P.; Russell, C.; Liable-Sands, L. M.; Rheingold, A. L.; Lough, A. J.; Manners, I. *Organometallics* **2001**, *20*, 3035.

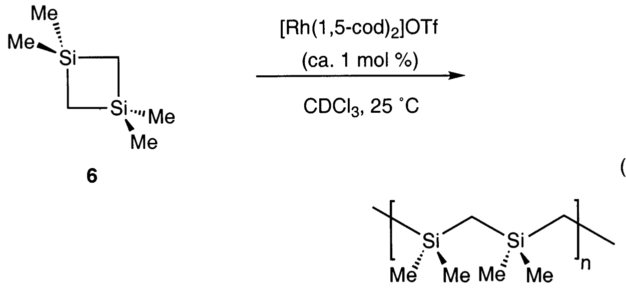
[37] Cundy, C. S.; Eaborn, C.; Lappert, M. *J. Organomet. Chem.* **1972**, *44*, 291.

[38] Wu, X. S.; Neckers, D. C. *Macromolecules* **1999**, *32*, 6003.

[39] Wang, F.; Neckers, D. C. *Macromolecules* **2001**, *34*, 6202.

[40] Interrante, L. V.; Wu, H. J.; Apple, T.; Shen, Q.; Ziemann, B.; Narsavage, D. M.; Smith, K. *J. Am. Chem. Soc.* **1994**, *116*, 12085.

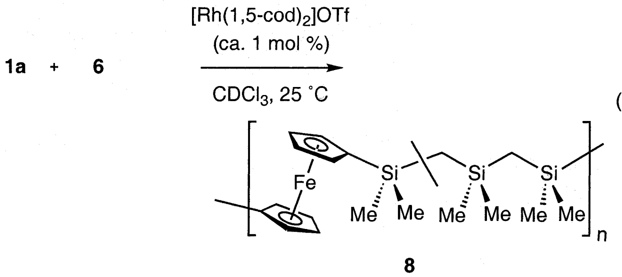
[41] For insertion of Pd or Pt into a silacyclobutane, see: (a) Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873. (b) Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246.



6 (3) 7

yield ($M_n = 1.08 \times 10^6$, PDI = 1.39). Thus, [Rh(1,5-cod)$_2$]OTf represents a highly active catalyst for the ROP of **6**, with only the platinum-based photocatalyst, Pt(acac)$_2$, exhibiting superior catalytic activity.[38,39] Importantly, in contrast to the degradation of **2a** following [Rh(1,5-cod)$_2$]OTf-initiated ROP of **1a**, no decrease in molecular weight was detected for **7**. Indeed, the molecular weights of **7** were unchanged over a period of 7 days.

We previously reported that random copolymers derived from **1a** and **6** and benzosilacyclobutane are readily accessible via platinum-catalyzed ROP.[42] Consequently, the catalytic effect of [Rh(1,5-cod)$_2$]OTf on both **1a** and **6** to afford high molecular weight homopolymers **2a** and **7** led us to explore the possible copolymerization of these two monomers. Previous copolymerization studies have shown that tetramethyldisilacyclobutane undergoes transition metal-mediated ROP at a slower rate than the dimethyl[1]-silaferrocenophane.[24] Therefore, to effectively copolymerize these two monomers, a higher concentration of the less reactive species was used. Thus compounds **1a** and **6** in a 1:9 mol ratio were dissolved in THF, after which a catalytic amount of [Rh(1,5-cod)$_2$]OTf (<1 mol %) was added. An immediate dramatic increase in the viscosity was accompanied by a color change from orange-red to amber. Due to the decreases in molecular weight when the [Rh(1,5-cod)$_2$]A catalyzes the polymerization, the polymer was precipitated prior to complete consumption of **6**. Therefore, after stirring for 20 min at room temperature, the solution was precipitated into MeOH, yielding an orange-colored gum (**8**) in 45% yield.



