Nucleophilically Assisted Ring-Opening Polymerization of Group 14 Element-Bridged [1]Ferrocenophanes

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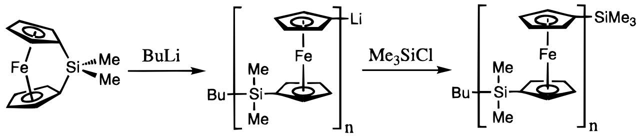
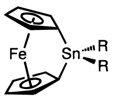
Ring-opening polymerization (ROP) of strained ring-tilted [1]- and [2]metallocenophanes has recently become a well-established route to high molecular weight poly(metallocene)s which possess a range of interesting properties.[1,2] Thermally induced ROP is currently the most general synthetic method. However, although evidence for cleavage of the silicon−*ipso* Cp carbon bond in silicon-bridged [1]ferrocenophanes has been presented, the detailed mechanism of these reactions is unclear but it appears to involve heterolysis.[3] In contrast to thermal ROP, the mechanism of anionic ROP 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.[4]



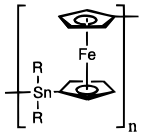
1 **2**

The recent discovery that tin-bridged [1]ferrocenophanes **3a** and **3b** can be successfully isolated if sterically demanding substituents are present on tin[5] and the observation of their apparent "spontaneous" ROP in solution to afford high molecular weight poly(ferrocenylstannane)s **4a** and **4b** (and small amounts of cyclics **5a** and **5b**) allows for a convenient mechanistic investigation of this ROP process.[5a,b] These studies may also provide insight into the thermal ROP reactions for metallocenophanes which proceed in the melt. In this paper we report our initial results and, in particular, the discovery of a new and potentially general method of polymerization which involves nucleophilic *assistance*.

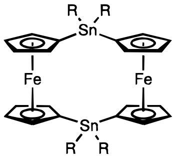
The [1]stannaferrocenophane **3a** polymerizes in benzene or toluene solution at 25 °C forming high molecular weight polymer **4a** (100% conversion, ca. 6 h, 0.1 M solution). For **3b** the



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



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



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

polymerization is much slower (ca. 50% conversion, 15 d, 0.1 M).[6] In either case high molecular weight polymer is formed at low conversion (for **3a** ca. 20% after 1 h, $M_n = 4.8 \times 10^5$, PDI $= 1.3$; for **3b** ca. 20% after 5 d, $M_n = 1.0 \times 10^6$, PDI $= 1.3$),[7] which is indicative of a chain growth process where the concentration of propagating centers is extremely low. As a radical mechanism was suspected, the effect of a variety of externally added radical traps was investigated under similar conditions. The observation that neither the traps (Galvinoxyl, TEMPO, BzSSBz, BHT, 1,4-cyclohexadiene) nor irradiation ($\lambda = 365$ nm) had a substantial effect on the rate of polymerization of **3a** or **3b** suggested that a homolytic ROP mechanism is unlikely.[8,9] This was supported by experiments in which the influence of stannyl radicals on the ROP of **3b** was investigated. Reaction of **3b** with an excess of Bu_3SnH and AIBN at 60 °C, which is known to generate $Bu_3Sn^\bullet$ species,[10] afforded the ring-opened product **6**. This process presumably involves a radical reaction with attack of $Bu_3Sn^\bullet$ on the ferrocenophane 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 AIBN or 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 (ca. 15 mol %) of AIBN and excess Bu_3SnH at 60 °C. An alternative ROP mechanism involving sequential ring-fusion via σ-bond metathesis was dismissed on the basis that ring-fusion of [1]stannaferrocenophanes **3a** and **3b** with the cyclic dimers **5a** and **5b** was not detected.[8] These results encouraged us to investigate the influence of polar additives on the ROP of **3a** and **3b** and a dramatic increase in the rate of ROP was observed on addition of amine nucleophiles.[11,12] 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 polymerization rate for **3b** was dramatically increased (in C_6D_6 ca. 95% conversion after 24 h compared to <3% in a control

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[1] (a) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131. (c) Manners, I. *Chem. Commun.* **1999**, 857.

[2] For other examples of poly(ferrocene)s obtained via ROP routes, see: (a) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (b) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (c) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (d) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507.

[3] Pudelski, J. K.; Manners, I. *J. Am. Chem. Soc.* **1995**, *117*, 7265.

[4] (a) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102. (b) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683.

