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Nucleophilically Assisted and Cationic Ring-Opening Polymerization of Tin-Bridged [1]Ferrocenophanes

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Abstract: To obtain mechanistic insight, detailed studies of the intriguing “spontaneous” ambient temperature ring-opening polymerization (ROP) of tin-bridged [1]ferrocenophanes $Fe(\eta\text{-}C_5H_4)_2SnR_2$ **3a** (R = t-Bu) and **3b** (R = Mes) in solution have been performed. The investigations explored the influence of non-nucleophilic additives such as radicals and radical traps, neutral and anionic nucleophiles, Lewis acids, protic species, and other cationic electrophiles. Significantly, two novel methodologies and mechanisms for the ROP of strained [1]ferrocenophanes are proposed based on this study. First, as the addition of amine nucleophiles such as pyridine was found to strongly accelerate the polymerization rate in solution, a new *nucleophilically assisted* ROP methodology was proposed. This operates at ambient temperature in solution even in the presence of chlorosilanes but, unlike the anionic polymerization of ferrocenophanes, does not involve cyclopentadienyl anions. Second, the addition of small quantities of the electrophilic species H^+ and Bu_3Sn^+ was found to lead to a *cationic* ROP process. These studies suggest that the “spontaneous” ROP of tin-bridged [1]ferrocenophanes may be a consequence of the presence of spurious, trace quantities of Lewis basic or acidic impurities. The new ROP mechanisms reported are likely to be of general significance for the ROP of other metallocenophanes (e.g., for thermal ROP in the melt) and for other metallacycles containing group 14 elements.

Introduction

Over the past decade the thermal,[1] anionic,[2] and transition metal-catalyzed[3] ring-opening polymerization (ROP) of strained ring-tilted [1]- and [2]metallocenophanes has become a well-established route to high molecular weight polymetallocenes which possess a range of interesting properties.[4] The resulting materials are attracting attention as redox-active gels,[5] sensors,[6] charge dissipation coatings,[7] plasma etching resists,[8] self-assembled materials,[9] and precursors to magnetic ceramics over various length scales.[10] Among the various possibilities, thermally induced ROP is currently the most general synthetic method. Although evidence for cleavage of the silicon ipso Cp[11] carbon bond in silicon-bridged [1]ferrocenophanes has been presented, the detailed mechanism of these reactions is still unclear. However, preliminary evidence based on the lack of ROP inhibition in the presence of radical traps suggests that hetero-

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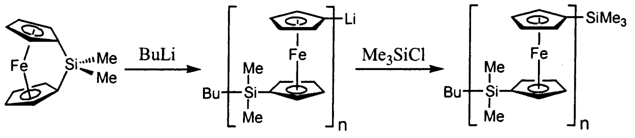
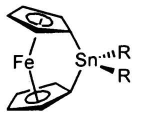
lytic processes may be involved in this case.[12] The mechanism of anionic ROP, on the other hand, is well-established. For silicon-bridged [1]ferrocenophanes (e.g., **1**), after initial attack of the nucleophile at silicon a cyclopentadienyl (Cp) anion is generated. The latter can attack further silicon centers of other monomer molecules in the propagation step, and the chain ends of the resulting living anionic polymer can be capped with, for example, $SiMe_3$ groups by the addition of Me_3SiCl (to give **2**) or used to prepare block copolymers.[13]

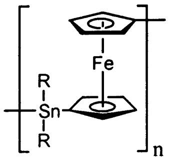


1 **2**

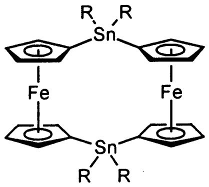
Although silicon and germanium-bridged [1]ferrocenophanes are easily prepared from the reaction of the dilithioferrocene–TMEDA complex with the appropriate dichloroorganosilane or -germane,[14,15] early attempts to prepare tin-bridged analogues in a similar manner were frustrated by the formation of cyclic and linear oligomers.[16] In the mid-1990s, tin-bridged [1]ferrocenophanes were successfully isolated by using sterically demanding substituents on tin.[17−19] Interestingly, although the two examples prepared in our group, **3a** and **3b**, were stable in the solid state, each was found to undergo "spontaneous" ROP in solution at ambient temperature. This afforded the high molecular weight polyferrocenylstannanes **4a** and **4b**, together with, in some cases, small amounts of the corresponding cyclic dimers **5a** and **5b**.[18] Encouragingly, these reactions appeared to offer the possibility of convenient mechanistic investigations of the ROP process, which might also provide much needed insight into the thermal ROP reactions for strained metallocenophanes that proceed in the melt. In this paper, we report full details[20] of our studies on the reactivity of [1]stannaferrocenophanes toward radicals, nucleophiles, and electrophiles and describe the discovery two new and potentially general methods of polymerization that involve *nucleophilically assisted* and *cationic* mechanisms.



3 a: R = *t*-Bu
b: R = Mes



4 a: R = *t*-Bu
b: R = Mes



5 a: R = *t*-Bu
b: R = Mes

Table 1. Representative NMR Experiments with **3a** (20 mg; 48 μmol; 0.10 M)[a]

additive	molar ratio *n*/*n* (**3a**)	approximate relative rate
		1
galvinoxyl	0.1	1
TEMPO	0.1	1
BzSSBz	0.1	1
BHT	0.1	1
$SiCl_4$	18	1
Me_3SiCl	8	1
TMEDA	15	30
pyridine	26	300
pyridine/Me_3SiCl	13/8/1	300

[a] Rates for ROP are given in comparison to reaction of **3a** in neat benzene (rate = 1) and are based on 50% conversion. The average molecular weights and PDI show a broad distribution (M_n = 10 000−900 000; PDI = 1.2−3.5) and vary from sample to sample for runs with the same combination of reagents. Reactions performed at 25 °C. For further details, see Supporting Information.

Results

We have previously shown that [1]stannaferrocenophane **3a** polymerizes in benzene or toluene solution at 25 °C, forming high molecular weight polymer **4a** (100% conversion, ~6 h, 0.1 M solution, $M_n > 10^5$). For the sterically more encumbered analogue, **3b**, the ROP is much slower (~50% conversion, 15 d, 0.1 M, $M_n > 10^5$). The rates of polymerization and the exact molecular weights as well as the polydispersities of the resulting polyferrocenylstannanes **4a** and **4b** were found to vary significantly from sample to sample and from experiment to experiment. In addition, in some cases, bimodal molecular weight distributions resulted. However, for both **3a** and **3b**, high molecular weight polymer is formed at low conversion, which is characteristic of a chain growth process where the concentration of propagating centers is extremely low.[18] Because of the slower rate of ROP for **3b**, the detection of rate enhancement effects caused by additives was expected to be more convenient with this species. Thus, although many experiments with additives were performed with both **3a** and **3b**, most of the following work involved the latter monomer.

1. Influence of Non-Nucleophilic Additives on the ROP of [1]Stannaferrocenophanes 3a and 3b. (a) Influence of Radical Initiators and Radical Traps. As a radical mechanism for the ambient temperature ROP of **3a** and **3b** was suspected, the effect of a variety of radical traps was investigated under similar conditions (Table 1 and Table 2). The observation that neither the traps galvinoxyl, TEMPO, $PhCH_2SSCH_2Ph$, BHT, and 1,4-cyclohexadiene nor UV irradiation (λ = 365 nm) had a substantial effect on the rate of polymerization of **3a** or **3b** suggested that a homolytic ROP mechanism is unlikely.[21]

This hypothesis was supported by experiments in which the influence of stannyl radicals on the ROP of **3b** was investigated.