(4) 8

GPC revealed a monomodal distribution of high molecular weight ($M_n = 4.63 \times 10^5$, PDI = 1.86). The ^{29}Si NMR spectrum (Figure 1) proved interesting and surprisingly showed only two detectable resonances. The peak at $\delta = 0.21$ is similar to that observed for the corresponding homopolymer **7** and was therefore attributed to the silicon resonances of polycarbosilane segments. In contrast, the second resonance falling slightly upfield at $\delta = -3.66$ is indicative of the switching group, CH$_2$*Si*Me$_2$fc. Noteworthy is the conspicuous absence of signals due to segments analogous to homopolymer **2a** at $\delta = -6.41$. Similarily, the resonances due to the methyl groups of homopolyferrocenylsilane (fcSi*Me$_2$*fc), which typically fall at $\delta = 0.58$ and $\delta = -0.55$ in ^{1}H and ^{13}C NMR spectra, respectively, were not observed. Consequently, copolymer **8** is comprised of segments derived from **6** with a single dimethylferrocenylsilane unit intermittently interrupting this homo-oligocarbosilane backbone. On the basis of the ^{29}Si NMR spectrum, the carbosilane segments average three repeat units.

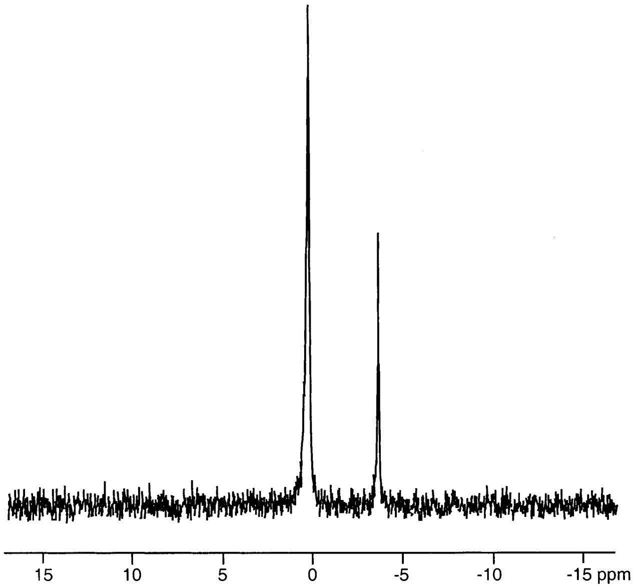


Figure 1. ^{29}Si NMR spectrum (C$_6$D$_6$) of copolymer **8**.

Switching groups detected in both the ^{1}H and ^{13}C NMR spectra provided further evidence supporting the formation of a random copolymer. The ^{1}H NMR spectrum displayed resonances at $\delta = 0.41$ and 0.44, which correlate with the methyl groups flanking the ferrocene moiety (CH$_2$Si*Me$_2$*fcSi*Me$_2$*CH$_2$). The resonances at $\delta =$ 0.14 and 0.20 correspond to the methylene switching groups (*CH$_2$*SiMe$_2$fcSiMe$_2$*CH$_2$*). Thus, the presence of these two sets of distinct switching group resonances arises from the unusual structure of short carbosilane segments, interrupted by single ferrocenylsilane moeities, and not due to head-to-head linkages. The ^{13}C NMR spectrum also proved informative. The resonance at $\delta = 2.9$ shouldering the signal of the methyl groups of polycarbosilane segments (cf. $\delta = 3.1$) was assigned to the switching group CH$_2$Si*Me$_2$*CH$_2$SiMe$_2$fc. Similarly, a series of peaks, observed between $\delta = 6.4-7.5$, was attributed to SiMe$_2$*CH$_2$*SiMe$_2$fc switching groups. More intense signals at $\delta = 3.1$ and 7.9 were attributed to the methyl and methylene resonances of homocarbosilane segments. Finally, the cyclopentadienyl ligands were found to resonate at $\delta = 71.6$ and 73.4, which are similar to the values for **2a**. Importantly, no degradation of the backbone was detected upon leaving the reaction solution in the presence of the catalyst for prolonged periods of time.