[5] (a) Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1805. (b) Jäkle, F.; Rulkens, R.; Zech, G.; Foucher, D. A.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 2117. (c) Sharma, H. K.; Cervantes-Lee, F.; Mahmoud, J. S.; Pannell, K. H. *Organometallics* **1999**, *18*, 399.

[6] The exact molecular weights as well as the polydispersities of polymers **4a** and **4b** vary from sample to sample and from experiment to experiment. In addition, we have studied the ROP of **3a** in different solvents. The ROP was found to be faster in coordinating and polar solvents (e.g. THF and CH_2Cl_2) than in PhCl or benzene. Only in the case of CH_2Cl_2 is a substantial amount of cyclic dimer **5a** formed.

[7] Polymerization of **3a** in benzene led to bimodal molecular weight distributions with a large amount of high molecular weight polymer (ca. 80%) and a small amount of low molecular weight polymer (ca. 20%; M_n ca. 10 000), whereas **3b** almost exclusively yielded high molecular weight polymer.

[8] For details see the Supporting Information.

[9] Homolytic cleavage of stannacycloalkanes with free radical sources has previously been reported. See: Davies, A. G.; Roberts, B. P.; Tse, M.-W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1499.

[10] Davies, A. G., Ed. *Organotin Chemistry*; VCH: Weinheim, 1997.

[11] 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 ref 10 and, for example: Suga, S.; Manabe, T.; Yoshida, J. *J. Chem. Soc., Chem. Commun.* **1999**, 1237 and references therein.

[12] 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.

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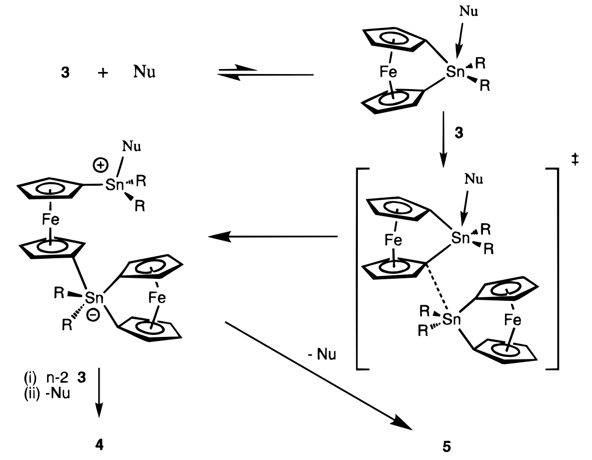
Scheme 1. Proposed Mechanism

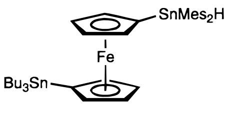


experiment without pyridine addition).[8,13] The use of the more basic 4-(dimethylamino)pyridine led to a further increase of the reaction rate for **3b** in benzene solution (ca. 95% conversion in 3.5 h), whereas for the more bulky NEt_3 the rate was much slower and for the highly sterically encumbered amine 2,6-di-*tert*-butylpyridine no accelerating effect was detected.

These observations initially suggested a mechanism, in which coordination of the amine to tin might induce heterolytic cleavage of the Sn−Cp bond to generate free anionic Cp sites in a manner similar to the anionic ROP mechanism. *However, crucially, the addition of silyl halides such as Me_3SiCl, which terminate chain ends in anionic ROP, had no significant effect on the rate of polymerization of **3a** or **3b** in the presence (or absence) of added amine*. This indicated a mechanism (Scheme 1) 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 may form.[14,15] Although examples of amine coordination to tetraorganotin compounds are still rare, evidence for the formation of stable pentacoordinate tetraorganostannanes has been reported.[16] Moreover, intramolecular coordination of amines is known to lead to elongated tin−carbon bonds trans to the incoming nucleophile, which display enhanced reactivity.[17] The increased nucleophilicity of the Cp carbon bonded to tin may allow for attack at the tin center of another monomer molecule **3** (Scheme 1). Crucially, heterolytic cleavage of the Sn−C bond trans to the coordinating amine does *not* generate a free anion but results in a tin ate complex as an intermediate. Pentacoordinate stannate complexes are known to show decreased reactivity toward electrophiles in comparison to the corresponding lithium carbanions,[18] 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 reactions.