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(11) In this paper, the abbreviation Cp is used to denote both substituted and unsubstituted cyclopentadienyl ligands.

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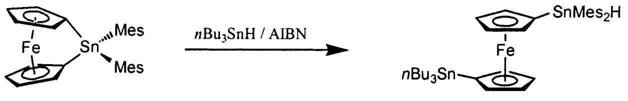
Table 2. Representative NMR Experiments with **3b** (20 mg; 37 μmol; 0.07 M)[a]

additive	25 °C molar ratio *n*/*n* (**3b**)	25 °C approx rel rate	60 °C molar ratio *n*/*n* (**3b**)	60 °C approx rel rate
		1		15
AIBN	1	1	1	15
Bu_3SnH			5	15
AIBN/Bu_3SnH			0.5/5/1	15
BHT	1	1		
TEMPO	1	1		
Me_3SiCl	11	1		
pyridine	33	300	1	1000
			0.03	300
4-(dimethylamino)pyridine	33	1000		
NEt_3	19	1		
2,6-di-*tert*-butylpyridine	12	<1		
1,4-diazabicyclo[2.2.2]octane	2	$\ll 1$		
pyridine/AIBN	33/1/1	300		
pyridine/TEMPO	33/1/1	300		
pyridine/1,4-cyclohexadiene	17/6/1	300		
pyridine/Me_3SiCl	17/11/1	300		

[a] Rates for ROP are given in comparison to reaction of **3b** in neat benzene (rate = 1) and are based on 50% conversion. The average molecular weights and PDI show a broad distribution (M_n = 10 000−500 000; PDI = 1.3−3.2) and vary from sample to sample for runs with the same combination of reagents. For further details, see Supporting Information.

Scheme 1. Ring Opening of **3b** with $Bu_3Sn\bullet$ Radicals



3b **6**

Reaction of **3b** with an excess of Bu_3SnH and AIBN at 60 °C, which is known to generate $Bu_3Sn^\bullet$ radical species,[22] afforded the ring-opened product **6** quantitatively (Scheme 1). This process presumably involves a radical reaction, with attack of $Bu_3Sn^\bullet$ on the ferrocenophane followed by hydrogen abstraction from the excess Bu_3SnH as the formation of **6** was not detected when **3b** was treated with Bu_3SnH, alone under the same conditions. Importantly, treatment of **3b** with either an equimolar amount of AIBN or an excess Bu_3SnH at 60 °C did not significantly influence the ROP rate. Moreover, no increase in the ROP rate was detected when **3b** was treated with a deficiency (~15 mol %) of AIBN and excess Bu_3SnH at 60 °C.

(b) Influence of Cyclic Dimers 5a and 5b. An alternative ROP mechanism involving sequential ring fusion via σ-bond metathesis processes was dismissed on the basis that ring fusion of the [1]stannaferrocenophane **3a** and **3b** with the cyclic dimers **5a** and **5b** was not detected. Thus, for example, with a 1:1 mixture of **3a** and **5a** in C_6D_6, **3a** was found to form high molecular weight polymer **4a** without consuming detectable quantities of **5a**. Similarly, a mixture of **3b** and **5a** afforded homopolymer **4b** and no copolymer, whereas **5a** remained unchanged.[23]

2. Influence of Neutral and Anionic Nucleophiles on the ROP of [1]Stannaferrocenophanes 3a and 3b. (a) Influence of Amine Nucleophiles. Next, we investigated the influence of polar additives on the ROP of **3a** and **3b**. A dramatic increase in the rate of ROP was detected on addition of amine nucleophiles.[24,25] Thus, on addition of excess pyridine, ROP of **3a** (0.1 M in C_6D_6) was complete after less than 90 s and the ROP rate for **3b** was dramatically increased (in C_6D_6, 0.07 M, ~95% conversion after 24 h compared to <3% in a control experiment without pyridine addition). At 60 °C, strongly accelerated polymerization of **3b** was observed even with an equimolar (95% conversion in 16 h; M_n = 10 000, PDI = 2.3) or catalytic amount of pyridine (95% conversion in 16 h; M_n = 111 000, PDI = 3.1). The use of more basic amines such as 4-(dimethylamino)pyridine led to further increases of the ROP rate (for **3b**, ~95% conversion in 3.5 h), whereas for the more bulky NEt_3, the rate was much slower. It is interesting to note that the highly sterically encumbered amines 2,6-di-*tert*-butylpyridine and 1,4-diazabicyclo[2.2.2]octane (DABCO) show no accelerating effects at all; ROP is inhibited (Table 2). The reaction of **3b** with 2 equiv of DABCO affords only small amounts of polymer **4b** as observed by ^1H NMR (<5%), even after prolonged reaction times (1 week) at 60 °C.

(b) Influence of Amine Nucleophiles in the Presence of Radical Traps and UV Light. Importantly, the accelerating effect of amines was also observed in the presence of a stoichiometric amount of the TEMPO free radical. Thus, a nucleophilically assisted radical mechanism appeared unlikely as treatment of **3a** with amines in the presence of radical traps (Table 2) or on irradiation with UV light (λ = 365 nm) or sunlight led to no significant change in the rate of ROP.

(c) Influence of Amine Nucleophiles in the Presence of Me_3SiCl as an Electrophilic Trap. If free Cp anions are generated during the amine-promoted ROP of **3a** and **3b**, the addition of electrophiles would be expected to terminate the polymerization process. However, significantly, even the presence of a large excess of the silyl halide Me_3SiCl, which is known to cap living chain ends formed in the anionic ROP of [1]silaferrocenophanes, was found to have no significant effect on the rate of polymerization of **3a** or **3b** in the presence of added pyridine. This important result strongly indicates that Cp anions are *not* generated during the amine-catalyzed ROP process.[26]

(d) Influence of Organolithium Reagents. To further investigate the possible formation and reactivity of free Cp anions derived from **3b**, we attempted to generate an anionic species via the ring-opening addition of an organolithium reagent. Reaction of **3b** with 10 mol % BuLi in THF followed by the addition of Me_3SiCl, conditions analogous to those used for the formation of Me_3Si-capped polyferrocenylsilanes by the anionic ROP polymerization of silicon-bridged [1]ferrocenophanes,[2,13]

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(22) Davies, A. G. *Organotin Chemistry*; VCH: Weinheim, 1997.

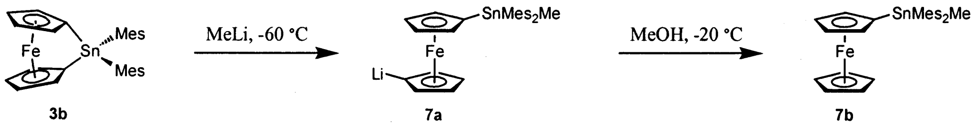
(23) For this reaction, a small amount of pyridine (see vide infra) was added so an appreciable reaction rate was detected.