Modeling the Catalytic Depolymerization Chemistry: Reaction of Fc$_2$SiMe$_2$ (Fc = (η^5-C$_5$H$_5$)(η^5-

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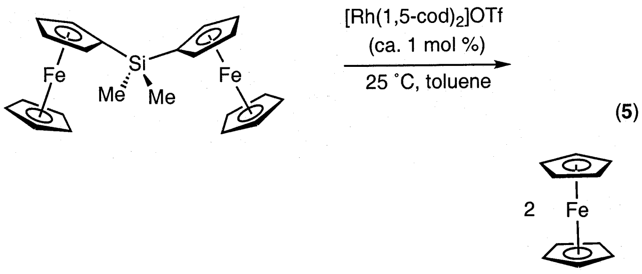
[42] Sheridan, J. B.; Gómez-Elipe, P.; Manners, I. *Macromol. Rapid. Commun.* **1996**, *17*, 319.

C_5H_4)Fe) with [Rh(1,5-cod)$_2$]OTf. To model the depolymerization of polyferrocenylsilane **2a**, we investigated the reaction of Fc_2SiMe_2 (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4)) with a catalytic amount (10 mol %) of [Rh(1,5-cod)$_2$]OTf. During the reaction, the initially orange-colored solution discolored somewhat, taking on a slight green hue. After 1 week at room temperature, the ^{1}H NMR resonances corresponding to Fc_2SiMe_2 had disappeared, while a new signal at $\delta = 4.05$, characteristic of ferrocene, was detected. The formation of ferrocene was confirmed by ^{13}C NMR and mass spectrometry. Furthermore, when the reaction was conducted in a deuterated solvent (C_6D_6), no Fe(η^5-C_5H_4D)(η^5-C_5H_5) was detected in the product as determined by mass spectrometry. The fate of the $SiMe_2$ fragment remains unknown, with numerous ^{1}H NMR peaks appearing in the region $\delta = 0.43-0.12$, upfield of the methyl resonance in Fc_2SiMe_2 ($\delta = 0.50$).



(5)

These results indicate that [Rh(1,5-cod)$_2$]OTf can cause Si−Cp bond cleavage in a model compound and, thus, suggest a similar mechanism may be operating in the case of high molecular weight polymer. Interestingly, no reaction occurred when Me_3SiPh was treated with [Rh(1,5-cod)$_2$]OTf, indicating that this Rh(I) complex is not active toward Si−Ph bonds at room temperature and that the presence of repeating ferrocenylsilane units may be a prerequisite for Si−C bond cleavage.[43] A detailed knowledge of the catalytic depolymerization mechanism is desirable and will be the subject of future work.

Summary

Catalytic amounts of the rhodium(I) complexes [Rh(1,5-cod)$_2$]A (A = OTf, PF_6) initiate the ROP of **1a**−**1c** to yield high molecular weight polymers **2a**−**2c**. While activity of these catalysts proved remarkably high with quantitative conversion within 2 min in the case of **2a** and **2b**, prolonged exposure of the polymer in the reaction medium resulted in oxidation and apparent degradation of **2a**.[33] Evidence for Cp−Si bond cleavage was provided through the reaction of Fc_2SiMe_2 and [Rh(1,5-cod)$_2$]OTf, which afforded ferrocene as the sole, isolable product. Although significantly less active than [Rh(1,5-cod)$_2$]A (A = OTf, PF_6), [Rh(1,5-cod)(dmpe)]OTf represents the first phosphine-ligated transition metal complex to be catalytically active toward the ROP of **1a**. Moreover, no subsequent cleavage of the resulting polyferrocenylsilane chains was detected in this case. The homopolymerization of tetramethyldisilacyclobutane (**6**) and copolymerization with **1a** also proved facile using the cationic rhodium(I) precatalysts. Significantly, no subsequent polymer degradation was observed. The absence of chain cleavage reactions may be due to the absence of repeating ferrocenylsilane units in these materials. Mechanistic studies showed that the presence of 1,5-cod arrested catalytic activity of all rhodium(I) precatalysts studied, suggesting that 1,5-cod may dissociate from the rhodium center prior to ROP. Catalytic activity of [Rh(1,5-cod)(dmpe)]OTf was also completely inhibited in the presence of dmpe presumably due to the substitution of the 1,5-cod ligand for dmpe, thereby rendering the rhodium complex ineffective toward the ROP of **1a**. Further studies will be directed at expanding the range of rhodium ROP catalysts bearing chelating diphosphine ligands and will also focus on the mechanism of the catalytic chain cleavage reactions.