Although the silicon centers of silyl halides appear insufficiently electrophilic to react with the nucleophilic Cp propagating centers, organotin halides such as Me_3SnCl should possess a Group 14 center of comparable (or greater) electrophilicity to that in **3b** and would therefore be expected to successfully compete with the monomer for the propagating sites. However, Me_3SnCl was found to react directly with **3b** to afford ring-opened addition products such as **7** and higher oligomers.[8,19]

To explore the generality of the new nucleophilically assisted ROP methodology we have also investigated the influence of amines on the ROP of germanium-bridged [1]ferrocenophane **8** and the silicon-bridged [1]ferrocenophanes **9** and **1**, for which the electrophilicity of the silicon center is **9** ≫ **1**.[1b,c] When pyridine was added to solutions of **1**, **3a**, **3b**, **8**, and **9** in C_6D_6, all apart from **1** underwent ROP; the order of decreasing rate was **3a** > **3b** ≈ **8** ≫ **9**. The relative ROP rates can be rationalized by the influence of the steric accessibility and electrophilicity of the bridging atom on the ease of formation of the proposed pentacoordinate intermediate.[15]



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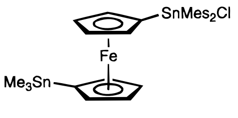

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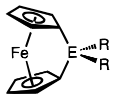

8: $ER_2 = GeMe_2$
9: $ER_2 = SiCl_2$

In summary, we report a new method for the ROP of metallocenophanes that operates at ambient temperature in solution, and which involves nucleophilic assistance by amines without the formation of free cyclopentadienyl anions. Intriguingly, the presence of trace amounts of amine (or other nucleophilic) impurities might be anticipated in the monomers as a result of their synthesis from amine (TMEDA) adducts of dilithioferrocene. Therefore, an analogous mechanism also needs to be considered for the thermal ROP of [1]ferrocenophanes in the melt. Further experiments are being performed to test this possibility and to explore the generality of this new ROP method, which should be applicable to many other strained rings containing Group 14 elements.

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Supporting Information Available: Tables of representative NMR experiments with **3a** and **3b** and experimental details and synthetic procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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[13] (a) The observed reaction rate can vary depending on the sample of **3a** and **3b**. Control experiments without addition of other reagents were performed to estimate the relative rate. (b) At 60 °C strongly accelerated polymerization of **3a** and **3b** was observed even with an equimolar or catalytic amount of pyridine. (c) A nucleophilically assisted radical mechanism appears unlikely as treatment of **3b** with amines in the presence of radical traps or under irradiation led to no significant change in the rate of ROP.

[14] In solution a pentacoordinate intermediate formed by the coordination of pyridine to **3b** could not be detected by ^1H, ^{13}C, or ^{119}Sn NMR. This may be attributed to a very low concentration of the adduct, which is consistent with the observed chain growth mechanism involving only a very small amount of propagating species. Furthermore, examples of tetraorganotin compounds which display a pentacoordinate geometry in the solid state without significant change of the NMR spectra in solution in comparison to tetracoordinate analogues have been previously reported. See, for example: (a) Podesta, J. C.; Chopa, A. B.; Koll, L. C. *J. Chem. Res. (S)* **1986**, 308. (b) Jousseaume, B.; Villeneuve, P.; Dräger, M.; Roller, S.; Chezeau, J. M. *J. Organomet. Chem.* **1988**, *349*, C1. (c) Jastrzebski, J. T. B. H.; Boersma, J.; Esch, P. M.; van Koten, G. *Organometallics* **1991**, *10*, 930.

[15] We have recently isolated a silicon-bridged analogue with an intramolecular Si−N interaction; in the solid-state $Fe(\eta-C_5H_4)_2SiMe(2\text{-}C_6H_4NMe_2)$ possesses a trigonal-bipyramidal Si center with an elongated Cp−Si bond trans to the amine substituent: Jäkle, F.; Lough, A. J.; Manners, I. Manuscript in preparation.

[16] See, for example: (a) Tzschach, A.; Jurkschat, K. *Pure Appl. Chem.* **1986**, *58*, 639. (b) Das, V. G. K.; Mun, L. K.; Wei, C.; Blunden, S. J.; Mak, T. C. W. *J. Organomet. Chem.* **1987**, *322*, 163.

[17] See, for example: (a) 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. (b) Yoshida, J.; Izawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 9361.

[18] Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102.

[19] Ring-opening reactions were also detected with species such as $Al\textit{i}Bu_3$ or $AlMe_3$.