(24) Other nucleophilically assisted or accelerated reactions with tin compounds include hydrogenation reactions with tin hydrides (homolytic and heterolytic reactions), the reaction of tin dihydrides to form tin−tin bonds, scrambling reactions of Sn_2R_6 with $Sn_2R'_6$, and oxidative cleavage of Sn−C bonds. See, for example: (a) Vedejs, E.; Duncan, S. M.; Haight, A. R. *J. Org. Chem.* **1993**, *58*, 3046. (b) Clive, D. J. L.; Yang, W. *J. Org. Chem.* **1995**, *60*, 2607. (c) Bulten, E. J.; Budding, H. A.; Noltes, J. G. *J. Organomet. Chem.* **1970**, *22*, C5. (d) Yoshida, J.; Izawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 9361. (e) Suga, S.; Manabe, T.; Yoshida, J. *Chem. Commun.* **1999**, 1237.

(25) An increased susceptibility of stannacyclopentanes and stannacyclobutanes toward oligomerization in polar solvents had been noted previously without mechanistic investigations or discussions. See, for example: (a) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1977**, *137*, 165. (b) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1983**, *105*, 3336.

(26) In an additional control experiment, Me_3SiCl was also found to have no significant effect on the ROP rate for **3a** and **3b** in the absence of added pyridine.

Scheme 2. Ring-Opening Reaction of **3b** with MeLi: Formation of **7a** and **7b**



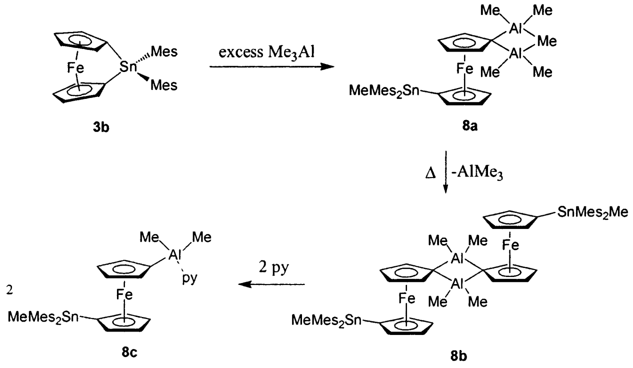
failed to generate any polyferrocenylstannane by ^{1}H NMR and GPC.

To gain insight into the lack of anionic ROP for **3b** under these conditions, this species was treated with a stoichiometric amount of MeLi in THF-d_8 at -196 °C. On warming to -20 °C, analysis by ^{119}Sn and ^{1}H NMR provided convincing evidence for the formation of the lithiated ring-opening addition product **7a** (Scheme 2). Thus, the ^{119}Sn NMR spectrum of the product showed a new singlet resonance at $\delta = -103.5$ consistent with the formation of a methyltriarylstannane-type product. Attachment of a Me group to the tin center was further confirmed by the presence of a new signal at $\delta = 0.87$ ppm in the ^{1}H NMR spectrum, which showed satellites due to coupling to the Sn center (J (H$-^{117/119}$Sn) = 53 Hz). In addition, the observation of four signals in the Cp region of the ^{1}H NMR spectrum was indicative of the generation of an unsymmetrically disubstituted ferrocene derivative. Interestingly, two of these resonances were found at unusually high field ($\delta = 3.79$, 3.62) and were assigned to the α- and β-carbons of a lithiated Cp ring. When the THF solution of **7a** was treated with MeOH at -30 °C, the protonated, monosubstituted ferrocene **7b** was obtained in 61% yield. The ^{119}Sn NMR spectrum of **7b** showed a signal at $\delta = -109.0$, which is upfield shifted by 5.5 ppm in comparison to the lithiated precursor **7a**. The ^{1}H NMR spectrum of **7b** also provided key characterization, displaying two pseudotriplet resonances for the substituted Cp ring ($\delta = 4.24$ and 4.17) and a singlet resonance for an unsubstituted Cp ring ($\delta = 3.94$). Significantly, when the reaction mixture containing **7a** was not quenched at -30 °C, but was allowed to warm to room temperature, fast decomposition to a range of uncharacterized products occurred. This may be a consequence of transmetalation reactions between the lithium and tin centers. The thermal instability of the lithiated ring-opened species **7a** and the inability of this compound to induce anionic ROP of **3b** was apparent from the reaction of the latter with 0.1 equiv of MeLi in THF. Analysis of the products formed on slow warming from -78 to 25 °C by ^{1}H NMR showed the generation of ~10% of unidentified species in addition to ~90% of unreacted **3b**. Significantly, no polymer **4b** was detected. These experiments therefore indicate that **3b** does not undergo anionic ROP with organolithium reagents as the intermediates with free Cp anions, such as **7a**, are unstable at room temperature and do not appear to participate in a ring-opening propagation step with **3b** at the low temperatures where such species are stable. These results provide additional support for the assertion that amine-promoted ROP reactions cannot proceed by a mechanism involving Cp anions as intermediates.

3. Influence of Lewis Acids on the ROP of [1]Stannaferrocenophane 3b. The discovery that amines have a dramatic effect on the ROP rate for tin-bridged [1]ferrocenophanes suggests that such species may be responsible for the "spontaneous" ROP of the latter at room temperature. Indeed, amines are likely trace impurities in the monomers formed in their synthesis in the presence of TMEDA catalyst. This prompted us to investigate the addition of Lewis acids, which would be expected to act as scavengers for nucleophilic impurities.

(a) Addition of Organoaluminum Reagents. When **3b** was treated with excess AlMe$_3$ (hexanes or toluene, 25 °C), however, the ring-opening addition product **8a** was formed as an orange oil (Scheme 3).[27] The ^{119}Sn NMR spectrum of **8a** showed a signal at $\delta = -111.6$, which is in a region similar to that for **7a** ($\delta = -103.5$) and **7b** ($\delta = -109.0$) but at higher field than for **3b** ($\delta = -128.3$). In the ^{27}Al NMR spectrum, a broad resonance was observed for **8a** at 152 ppm indicative of a dimeric triorganoaluminum species.[28] Ring-opening of **3b** was further confirmed by the fact that the ^{13}C NMR spectrum showed no *ipso*-Cp resonances in the 30−40 ppm range characteristic of a tin-bridged [1]ferrocenophane. Instead, the ^{13}C NMR spectrum revealed four signals in the Cp region ($\delta = 86.1$, 77.3, 75.7, 73.7), of which one was strongly downfield shifted as expected for the attachment of a Lewis acidic aluminum center to a Cp ring. A signal at -1.8 ppm was assigned to the methyl group transferred from the aluminum to the tin center as supported by the appearance of tin satellites ($J = 356$, 367 Hz). A singlet displaying tin satellites was also observed in the ^{1}H NMR spectrum at 0.82 ppm ($J = 52$ Hz). Importantly, a broad signal with an intensity of ~15 protons at -0.32 ppm indicated that **8a** was an adduct with AlMe$_3$, which is consistent with the structures of previously reported ferrocenylalanes.[29]

Scheme 3. Ring-Opening Reaction of **3b** with AlMe$_3$: Formation of **8a**, **8b**, and **8c**



When **8a** was heated under vacuum at 50 °C, 1 equiv of AlMe$_3$ was removed according to ^{1}H NMR and **8b** was formed (Scheme 3). Interestingly, the ^{1}H and ^{13}C NMR chemical shifts for the methyl groups changed significantly (**8a**, $\delta = -0.32/-5.8$; **8b**, $\delta = -0.38/-4.5$). The dimeric nature of **8b** was corroborated by the broad ^{27}Al NMR signal at $\delta = 154$ ppm, which is comparable to the signal observed for **8a**. In both species, the Cp ring acts as a bridging ligand between two aluminum centers bearing additional methyl substituents. The

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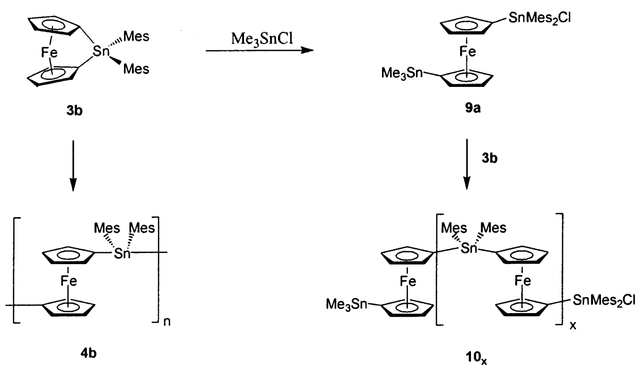
[27] A similar reaction was detected with the more encumbered species Al*i*Bu$_3$. See: Supporting Information.