Experimental Section

Materials. Solvents were dried by standard procedures and distilled immediately prior to use. [1]Silaferrocenophanes (**1a**−**1c**) were synthesized as described in the literature.[20,27] [Rh(1,5-cod)$_2$]OTf was purchased from Strem, while [Rh(1,5-cod)$_2$]PF_6, [Rh(1,5-cod)dmpe]PF_6,[44] Fc_2SiMe_2,[45] and polymer **5**[21] were synthesized as described in the literature.

Equipment. All reactions and manipulations were performed under an inert atmosphere (prepurified N_2) using either standard Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies), except for the polymers for which manipulations were carried out in air. The reactions and polymerizations were monitored by ^{1}H NMR spectroscopy. Solution NMR spectra were recorded on Varian XL 400 instruments. ^{1}H NMR spectra (400 MHz) were referenced to residual protonated solvent, and ^{13}C NMR spectra (100.5 MHz) were referenced to the residual carbons of the deuterated solvent. ^{29}Si NMR (79.5 MHz) spectra were referenced externally to TMS utilizing a normal (proton-decoupled) pulse sequence. Molecular weight distributions were analyzed by gel permeation chromatography using a Waters Associates 2690 Separations Unit. Ultrastyragel columns with a pore of 500, 10^3, and 10^5 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 of 0.1% tetra-*n*-butylammonium bromide. Polystyrene standards purchased from Aldrich were used for calibration purposes.

ROP of 1a−1c Using [Rh(1,5-cod)$_2$]OTf as a Precatalyst. As the experimental conditions were identical for monomers **1a**−**1c**, the ROP of only one example, **1a**, will be described. Silaferrocenophane (**1a**) (0.28 g, 1.16 mmol) was dissolved in toluene (4.0 mL). To this red solution was added the catalyst [Rh(1,5-cod)$_2$]OTf (ca. 0.3 mol %), which had been previously dissolved in THF (0.1 mL) The solution rapidly changed from red to amber. The resulting polymer (**2a**) was precipitated into hexanes (ca. 250 mL) after 2 min, isolated by filtration, and dried under high vacuum. Repeated reactions were monitored by ^{1}H NMR spectroscopy and were complete by the time the NMR experiment was over. Yield **2a**: 182 mg (65%). ^{1}H NMR (δ, C_6D_6) monomer **1a**: 0.35 (s, 6H, fcSiMe_2), 3.95 (br, 4H, Cp), 4.40 (br, 4H, Cp); polymer **2a**: 0.58 (s, fcSiMe_2), 4.02 (br, Cp), 4.23 (br, Cp). GPC analysis: $M_n = 1.00 \times 10^5$, PDI = 1.94. ^{1}H NMR (δ, C_6D_6) monomer **1b**: 0.32 (s, 3H, fcSiMe(CH_2CH_3)), 0.88 (q, 2H, fcSiMe(CH_2CH$_3$)), 1.12 (t, 3H, fcSiMe(CH$_2$CH_3)), 3.95 (m, 4H, Cp), 4.41 (m, 4H, Cp); polymer **2b**: 0.28 (s, fcSiMe(CH_2CH_3)), 1.00 (br, fcSiMe(CH_2CH$_3$)), 1.17

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[43] While triflic acid is known to cleave Si−Ar bonds to generate Si−OTf bonds (see Schröck, R.; Angermaier, K.; Schmidbaur, H. *Z. Naturforsch.* **1995**, *50*, 613, and references therein), it should be noted that Rh-catalyzed depolymerization of **2a** was observed irrespective of the counteranion (OTf or PF_6) employed.

