

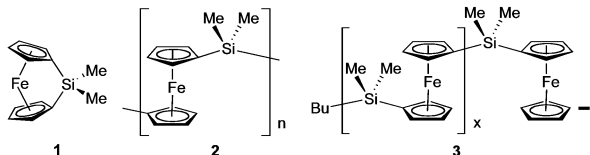
Photolytic Living Anionic Ring-Opening Polymerization (ROP) of Silicon-Bridged [1]Ferrocenophanes via an Iron-Cyclopentadienyl Bond Cleavage Mechanism

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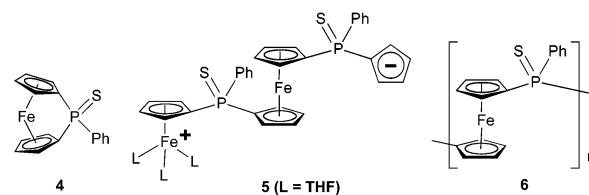
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High-molecular weight metal-containing polymers with well-defined and controlled architectures are of growing interest as a result of their interesting physical properties and self-assembly to yield functional supramolecular materials.^{1–3} Ring-opening polymerization (ROP) of strained metallocenophanes has been shown to provide a convenient route to polymetalloenes.⁴ Thermal, metal-catalyzed, or living anionic ROP of silicon-bridged [1]ferrocenophanes such as **1** yields polyferrocenylsilanes (PFSs, e.g., **2**).⁴ In each of these cases, the polymerization mechanism is believed to involve cleavage of the bond between the ipso cyclopentadienyl (Cp) carbon and the bridging silicon atom in the monomer. The enhanced reactivity of the Si–Cp bonds in **1** is clear from the treatment with protic reagents⁵ or platinum(0) complexes.⁶ Living anionic ROP of **1** induced by organolithium reagents such as BuLi, for example, proceeds via attack of the anionic initiator at the bridging silicon atom followed by Si–Cp bond cleavage.⁷ Chain propagation involves intermediates **3** with a metal-coordinated Cp anion. This route has permitted access to PFS block copolymers that undergo self-assembly to form phase-separated metal-rich nanodomains in thin films⁸ or micellar structures in block-selective solvents,⁹ with a variety of potential applications.

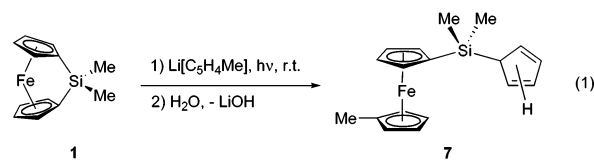


The cleavage of the Fe–Cp bonds in strained metallocenophanes was first observed in the reaction of highly strained boron-bridged [1]ferrocenophanes with metal–carbonyls.¹⁰ In an important recent development, Miyoshi and co-workers have shown that UV photolysis of phosphorus-bridged [1]ferrocenophane **4** in donor solvents (e.g., THF) leads to Cp ligand slippage (from η^5 to η^1) and ultimately Fe–Cp bond cleavage to form reactive intermediates of possible structure **5**, which subsequently further react with **4** to generate ring-opened organophosphorus metallopolymers **6** ($M_n = 2.9 \times 10^4$) with broad polydispersities (PDI = $M_w/M_n = 1.63$).¹¹ Encouraged by both these observations and a previous report¹² that benzoylferrocene derivatives can function as photoinitiators for anionic polymerizations via Fe–Cp bond cleavage, we have investigated the photolytic reactivity of silicon-bridged [1]ferrocenophanes. In this communication, we report our initial observations of photodissociation of an Fe–Cp bond of **1** and, by the use of an appropriate anionic initiator, the discovery of a new photolytic living anionic ROP method.