[28] *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1993; Vol. 2, p 166.

[29] (a) Atwood, J. L.; Shoemaker, A. L. *Chem. Commun.* **1976**, 536. (b) Rogers, R. D.; Cook, W. J.; Atwood, J. L. *Inorg. Chem.* **1979**, *18*, 279.

Scheme 4. Homopolymerization versus Addition−Oligomerization in the Reaction of **3b** with Me_3SnCl



preference of aryl groups over alkyl groups for the bridging positions in organoaluminum dimers was previously reported for the analogous species Al_2Me_5Ph and $[PhAlMe_2]_2$.[30,31]

When **8b** was reacted with 2 equiv of pyridine, the monomeric adduct **8c** was formed. The existence of a monomeric species was indicated by the ^{27}Al NMR signal at $\delta = 167$ ppm, which is similar to the previously reported shift of the adduct $AlMe_3{\cdot}py$ ($\delta = 167$ ppm).[28] Due to the reduced Lewis acidity of the aluminum center in **8c**, no strongly downfield shifted Cp carbon atom was observed by ^{13}C NMR ($\delta = 76.7$, 74.2, 74.1, 72.1, 71.1, 68.6), and the resonance of the methyl groups bound to aluminum was high-field shifted ($\delta = -8.9$).

(b) Addition of Tin Halides. Although silyl halides had no effect on the ROP rate for **3a** or **3b** (see above), organotin halides such as Me_3SnCl would be expected to be more effective scavengers for nucleophilic impurities. However, as with the case of organoaluminum reagents, Me_3SnCl was found to react directly with **3b** to afford ring-opening addition products. Thus, reaction of 1 equiv of Me_3SnCl with **3b** (25 °C, C_6D_6) gave approximately equal amounts of **9a** and the dimer $\mathbf{10_1}$. The latter was presumably formed by the further reaction of **9a** with **3b** (Scheme 4).[32] With a 2:1 ratio of Me_3SnCl to **3b**, the addition product **9a** was obtained almost exclusively.

Formation of **9a** and $\mathbf{10_1}$ was confirmed by multinuclear NMR spectroscopy and by mass spectrometry. The ^{119}Sn NMR spectrum of **9a** showed two signals at −6.2 and −27.9 ppm, which were assigned to the $SnMe_3$ and $SnMes_2Cl$ substituents, respectively. Formation of a product bearing two different substituents on the Cp rings was apparent in the ^1H NMR spectrum, which showed four pseudotriplets at $\delta = 4.47$, 4.42, 4.30, and 4.11. A signal at 0.19 ppm was assigned to the trimethylstannyl group. The ^{13}C NMR spectrum of **9a** shows four signals for the Cp−H resonances at 75.4 (48 Hz), 73.9 (81 Hz), 72.3 (38 Hz), 71.6 (55 Hz) ppm, two of which show strong coupling to tin. For the higher homologue $\mathbf{10_1}$, additional signals in the NMR spectra for an internal $-Mes_2SnfcSnMes_2-$ fragment would be expected in a region similar to those for polyferrocenylstannane **4b**. Indeed, the ^{119}Sn NMR spectrum for $\mathbf{10_1}$ showed signals at −6.0 and −27.9 ppm for the terminal stannyl groups and a resonance at −128.1 ppm assigned to the interior tin center (cf. **9a**, $\delta = -6.2, -27.9$; **4b**, $\delta = -127.0$). Furthermore, the ^1H NMR spectrum displays eight Cp resonances and two sets of signals for the mesityl groups and in the mass spectrum of $\mathbf{10_1}$ the molecular ion peak was observed ($m/z = 1282$).

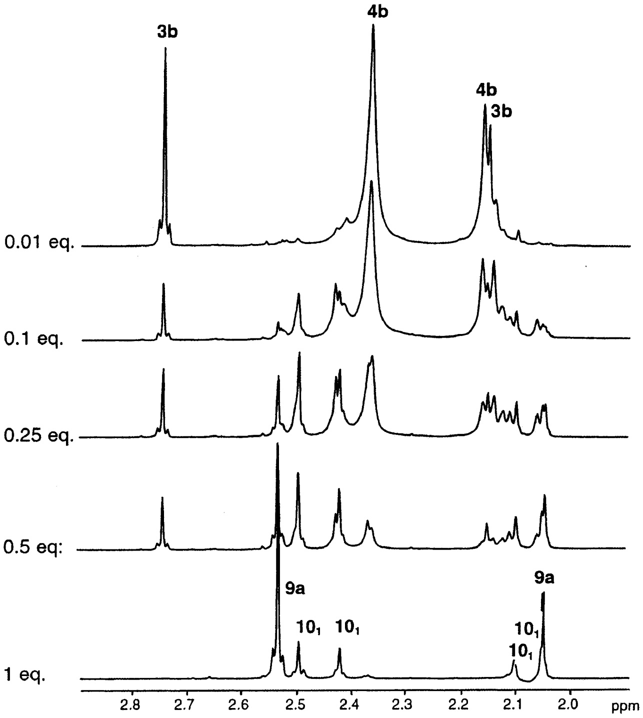


Figure 1. ^1H NMR spectra (in C_6D_6) after 14 d for reactions of **3b** with varying amounts of Me_3SnCl. Only the region for the methyl groups on the mesityl substituents is shown.

When the reaction of Me_3SnCl and **3b** was performed in ratios of 1:2−1:10 (C_6D_6, 14 d), increasing amounts of higher oligomers $\mathbf{10}_x$ ($x \geq 2$) were formed (see Figure 1). However, significantly, unreacted **3b** was also detected.[33] This suggested that the reactivity of **9a** and the oligomers $\mathbf{10}_x$ toward **3b** is lower than that of Me_3SnCl. This would be expected based on steric effects. When Me_3SnCl and **3b** were reacted in C_6D_6 in a 1:100 ratio under the same conditions, the major products were polyferrocenylstannane **4b** (GPC, $M_n > 10^5$) together with small amounts of $\mathbf{10}_x$ ($x \geq 2$; GPC, $M_n < 10^3$) and significant quantities of unreacted monomer **3b** were detected (Figure 1, top). These results, together with the observation that the conversion of **3b** strongly decreased with decreasing amounts of Me_3SnCl (see Figure 1), suggest that **4b** and $\mathbf{10_x}$ are formed by *different* competing mechanisms in such reactions. The formation of **4b** appears typical of the "spontaneous" ROP of **3b** via a chain growth process whereas $\mathbf{10}_x$ is formed by a sluggish ring-opening polycondensation process in which **3b** successively reacts with the moderately reactive $SnMes_2Cl$ group of **9a** and subsequently $\mathbf{10}_x$. The results of these experiments therefore indicate that the "spontaneous" ROP of **3b** is unaffected by the Lewis acidic tin centers present in $\mathbf{10}_x$.