[44] Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. (A)* **1971**, 2334.

[45] Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502.

(br, fcSiMe(CH$_2$C*H*$_3$), 4.10 (br, Cp), 4.12 (br, Cp), 4.28 (br, Cp). GPC analysis (isolated after 5 min): $M_n = 1.51 \times 10^5$, PDI = 2.05. ^{1}H NMR (δ, C_6D_6) monomer **1c**: 0.56 (s, 3H, fcSi*Me*Ph), 3.97 (br, 2H, Cp), 4.40 (br, 2H, Cp), 4.38 (br, 2H, Cp), 4.43 (br, 2H, Cp), 7.26 (br, 3H, fcSiMe*Ph*), 7.91 (br, 2H, fcSiMe*Ph*); polymer **2c**: 0.72, (s, fcSi*Me*Ph), 0.74 (s, fcSi*Me*Ph), 0.76 (s, fcSi*Me*Ph), 3.97 (br, Cp, *fc*SiMePh,), 4.06 (br, Cp, *fc*SiMePh), 4.14 (br, Cp, *fc*SiMePh), 4.21 (br, Cp, *fc*SiMePh), 7.24 (br, fcSiMe*Ph*), 7.75 (br, fcSiMe*Ph*). GPC analysis (isolated after 1.5 h): $M_n = 9.57 \times 10^4$, PDI = 2.12.

Effects of Reaction Time on the ROP of 1a−1c Catalyzed Using [Rh(1,5-cod)$_2$]OTf as a Precatalyst in THF. In a typical experiment when **1a** (0.74 g, 3.09 mmol) was dissolved in ca. 5 mL of THF containing a catalytic amount of [Rh(1,5-cod)$_2$]OTf (<1 mol %), the solution viscosity increased very rapidly followed by a continuing decrease in solution viscosity with respect to time. Removing aliquots at given time intervals and purifying the polymer via precipitation into hexanes (ca. 50 mL) revealed an apparent decrease in molecular weight by GPC analysis: see Table 1 for **2a**. **2b** (over 132 h): M_n ranged from 1.36×10^5 to 3.61×10^4, PDI = 1.75−2.12; **2c** (over 24 h), 6.00×10^4 to 3.28×10^4, PDI = 2.12−2.85.

Effects of Reaction Time on the ROP of 1a Catalyzed Using [Rh(1,5-cod)$_2$]OTf as a Precatalyst in CH$_2$Cl$_2$. When a catalytic amount of [Rh(1,5-cod)$_2$]OTf (<1 mol %) was added to a CH_2Cl_2 (5 mL) solution of **1a** (435 mg, 1.80 mmol), a trend of decreasing molecular weights was observed that was similar to that in THF. Thus, the solution immediately became viscous and amber in color followed by a pronounced decrease in viscosity. Aliquots were precipitated into hexanes (50 mL) at the 0.2, 3, 24, 48, and 72 h. GPC analysis: **2a** over a period of 72 h, M_n ranged from 2.33×10^5 to 4.95×10^4, PDI = 1.45−2.23.