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Unlike the case of **4**, UV photoirradiation of **1** in THF or acetonitrile led to no observation of a ring-opening reaction by ¹H NMR. We therefore explored the addition of more nucleophilic, anionic initiators. Treatment of **1** with a 5-fold excess of moderately nucleophilic Li[C₅H₄Me] in THF at room temperature in the absence of UV light also led to no reaction. Upon UV irradiation for 1 h, however, the solution turned from red to yellow in color. Analysis of the reaction mixture by ¹H NMR spectroscopy indicated that **1** was completely converted to yield a ring-opened product with two multiplets for the SiC₅H₄ anion at δ 5.64 and 5.75.¹³ Subsequently, the photoproduct was terminated with H₂O to afford a ferrocenylsilane with a dangling silyl substituent, (η^5 -C₅H₄Me)-Fe(η^5 -C₅H₄SiMe₂C₅H₅) (**7**), in 32% isolated yield, which contains three regioisomers due to slow hydrogen migration on the Cp ring (eq 1).¹⁴ This demonstrated that the conjugated 6 π electron Cp[–] anion species efficiently promoted dissociation of the Fe–Cp bond of ring-strained ferrocenophane **1** on photoirradiation.



Treatment of **1** with Li[C₅H₄R] (R = Me, H) in a 10:1 ratio in the presence of UV light at room temperature led to analogous regioisomeric chain end-capped low-molecular weight PFSs (**8a**, R = Me, 72%, $M_n = 3.5 \times 10^3$, PDI = 1.18; **8b**, R = H, 61%, $M_n = 3.3 \times 10^3$, PDI = 1.35) (eq 2). The signals for each end group were clearly observed in the ¹H and ¹³C{¹H} NMR spectra. The use of smaller quantities of Li[C₅H₄R] to obtain a higher molecular weight and an attempt to control the molecular weight by varying the monomer:initiator ratios at room temperature were not successful.

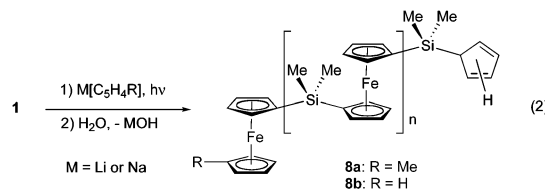
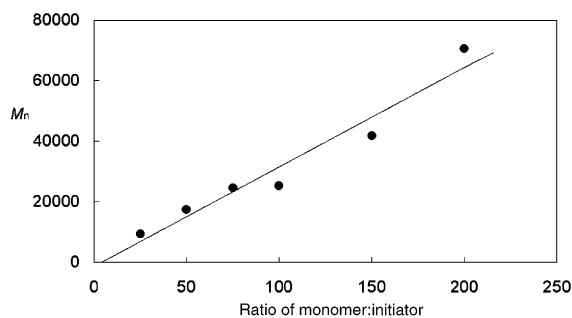


Table 1. Photolytic Living Anionic ROP of **1**^a

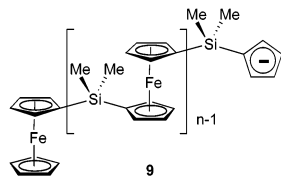
run	M:P	reaction time (h)	isolated yield (%)	M_n ($\times 10^3$)		M_w/M_n
				calcd	found	
1	25:1	2	76	6.0	9.3	1.04
2	50:1	2	91	12	17	1.05
3	75:1	4	85	18	24	1.04
4	100:1	4	90	24	25	1.06
5	150:1	6	91	36	41	1.21
6	200:1	6	93	48	70	1.12

^a Photopolymerizations were run in dry THF at 5 °C under nitrogen with 2.0 M Na[C₅H₅] in THF (from Aldrich) as an initiator. Polymer **8b** was isolated after termination with H₂O and precipitation into hexane.

**Figure 1.** Plot of the mole ratios of monomer:initiator versus M_n of polymer **8b**.

Living photolytic anionic ROP of **1** was successfully accomplished, however, by the use of the more ionic, commercially available initiator Na[C₅H₅] (2 M in THF from Aldrich) at subambient temperature (eq 2).¹⁵ Variation of the ratio of **1** to Na[C₅H₅] from 25:1 to 200:1 under UV irradiation at 5 °C, followed by chain termination with water, afforded samples of PFS **8b** with controlled molecular weights and narrow polydispersities (PDI = 1.04–1.21) (see Table 1). Figure 1 shows the plot of molecular weights ranging from $M_n = 9.3 \times 10^3$ to 7.0×10^4 .