4. Reactivity of [1]Stannaferrocenophane 3b toward Protic Species. Studies of the reactivity of silicon-bridged [1]ferrocenophanes have shown that ring-opening addition processes occur in the presence of protic agents such as MeOH, H_2O, and HCl.[34,35] To explore whether similar chemistry is possible

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(30) Mole, E. A. J.; Saunders: J. K. *Chem. Commun.* **1967**, 697.

(31) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2649.

(32) Reaction of **3b** with **9a** results in a mixture of higher oligomers $\mathbf{10}_x$ and polymer **4b** (see Supporting Information).

(33) Similar results and reaction rates were observed when the experiments were performed in CH_2Cl_2.

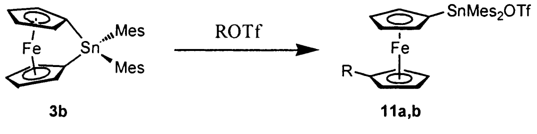
with the tin-bridged [1]ferrocenophane system, we performed a set of reactions that involve protic species.

(a) Reaction with HCl. The reaction of **3b** with 0.1 equiv of HCl (1 M in Et_2O) in either C_6D_6 or CD_2Cl_2 at ambient temperature led to chemistry similar to that observed in the case of Me_3SnCl. Thus, HCl reacted directly with **3b** to afford the ring-opened addition product **9b**. However, the formation of oligomeric/polymeric products was very sluggish, presumably for the same reasons as in the case of Me_3SnCl, and complete reaction required prolonged reaction times and slightly elevated reaction temperatures (50−60 °C). A more facile formation of oligomeric/polymeric products (M_n = 6,450, PDI = 1.4) was observed in the case of monomer **3a** with 0.1 equiv of HCl (1 M in Et_2O) in benzene, which is consistent with the lower kinetic stability of **3a** compared to **3b**. In this case, the reaction is complete after 2 d at room temperature.

On the basis of these and the aforementioned studies with Me_3SnCl, we chose triflate (OTf) as an alternative counteranion based on the expectation that the resulting $SnMes_2OTf$ chain end should provide a more reactive site for the induction of ring-opening processes of the type identified in the formation of oligomers $\mathbf{10}_x$. We anticipated that this might allow polyferrocenylstannanes of appreciable molecular weight to be rapidly formed.

(b) Reaction with HOTf. (i) Reaction of 3b with 1 Equiv of HOTf: Synthesis of Ring-Opening Addition Product 11a and the Pyridine Adduct 12. When a solution of **3b** in CH_2Cl_2 was treated with 1 equiv of HOTf at ambient temperature, the reaction mixture immediately turned dark green, indicating that a significant amount of oxidation of the ferrocene units had occurred. However, when the addition was performed at low temperature (−78 °C) and the reaction mixture was slowly allowed to warm to 25 °C, only a small amount of oxidation was detected in the form of a slight darkening of the solution. The ring-opening addition product **11a** was subsequently isolated as a yellow oil in ~90% purity (Scheme 5).[36] This species was characterized by multinuclear NMR. The ^1H NMR spectrum was consistent with the assigned structure as a monosubstituted ferrocene derivative, with two triplets at 4.41 and 4.20 ppm and a singlet at 4.13 ppm in the Cp region. Similarly, the Cp region of the ^{13}C NMR spectrum of **11a** showed two Cp−H signals displaying satellites due to coupling to the tin center ($\delta = 74.7$, $J = 79$ Hz; $\delta = 72.4$, $J = 60$ Hz) and a singlet for an unsubstituted Cp ring ($\delta = 69.5$). The ^{119}Sn NMR spectrum showed a strongly downfield shifted signal at $\delta = 36.9$.

Scheme 5. Ring-Opening Addition Reaction of **3b** with ROTf[a]



[a] Conditions: **11a**: R = H, −78 °C, CH_2Cl_2. **11b**: R = nBu$_3$Sn. Ambient Temperature, C_6D_6. OTf = OSO_2CF_3.

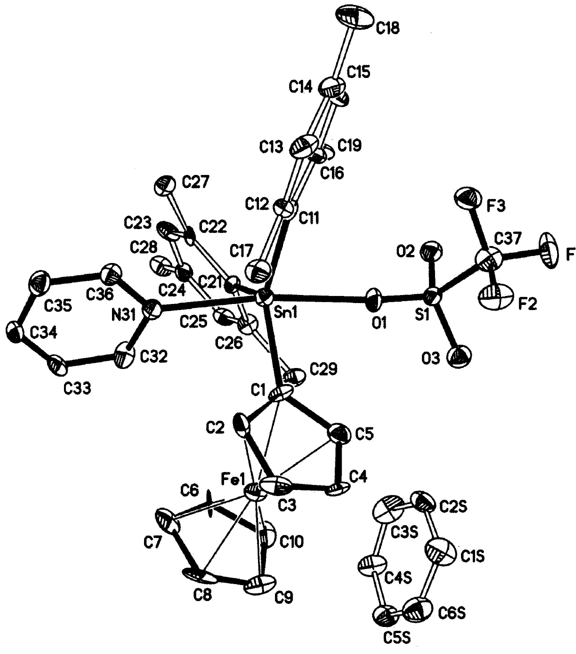
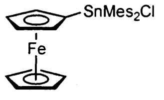
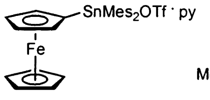


Figure 2. Molecular Structure of $\mathbf{12}\cdot C_6D_6$.

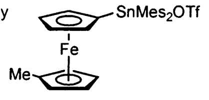
As the ring-opening addition product **11a** could not be obtained completely pure, an attempt was made to isolate an adduct of this species with pyridine for further characterization. Species **11a** was generated from the reaction of 1 equiv of HOTf and **3b** at −78 °C in CH_2Cl_2; the reaction mixture was subsequently treated with neat pyridine and the solution was allowed to slowly warm to ambient temperature. Formation of the adduct **12** was confirmed by multinuclear NMR spectroscopy and a single-crystal X-ray diffraction study (Figure 2, Tables 3 and 4). Complexation of **11a** is apparent from a significant upfield shift of the ^{119}Sn NMR signal ($\delta = -66.1$). Signals at $\delta = 8.42$, 6.95, and 6.59 in the ^1H NMR spectrum and at $\delta = 149.4$, 136.4, and 123.8 in the ^{13}C NMR spectrum were assigned to the coordinated pyridine moiety. Orange crystals of $\mathbf{12}\cdot C_6D_6$ for the X-ray study formed over a period of 2 days at ambient temperature and were isolated by decanting the solvent.