Reduction of 2a after Observed Decreases in GPC-Derived Molecular Weights. Complex **1a** (0.20 g, 0.83 mmol) dissolved in THF (5 mL) was exposed to catalytic amounts of [Rh(1,5-cod)$_2$]OTf (<1 mol %). An aliquot was precipitated into hexanes (50 mL) after 15 min, and the remaining reaction medium was allowed to stir for 20 h. The samples were subjected to purification and reduction via reprecipitation into a 10% solution of hydrazine in MeOH in an attempt to return the polymer to its original GPC-derived molecular weight. GPC results: (after 15 min) monomodal distribution $M_n = 1.00 \times 10^5$, PDI = 1.77; (20 h followed by reduction) bimodal distribution, $M_n = 7.90 \times 10^3$, PDI = 1.11, $M_n = 1.08 \times 10^5$, PDI = 1.31 (ratio = 2.1).

Effect of the Precatalyst's Counteranion on the Apparent Decrease in Molecular Weight. Complex **1a** (0.20 g, 0.83 mmol) was dissolved in ca. 5 mL of THF. On addition of catalytic amounts of [Rh(1,5-cod)$_2$]PF$_6$ (<1 mol %), the solution become highly viscous, with quantitative conversion to polymer within 15 min as evidenced by ^{1}H NMR. GPC: (after 15 min) $M_n = 1.78 \times 10^5$, PDI = 2.05. However, extending the reaction time led to a decrease in molecular weight by GPC. GPC: (2 h) $M_n = 1.60 \times 10^5$, PDI = 2.01; (48 h) $M_n = 3.60 \times 10^4$, PDI = 1.64. In this case, reprecipitation into a 10% solution of hydrazine in MeOH reduced the polymer back to high GPC-derived molecular weight. GPC analysis: $M_n = 1.95 \times 10^5$, PDI = 2.14. This experiment was repeated several times, and the regeneration of the fraction with $M_n \approx 10^5$ was often not complete and a lower M_n fraction (ca. 10^4) remained.

Reaction of [Rh(1,5-cod)$_2$]OTf with Polymer 5. Polymer **5** (0.08 g, $M_n = 1.10 \times 10^5$, PDI = 1.12) was dissolved in THF (4 mL) containing ca. 1 mol % [Rh(1,5-cod)$_2$]OTf. Aliquots were precipitated into hexanes (50 mL) at 44, 66, and 102 h. GPC analysis: (44 h) $M_n = 4.80 \times 10^4$, PDI = 1.48; (66 h) $M_n = 3.40 \times 10^4$, PDI = 1.59; (102 h) $M_n = 2.50 \times 10^4$, PDI = 1.80. Attempts to reduce the samples, after 102 h, by reprecipitating into a 10% v/v solution of hydrazine in MeOH produced a bimodal distribution. GPC analysis: $M_n = 1.2 \times 10^5$, PDI = 1.2; $M_n = 1.4 \times 10^4$, PDI = 2.5 with an approximate ratio of 2:1.

Attempted Reaction of NaOTf with 5. Polymer **5** (0.08 g, $M_n = 1.10 \times 10^5$, PDI = 1.12) and NaOTf (0.11 g, 0.64 mmol) were dissolved in THF (4 mL). After stirring the reaction at room temperature for 11 days, the polymer was purified by precipitation into MeOH (ca. 20 mL) after 24 and 48 h. GPC analysis: (24 h) $M_n = 9.40 \times 10^4$, PDI = 1.16; (48 h) $M_n = 1.01 \times 10^5$, PDI = 1.12. No appreciable change was detected after 11 d.

ROP of 1a Initiated by [Rh(1,5-cod)(dmpe)]OTf Precatalyst. In a typical experiment, **1a** (0.08 g, 0.33 mmol) was dissolved in 0.5 mL of C_6D_6, after which a catalytic amount of [Rh(1,5-cod)(dmpe)]OTf (<1 mol %) was added. The solution became immobile after 4 h, accompanied by a color change from red to amber, characteristic of polymer formation. After 1 week at room temperature, the solution remained immobile. The polymer **2a** was then precipitated into hexanes (ca. 100 mL), isolated by filtration, and dried at reduced pressure. Yield: 68 mg (85%). ^{1}H NMR (δ, C_6D_6) monomer **1a**: 0.35 (6H, Me), 3.95 (4H, Cp), 4.40 (4H, Cp); polymer **2a**: 0.58 (6H, Me), 4.02 (4H, Cp), 4.23 (4H, Cp). GPC analysis: $M_n = 1.54 \times 10^5$ to 3.44×10^5, PDI = 1.61−2.13.