In summary, we report a new photolytic living anionic ROP reaction for silicon-bridged [1]ferrocenophane **1** that proceeds in the presence of anionic initiator Na[C₅H₅] via cleavage of the Fe–Cp bonds in the monomer.¹⁶ This method differs fundamentally from the previously reported living anionic ROP in the presence of organolithium initiators such as BuLi,⁷ which proceeds in the absence of UV irradiation and involves Si–Cp bond cleavage. Moreover, the propagating centers for the new photolytic methodology are less basic free silyl-substituted cyclopentadienyl anions (as in **9**) rather than more basic iron-coordinated Cp anions (as in **3**).



This new living photolytic anionic ROP method should offer opportunities to complement the previous, more conventional approach by permitting (i) living anionic polymerization of strained metallocenophanes and (ii) block copolymerizations with monomers (such as acrylates¹⁷) that, in either case, might undergo side reactions with more basic anionic propagating centers. Research aimed at the use of this new methodology to allow access to new metallopolymer architectures is in progress. We are also performing detailed studies of the polymerization mechanism.

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Supporting Information Available: Experimental procedures for the synthesis and characterization of **7** and **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) The ¹H NMR spectrum in CD₃CN showed a mixture of (η^5 -MeC₅H₄)-Fe(η^5 -C₅H₄SiMe₂C₅H₄Li) and excess Li[C₅H₄Me]. The Cp⁻ ring protons for the latter were observed as two multiplets at δ 5.20 and 5.28.
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- (15) The higher ionic character of the Na salt may lead to more rapid initiation, which could generate polymers with narrow polydispersities.
- (16) Pyrex-filtered Hg light was used (i.e., $\lambda > \text{ca. } 300 \text{ nm}$). On the basis of previous work on the use of benzoylferrocenes as anionic photoinitiators (see ref 12), we propose that the ring-opening of **1** is facilitated via photoinduced metal to ligand charge transfer (MLCT) which weakens the Fe–Cp bond and promotes nucleophilic attack at the Fe center. In the case of [1]ferrocenophanes such as **1**, this bond is already weakened due to the strained, ring-tilted structure (Cp ring tilt angle = ca. 21°); moreover, the HOMO–LUMO transition at 481 nm (in THF) has been shown by theoretical calculations to possess significant MLCT character compared to that in ferrocene (at 440 nm in hexane), which is an Fe-centered d–d transition. Mechanistically relevant photoexcitation of the Cp anion is highly unlikely, as this absorbs only at short wavelengths ($\lambda < \text{ca. } 240 \text{ nm}$) in a π – π^* transition. We postulate that chain initiation and subsequent chain propagation occur via bimolecular attack on the Fe center of photoexcited **1** by the nucleophilic Cp anion and by the terminal silyl-substituted Cp anions, respectively. This bimolecular reaction may well proceed via Fe–Cp ring-slipped (η^5 , η^3) and (η^5 , η^1) intermediates. Note that the resulting PFS **2** is not photoactive under the conditions of the experiment, as the lowest energy HOMO–LUMO transition for this material (at 430 nm in THF) is similar to that in ferrocene and is Fe-centered d–d in nature with no significant MLCT character, as the Cp ligands are no longer tilted. For discussions of the bonding, UV–vis spectra, and theoretical calculations for [1]ferrocenophanes such as **1** that support the presence of low-lying excited states with ligand character, see: (a) Rulkens, R.; Gates, D. P.; Balaisis, D.; Pudelski, J. K.; McIntosh, D. F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1997**, *119*, 10976–10986. (b) Barlow, S.; Drewitt, M. J.; Dijkstra, T.; Green, J. C.; O'Hare, D.; Whittingham, C.; Wynn, H. H.; Gates, D. P.; Manners, I.; Nelson, J. M.; Pudelski, J. K. *Organometallics* **1998**, *17*, 2113–2120. For considerations of photochemically generated ring-slipped intermediates in benzoylferrocene photochemistry, see refs 12a and 12c.
- (17) Cyanoacrylates have been successfully polymerized using the photo-generated free Cp anions from benzoylferrocenes: see ref 12b.

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