9b



12



14

The crystal structure of $\mathbf{12}\cdot C_6D_6$ confirmed the formation of a monosubstituted ferrocene derivative via addition of HOTf across one of the *ipso*-C−Sn bonds of **3b**. Compound **12** represents the first structurally characterized triorganotin triflate containing an additional donor ligand.[37] A distorted trigonal bipyramidal geometry around the tin center with a triflate and a pyridine ligand in axial positions is apparent from the N(31)−Sn(1)−O(1) angle of 172.6°. The angles between axial and equatorial ligands are in the range of 86.0−99.5°, and the angles between the equatorial ligands were found to be 116.8, 120.1,

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(34) (a) Fischer, A. B.; Kinney, R. H.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501. (b) O'Brien, S.; Tudor, J.; Barlow, S.; Drewitt, M. J.; Heyes, S. J.; O'Hare, D. *Chem. Commun.* **1997**, 641.

(35) (a) MacLachlan, M. J.; Ginzburg, M.; Zheng, J.; Knöll, O.; Lough, A. J., Manners, I. *New J. Chem.* **1998**, *22*, 1409. (b) MacLachlan, M. J.; Bourke, S. C.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 2126.

(36) We found that formation of **11a** can also be achieved at ambient temperature when **3b** and HOTf are reacted in benzene.

(37) For related structures of tin(IV) sulfonates and sulfates, see: (a) Harrison, P. G.; Phillips, R. C.; Richards, J. A. *J. Organomet. Chem.* **1976**, *114*, 47. (b) Molloy, K. C.; Quill, K.; Cunningham, D.; McArdle, P.; Higgins, T. *J. Chem. Soc., Dalton Trans.* **1989**, 267. (c) Hiemisch, O.; Henschel, D.; Jones, P. G.; Blaschette, A. *Z. Anorg. Allg. Chem.* **1997**, *623*, 147. (d) Westerhausen, M.; Schwarz, W. *Main Group Met. Chem.* **1997**, *20*, 351. (e) Nakazawa, H.; Yamaguchi, Y.; Kawamura, K.; Miyoshi, K. *Organometallics* **1997**, *16*, 4626.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **12**·C_6D_6

Sn(1)−C(1)	2.117(10)	C(1)−Sn(1)−C(11)	116.8(4)	C(21)−Sn(1)−O(1)	93.5(4)
Sn(1)−C(11)	2.135(12)	C(1)−Sn(1)−C(21)	123.0(4)	N(31)−Sn(1)−O(1)	172.6(3)
Sn(1)−C(21)	2.160(13)	C(11)−Sn(1)−C(21)	120.1(4)	O(1)−S(1)−O(2)	115.1(5)
Sn(1)−N(31)	2.332(11)	C(1)−Sn(1)−N(31)	88.0(4)	O(1)−S(1)−O(3)	113.4(5)
Sn(1)−O(1)	2.340(8)	C(11)−Sn(1)−N(31)	99.5(4)	O(2)−S(1)−O(3)	116.2(6)
S(1)−O(1)	1.445(9)	C(21)−Sn(1)−N(31)	86.2(4)	Sn(1)−O(1)−S(1)	166.6(6)
S(1)−O(2)	1.456(9)	C(1)−Sn(1)−O(1)	86.0(4)		
S(1)−O(3)	1.421(9)	C(11)−Sn(1)−O(1)	87.1(4)		

Table 4. Crystal Data and Structure Refinement for **12**·C_6D_6

formula	$C_{40}H_{42}F_3FeNO_3SSn$
M_r	848.35
T, K	100.0(1)
wavelength, Å	λ(Mo Kα) = 0.710 73
crystal system	monoclinic
space group	$P2_1/n$
a, Å	12.989(1)
b, Å	9.922(1)
c, Å	28.220(2)
α, deg	90
β, deg	91.463(5)
γ, deg	90
V, Å^3	857.7(2)
Z	4
ρ_{calc}, g cm^{-3}	1.550
μ(Mo Kα), mm^{-1}	1.198
F(000)	1728
crystal size, mm	0.27 × 0.25 × 0.20
diffractometer	Kappa-CCD
scan type, range	ϕ, 1
θ range, deg	4.11−25.40
limiting indices	$0 = h = 15$, $0 = k = 11$, $-34 = l = 34$
reflns collected	11331
independent reflns	6321 (R_{int} = 0.098)
abs correction/ min and max transmn coeff	empirical, multiscan/ 0.7956, − 0.7380
data/parameters	6321/457
GoF on F^2	1.092
$R1^a$ ($I > 2\sigma(I)$)	0.0806
$wR2^b$ (all data)	0.2218
ext coefficient	0.0005(5)
peak/hole (eÅ^{-3})	2.504/−0.861

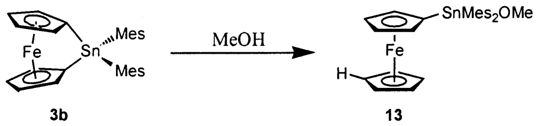
^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

and 123.0°, respectively. The Sn−N bond length of 2.33(1) Å is typical for pyridine adducts with tin(IV) centers, which range from 2.24 to 2.44 Å.[38] The Sn−O bond length of 2.340(8) Å is similar to that in trimethyltin benzenesulfonate hydrate (2.37(1) Å).[37,39] As a result of the bulky substituents, the tin atom is bent out of the Cp plane by an angle of −11(1)° and the tilt-angle between the Cp planes was found to be −9(1)°.

(ii) Reaction of 3b with 0.05 Equiv of HOTf. To explore whether adduct **11a** was capable of further reaction with **3b**, a small quantity (0.05 equiv) of HOTf was added dropwise to a solution of **3b** in CH_2Cl_2 at −78 °C. After 30 min, the solution was slowly warmed to 25 °C and an amber precipitate of polyferrocenylstannane **4b** formed. The formation of the latter was confirmed by ^{1}H and ^{119}Sn NMR analysis in C_6D_6 and GPC (in THF) indicated that the material was of high molecular weight (M_n = 385 000; PDI = 2.2).

These results indicate that HOTf reacts at −78 °C with **3b** to give the ring-opened species **11a**, which can be isolated as the pyridine adduct **12**. Rapid polymerization of **3b** is induced in the presence of catalytic amounts of HOTf in CH_2Cl_2, presumably via the reaction of **11a** with the monomer.[40]

Scheme 6. Ring-Opening Addition Reaction of **3b** with MeOH



(c) Reaction with MeOH. To establish the generality of this chemistry, we also investigated the reaction of **3b** with the weak proton source MeOH. However, only when a large excess of MeOH was added to a solution of **3b** in C_6D_6 at ambient temperature was slow conversion to the ring-opening addition product **13** detected by ^{1}H NMR spectroscopy (C_6D_6, 6 d) (Scheme 6). Formation of **13** was confirmed by multinuclear NMR spectroscopy and mass spectrometry. Ring-opening of **3b** is apparent from a significant downfield shift of the ^{119}Sn NMR signal, which is consistent with the attachment of the electronegative methoxy substituent ($\delta = -35.5$). The ^{1}H NMR spectrum of **13** was also consistent with the assigned structure and showed two pseudotriplets and a singlet in the Cp region. Furthermore, signals at $\delta = 3.73$ (J (H−$^{117/119}$Sn) = 42 Hz) in the ^{1}H NMR spectrum and at $\delta = 53.9$ (J (C−$^{117/119}$Sn) = 22 Hz) in the ^{13}C NMR spectrum showed Sn satellites and were assigned to the methoxy substituent on tin.