Effects of Reaction Time on the ROP of 1a−1c Catalyzed Using [Rh(1,5-cod)dmpe]OTf as a Precatalyst. In a similar reaction, **1a** (0.25 g, 1.03 mmol) was dissolved in toluene (ca. 4 mL). A catalytic amount of [Rh(1,5-cod)(dmpe)]-OTf (<1 mol %) was added. At selected time intervals, aliquots of the reaction medium were removed, precipitated, and dried under reduced pressure prior to GPC analysis: (4 h) $M_n = 1.00 \times 10^5$, PDI = 1.94; (1 week) $M_n = 1.54 \times 10^5$, PDI = 1.63.

Inhibition Studies for the Rhodium-Catalyzed Polymerization of 1a. A. Equimolar amounts of 1,5-cod (25 μL, 0.21 mmol) and **1a** (0.05 g, 0.21 mmol) were dissolved in ca. 0.5 mL of C_6D_6. To this solution was added a catalytic amount of [Rh(1,5-cod)$_2$]OTf (<1 mol %). Monitoring by ^{1}H NMR revealed less than 5% conversion to polymer after 12 h at room temperature.

B. [1]Silaferrocenophane **1a** (0.05 g, 0.21 mmol) and 1,5-cod (25 μL, 0.21 mmol) were dissolved in 0.5 mL of C_6D_6. To this solution was added a small amount of the [Rh(1,5-cod)-dmpe]PF$_6$ precatalyst (<1 mol %). No polymerization occurred over a period of 7 days as monitored by ^{1}H NMR spectroscopy.

C. When equimolar amounts of **1a** (0.05 g, 0.21 mmol) and dmpe (35 μL, 0.21 mmols) were dissolved in 0.5 mL of C_6D_6 followed by a catalytic amount of [Rh(1,5-cod)dmpe]PF$_6$ precatalyst (<1 mol %), no reaction was observed over a period of 1 week as monitored by ^{1}H NMR spectroscopy.

Attempted ROP of 1a Using [Rh(dmpe)$_2$]OTf as a Precatalyst. To a solution of **1a** (0.05 g, 0.21 mmol) dissolved in CH_2Cl_2 (ca. 5 mL) was added a catalytic amount of [Rh-(dmpe)$_2$]OTf (<1 mol %). The reaction was allowed to stir at room temperature for over 1 week. Throughout this time, polymer formation was not detected by ^{1}H NMR spectroscopy.

ROP of 6 Catalyzed Using [Rh(1,5-cod)$_2$]OTf as a Precatalyst. Compound **6** (0.05 g, 0.35 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$ to which a catalytic amount of [Rh-(1,5-cod)$_2$]OTf (<1 mol %) was added. Within 15 min the solution became immobile, and the reaction reached 85% conversion after 45 min. Yield: 40 mg (80%). ^{1}H NMR (δ, $CDCl_3$) monomer: −0.01 (4H, [*CH*$_2$SiMe$_2$]$_2$), 0.22 (12H, [CH$_2$-Si*Me*$_2$]$_2$); polymer **7**: −0.25 (4H, [*CH*$_2$SiMe$_2$]$_2$), 0.04 (12H, [CH$_2$-Si*Me*$_2$]$_2$). GPC analysis: $M_n = 1.08 \times 10^6$, PDI = 1.39.