The sluggish formation of **13** is consistent with the low acidity of MeOH compared to HCl and triflic acid, and the resulting $SnMes_2OMe$ group is insufficiently reactive for further reaction with **3b**. The latter is corroborated by the reactions of **3b** with smaller amounts of MeOH (0.1 and 0.01 equiv), which show the generation of the ring-opened product **13** (10 or 1%, respectively), which does not react with the remaining **3b** even after prolonged reactions times (3 weeks) at ambient temperature.

5. Reactivity of [1]Stannaferrocenophane 3b toward other Electrophilic Cations. (a) Reaction with MeOTf. To further investigate whether other electrophilic cations are capable of inducing the ROP of **3b** in a manner similar to HOTf, we explored the reactions of **3b** with methyl triflate, a widely used source of methyl electrophiles.

When an equimolar amount of neat MeOTf was added dropwise to a solution of **3b** in CH_2Cl_2 at ambient temperature, a yellow precipitate gradually formed over a period of 1−2 h. ^{1}H and ^{119}Sn NMR analysis in C_6D_6 indicated the formation of high molecular weight polymer **4b**, which was confirmed by GPC (M_n = 116 900, PDI = 2.4). However, no evidence for the ring-opening addition product **14** was apparent. Similar observations were made during the reaction of 0.1 equiv of MeOTf with **3b** in CH_2Cl_2 at 25 °C, except that in this case,

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[38] A CSD search gave eight structures of tin(IV) pyridine adducts.

[39] Harrison, P. G.; Phillips, R. C.; Richards, J. A. *J. Organomet. Chem.* **1976**, *114*, 47.

[40] Reaction of **3b** with ∼0.1 equiv of **11a** also results in the formation of polymer **4b** (see Supporting Information).

the yellow precipitate of high molecular weight **4b** formed more slowly over a period of 5−6 h ($M_n = 222\,700$, PDI = 3.0).

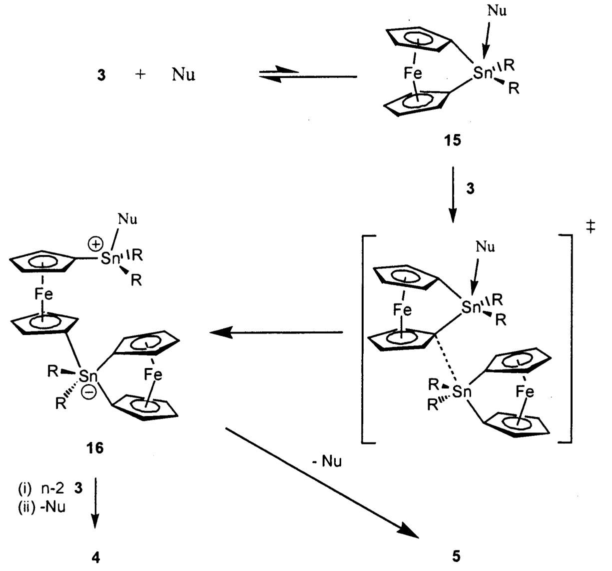
The observation that no ring-opening addition product was formed despite the fact that polymer **4b** formed relatively slowly suggests that the ROP is induced by the small concentration of HOTf impurities present in the MeOTf. This assumption is further supported by the observation that the addition of 1 equiv of the proton scavenger 2,6-di-*tert*-butylpyridine slowed the polymerization process significantly (95% conversion after 10−12 h). The formation of the polymer **4b** even under these conditions might be explained by the presence of an equilibrium between free HOTf and the corresponding pyridinium triflate species in the reaction mixture, which could still allow catalytic quantities of HOTf to initiate the ROP.

(b) Reaction with *n*Bu$_3$SnOTf. (i) Reaction of 3b with 1 Equiv of *n*Bu$_3$SnOTf. To probe the possibility that a source of highly electrophilic Sn centers could induce ROP of tin-bridged [1]ferrocenophanes, we investigated the reactivity of *n*Bu$_3$SnOTf toward **3b** at ambient temperature. The 1:1 reaction between these compounds in C_6D_6 led to the formation of ring-opening addition species **11b** as the main product according to NMR analysis of the reaction mixture after 1 d (Scheme 5). The ^{1}H NMR spectrum of **11b** showed four pseudotriplets at 4.62, 4.56, 4.42, and 4.13 ppm in the Cp region, which suggested the formation of a disubstituted ferrocene compound. This feature was also apparent in the Cp region of the ^{13}C NMR spectrum, which displayed four signals with tin satellites for the Cp−H resonances ($\delta = 75.8$, $J = 40$ Hz; 74.4, $J = 79$ Hz; 72.6, $J = 60$ Hz; $\delta = 72.3$, $J = 34$ Hz). The signals at 74.4 and 72.6 ppm showed strong coupling to tin and were therefore assigned to the electron-deficient tin center bearing a triflate substituent (cf. 1,1′-fc(SnBu$_3$)$_2$, $\delta = 74.7$, $J = 43$ Hz; 71.1, $J = 34$ Hz). Formation of a new tin triflate species was also apparent from the ^{119}Sn NMR spectrum, which showed a strongly downfield-shifted signal at $\delta = 34.7$ and a signal at −20.5 ppm, which was assigned to the tributylstannyl group by comparison with that for 1,1′-fc(SnBu$_3$)$_2$ ($\delta = -17.4$). Furthermore, the ^{19}F NMR spectrum gave rise to a signal at $\delta = -77.9$, which was assigned to the triflate group.

(ii) Reaction of 3b with 0.3 Equiv of *n*Bu$_3$SnOTf. With the analogous reaction involving 30 mol % *n*Bu$_3$SnOTf in C_6D_6, initial formation of **11b** was detected followed by ROP to give polymer **4b** over 14 d. Polymer **4b** was isolated as a yellow solid after precipitation into MeOH, and the molecular weight was found to be high by GPC ($M_n = 58\,100$, PDI = 2.2). The analogous process in CH_2Cl_2 was complete within 3 d by ^{1}H NMR (GPC: $M_n = 244\,000$; PDI = 2.3). These results suggest that the reactivity of the SnMes$_2$OTf end group is dependent on the ability of the solvent to promote ionization to form a cationic tin center.

6. Attempted Inhibition of Cationic ROP: Reaction of 3b with HOTf or *n*Bu$_3$SnOTf in the Presence of Excess [NBu$_4$]OTf. If stannyl cations are generated during the polymerization of **3b** with HOTf or *n*Bu$_3$SnOTf, then the presence of a large concentration of triflate anions would be expected to terminate or at least hinder the ROP process. Indeed, on treatment of **3b** with catalytic amounts of either HOTf or Bu$_3$SnOTf in the presence of 100 equiv of [NBu$_4$]OTf no polymer formation was detected. ^{1}H NMR spectroscopy and GPC revealed the formation of only oligomeric products in both cases ($M_n < 1000$). These results for the cases of the ROP of **3b** initiated by *n*Bu$_3$SnOTf and HOTf are clearly indicative of an inhibiting effect for excess triflate anion. This strongly suggests that a cationic or “cation-like” tin center functions as the propagating species in the ROP mechanism.

Scheme 7. Proposed Mechanism for the Nucleophilically Assisted ROP of [1]Stannaferrocenophanes



Discussion

Two New Polymerization Mechanisms for [1]Ferrocenophanes: Nucleophilically-Assisted ROP and Cationic ROP. Our studies of the influence of additives on the “spontaneous” ROP of tin-bridged [1]ferrocenophanes have led to the discovery of two new polymerization mechanisms.

The rate enhancement detected for **3a** and **3b** in the presence of amines points to a mechanism (Scheme 7), in which amine coordination to tin increases the nucleophilicity of the Cp carbon bonded to tin *without* generating a free anion. In the initiation step, a small equilibrium concentration of a pentacoordinate tin species **15** may form.[24,41] Although examples of amine coordination to tetraorganotin compounds are still rare, evidence for the formation of stable pentacoordinate tetraorganostannanes has been reported.[42] Moreover, intramolecular coordination of amines is known to lead to elongated tin−carbon bonds trans to the incoming nucleophile, which display enhanced reactivity.[43] The increased nucleophilicity of the Cp carbon bonded to tin in **15** may allow for attack at the tin center of another monomer molecule of **3** (Scheme 7). Crucially, heterolytic cleavage of the Sn−C bond trans to the coordinating amine does

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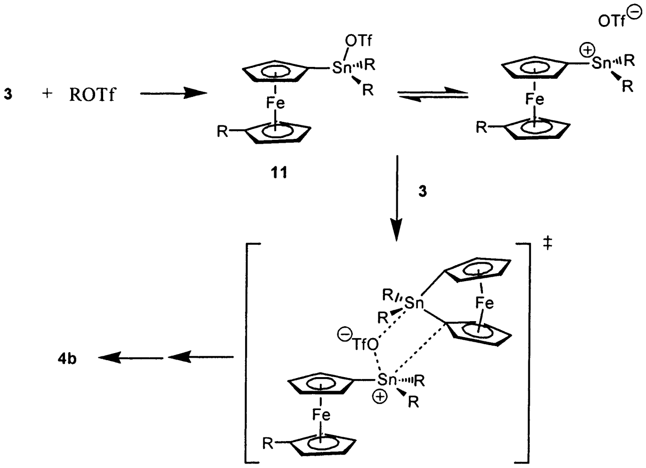
(41) (a) We have isolated a 5-coordinate silicon-bridged [1]ferrocenophane with an intramolecular Si−N interaction; in the solid state, Fe(η-C$_5$H$_4$)$_2$SiMe(2-C$_6$H$_4$NMe$_2$) possesses a trigonal bipyramidal Si center with an elongated Cp−Si bond trans to the amine substituent. Jäkle, F.; Vejzovic, E.: Power-Billard, K. N.; MacLachlan, M. J.; Lough, A. J.; Manners, I. *Organometallics* **2000**, *19*, 2826. (b) The formation of 5-coordinate [1]ferrocenophanes is favored by the contracted Cp−E−Cp bond angle (E = bridging element) relative to analogous acyclic species.

(42) See, for example: (a) Tzschach, A.; Jurkschat, K. *Pure Appl. Chem.* **1986**, *58*, 639. (b) Jurkschat, K.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1986**, *315*, 45. (c) Kumar-Das, V. G.; Mun, L. K.; Wei, C.; Blunden, S. J.; Mak, T. C. W. *J. Organomet. Chem.* **1987**, *322*, 163. (d) Kumar-Das, V. G.; Mun, L. K.; Wei, C.; Mak, T. C. W. *Organometallics* **1987**, *6*, 10.

(43) See for example: (a) Yoshida, J.; Izawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 9361. (b) Steenwinkel, P.; Jastrzebski, J. T. B. H.; Deelman, B.-J.; Grove, D. M.; Kooijman, H.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 5486.

Scheme 8. Proposed Mechanism for the Cationic ROP of [1]Stannaferrocenophanes



not generate a free anion but results in a tin ate complex (**16**) as an intermediate. Pentacoordinate stannate complexes are known to show decreased reactivity toward electrophiles in comparison to the corresponding lithium carbanions,[44] which may account for the fact that silicon halides have no significant influence on the polymerization process. The formation of cyclic dimer **5** can be explained by backbiting and the regeneration of the amine catalyst and would be expected to occur in situations of lower monomer concentration.[45]

The surprising inhibition of the ROP process by the highly sterically emcumbered, strongly basic amines 2,6-di-*tert*-butylpyridine and 1,4-diazabicyclo[2.2.2]octane can be attributed to two effects. First, the inacessability of the tin center of **3** due to the steric bulk of the amine nucleophile, which hinders the formation of key intermediate **15**, and second, their ability to act as scavengers for electrophiles (e.g., protons). The latter suppresses a possible ROP process through a *cationic* mechanism induced by, for example, acid impurities present in the reaction mixture.

Our studies indicate that a *cationic* mechanism operates in the case of the ROP of **3b** in the presence of small quantities of HOTf or *n*Bu$_3$SnOTf. An initial rapid reaction of **3b** with these species forms the ring-opened tin triflate species **11a** or **11b**, which reacts further with **3b** via a chain growth ROP process. The observation that the reaction is faster in more polar solvents (CH_2Cl_2 vs C_6D_6) and the observed inhibition by excess triflate anions supports the assertion that the propagating tin center is either cationic or cation-like (Scheme 8). The ROP of **3a** in the presence of HCl as initiator is presumed to occur by an analogous mechanism.

We recently found that MeOTf and $BF_3{\cdot}OEt_2$ induce the ROP of a [2]carbathiaferrocenophane.[1b] Methyl cations and (hydrolytically derived) protons were shown to be the likely initiators, respectively, and attack at the sulfur lone pair was tentatively proposed to be the key step. By contrast, the proposed mechanism for the cationic ROP process discovered for **3a** and **3b**, the first for a [1]ferrocenophane, appears to involve a propagating cationic or cation-like tin site.

Although the mechanism for the spontaneous ROP of tin-bridged [1]ferrocenophanes is still not known with certainty, the results reported clearly indicate that trace quantities of bases or perhaps strong protic acids may explain this phenomenon. For example, minute amounts of amines are likely impurities in the monomers, which are prepared from dilithioferrocene−TMEDA complex, and catalytic quantities of acids are possible as impurities in many solvents and reagents. Indeed, the noted variation of the rate of ROP and molecular weight from sample to sample is also consistent with this explanation.

Summary

Our investigations of the reactivity of tin-bridged [1]ferrocenophanes toward a variety of reagents including radicals and radical traps, nucleophiles, and electrophiles have led to the discovery of two new ROP mechanisms for [1]ferrocenophanes. One involves nucleophilic assistance by amines and the other proceeds via a cationic process.

The observed “spontaneous” ambient temperature ROP of tin-bridged [1]ferrocenophanes in solution can be tentatively explained in terms of the presence of trace quantities of amine (or other nucleophilic) impurities or electrophilic species, such as protons. Significantly, similar impurities might also be anticipated in other, less labile metallocenophane monomers such as silicon-bridged [1]ferrocenophanes, and as a consequence, analogous mechanisms need to be considered for the thermal ROP of these species in the melt as well. Future experiments will test this possibility and will also explore the generality of these new ROP methods, which should be applicable to many other strained rings containing group 14 elements.

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Supporting Information Available: Full experimental procedures and ^{1}H, ^{13}C, and ^{119}Sn NMR, MS, and GPC data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA020206V

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(44) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102.

(45) In the case of polymer formation, we anticipate that the coordinated amine and ferrocenophane chain termini remain intact until workup where hydrolysis would likely generate SnR_2OH and $SnR_2(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ end groups.