ROP of 6 Initiated by [Rh(1,5-cod)$_2$]OTf as the Precatalyst: The Effect of Prolonged Reaction Times. In a typical experiment when **6** (0.25 g, 1.74 mmol) was dissolved in ca. 5 mL of THF containing a catalytic amount of [Rh(1,5-cod)$_2$]OTf (<1 mol %), the viscosity of the solution increased and remained high for the duration of the experiment. Aliquots of the reaction mixture were removed at specific time intervals.

The resulting polymer (**7**) was purified by precipitation into hexanes (ca. 50 mL). GPC analysis: M_n values ranged from 4.20×10^5 to 6.60×10^5 and the PDI from 1.58 to 2.08 over a reaction period of 5 days with no significant molecular weight decline detected.

Copolymerization of 1a and 6 Catalyzed Using [Rh(1,5-cod)$_2$]OTf Precatalyst. After dissolving compounds **1a** (0.04 g, 0.16 mmol) and **6** (0.20 g, 1.39 mmol) in 2 mL of THF, a catalytic amount of [Rh(1,5-cod)$_2$]OTf (<1 mol %) was added to the solution. In addition to a color change from orange-red to light amber, a dramatic increase in viscosity was noted within less than 30 s. After stirring for 20 min at room temperature, the solution was precipitated into ca. 100 mL of MeOH, yielding an orange-colored elastomer **8**. Yield: 108 mg (45%). ^{1}H NMR (δ, C_6D_6): −0.06 (SiMe*CH$_2$*SiMe$_2$), 0.14, 0.20 (switching group, SiMe$_2$*CH$_2$*fc), 0.27 (CH$_2$Si*Me$_2$*CH$_2$), 0.41, 0.44 (switching group, CH$_2$Si*Me$_2$*fc), 4.12 (*fc*SiMe$_2$CH$_2$), 4.32 (*fc*SiMe$_2$CH$_2$). ^{13}C NMR (δ, C_6D_6): 1.1 (CH$_2$Si*Me$_2$*fc), 2.9 (switching group, CH$_2$Si*Me$_2$*CH$_2$SiMe$_2$fc), 3.1 (CH$_2$Si*Me$_2$*CH$_2$), 6.4−7.5 (switching group, SiMe$_2$*CH$_2$*SiMe$_2$fc), 7.9 (SiMe$_2$*CH$_2$*SiMe$_2$), 71.6 (Cp), 73.4 (Cp). ^{29}Si NMR (δ, C_6D_6): 0.21 (CH$_2$SiMe$_2$CH$_2$), −3.66 (CH$_2$SiMe$_2$fc). GPC analysis: $M_n = 4.63 \times 10^5$, PDI = 1.86.

Reaction of Fc$_2$SiMe$_2$ with [Rh(1,5-cod)$_2$]OTf. To an orange solution of Fc$_2$SiMe$_2$ (0.20 g, 0.47 mmol) in toluene (ca. 3.5 mL) was added a catalytic amount of [Rh(1,5-cod)$_2$]OTf (0.02 g, 0.04 mmol, 9 mol %). During the reaction the solution became slightly green. After allowing the reaction to stir over 1 week, the resulting solution was analyzed by NMR spectroscopy. The product was purified by filtration through Celite and recrystallized from hexane at 25 °C. Yield: 0.15 g (85%). ^{1}H NMR (δ, C_6D_6): 4.05 (10H, Cp). ^{13}C NMR (δ, C_6D_6): 68.3 (Cp). MS (EI, 70 eV): m/z 186 [M^+ = Fc] 121 [$M^+ - Cp$], 56 [$M^+ - 2Cp$]. Comparison with an authentic sample of ferrocene confirmed the identity of the product of this reaction.

Attempted Reaction of PhSiMe$_3$ with [Rh(1,5-cod)$_2$]OTf. PhSiMe$_3$ (0.12 g, 0.80 mmol) was dissolved in C_6D_6 followed by the addition of a catalytic amount of [Rh(1,5-cod)$_2$]OTf (ca. <1 mol %). The reaction was monitored over a period of 1 week by ^{1}H NMR spectroscopy. No reaction was detected.

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